

Heterogeneous acid catalysts for acetylation in glycerol

INMACULADA DOSUNA-RODRÍGUEZ

May 2012

Thèse présentée en vue de l'obtention
du grade de docteur en sciences agronomiques et
ingénierie biologique

Faculté d'ingénierie biologique,
agronomique et environnementale

Université catholique de Louvain

Composition du Jury :**Président :**

Pr. Michel Devillers (Université Catholique De Louvain, Belgium)

Promoteur :

Pr. Eric Gaigneaux (Université catholique de Louvain, Belgium)

Lecteurs :

Pr. Juray De Wilde (Université catholique de Louvain, Belgium)

Pr. Patrick Gerin (Université catholique de Louvain, Belgium)

Pr. Jacqueline Marchand-Brynaert (Université catholique de Louvain, Belgium)

Pr. Elio Santacesaria (University of Naples Federico II, Italy)

Pr. Pascal Van Der Voort (University of Ghent, Belgium)

ACKNOWLEDGMENTS

Once upon a time, in a rainy country far, far away from sunny-land, a little pixie was engaged in a battle that would last four years. A battle against dragons, glycerol molecules, unexpected results, surrounded by vinegar and cheese perfume, a battle against herself. Amazing people passed on her way, sharing their journeys, fighting their own battles and helping with a powerful weapon to keep going: a smile. Here is to all these people who participated to the story that lays hidden behind these lines...

I would like to express my gratitude to Prof. Eric Gaigneaux for giving me the opportunity to join his laboratory. For the confidence he deposited on me, and his guidance throughout this research. I appreciate the time we dedicated to scientific discussions and his corrections, despite his busy schedule and my “just in time” timing.

I wish to thank Prof. Michel Devillers for the honor of chairing the jury. I am also grateful to the jury members: Prof. Juray De Wilde, Prof. Patrick Gerin, Prof. Jacqueline Marchand-Brynaert, Prof. Elio Santacesaria and Prof. Pascal Van Der Voort, for sharing their expertises with me, as well as for their advices which contributed to the writing of the thesis.

I gratefully acknowledge the financial support from the «DGTRE, Région Wallonne» within the frame of the project «FuturEnergy-LIGNOFUEL» (Convention number 716721).

I thank again Prof. Pascal Van Der Voort and Els De Canck for the scientific discussions and for performing the tests in presence of propanol.

J'aimerais aussi remercier Pr. Rouxhet et Pr. García pour leur disponibilité et les discussions scientifiques menées avec eux.

J'aimerais remercier Françoise, pour les corrections du français et ses « moments culturels » : on ne parle pas avec elle sans apprendre un nouveau truc. À Nathalie, la fée magique, on écrit le produit désiré dans le cahier et il apparaît le lendemain comme par magie, merci pour cet excellent travail et pour ton aide. Merci à Pierre, pour sa patience à m'expliquer les écolages, pour les analyses XPS, GC, et pour le bon souvenir des 24h vélo. Merci aussi à Pascal et sa célèbre moustache, pour son aide, pour les blagues et pour donner vie au vélo CATA tous les 24h vélo.

Quand même je devrais dire que cette thèse est la faute de d'Églantine et de Damien. Églantine assistante de mes cours Erasmus, est devenue un peu ma sœur aînée des HPA, merci, pour ta gentillesse, et pour partager avec moi tellement de moments. Damien Debecker, mon encadrant dans mes premier mois au labo CATA, qui a partagé son goût pour la catalyse, ainsi que des soirées, des soupers, des courses et son amitié... Un grand MERCI à vous deux.

Je voudrais remercier aussi Romain, avec qui j'ai eu le plaisir de partager de parcours thésard, le fameux rangement de la salle des composants organiques, et la découverte de Pékin...

Je remercie aussi Marc, Damien H, Benji, Colas, Alejandro, Camila, Melissa, Maryna, Robert, Nawfal, Siham, et tous les collègues avec lesquels j'ai eu le plaisir de partager des discussions scientifiques, un bureau et des bons moments. Spécial dédicace à Corentin, qui a aussi souffert des embrouilles du glycérol.

Je tiens à remercier Deepak, Aneesh et Gijo pour leur sourire, leur amitié et pour me faire découvrir un peu les trésors de la culture indienne.

Je voudrais exprimer ma gratitude au Docteur François Varchon, pour ses conseils avisés concernant la rédaction de la thèse ainsi que pour empêcher mon passage irréversible au «Dark Side».

Qué hubiera sido de esta tesis sin mi familia latina: Teresa, que presencié mi inmersión en el país de la cerveza, entre tantas otras cosas, Belén, que aunque sólo pasaste 6 meses en este pueblecito parece como si no te hubieras ido nunca; Tiuh, que se vino y se fue, tímido como siempre, Óscar, con el que he compartido tantas cosas, Natalia, el tenedor más rápido de LLN, Víctor y a Raquel, que conocí como compañeros de laboratorio y terminaron siendo parte indispensable de esta familia. Tantas cosas que debería agradecerlos que se quedan pequeñas si las plasmo en papel... Y a todo el combo latino... También a Chispito, porque si una pata de conejo da buena suerte, con cuatro nada puede fallar.

Esta batalla nunca hubiera empezado ni mucho menos terminado sin mis amuletos mágicos, mis catalizadores de sueños, mi familia. Por ser mis solecitos andantes, y enseñarme tantas cosas y las que quedan, en especial a mis padres, mi hermano, Anni y Alexis...

TABLE OF CONTENTS

PART I: INTRODUCTION	13
CONTEXT OF THE THESIS	15
First and second generation biodiesel	15
Glycerol as raw material, glycerol revaluation.....	16
CATALYTIC PROCESSES.....	18
The importance of catalysis in industry	18
Catalyst definition and concepts	20
Heterogeneous catalysts.....	21
Different stages of the heterogeneous catalytic cycle	21
Acid solids.....	24
ESTERIFICATION OF CARBOXYLIC ACIDS	25
Acid catalysed esterification model in homogeneous phase	26
Acid catalysed esterification models in heterogeneous phase	27
Glycerol acetylation	33
OBJECTIVES OF THE THESIS AND STRATEGY APPLIED.....	36
Main objectives.....	36
Strategy.....	38
PART II: EXPERIMENTAL.....	41
CHAPTER 1: CATALYSTS PREPARATION AND PHYSICOCHEMICAL CHARACTERISATION.....	43
1.1. CATALYSTS PREPARATION	43
1.1.1. Niobium oxide supported on commercial silica-alumina (Nb- SA).....	43
1.1.2. Amorphous aluminophosphate (PA).....	44
1.1.3. Tungstated zirconia (WZ)	45
1.1.3.1. Tungstated zirconia obtained by wet impregnation technique (WZ-WI).....	45
1.1.3.2. Tungstated zirconia obtained by co-precipitation technique (WZ-CP)	46
1.1.4. Sulphated zirconia (SZ)	47
1.1.5. Immobilised heteropolyacids	48
1.1.5.1. Immobilised heteropolyacid by sol-gel method (Zr-SG and Si-SG).....	48

1.1.5.2. Immobilised heteropolyacid by wet impregnation technique (Zr-WI and Si-WI)	49
1.2. PHYSICOCHEMICAL CHARACTERISATION	50
1.2.1. Textural properties measurements	50
1.2.2. Crystallographic structure	50
1.2.3. Bulk chemical composition	51
1.2.4. Surface chemical composition	52
1.2.5. Fourier Transform Infrared Spectroscopy.....	53
1.2.6. Acidity measurements.....	54
1.2.6.1. Temperature programmed desorption of ammonia	54
1.2.6.2. Ammonia chemisorption.....	55
CHAPTER 2: CATALYTIC PERFORMANCES AND RECYCLABILITY.....	57
2.1. STANDARD TEST.....	57
2.2. SAMPLE ANALYSIS	58
2.3. CALIBRATION CURVES.....	60
2.4. EXPRESSION OF THE CATALYTIC PERFORMANCES.....	60
2.3. HOMOGENOUS CATALYSIS AND CATALYST RECYCLABILITY TESTS	62
PART III: RESULTS.....	65
CHAPTER 3A. GLYCEROL ACETYLATION OVER CATALYSTS OF DIFFERENT NATURE	67
3A.1. INTRODUCTION	69
3A.2. NIOBIUM OXIDE SUPPORTED ON COMMERCIAL SILICA-ALUMINA	69
3A.2.1. Introduction	69
3A.2.2. Solid characterisation.....	74
3A.2.3. Catalytic activity	76
3A.3. ALUMINOPHOSPHATES.....	77
3A.3.1. Introduction	77
3A.3.2. Solid characterisation.....	80
3A.3.3. Catalytic activity	82
3A.4. TUNGSTATED ZIRCONIA.....	83
3A.4.1. Introduction	83
3A.4.2. Solid characterisation.....	88
3A.4.3. Catalytic activity	95
3A.5. SULPHATED ZIRCONIA.....	96
3A.5.1. Introduction	96
3A.5.2. Solid characterisation.....	99
3A.5.3. Catalytic activity	102
3A.6. DISCUSSION OF THE RESULTS	103

3A.6.1. Diffusion limitations	105
3A.6.2. Interaction reactants-solid.....	106
3A.6.2.1. Influence of the reaction medium.....	106
3A.6.2.2. Acidic properties of the samples.....	108
CHAPTER 3B. PROPANOL ACETYLATION OVER CATALYSTS	
OF DIFFERENT NATURE	115
3B.1. PROPANOL ACETYLATION.....	116
3B.2. EXPERIMENTAL	117
3B.3. RESULTS	118
3B.4. DISCUSSION OF THE RESULTS	120
3B.4.1. Diffusion limitations	120
3B.4.2. Interaction reactants-solid.....	121
3B.4.2.1. Influence of the reaction medium.....	121
3B.4.2.2. Acidic properties of the samples.....	124
CHAPTER 3C. GENERAL DISCUSSION AND CONCLUSIONS	125
3C.1. DIFFERENT HYPOTHESES TO EXPLAIN THE CATALYTIC BEHAVIOUR OF	
THE SOLIDS.....	126
Hypothesis 1: Different synthesis method, different catalytic properties	
.....	126
Hypothesis 2: the nature of the solids: amphoteric character	127
Hypothesis 3: Solubility of solids	129
Hypothesis 4: Secondary reactions in the reaction medium for glycerol	
acetylation	130
3C.2. THE CATALYTIC BEHAVIOUR OF THE SYNTHESISED SOLIDS	136
3C.1.1 Niobium oxide supported on commercial silica-alumina.....	137
3C.1.2. Amorphous aluminophosphates	142
3C.1.3. Tungstated zirconia.....	144
3C.1.4. Sulphated zirconia	146
3C.3. CONCLUSIONS.....	148
CHAPTER 4: FURTHER STUDIES ON SULPHATED ZIRCONIA	
CATALYSTS.....	151
4.1. INTRODUCTION	152
4.1.1. Main objectives of this chapter	153
4.1.2. The nature of sulphated zirconia species	154
4.2. EXPERIMENTAL	158
4.2.1. Preparation of the catalysts	158
4.2.2. Further solid characterisation	158
4.2.3. Catalytic performances measurements	159
4.2.3.1. Esterification tests	159
4.2.3.2. Effect of glycerol excess.....	160
4.2.3.3. Esters distribution	161

4.2.3.4. Leaching tests	161
4.2.3.5. Homogeneous and recyclability tests.....	162
4.3. RESULTS AND DISCUSSION.....	162
4.3.1. Further solid characterisation	162
4.3.2. Catalytic performances	169
4.3.2.1. Esterification tests	169
4.3.2.2. Effect of glycerol excess.....	175
4.3.2.3. Esters distribution.....	177
4.3.2.4. Leaching tests	179
4.3.2.5. Homogeneous catalysis and catalyst recyclability tests ...	181
4.4. CONCLUSIONS.....	185

CHAPTER 5: IMMOBILISED HETEROPOLYACIDS IN SILICA AND ZIRCONIA MATRIX BY SOL-GEL AND WET IMPREGNATION TECHNIQUES FOR GLYCEROL ACETYLATION

.....	189
5.1. INTRODUCTION.....	190
5.1.1. Keggin heteropolyacids.....	190
5.1.2. From homogeneous to heterogeneous systems	193
5.1.2.1. Matrix interactions	194
5.1.2.2. Change in acidity strength.....	196
5.1.3. Immobilised heteropolyacids in esterification reactions.....	199
5.1.3.1. Glycerol acetylation	203
5.1.4. Main objectives of this chapter	204
5.2. EXPERIMENTAL	205
5.2.1. Preparation of the catalysts	205
5.2.1.1. Soxhlet washing	206
5.2.2. Characterisation.....	207
5.2.3. Catalytic performances measurements	208
5.2.3.1. Esterification tests	208
5.3. RESULTS	209
5.3.1. Solid characterisation.....	209
5.3.1.1. Textural properties	209
5.3.1.2. Structure	211
5.3.1.3. Immobilisation yield	213
5.3.1.4. Stability of the Keggin units.....	215
5.3.1.5. Number of acid sites.....	219
5.3.2. Catalytic performances	219
5.3.2.1. Esterification tests in homogeneous phase.....	219
5.3.2.2. Esterification tests with immobilised HPW	221
5.4. DISCUSSION OF THE RESULTS	223
5.5. CONCLUSIONS.....	227

CHAPTER 6: GLYCEROL ACETYLATION CATALYSED BY ION EXCHANGE RESINS.....	231
6.1. INTRODUCTION: ION EXCHANGE RESINS AS CATALYSTS	232
6.1.1. Ion exchange definition and classification	233
6.1.2. Swelling of ion exchange resins	235
6.1.3. Esterification mechanism over ion exchange resins.....	238
6.1.4. Influence of water.....	239
6.1.4.1. Effect of catalyst moisture content	240
6.1.4.2. Effect of water adding.....	240
6.1.5. Main objectives of the chapter	242
6.2. EXPERIMENTAL	244
6.2.1. Ion exchange resins.....	244
6.2.2. Esterification tests.....	245
6.2.3. Catalyst loading optimisation	246
6.2.4. Catalysts pre-treatment optimisation	246
6.2.5. Effect of water addition	246
6.2.6. Homogeneous catalysis and catalyst recyclability tests	247
6.3. RESULTS AND DISCUSSION	249
6.3.1. Esterification tests.....	249
6.3.2. Catalyst loading optimisation	252
6.3.3. Catalysts pre-treatment optimisation	254
6.3.4. Effect of water addition	257
6.3.5. Homogeneous catalysis and catalyst recyclability tests	258
6.4. CONCLUSIONS.....	261
 PART IV: GENERAL DISCUSSION CONCLUSIONS AND PERSPECTIVES	 265
GENERAL DISCUSSION.....	267
Glycerol acetylation reaction conducted in excess of glycerol.....	268
Heterogeneous catalysts for glycerol acetylation.....	271
CONCLUSIONS.....	279
PERSPECTIVES.....	283
 REFERENCES	 285
 PUBLICATIONS.....	 303
Published articles.....	303
Submitted articles	303

CONFERENCE ABSTRACTS.....	305
Oral communications.....	305
Poster communications.....	306
PART V: ANNEXE	307
ANNEXE 1	309
1. OBJECTIVES.....	309
2. EXPERIMENTAL	309
3. RESULTS	310
4. CONCLUSIONS.....	311

PART I: INTRODUCTION

This first part encloses a brief introduction to biodiesel production thence leading to the justification of the present work and the main objectives. In addition, some theoretical concepts about heterogeneous catalysis and the esterification reaction are presented. The comprehension of these concepts is essential to the construction of different hypotheses that are discussed throughout this current work. Finally, the main objectives of this work and the strategy applied to accomplish them are described.

CONTEXT OF THE THESIS

Due to environmental issues, the production of biodiesel and green chemicals has become a centre of interest in industry. New synthesis routes and environmental friendly processes are continuously emerging. In consequence, numerous catalytic materials are being applied to improve reaction yield and selectivity. Furthermore, there is a continuously growing search for new materials and for improved formulations of existing materials in order to be applied to these new green processes.

First and second generation biodiesel

Due to problems related to finite fossil resources as an energy source and their negative effect on the environment, the development of technologies using renewable energy sources, with lower environmental impact creates an everyday growing interest. In this context, biodiesel produced from vegetable oils and animal fats is emerging as an alternative to fossil fuels. The biodiesel is composed of monoalkyl esters of fatty acids, and can be used pure or blended with fossil diesel fuel without engine modification. Depending on the type of feedstock used as raw material, biodiesel can be classified as first generation or second generation. The main advantages of biodiesel are its renewable, nontoxic and biodegradable character, and the absence of sulphur and aromatics species [1].

The current technologies have favoured the production of first generation biodiesel, which is obtained from triglycerides of animal or vegetable origin, rather than second generation biodiesel, which is produced from lignocellulosic materials such as agricultural and forest residues and non-food crop feedstocks [2-3]. Transesterification (reaction producing monoalkyl esters and glycerol and biodiesel) seems to be the currently most worldwide used method to produce biodiesel industrially. However, due to the origin of the raw material, first generation biodiesel creates a competition for land and water for food production and generates a large amount of by-products like glycerol [2]. This increases the interest in developing second generation biofuels. Potential applications for food and agricultural waste and by-products have already been identified in scientific research [3]. However, the scaling-up of the manufacture of second generation biodiesel is still unfeasible due to several technical drawbacks as low yield and purity of raw materials [4].

Glycerol as raw material, glycerol revaluation

The revaluation of glycerol has become a necessity, as the manufacture of first generation biodiesel produces a large glut of this organic compound (which represents the 10%_{wt} of the total product) [5]. Thus, the market for glycerol (a component of some soaps, cosmetics or medicines, food additive (E422)) is now saturated and the production of valuable chemicals such as fuel and raw molecules for polymer industry seems to be a promising solution leading to large

novel market opportunities. Concerning biodiesel production, research has been directed toward reactions forming molecules reducing the viscosity and cloud point of biodiesel. The products issued from the etherification of glycerol with tert-butanol and isobutylene can be used as additives in biodiesel in order to lower the cloud point and to decrease the particulate, carbon oxide and carbonyl compounds emissions in exhaust gases [6-8]. Glycerol can also react with aldehydes, ketones, acetic acid, methyl and ethyl acetates forming acetals, cetal and glycerine acetates that can be used for reducing the particulate emission and for improving combustion and the biodiesel behaviour at low temperature [9-10]. Moreover, products obtained from glycerol acetylation: glycerol monoacetate, MAG, glyceryl diacetate, DAG, and glyceryl triacetate, TAG, find applications in cryogenics, the sector of biodegradable polymers and many others such as cosmetics and food industry. In addition, DAG and TAG are used as fuel additives for viscosity reduction. The TAG meets the specifications of flash point and oxidation stability (EN 14214 and ASTM D6751). Biodiesel shows lower oxidation stability than fossil fuel carburant. The oxidation reaction produces as main products aldehydes and polymers from hydroperoxides and peroxide radicals, and, as secondary products, alcohols and carboxylic acids. These products cause an increase of the viscosity and corrosion problems which can damage the engine [11-14]. Further details about new ways to reevaluate glycerol surplus in liquid and gas phase reactions can be found in [15-17] and references therein.

Among all the existing possibilities to tackle glycerol overproduction, this work focuses on the reaction of esterification of carboxylic acids with glycerol, as both glycerol and carboxylic acids can be produced from biodiesel industries (first generation and second generation biodiesel respectively). Carboxylic acids can be produced from acidogenic fermentation of pre-treated cellulose.

The principal objective of this research is to re-value the glycerol by esterification with carboxylic acids, consuming the largest quantity of glycerol possible. In order to accelerate the reaction a catalyst is needed.

CATALYTIC PROCESSES

The importance of catalysis in industry

In chemical industry approximately 85-90% of the products are made by catalytic processes [18]. A catalyst allows improving the kinetics of a chemical reaction. Moreover, the reaction can be conducted at lower temperature and pressure which means a significant gain in energy and thereon in production costs.

Catalytic processes are essential to all branches of chemical industry: petrochemical and polymers production, bulk and fine chemicals synthesis among others. In addition, catalysts could also converge toward the «green chemistry» as they can improve the

selectivity to the desired products, hence involving better use of raw materials, avoidance of the production of toxic substances, namely decrease of the waste and harmful molecules production. Moreover, they can be used to prevent the pollution and to avoid formation of waste [19].

Catalysts are also applied in the production of biofuel from transesterification and esterification reactions and other numerous green chemical reactions concerning the production of biopolymers and high value molecules from renewable raw materials.

Nowadays, liquid catalysts such as H_2SO_4 , HF, HClO_4 and H_3PO_4 , are still employed in industry. However, the environmental policies and the need to make production economically more advantageous lead the manufacture process towards the increasing use of solid catalysts. Solid (or heterogeneous) catalysts present multiple advantages when compared to homogeneous catalysts. Among them, it can be remarked the absence of contamination of the final products, the avoidance of further processes of purification and so waste, lower toxicity, reduction of corrosion problems and increased recyclability. This is mainly due to the fact that they can be easily separated from the reaction products by physical processes [20]. **This is the reason why in this work heterogeneous catalysts were selected to improve the glycerol acetylation rate.**

Catalyst definition and concepts

«A catalyst is a substance that increases the rate of a reaction without modifying the overall standard Gibbs energy change in the reaction» [21]. Depending on the phase in which the reaction takes place, catalysts can be divided into homogeneous, when only one phase is implicated in the reaction, and heterogeneous catalysts, when the reaction occurs at or near an interface between different phases.

It is important to remark that the concept «autocatalysis» is applied when one of the products of a reaction acts itself as a catalyst [21]. In addition, when the catalytic effect is brought by a group on a reactant molecule, the phenomenon is called intramolecular catalysis, with the cited molecule often called «activator». If the molecule which acts as a catalyst is being consumed during the reaction, this process is called a pseudo-catalysed reaction [21-22]. This is the case of esterification where carboxylic acid acts as a catalyst, due to the release of the proton.

Finally, it is important to provide a brief definition of «active site in heterogeneous catalysis», as this term will be cited several times during this work. «Active sites are those sites for adsorption which are the effective sites for a particular heterogeneous catalytic reaction» [22].

Heterogeneous catalysts

In summary, a catalyst presents the ability to accelerate a chemical reaction without being consumed. This phenomenon is possible as the catalyst provides the ability to operate according to a different reaction mechanism than the non-catalysed reaction. It does so by creating a bond with the reacting molecules, hence lowering the activation energy of the reaction. In the case of a solid catalyst, the adsorbed reagents form a product that detaches from the catalyst, thus leaving the active site available for the next reaction [18].

Different stages of the heterogeneous catalytic cycle

It is essential to consider the different stages of the catalytic process in order to understand the phenomenon and to determine the required properties of the solid. In heterogeneous catalysis, the reaction takes place at the solid-fluid interface. If a bimolecular reaction is considered ($A+B \rightarrow C$), the entire process can be divided in seven stages:

- 1- The external diffusion of the reactants from the reaction medium to the solid external surface. This mass transfer takes place in the layer surrounding the catalyst grain and is due to the difference of reactants concentration in the reaction medium and at the solid external surface.
- 2- The internal diffusion of the reactants from the external surface to the surface inside the pores. This mass transfer is

controlled among other factors by the pore size and their tortuosity and is more complex than the external diffusion.

- 3- Adsorption of one or both reactants on the catalyst (Eley-Rideal and Langmuir-Hinshelwood model respectively).
- 4- Chemical interaction between the reactants to form the product species.
- 5- Desorption of the products from the catalytic surface.
- 6- Migration of the products from the internal surface of the solid (pores) to the external surface of the grain.
- 7- External diffusion of the products from the layer surrounding the catalyst grain to the reaction medium.

The steps 1-2 and 6-7 correspond to physical processes concerning matter transfer whose rate is determined by the external and internal diffusions [23]. The remaining steps have a chemical nature.

The external diffusion considers the migration of molecules in the immediate vicinity of the surface. The external diffusion rate depends on several factors such as the stirring rate, the temperature and the chemical reaction taking place over the solid. Concerning internal diffusion, the presence of micropores, or too deep and tortuous pores in the solid could impede the efficient mass transfer of reactants from the vicinity of the solid surface to the active sites. The presence of diffusion limitations can lead to a decrease or even absence of chemisorption of the molecules as they cannot reach the active sites, which are thus unavailable.

The most important step in the heterogeneous catalysis is the adsorption, which is exothermic. There are two types of adsorption. First, physical adsorption where attraction forces between the adsorbed molecules and the solid are weak intermolecular non-selective forces that do not involve a significant change in the electronic orbital patterns of the adsorbed molecules (i.e Van der Waals forces) [22-23]. And second, chemical adsorption which results in a chemical bond between the adsorbed molecule and the adsorbate in a monolayer on the surface [22-23]. This type of adsorption is specific and selective and it involves higher energy than physical adsorption.

Depending on the chemical reaction studied, the limiting step that dictates the rate of the full catalytic process and determines the activation energy is generally the reaction between the adsorbed molecules of reactants to form the products.

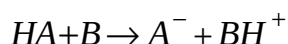
The catalytic performance of one solid in a given reaction depends on several variables: the diffusion rate of the reactive to the active site (active sites must be numerous and available to the reactant molecules) and the strength of the chemical bond formed between the reactants and the active sites, determining the occurrence of the chemical reaction. If the bond is too weak, the molecule may desorb prior to reacting; if it is too strong, the molecule may not react, or the release of the product and regeneration of the site may be retarded [23].

Acid solids

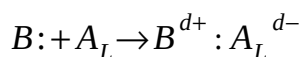
The esterification reaction can be conducted in the presence of base or acid catalysts. Base catalysts show higher reaction rates but they are often not as robust as acid catalysts, showing a marked trend to leaching and thus a lower recyclability [24]. This is the reason why acid solid catalysts were studied herein.

Several families of solids can be distinguished on the basis of the nature of the solid and thus on the properties and number of acid sites, as well as on their acid strength [19, 25-26].

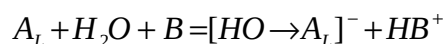
Two types of acid sites can be found in solids: Brønsted and Lewis acid sites. Brønsted acid sites (HA) are those capable of donating a proton to a base (B), a base being a compound able to accept the proton [25-27]. Thus the acid-base reaction taking place in presence of Brønsted acid sites can be defined as a transfer of proton.



A Lewis acid site participates in an acid-base reaction via the redistribution of valence electrons of compounds. The electronic configuration of the acceptor (acid, A_L) is completed with the lone pair of electrons belonging to the donor (base, B :) [25, 28].



It must be considered that in some cases, the Lewis type acid sites can be converted into Brønsted acid sites by including a molecule of water in the following manner [25]:



A brief summary of the most common solid acids can be found in the following references: zeolites [25, 29]; amorphous silica-aluminas [25], supported metal oxides [25, 30]; sulphated metal oxides [25-26, 29]; solids based on phosphorus and aluminium [26]; heteropolyacids (HPA) [29-31]; supported sulphonic acids [29-30]; organic-inorganic composites concerning «Periodic mesoporous organosilica (PMO)» [32-33], «Metal organic framework (MOF)» [34] and «Ordered mesoporous polymers (OMP)» [33].

Details concerning the acid solids studied in this work can be found from Chapter 3 to Chapter 6.

ESTERIFICATION OF CARBOXYLIC ACIDS

Detailed studies concerning the kinetic of the reaction were not conducted in the present work. Nevertheless, it is useful to describe briefly the different mechanisms proposed in the literature for the esterification reaction in order to better understand the results presented in the Part II of the manuscript.

Acid catalysed esterification model in homogeneous phase

The mechanism of carboxylic acids esterification catalysed in homogeneous phase by protons follows five different steps (Figure 1). First, the carboxylic acid is reversibly protonated (step 1), thus the positive charge of the carbon is increased. This phenomenon facilitates the nucleophilic attack of the hydroxyl group of the alcohol resulting in the formation of a new C-O bond (step 2). After the transfer of the proton (step 3) the break of one C-O bond produces the elimination of a water molecule (step 4). Finally, the ester is stabilised by a deprotonation (step 5), thus regenerating the proton for further catalytic cycles [35].

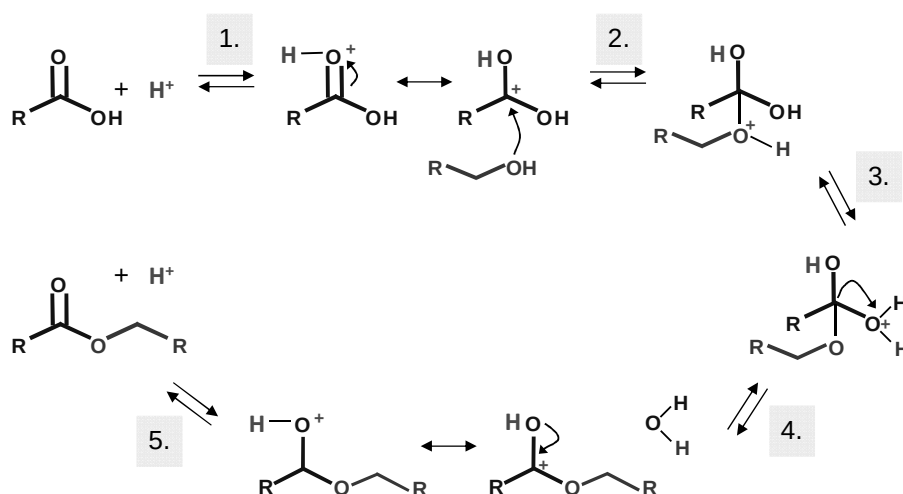


Figure 1. Mechanism of acid catalysed esterification in homogenous phase.

Acid catalysed esterification models in heterogeneous phase

Even if the mechanism for the esterification reaction in homogenous phase is well known and accepted unanimously, the mechanism concerning heterogeneous catalysed reaction is still much discussed. Several authors have tried to understand this phenomenon, but there is still no acceptance of one reaction mechanism.

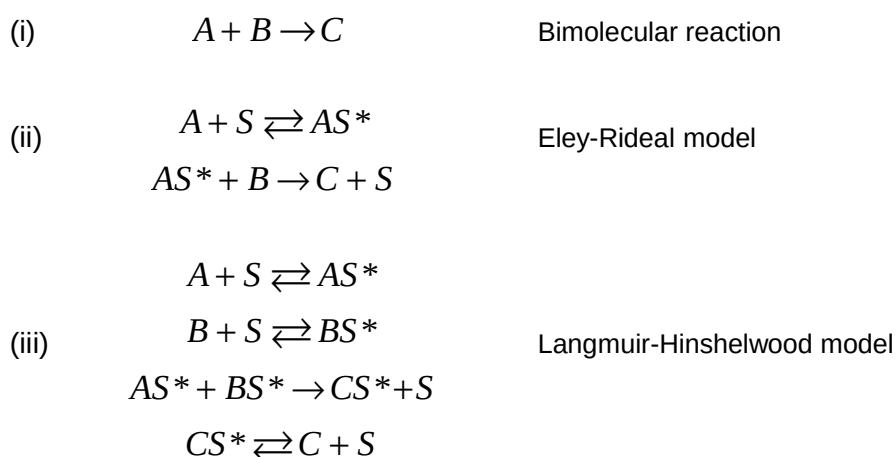


Figure 2. Different models of heterogeneous catalysed reactions.

Different models have been proposed in order to explain the different mechanisms of heterogeneous catalysed bimolecular reaction (i), (Figure 2): Eley-Rideal model states that only one molecule is adsorbed and reacts with a molecule from the gas or liquid phase (ii) [22], (S indicates the active site of the solid and * represent the adsorbed molecule over the solid surface); Langmuir-Hinshelwood model proposes that the two reactant molecules are adsorbed when the

Part I

chemical reaction occurs (iii) [22]. The main difference between the Eley-Rideal and Langmuir-Hinshelwood models is that in the former there is no competition between the species for the active sites [18].

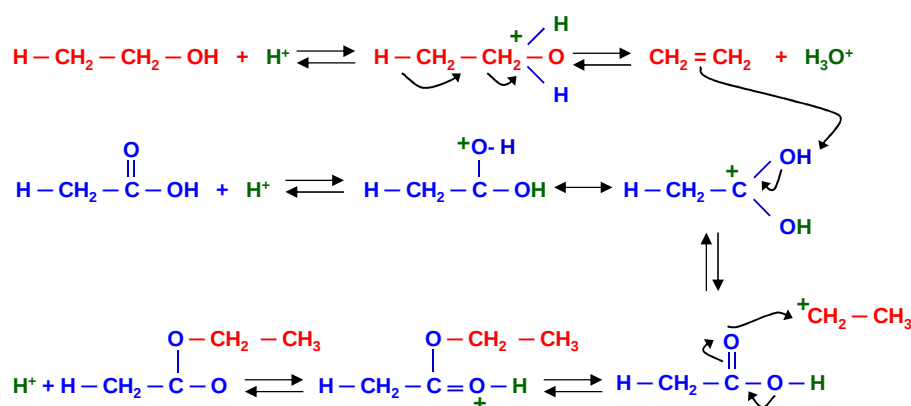


Figure 3. Esterification route via carbonium ion from ethanol based on the Langmuir-Hinshelwood model. For alumina a similar model can be applied substituting the proton by an Al ion.

A wide range of research related to carboxylic acid esterification with mono-alcohols can be found in literature, related both to short [36-39] and long chain carboxylic acids [40-47]. Gas phase esterification of acetic acid with ethanol by pulse technique was studied over silica-alumina, alumina-boria, sodium poisoned silica-alumina (silica group) and alumina [48]. In the silica group the active sites were Brønsted type. On the contrary, in alumina they were Lewis acid sites. Applying Langmuir-Hinshelwood model to kinetics, it was found that acetic acid adsorbed more strongly than ethanol on alumina and the reverse on the silica group. However, adsorbed acetic acid on alumina was only slightly reactive. The proposed mechanism proceeded via a carbonium ion formed from ethanol which was first

dehydrated and then esterified via the Langmuir-Hinshelwood mechanism (Figure 3).

Focalising in liquid phase esterification, it can be seen that single-site mechanism and Langmuir-Hinshelwood models can be applied to fit the experimental data depending on the esterification reaction (reactants, temperature conditions) and the catalyst used.

In general, water addition during esterification tests allowed concluding that water has a stronger affinity for the solid catalyst than carboxylic acids. Liquid phase esterification between acetic acid and methanol with sulphuric acid and Nafion/silica nanocomposite SAC-13 presenting Brønsted acid sites revealed that water had a stronger deactivation effect over the solid catalyst than over sulphuric acid [49]. Eley-Rideal model analogous to the homogeneous one was accepted. Another example is the esterification of hexanoic acid with 1-octanol in cumene as a solvent over Nafion SAC-13 and zeolite BEA [50]. The assumed esterification model was Eley-Rideal, however, carboxylic acid adsorption was hindered by the competitive adsorption of the alcohol. An additional work [51] concludes that the esterification reaction can be modelled by an Eley-Rideal model and includes studies about the influence of the carbon chain of the different compounds. It was shown that the increase of the length and branching of the alcohol chain had a retarding effect on the reaction rate. Similarly, the increase of the acid chain length retarded the reaction rate due to the steric hindrance. The assumption of an Eley-Rideal model in which active site competition between carboxylic

Part I

acid and water occurs has been discussed [52-54]. The authors proposed a pathway mechanism very similar to the homogeneous reaction. The proton is transferred to the oxygen that acquires a positive charge which is then delocalized over the carbon atom. Afterwards, the carboxylic acid undergoes a nucleophilic attack by the hydroxyl group of the alcohol (R'OH). The formation of the short living intermediate causes the release of one molecule of water. Finally the proton is transferred to the solid thus regenerating the active site [53].

Moreover, the authors assumed the subsequent competitive adsorption over the active sites (

Figure 4): (a) water molecules interact with sulphonic acid through protolysis equilibria, and (b) alcohol molecules can act as weak bases and receive the proton from sulphonic acid. The adsorption of ester was considered negligible. The adsorbed alcohol molecule was considered as inert for the esterification reaction.

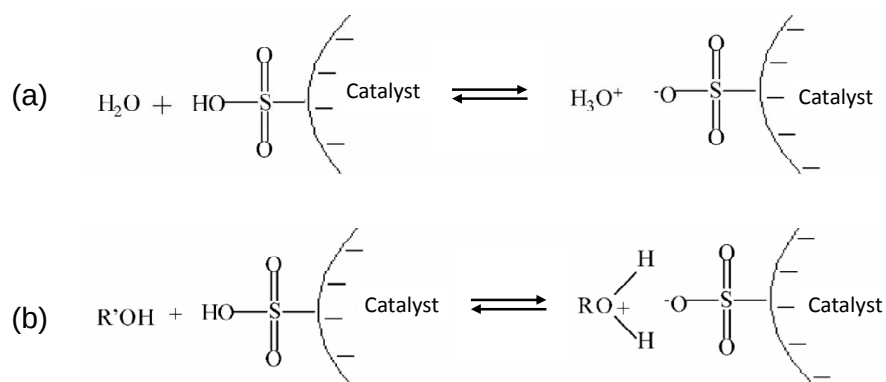


Figure 4. Competitive adsorption over the active sites of resins [53].

Another study conducted by Altiokka and co-workers [55] over Amberlite IR-120 proposed a Eley-Rideal model involving the reaction of isobutanol adsorbed on the acid sites with free acetic acid from the bulk solution, contrary to most of the works. This was deduced from the following experimental observations: the initial reaction rate increases linearly with the acid concentration, but it is nearly independent of the alcohol concentration at high levels. In addition, the increase of water concentration lowers the initial reaction rate. The adsorption of solvent (dioxane) and ester were reported to be negligible. This mechanism was also proposed by Parida et al. [56] who worked on the esterification of acetic acid with various alcohols over zirconia supported silicotungstic acid. The assumptions of this work were based on previous studies related to the formation of butylacetate in liquid phase catalysed by solid acids. Experimental data was adjusted to an equation rate having first and zero orders with respect to acetic acid and *n*-butyl alcohol.

A different approach was presented by Barbosa and co-workers for the esterification of acetic acid with methanol over commercial tungstated zirconia [57]. This work assumed three types of mechanisms, which were discarded on the basis of experimental data. The authors determined that the reaction mechanism was better described by the Eley-Rideal model, based on the absence of a maximum value of the esterification rate within the studied concentration range and previous works concerning the poisoning of acid sites [49].

Studies concerning the esterification of acetic acid with amyl alcohol over ion exchange resin: Purolite CT-175 [58] and Dowex 50Wx8-100 [59] stated that the Langmuir-Hinselwood modified model, corresponding to dual-site kinetic calculations, fitted better to the experimental data than the Eley-Rideal model. It was assumed that the adsorption of acetic acid and amyl acetate over the resins was negligible compared to that of water and alcohol whose affinity for the resin was stronger.

All the previous studies consider the Brønsted acid sites as unique active sites for esterification. However, there are studies which present satisfactory esterification rates using Lewis acid catalyst. Solvent free esterification between benzoic acid and ethanol has been conducted over SiO_2/ZnCl solids [60]. The mechanism presented by the authors is based on a conventional homogeneous mechanism where the Lewis acid sites play the role of a proton. Another esterification conducted over alumina, tin oxide and doped alumina with a mix issued from soybean oil (linoleic acid, 52%; oleic acid, 24%; palmitic acid, 14%; stearic acid, 4%; and other acids, 6%) and methanol in an autoclave showed that Lewis acids were active catalysts for this reaction [61]. The author revisited the esterification mechanism presented elsewhere [62]. This mechanism established that methanol reacts with the metal oxide, producing methoxide and hydroxyl groups. Then, the fatty acid reacts with the hydroxyl group producing water, which leaves the metal centre. Intramolecular attack on the carbonyl group by the methoxide ligand produces the desired

ester and restores the starting metal oxide (Figure 5). The most active catalysts for esterification were alumina and tin oxide, which also present the lowest acid site density. This behaviour was explained by the lower effective coordination of the intermediates and the produced ester species which favoured the last step of the catalytic cycle.

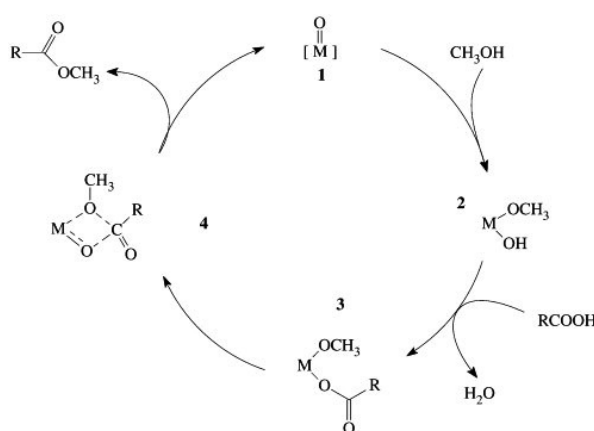


Figure 5. Esterification route via Eley-Rideal model proposed by Mello and co-workers [61].

In summary, the esterification reaction rates depend on several parameters such as temperature, pressure, carboxylic acids and alcohol used, their molar ratio and the nature of the catalyst participating in the reaction.

Glycerol acetylation

Concerning the esterification of glycerol, inorganic materials functionalised with sulphonic groups $\text{-SO}_3\text{H}$ have attracted much attention. Functionalised mesoporous silica-type SBA-15 showed high selectivity and conversion in the acetylation of glycerol [63].

Moreover, this solid could be reused, although a regeneration step is required [63]. Mesoporous silica MCM-41 sulphonated and functionalised with different alkyl chains (methyl, ethyl, propyl and phenyl) presented a good combination between the hydrophobic character of alkyl groups and the acidity of $\text{-SO}_3\text{H}$ species, thus favouring the selectivity to monosubstituted glycerol in the esterification of lauric and oleic acids. Nevertheless, the recyclability of these materials remains unclear [64-66]. The application of these solids at industrial scale presents a drawback related to the high cost of the copolymer involved in their preparation and to the complexity of the functionalisation process [11]. Studies comparing the different performances of Amberlyst-15, montmorillonite K-10, niobium oxide and zeolite HZSM-5 and H-USY have been published [67]. Amberlyst-15 showed the best catalytic activity in terms of conversion of glycerol (result expressed in acetic acid conversion) and selectivity to triacetin. Liao et al. compared the behaviour of Amberlyst-15 and Amberlyst-35 ion exchange resins and HY and HZSM-5 zeolites [11]. For their experiments, the reaction conditions were set to lead to a selective production of triacetin. Under these conditions, the Amberlyst-35 could be recycled without losing catalytic activity. The combinations of Starbon[®] (mesoporous carbon material derived from starch with sulphonic functions) and the use of microwave radiation, allowed an almost complete conversion of glycerol in presence of acetic acid [68].

Even if the most active materials are those whose acid sites consist of functions based on sulphonic acid, solids presenting different nature such as heteropolyacids can also catalyse the glycerol acetylation. Dodecamolybdophosphoric acid ($\text{H}_3\text{PMo}_{12}\text{O}_{40}$), immobilised in zeolites NaUSY presented an acceptable conversion and selectivity values. The activity decreased slightly during the first use but remained constant in the following applications [69]. The same authors also tested the catalytic performance of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ immobilised on silica by wet impregnation and sol-gel methods. The catalysts prepared by sol-gel have proven to be the most active. Moreover, the determination of optimal working conditions and stability tests were performed [70]. Supported heteropolyacids on activated carbon has been also tested in this reaction leading to satisfactory yields [71].

Esterification is an equilibrium reaction, thus to direct the reaction equilibrium towards the products a reagent is always used in excess. This reagent is generally the carboxylic acid whose cost is lower compared to alcohol [11]. In the case of glycerol acetylation, the excess reactant is acetic acid, whose purpose is maximising the selectivity towards triacetin.

OBJECTIVES OF THE THESIS AND STRATEGY APPLIED

Main objectives

In this work, the main objectives, concerning the glycerol acetylation reaction, aim to answer the following questions:

- (i) Is it possible to carry out the glycerol acetylation reaction in presence of a large excess of glycerol in order to consume the latter which is the low value molecule?
- (ii) Otherwise, could the equilibrium of the reaction be shifted towards the products by using an excess of glycerol, instead of an excess of carboxylic acid?
- (iii) Is it possible to modify the selectivity to the different products under the defined reaction conditions by using different catalysts?

The above, to the best of our knowledge, has not been reported in literature. Moreover, in this work the solid acid catalysts usually employed for esterification with monoalcohols are also tested in presence of a polyalcohol such as the glycerol whereas works in the literature concerning glycerol acetylation, only used ion exchange resins, sulphonated solids and immobilised heteropolyacids.

We must remember that each catalyst must fulfil requirements such as low internal diffusion problems, optimal surface characteristics, thermal stability, high resistance to leaching and recyclability. Furthermore, the catalytic performances of a solid depend on the characteristics and nature of the material and on the chemical reaction studied. Thus, there is an inherent specificity related to the whole reaction system. Moreover, the recyclability is directly related to the solubility of the active species which depends on the reaction conditions and on the composition of the reactive medium.

This research project was focused on the study and development of heterogeneous catalysts for the esterification of acetic acid with an excess of glycerol.

The main objectives, concerning the use of catalyst in glycerol acetylation, are:

- (i) To identify and synthesise solid acid catalysts having suitable properties (texture, structure and acidity) for glycerol acetylation leading to a satisfactory acetylation yield.**
- (ii) To analyse the solids recyclability during several successive esterification runs, namely, the leachability of active species and the presence of eventual homogeneous catalysis. Moreover, the deactivation of the catalyst due to the adsorption of water or other products occurring during the acetylation reaction is**

also studied, as well as, the different regeneration steps needed for the recovery of the initial performances of the solid.

- (iii) Ultimately, to understand the phenomena occurring in the esterification reaction (reaction mechanism, effect of acidity in the reaction, identification of active sites etc.).**

Strategy

This work provides a comparative study of the catalytic performances of a large scope of acid solids in glycerol acetylation conducted with a large excess of glycerol. To our knowledge, such a systematic study has not yet been reported in open literature. The synthesis and characterisation of catalysts required for the processing of glycerol-acetylated molecules in liquid phase was the main point of this thesis.

Briefly this research addresses the following issues presented in the different chapters:

Chapter 1 is related to the experimental techniques used for the synthesis of the catalysts and their physicochemical characterisation. Chapter 2 presents the experimental parameters applied to the catalytic test in liquid phase.

In Chapter 3, an experimental approach based on an initial broad screening in order to find the adequate catalyst for our reaction is presented. The selected families of solid acids studied in Chapter 3 are: niobium oxide supported on silica (Nb-SA), aluminium phosphates (PA), tungstated and sulphated zirconia (WZ and SZ). These solids have been reported to be active in the presence of monoalcohols and carboxylic acids and in transesterification reactions. The advantages of these solids are: the well known synthesis and characteristics and low production cost. The aim of this chapter is to determine which type of solid presents the best catalytic performances in glycerol acetylation. From this chapter, it can be seen that only sulphated zirconia samples are active in the esterification reaction likely due to the presence of active Brønsted acid sites on the surface.

Chapter 4 focuses on the different parameters that lead the sulphated zirconia samples to a high esterification yield. A correlation between their acidic properties and the esterification yield is presented. Recyclability properties and the presence of homogeneous catalysis possibly due to leached species are also studied. From recyclability tests, it can be concluded that sulphated zirconia samples although active are not recyclable in our system.

The research is thus directed towards the use of immobilised heteropolyacids in the esterification reaction. Heteropolyacids (HPA) possess strong Brønsted acidity and very high solubility in polar media. They show higher activity and lower toxicity than sulphuric acid in esterification reactions. With the purpose of avoiding the

drawbacks of the homogeneous catalysis the immobilisation of these substances over oxide carriers or inside matrixes is necessary. In Chapter 5, the study concerning HPA consists in a comparison between two different synthesis methods for immobilising HPA: wet impregnation and sol-gel technique, over two different matrixes, namely SiO_2 and ZrO_2 . As far as we know, this was not reported yet in the literature. Again, a correlation between the nature of the solids and the catalytic performances in glycerol acetylation is discussed.

Due to the absence of catalytic effects from immobilised heteropolyacids, the research was finally focused on commercial ion-exchange resins which to the best of our knowledge have not been tested in glycerol acetylation conducted in presence of a large excess of glycerol (Chapter 6). The catalytic performances of macroreticular and gel resins are compared, while the optimisation of the operational conditions, recyclability and pre-treatment steps are analysed. These solids stand also as reference materials for the previously cited catalysts. The use of ion exchange resins concludes the study; they showed high catalytic activity, good recyclability properties and low deactivation by water adsorption.

PART II: EXPERIMENTAL

This section compiles all the experimental details. In Chapter 1, the catalysts preparation and the summary of the principal physicochemical characterisations applied to the solids are described. It should be remarked that this section includes the techniques applied almost systematically to all the studied solids (N_2 -adsorption-desorption, XRD, ICP), but also techniques that are only punctually used for some specific solids (FTIR, XPS and acidity measurements). However, details concerning the latter techniques will be given in the corresponding sections for the sake of clarity.

Finally, the description of the esterification reactions, from the standard tests to recyclability cycles, is presented in Chapter 2. Once more, specific details will be given or occasionally repeated in the corresponding sections for clarity.

CHAPTER 1: CATALYSTS PREPARATION AND PHYSICOCHEMICAL CHARACTERISATION

1.1. Catalysts preparation

1.1.1. Niobium oxide supported on commercial silica-alumina (Nb-SA)

Different samples of catalysts based on supported niobium oxide were obtained by wet impregnation, varying the Nb mass composition. 10 g of commercial silica-alumina (catalyst support grade 135, Aldrich) previously calcined at 550 °C 12 hours in air were suspended in 100 ml of distilled water where a quantity of ammonium niobate (V) oxalate hydrate, $(\text{NH}_4\text{NbO}(\text{C}_2\text{O}_4)_2 \cdot x(\text{H}_2\text{O}))$, 99.99% Aldrich) was diluted. After stirring the mixture for 2 hours, the excess of water was removed under vacuum at ~ 45 °C in a rotary evaporator. The resulting powder was dried overnight at 120 °C and then calcined at 300 °C in air for 6 hours (heating rate 10 °C/min). This calcination temperature leads to a good compromise between the high acidity of the catalyst and the anchoring strength of niobium species on the support [72].

The nominal loading of the samples expressed in niobium was 2.5, 5, 7.5, 15 and 30 %_{wt} that correspond to loadings equal to 3.6, 7.2, 10.7, 21.5 and 42.9 %_{wt} in niobium oxide. These samples are named as follows: «NbxxSA300», where «Nb» stands for niobium oxide,

Part II: Experimental

«xx» is the loading of Nb expressed in %_{wt}, «SA» corresponds to silica-alumina and «300» is the calcination temperature. Abbreviated nomenclature could be also be used as «Nbxx».

1.1.2. Amorphous aluminophosphate (PA)

Aluminophosphate solids were prepared by a hydrogel method [73-74]. The P/Al molar ratio was modulated in order to obtain the values 1, 0.66 and 0.33. The aluminium salt, $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (Aldrich, 99%) was dissolved in an aqueous solution of H_3PO_4 2M (Fluka, 85%) at 0 °C. At this temperature, ammonia (Merck, 25%) was slowly added to the solution under mechanical stirring (anchor shaped stirrer) until pH = 1.3 is reached. Thereafter, three moles of propylene oxide ($\text{C}_3\text{H}_6\text{O}$; Aldrich, 99%) per mole of desired product (AlPO_4) were added very slowly until a pH value of 2.5. The reaction mixture was allowed to stand at room temperature to form a gel. The gelation time was influenced by the P/Al molar ratio. The gel obtained was washed three times with two volumes of isopropanol ($\text{C}_3\text{H}_8\text{O}$, technical grade) per volume of gel through 30 minutes under magnetic stirring; separation of the washed gel from the solvent was made by centrifugation. Finally, the gel was dried in an oven at reduced pressure (1.33 Pa) at 110 °C for 15 hours. The resulting powder was grounded and sieved to obtain grains smaller than 500 μm to facilitate the burning of organic species. The calcination was performed in air for 3 hours at 650 °C with a temperature increase equal to 5 °C/min. During this step, the residual organic solvents were removed and the

final oxide was obtained [74]. These solids are denoted by «PA» for aluminium phosphate, followed by the P/Al nominal molar ratio (1, 0.66 or 0.33).

1.1.3. Tungstated zirconia (WZ)

Tungstated zirconia samples were obtained by two different techniques in order to compare the final properties of the solids.

The main difference between the wet impregnation and the co-precipitation technique is that in the latter the tungsten salt was dissolved in the same solution where the zirconium oxide was synthesised. Thus the solid obtained could be a priori considered as a bulk catalyst and not as a supported solid. This could influence the resistance to leaching of the tungsten species as they are in principle in the network of the zirconium oxide.

1.1.3.1. Tungstated zirconia obtained by wet impregnation technique (WZ-WI)

A desired quantity of ammonium metatungstate pentahydrate ((NH₄)₆H₂W₁₂O₄₀.xH₂O, 99% Fluka) was dissolved in distilled water and added to hydrated zirconia (HZ) in order to obtain a homogeneous slurry (0.4 ml precursor solution/g HZ solid). This slurry was dried in an oven at 120 °C overnight. The powder was divided in two different fractions which were calcined at 500 or 700 °C in air for 3 hours, with a temperature increase equal to 10 °C/min. Nominal values of W

Part II: Experimental

loading were fixed at 6, 15 and 25%_{wt} which correspond to 7.57, 18.92 and 31.53 WO₃%_{wt}.

The nomenclature for the samples is: «WZxxWItt» where «WZ» stands for tungstated zirconia, «xx» is the W nominal loading in %_{wt}, «WI» stands for wet impregnation technique and «tt» corresponds to the thermal treatment temperature: «D» meaning that the samples has not been submitted to a calcination step.

The hydrated zirconia «HZ» used as support was synthesised as follows: the precursor, zirconium (IV) oxychloride octahydrate (ZrOCl₂.8H₂O) was dissolved in distilled water (25 g/150 ml). A solution of aqueous ammonia (NH₃aq) 25% was added drop wise until pH=10-10.5, while stirring vigorously. The mixture was allowed to stand for 22 hours and then it was filtered and washed until no Cl⁻ ions were detected by the Mohr test. The solid was dried at 120 °C overnight and then it was grounded and sieved (particle size <200 µm).

1.1.3.2. Tungstated zirconia obtained by co-precipitation technique (WZ-CP)

In the same manner, samples containing W loadings equal to 6, 15 and 25%_{wt} were prepared by the co-precipitation method. A solution of zirconium (IV) oxynitrate hydrate (99%, Sigma-Aldrich) and a solution of ammonium metatungstate hydrate were prepared with distilled water in order to obtain a concentration equal to 0.17 M for each solution. The pH of the ammonium metatungstate hydrate

solution was adjusted to 10 with a solution of aqueous ammonia (NH₃aq) 14%. The solution of zirconium (IV) oxynitrate hydrate was added dropwise maintaining the pH at the initial value. The resulting white precipitate was allowed to stand 24 hours at room temperature, and then it was filtered and dried in an oven at 120 °C under vacuum (1.3 Pa) overnight. The solid obtained was grounded and divided into two fractions that were calcined at 500 or 700 °C in air for 3 hours, with a heating rate equal to 10 °C/min [75].

1.1.4. Sulphated zirconia (SZ)

The sulphated zirconia solids were synthesised by one-step sol-gel technique. A mixture of zirconium propoxide (70% wt. in 1-propanol, Aldrich) and 1-propanol (> 99.5%, Acros Organic) with a concentration of Zr in propanol equal to 1M was prepared. Sulphuric acid (96%, Merck) was added dropwise under continuous mechanical stirring (200 rpm, propeller type stirrer in PTFE) and at room temperature. The quantity of sulphuric acid was calculated according to an initial atomic ratio S/Zr=0.5. Sulphuric acid was used both as the sulphating agent and as the catalyst for the polycondensation of the gel. After 1 hour under stirring, a defined quantity of distilled water was added in order to accomplish the desired hydrolysis molar ratio H₂O/alkoxide, hereafter abbreviated H, which was modulated from 0 to 6. The gelation time increased when the hydrolysis ratio decreases and is about 30 minutes for high ratios of hydrolysis and 90 minutes for lower H ratios. The gels obtained were dried at 120 °C for 12

hours, and then calcined in air at 560 °C for 3 hours (heating rate 3.5 °C/min). Catalysts are denoted «SZH», where «SZ» stands for sulphated zirconia and «H» represents the hydrolysis ratio employed.

1.1.5. Immobilised heteropolyacids

1.1.5.1. Immobilised heteropolyacid by sol-gel method (Zr-SG and Si-SG)

The tungstophosphoric acid (HPW, $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$, Fluka) immobilised in zirconia samples were prepared by one-step sol-gel technique by hydrolysis of zirconium (IV) propoxide (70% in propanol, Aldrich) with distilled water. After stirring the mixture (1mole Zr/l propanol) for 90 min at 40 °C under nitrogen atmosphere, the heteropolyacid dissolved in a mixture of distilled water and propanol (50 % vol.) was added slowly. The amount of water was fixed in order to reach a hydrolysis molar ratio $\text{H}_2\text{O}/\text{Zr}$ equal to 1. The gel obtained was aged 5 days and then dried at 80 °C under vacuum. The resulting powder was divided into different fractions which underwent different treatments: calcination in air for 3 hours at 200 °C or Soxhlet extraction with distilled water for 24 hours at approximately 70 °C.

The tungstophosphoric acid immobilised in silica solids were synthesised by the sol-gel technique proposed by Izumi and co-workers [76], with some modifications [70]. A mixture of water (2.0 mol), ethanol (0.2 mol) and heteropolyacid was added slowly to

tetraethyl orthosilicate (0.2 mol) at 80 °C under nitrogen atmosphere. After gelation, the mixture was dried at 80 °C under vacuum. A fraction of the resulting powder was washed with distilled water for 24 hours with a Soxhlet apparatus at approximately 70 °C.

Tungstophosphoric acid immobilised samples were named as: «Nn-xx-SG-ht-S», where «Nn» is the matrix (Zr for zirconia and Si for silica), «xx» is the nominal loading of heteropolyacid expressed in %_{wt}, «SG» stands for sol-gel method, «tt» is the thermal treatment applied (D for dried samples at 120 °C and C for calcined samples at 200 °C in air) and «S» stands for Soxhlet extraction.

1.1.5.2. Immobilised heteropolyacid by wet impregnation technique (Zr-WI and Si-WI)

Zirconia and silica solids were prepared by the previously described sol-gel method without adding HPW, and used as supports for the wet impregnation technique. For samples obtained by wet impregnation method (WI), the support was suspended in distilled water in which a quantity of HPW was dissolved (1 g support/ 50 ml of water). The mixture was stirred for 2 hours, and then water was eliminated by vacuum drying in a rotary evaporator. The resulting powders were dried in an oven at 120 °C overnight. A fraction of the obtained solids was washed by Soxhlet extraction with distilled water at approximately 70 °C during 24 hours.

The nomenclature for wet impregnation samples is the same as for sol-gel samples but «WI» is added to indicate the synthesis method as follows: «Nn-xx-WI-tt-S».

1.2. Physicochemical characterisation

1.2.1. Textural properties measurements

N₂-physisorption experiments were carried out on a Micromeritics Tristar 3000 at -196 °C working with relative pressures P/P_0 in the range of 10^{-2} to 1.0. Samples were degassed overnight under vacuum (0.67 Pa) at 150 °C unless specified otherwise. The specific surface area was calculated from the adsorption isotherm in the 0.05-0.30 P/P_0 range using the BET method. The error of the surface area measurement is estimated at 5%. The pore size distribution, mean pore diameter and pore volume were determined by the BJH method (Barrett, Joyner and Halenda) exploiting the desorption data. The micropore volume was estimated using t-plot analysis in the 0.25-0.5 nm range. These parameters are applied to all measurements unless specified otherwise in the corresponding section.

1.2.2. Crystallographic structure

X-ray diffraction (XRD) technique was used to determine the crystalline structures of the different solids. Measurements were performed on the fresh samples with a Siemens D5000 diffractometer

equipped with a source providing 1.6 kW and using the $K\alpha$ radiation of Cu ($\lambda = 1.5418 \text{ \AA}$). The 2θ range was scanned between 5° and 90° at a rate of $0.02^\circ/\text{s}$. In every case, the diffraction lines were compared with those reported in literature.

1.2.3. Bulk chemical composition

The mass composition of the samples was measured by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) on an Iris Advantage apparatus from Jarrell Ash Corporation.

The principle of the technique is based on the formation of plasma in a flow of inert gas. This plasma is formed from an electrical discharge created in a stream of argon gas flowing through a series of concentric quartz tubes (torch) surrounded by a coil (inductor). The passage of an alternating current in the inductor produces an electromagnetic field that generates induced currents. The excitation of argon gas supplies through the acceleration of electrons, a plasma temperature of 10000 K. Previous to the analysis, samples were decomposed via sodium peroxide fusion in glassy carbon crucibles. The sample undergoes an excitation of atoms and ions due to decomposition, atomization and ionization phenomena. These atoms, while relaxing, emit a characteristic light which is transmitted through the optical system to the detector (CID type, collision-induced dissociation) which covers wavelengths from 175 to 800 nm. The detection limits of trace elements vary depending on the element, they are in the order of ppb or ten ppb.

1.2.4. Surface chemical composition

X-ray photoelectron spectroscopy (XPS) provides information on the elemental composition and oxidation state of the elements present on the surface of a sample, within the 2 to 10 nm depth.

XPS analysis was performed on a Kratos Axis Ultra spectrometer (Kratos Analytical - Manchester - UK) equipped with a monochromatized aluminium X-ray source, powered at 10 mA and 15 kV ($K\alpha$ line with an energy of 1486.6 eV) and an eight channeltrons detector. A workstation Sun Ultra 5 controlled the device and acquired the data. Prior to analysis, the samples were pressed into stainless steel cups and inserted the day before scanning in the pre-treatment chamber of the spectrometer at room temperature, (10^{-6} Pa). The size of analysed area was 700 μm x 300 μm . The pass energy was set at 160 eV for the wide scan and 40 eV for individual spectra. The detection angle was fixed at 0 °. In these conditions, the full width at half maximum (FWHM) of the Ag 3d_{5/2} peak of a standard silver sample was about 0.9 eV. The lenses were used in hybrid mode as a combination of electrostatic and magnetic lenses. The C1s spectrum was recorded twice, once at the beginning of the sequence of the spectra and once at the end, so as to check the stability of charge compensation in function of time and the absence of degradation of the sample during the analyses. Charge stabilisation was achieved by using the Kratos Axis device. The charge balance plate was set at -2.8 eV and the current of the filament was fixed at 1.8 A. The C-(C,H) component of the C 1s peak of carbon was fixed to 284.8 eV to set the

binding energies. Data treatment was executed with the CasaXPS program (Casa Software Ltd, UK), some spectra were decomposed with the least squares fitting routine provided by the software with a Gaussian/Lorentzian (70/30) product function and after a linear baseline subtraction.

1.2.5. Fourier Transform Infrared Spectroscopy

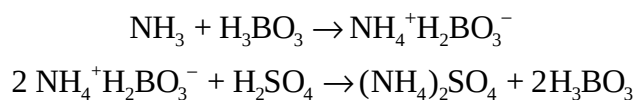
Fourier Transform Infrared Spectroscopy (FTIR) is an analytical technique which measures the radiation absorption as a function of frequency. The obtained spectrum provides specific information about chemical functions as they absorb characteristic vibration frequencies when exposed to infrared radiation. This technique can be applied to organic and inorganic materials.

FTIR spectra were recorded in transmission mode using a spectrometer IFS55 Equinox (Bruker) equipped with a DTGS detector. The spectra were obtained by recording 100 scans between 400 and 4400 cm^{-1} with a resolution of 4 cm^{-1} . The samples were analysed after dilution in KBr (Janssens Chimica 99 +%) by a weight factor of 50. The characteristic absorption peaks of the different chemical groups present were collected from literature.

1.2.6. Acidity measurements

1.2.6.1. Temperature programmed desorption of ammonia

Acidity properties of samples can be evaluated by temperature programmed desorption of ammonia (NH₃-TPD). Prior to TPD studies, samples were pre-treated at the desired temperature (usually the calcination temperature) for 1 hour in a flow of helium gas (Praxair, 60 ml/min). After the pre-treatment, the sample was cooled to 35 °C and then saturated with 5% anhydrous ammonia gas (Praxair, NH₃-He, 60 ml/min) for 1 hour. The physisorbed ammonia was flushed out by a flow of He (60 ml/min) at 35 °C. The ammonia desorption profile was monitored with a mass spectrometer equipped with a quadrupole (Balzers QMC 200) from 35 to 600 °C, with a heating rate equal to 10 °C/min. Three temperature zones were arbitrarily associated to the acid sites strength: weak (35 to 150 °C); medium (150 to 350 °C) and strong (350 to 600 °C). The NH₃ desorbed was neutralised in a boric acid solution (20 g/l) and quantified by back titration with a solution of sulphuric acid 0.005 M as presented here:



In addition, it was considered that each molecule of NH₃ adsorbed over the sample corresponds to one acid site, as represented in Figure 6.

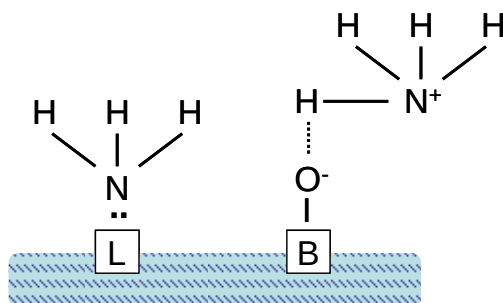


Figure 6. Schema of ammonia molecule adsorbed over a Lewis acid site (L) and over a Brønsted acid site (B).

1.2.6.2. Ammonia chemisorption

In order to evaluate the number of acid sites of the samples, ammonia chemisorption at 50 °C was performed in a Micrometrics ASAP 2010C apparatus (static volumetric adsorption analyser). Pre-treatments were performed at 120 °C for 2 hours under a helium flow of 30 ml/min. The analysis consists in performing adsorption isotherms of ammonia on the catalyst. The volume of ammonia adsorbed was measured at pressures of between $6.6 \cdot 10^{-4}$ and 1 atm. A first isotherm is performed in order to evaluate the volumes of ammonia physisorbed and chemisorbed at different pressures. After evacuation of the physisorbed NH_3 for 1 hour, a second isotherm was performed. The amount of chemisorbed ammonia at a temperature analysis is obtained after subtracting the first and second isotherms.

CHAPTER 2: CATALYTIC PERFORMANCES AND RECYCLABILITY

2.1. Standard test

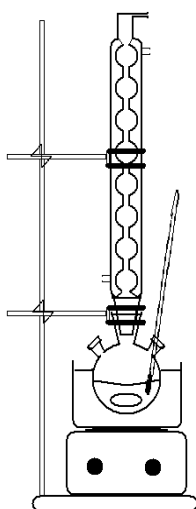


Figure 7. Representation of the batch reactor used for conducting the esterification tests.

Esterification reactions were carried out at 55 °C, unless otherwise specified, and at atmospheric pressure in a round bottom flask (100 ml) reactor equipped with a magnetic stirrer (~300rpm) and a refrigerator in order to minimise the losses of carboxylic acid. The temperature was maintained constant (± 1 °C) using an oil bath. The acetic acid (puriss. p.a., ACS reagent, $\geq 99.8\%$, GC/T, Fluka) concentration was 100 g/l of glycerol (puriss. p.a., ACS reagent, anhydrous, dist., $\geq 99.5\%$, Fluka) which corresponds to an initial molar ratio acetic acid: glycerol = 1:8.2; the catalyst concentration being

Part II: Experimental

6.25 g/l of glycerol. Therefore, the quantities used per run were: 3.8 ml of acetic acid, 40 ml of glycerol and 250 mg of catalyst.

The test procedure was conducted as follows: the catalyst was put in the reactor together with the glycerol and the mixture was brought to the reaction temperature. When the temperature was reached, acetic acid was injected. One minute after the injection, a sample was taken and analysed. This result was considered as the original chemical composition of the medium. This process was necessary to exclude the possibility that the catalytic measurements were interfered with the disappearance of acetic acid due to evaporation phenomenon during its injection.

2.2. Sample analysis

Samples of the reaction medium were analysed by gas chromatography in Varian CP-3800 with automatic injection (Autosampler Varian CP-8400) and equipped with a column of type Cp-Sil 8CB (50 m x 0.25 mm x 0.4 microns) Varian and a FID detector fuelled by hydrogen (30 ml/min) and dry air (300 ml/min). The carrier gas was helium (25 ml/min). The pressure was set at 1.7 atm. The temperature programme was fixed as follows: after maintaining the column at 84 °C for 2 minutes, a ramp of 4 °C/min was applied until reaching 184 °C. This temperature was kept for 2 min. The final temperature, 280 °C was reached after a ramp of 30 °C/min. The temperature program was accomplished in 27.20 min.

Chapter 2: Catalytic performances and recyclability

The injection volume was 0.5 μ l and the split ratio was set to 40, meaning that 40 parts of the sample were vaporised but only 1 part was introduced in to the column. The injector and the detector temperatures were fixed to 310 and 330 °C respectively.

As the injection of glycerol in the gas chromatography column resulted in a poorly defined peak, which influences variably the baseline of the chromatograph, the acetic acid and the esters produced were extracted before analysis in 1-heptanol (98%, Sigma Aldrich). The volume of the withdrawn sample was 0.4 ml. The extraction is performed with a volume ratio sample/1-heptanol = 1:3. O-xylene (98%, Aldrich) was used as internal standard (16.7 μ l/ml 1-heptanol). Then, the sample is mixed using a vortex (Lab-line Super-mixer) for 30 seconds and centrifuged (Heraeus Christ Biofuge A) 10 minutes at 6000 rpm. The upper phase was collected and injected into the gas chromatography. The retention times of different compounds are presented in Table 1.

Table 1. Retention times of the compounds analysed by gas chromatography on a column of type Cp-Sil 8CB.

Compound	Retention time (min)
Acetic acid	3.600
O-xylene	6.380
1-Monoacetin (1-MAG)	10.685
2-Monoacetin (2-MAG)	11.773
1,3-Diacetin (1-DAG)	15.050
2,3-Diacetin (2-DAG)	15.150
Triacetin (TAG)	18.585

2.3. Calibration curves

Calibration curves were calculated using different commercial compounds for determining the retention time and calculate the concentration of the different products participating in the reaction: a mixture of esters containing 40% of monoacetin (Monoacetin, 40%, Acros), diacetin (technical grade ~50%, Fluka) and triacetin (Glyceryl triacetate 99.0% Fluka) was used. Several injections were made in order to determine the stability of the extracted sample, the influence of the stirring time over the extraction yield. From these experiments (data not shown) it could be confirmed that in our conditions the analyses were stable and repeatable. Interaction test were also carried out with acetic acid and monoacetin (40%), in order to verify if the extraction in heptanol and the calibration were valid for the mixed samples and not only for the isolated compounds (carboxylic acid and esters). To do so, several samples were prepared with a determined quantity of acetic acid and esters and analysed in the gas chromatography. It could be concluded that the extraction in heptanol and the quantification of the samples was adequate and fitted correctly the experimental data.

2.4. Expression of the catalytic performances

In a closed system, the conversion is defined as the fraction of the limiting reagent that reacts to form a product. If we consider our system: a liquid phase reaction carried in batch mode, the conversion

can be defined as the fraction of reactant that is consumed during the reaction (assuming that losses of carboxylic acid are negligible). Mathematically, the conversion rate is expressed using the following formula:

$$\text{Conversion}_t(\%) = \frac{[\text{HAc}]_0 - [\text{HAc}]_t}{[\text{HAc}]_0} \times 100$$

Where $[\text{HAc}]_0$ is the initial concentration of carboxylic acid in the system and $[\text{HAc}]_t$ represents the concentration at a given reaction time, t . Concentrations are expressed in mol/g of sample.

Likewise, the yield expresses the amount of product obtained in the chemical reaction divided by the initial amount of limiting reagent. A stoichiometric factor is necessary to take into account the reaction stoichiometry. In our conditions, the esterification yield can be defined as follows:

$$\text{Yield}_t(\%) = \frac{[\text{P}]_t}{[\text{HAc}]_0} \frac{v_{\text{HAc}}}{v_p} \times 100$$

Where $[\text{P}]_t$ represents the concentration of product formed after a given reaction time, t ; v_{HAc} and v_p are the stoichiometric coefficients of the carboxylic acid and ester formed respectively. The value of the stoichiometric coefficients ratio is equal to 1 for mono-substituted esters, 2 for di-substituted esters and 3 for the fully substituted ester.

Generally, the results of the catalytic performances are presented by means of the reaction yield versus the reaction time. However, conversion graphics can be used to facilitate the discussion of the results.

Carbon balance results in an error near 20%, maybe due to losses of acetic acid during the injection or during the reaction, or to the production of some secondary substances that could not be identified.

Carboxylic acids present protons that lead to a pseudo-catalytic activity, for this reason, every catalyst performance is compared to the activity of the blank reaction, conducted in the absence of a catalyst.

2.3. Homogenous catalysis and catalyst recyclability tests

To identify the presence of leached species which could lead to an activity in the homogeneous phase and to analyse the reusability of the solid a cycle of tests called «Homogenous catalysis and catalyst recyclability tests» was conducted. The experimental procedure is represented in Figure 8.

These tests were carried out in the same conditions as the catalytic standard tests (250 mg of catalyst, 3.8 ml of acetic acid and 40 ml of glycerol) with some modifications. At a determined reaction time (before achieving the reaction equilibrium), the solid was

separated from the liquid medium by centrifugation using a Sigma 6K15 centrifuge (1500 rpm for 15 min, then 1000 rpm for 15 min). In one hand, the liquid medium was recovered and filtered (Whatman 6, filtration threshold: 3 μm) and kept under the reaction conditions. Aliquots were taken and analysed so as to identify the presence of homogenous catalysis in the reaction medium due to potential leached species.

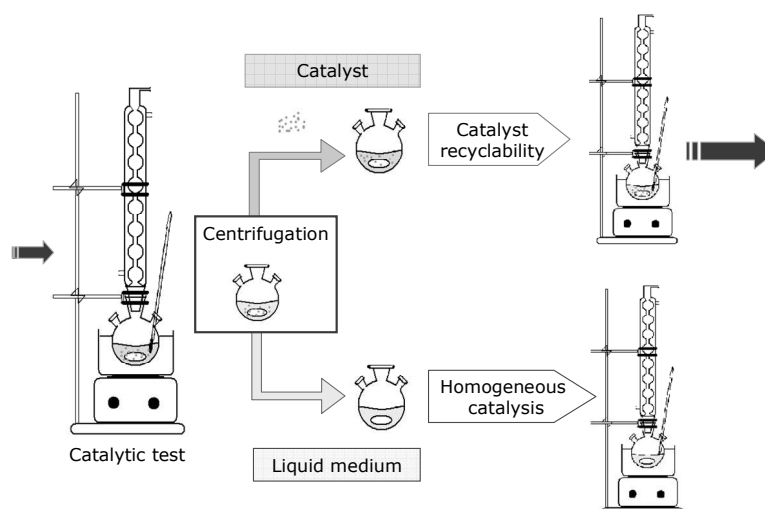


Figure 8. Schema of the experimental procedure applied for the homogeneous catalysis and catalyst recyclability tests. Dark arrows indicate that the schema is repeated several times for the same catalyst.

The comparison of the conversion rate of the separated liquid medium and the fresh liquid medium (blank) is performed by shifting the first point of the curve in homogeneous catalysis reaction to the point of the blank reaction with similar composition. On the other hand, the solid recovered by centrifugation was put in a fresh reaction medium without further pre-treatment. The volume of liquid accompanying the solid was less than 2 ml and was considered to have

Part II: Experimental

a minor effect over the esterification rate of the following run. Samples of the reaction medium were analysed periodically. After several cycles a complete catalytic test was performed to compare the final catalytic activity of the solid with the activity exhibited in the standard test.

PART III: RESULTS

Presentation of the complete studies of every family of solids analysed from the physicochemical properties to the catalytic performances in the esterification of acetic acid with glycerol.

CHAPTER 3A. GLYCEROL ACETYLATION OVER CATALYSTS OF DIFFERENT NATURE

Which is the main parameter needed to achieve a satisfactory acetylation yield?

In this chapter, the initial screening conducted in order to identify the solid exhibiting the best catalytic activity is presented. The families of solids studied are: niobium oxide supported on commercial silica-alumina, aluminophosphates, tungstated zirconia and sulphated zirconia. The synthesis of the solids is described in PART II EXPERIMENTAL Chapter 1. The physicochemical properties presented here are: texture, structure and chemical composition. The catalytic performances were tested in the acetic acid esterification with glycerol conducted at 55 °C. Reaction conditions are described in detail in Chapter 2.

3A.1. Introduction

There is a large number of solid acid catalysts that can be used in esterification reactions. For the initial screening, some families have been chosen based on a literature study which is presented in the following sections. It is important to remark that any of the solids presented in this chapter have been tested in an esterification reaction concerning a polyalcohol molecule such as glycerol, but according to the literature, they were all active in different esterification reactions performed with a monoalcohol.

3A.2. Niobium oxide supported on commercial silica-alumina

3A.2.1. Introduction

The niobic acid ($\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$) and its compounds are widely used in the field of heterogeneous catalysis due to their acidic properties. Acid strength of hydrated niobium oxide measured by Hammet indicator is $H_0 \leq -5.6$ which represents 70% of the strength of a sulphuric acid solution [77]. Moreover, this solid shows good catalytic performances in reactions involving water molecules, as its acidity properties can be improved by contact with water: dehydration and synthesis of alcohols, hydrolysis, polycondensation, esterification, liquid phase alkylation, oxidation and ammoxidation [78-82]. In gas phase esterification, niobic acid is resistant to deactivation by water

Part III: Results

and leads to higher catalytic performances than sulphated zirconia, alumina and silica [78, 82]. Acetic acid esterification with 1-decanol in liquid phase was accelerated better by niobic acid than by $\text{SiO}_2\text{-TiO}_2$ and $\text{SiO}_2\text{-Al}_2\text{O}_3$ [78, 83]. In recent decades, new synthesis routes and formulations have been performed (zeolites, MCM-41, mixed oxides Mo-V-Nb, carbides and sulphides of niobium) either to understand and master the properties of the catalysts or to meet specific applications principally in gas phase reactions [78-82, 84-85].

Treatments with phosphoric or sulphuric acid enhance the acid strength of niobic acid by forming a niobium phosphate or sulphate which present higher acidity and stability at elevated temperatures than the untreated solid [82]. This phenomenon leads to an improvement of the catalytic performances in organic reactions. Mixed oxides of niobium compounds can also show redox and photocatalytic properties [78-82, 86].

Several studies have been directed towards the elucidation of the structures formed by niobium species on the solid surfaces, the acidic properties and their catalytic role. The main parameters studied were the influence of the support used, the preparation method and the loading of Nb [87-90]. Wachs studied the acidic properties of bulk and supported niobic acid by Raman and IR of adsorbed pyridine [85]. Moreover, the stabilisation of the different surface species over bulk niobic acid prepared from aerogel, precipitated and commercial niobic acid were compared by Maurer and Ko [80, 91]. The aerogel preparation method leads to a porous network consisting of NbO_6

octahedra with Nb=O bonds, associated to strong Lewis acid sites. Carniti and co-workers studied the different acidity shown by niobium and niobium phosphate in presence of organic solvents such as methanol and cyclohexane [77].

Supports such as alumina and silica are further studied due to their ability to develop both Brønsted acid sites and Lewis in comparison to other oxides (magnesia, titania and zirconia systems) where only Lewis acid sites have been identified [82, 92]. Highly distorted surface NbO₆ octahedral sites in supported niobium oxide correspond to Lewis acid sites, while slightly distorted surface NbO₆ sites, as well as NbO₇ and NbO₈ sites are associated with Brønsted acid centres [93]. In general, the different surface niobium species that can be identified on oxide supports depend on the surface coverage: NbO₄ species are found at very low surface coverages ($\theta_{\text{Nb}} \ll 1$), NbO₅ species at intermediate surface coverages ($\theta_{\text{Nb}} < 1$), and surface NbO₆ species at surface coverages ($0.5 < \theta_{\text{Nb}} < 1$) [82]. More specifically, niobium species on silica obtained by the equilibrium impregnation method, varying the pH and the amount of precursor used, were present as isolated tetrahedral, as monomers, or as oligomers [89]. The existence of monomers, dimers, oligomers and clusters has been correlated to the catalytic performance in ethanol dehydrogenation [90]. Another work, revealed the presence of niobium oxide tetrahedra and distorted octahedra in niobium oxide supported on silica related to strong Lewis and weak acid sites respectively [88]. Three types of niobium oxide species were

Part III: Results

determined over alumina: NbO_4 monomers, dimeric and polymeric species Nb_2O_7 , and niobium acid [87].

Niobium-silicon mixed oxides synthesised by sol gel, presenting both Brønsted and Lewis acid sites, were active and recyclable in cyclooctane epoxidation with H_2O_2 in the presence of methanol as solvent [94]. Acid titration of Nb samples by 2- phenylethylamine ($\text{pK}_a=9.90$) performed in different solvents: cyclohexane (aprotic/apolar), and water (protic/polar), showed that the acidity was highly influenced by the presence of water. This was explained by the interaction of water molecules with the acidic groups at the surface of the solid preventing the interaction of the probe molecule. The effective acidity increased with niobium loading, as the niobium species are stronger than those of the silica phase [95].

Concerning esterification reactions, niobic acid calcined at 120-300 °C exhibited high catalytic activity and selectivity in gas-phase reaction between acetic acid and ethanol (temperature reaction 120-160 °C) [36]. The same study showed that these catalysts are more effective than ion exchange resins, $\text{SiO}_2\text{-Al}_2\text{O}_3$, HZSM-5 and solid superacids such as $\text{ZrO}_2\text{-SO}_4^{2-}$, $\text{TiO}_2\text{-SO}_4^{2-}$ and $\text{Fe}_2\text{O}_3\text{-SO}_4^{2-}$. Supermicroporous niobium oxide solids and $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ were tested in the esterification of acetic acid with ethanol at 70 °C. The study concludes that even if niobic acid was active in this reaction, microporous solids showed very similar catalytic performance as the self-catalysed reaction (without catalyst), due to diffusion problems inside the pores [96]. Niobium oxide supported on commercial silica-

alumina samples were tested in acetic acid esterification with several monoalcohols [37]. Two preparation methods were used: grafting and wet impregnation. Several characterisations were performed on the catalysts calcined at 800 °C. It was determined that this calcination temperature caused a decrease in the number of Brønsted acid sites, leading to a decrease in the catalytic performance of the solid. Solids prepared by the two synthesis methods and calcined at 300 °C in air exhibited similar Brønsted acidity and catalytic properties.

More recently, a study carried out by Brandão et al. revealed that $\text{Nb}_2\text{O}_5/\text{H}_3\text{PO}_4$ and $\text{Nb}_2\text{O}_5/\text{H}_2\text{SO}_4$ solids showed better activity in esterification than $\text{Nb}_2\text{O}_5 \cdot x\text{H}_2\text{O}$ and Nb_2O_5 [97]. An Eley-Rideal model was considered, where the adsorption of alcohol molecules proceeds over the Lewis acid sites. The lack of activity in the esterification of the untreated $\text{Nb}_2\text{O}_5 \cdot x\text{H}_2\text{O}$ was explained by the strong interaction between water molecules and the active site, hence, hindering the coordination of the alcohol [97].

Methyl esterification of oleic acid assisted by microwave heating was conducted over Nb_2O_5 and sulphated zirconia. Both catalysts presented similar esterification rates, but the recyclability properties of niobium oxide were higher than those of the sulphated zirconia sample [98].

Therefore, niobium oxide supported solids appear to be promising catalysts for glycerol acetylation. A series of Nb_2O_5

supported on commercial silica-alumina by wet impregnation were prepared varying the Nb content from 2.5 to 30%_{wt.}

3A.2.2. Solid characterisation

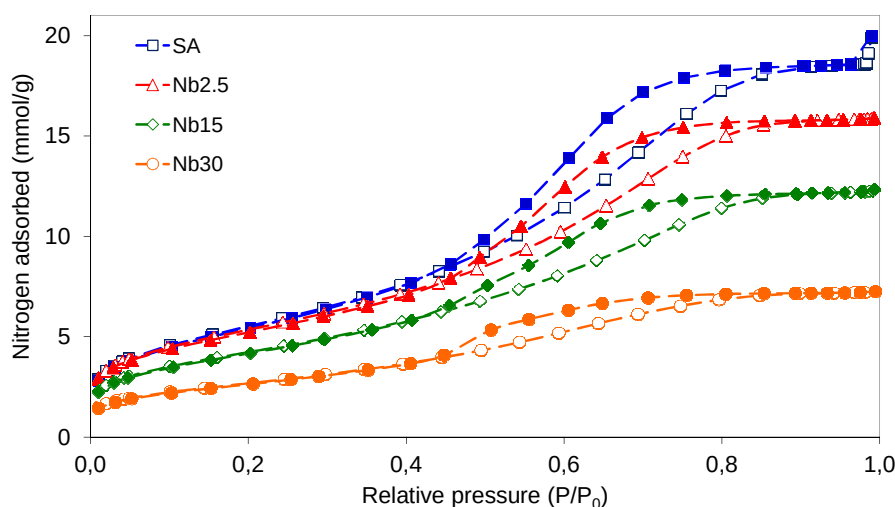


Figure 9. N₂-adsorption-desorption isotherms for niobium oxide supported on commercial silica-alumina samples. The isotherms of Nb5 and Nb7.5 are not shown for the sake of clarity. Open symbols are used for adsorption isotherms and the corresponding filled symbols are used for desorption isotherms.

As shown in Figure 9, all the Nb-SA solids present a type IV isotherm with both adsorption and desorption branches, very similar to the adsorption-desorption isotherm of the support. A decrease in the total surface area is observed when increasing niobium loading. In addition, the pore size and volume were also reduced. These results indicate a pore blockage by niobium oxide species. This is a typical phenomenon observed in solids prepared by the wet impregnation

technique. However, the obtained solids maintain the mesoporosity and a high surface area value. (Table 2).

Table 2. Textural properties of niobium oxide supported on commercial silica-alumina samples.

Sample	A _{BET} (m ² /g)	Pore volume (cm ³ /g)	Average pore diameter (nm)
Support	452	0.85	5.7
Nb2.5	434	0.53	4.1
Nb5	417	0.59	4.6
Nb7.5	406	0.54	4.5
Nb15	346	0.41	3.9
Nb30	218	0.24	3.6

XRD analyses confirmed that there was no formation of niobium oxide crystals after calcination at 300 °C. The support remained amorphous (figure not shown).

Table 3. Bulk chemical composition of niobium oxide supported on commercial silica alumina samples analysed by ICP-AES.

Sample	Nb loading (% _{wt})	Error (%)
Nb2.5	2.14	14.4
Nb5	4.39	12.1
Nb7.5	6.57	12.4
Nb15	12.77	14.9
Nb30	26.42	11.9

In our series of samples, the presence of water in the niobium precursor (NH₄NbO(C₂O₄)₂.x(H₂O)) was taken into account by considering x approximately equal to 10. Chemical composition of the samples is presented in Table 3. It can be seen that the error is always

below 15%, which agrees with literature where the final loading of supported niobium oxide is very close to the theoretical one [37].

3A.2.3. Catalytic activity

The catalytic performance in the esterification reaction is plotted as the esterification yield versus time and compared with the pseudo-catalysed reaction, that is to say, the reaction performed in the absence of catalyst (blank reaction). Under these reaction conditions, the points can be fitted to a straight line, meaning that the equilibrium of the reaction was not achieved at the end of the experiment. When the reaction was conducted in the absence of a catalyst, the final total esterification yield at 24 hours of reaction was about 20%, likely due to the activity of the acetic acid protons. Amberlyst-15 (dried overnight at 105 °C under vacuum) was used as a reference catalyst: after 20 hours of reaction the conversion of acetic acid obtained was equal to 95% and the acetylation total yield was close to 80% (see Figure 21). This may be reasonably regarded as the equilibrium point of the reaction.

Figure 10 displays the esterification yield of glycerol acetylation tests carried out in presence of niobium oxide supported on commercial silica-alumina samples. It can be observed that these solids lead to a lower esterification rate than the blank reaction, in both cases the equilibrium of the reaction is not achieved. In addition, the difference between the activity of the blank reaction and the tests in the presence of the Nb-SA solids diminishes when the Nb loading

increases. As the solids were stored after synthesis in a desiccator and used without further pre-treatment, another test (Nb7.5*) was carried out with a pre-dried sample (drying overnight at 120 °C in air). The drying of the solid before use did not result in an improvement of catalytic performance.

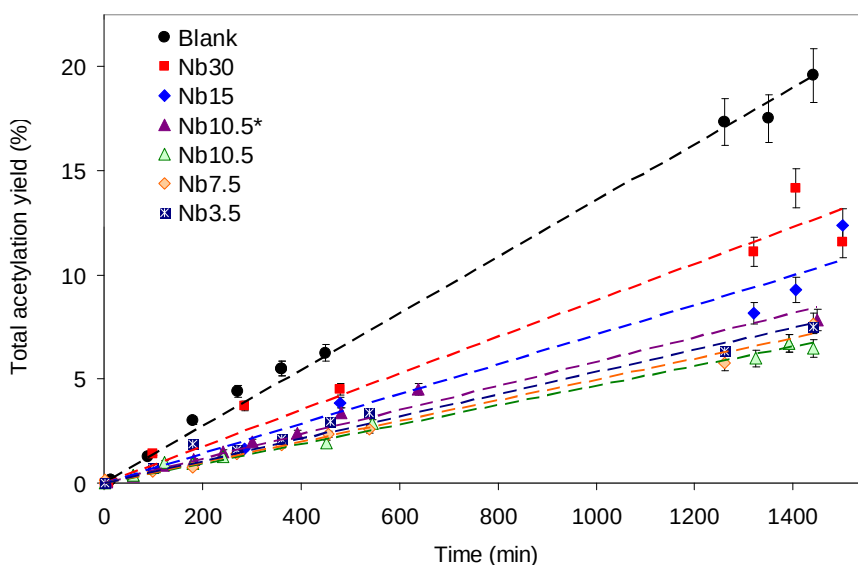


Figure 10. Acetylation yield in the esterification reaction conducted over niobium oxide supported on commercial silica-alumina samples at 55 °C. (*) sample dried overnight at 120 °C.

3A.3. Aluminophosphates

3A.3.1. Introduction

Aluminium phosphates present a high surface area, a hygroscopic character and acid properties [26]. The physicochemical

Part III: Results

properties of these solids can be modulated by the use of different synthesis methods (precipitation [99-100], citrate method [101] or sol-gel [102]), and the parameters applied (P/Al molar ratio, starting precursors, solvent, pH and calcination temperature [103]). Non stoichiometric aluminium phosphates are structurally stable in a wide range of P/Al molar ratio from 0.05 up to 2 [103-105]. Thermal and hydrothermal treated AlPO_4 present an equivalent stability close to those of zeolites [26] which allows to apply these solids to several organic processes: dehydration and dehydrogenation of alcohols [104], cracking and isomerisation reactions [106]. Ni, Pd, Pt supported on aluminium phosphates and mixed with other oxides (Al_2O_3 , SiO_2 , TiO_2 , ZrO_2 , B_2O_3) are often applied to hydrogenation of olefins in liquid-phase and to isomerisation reactions [104, 107-109]. The acid-base properties of the final solid can also be modulated by the substitution of Al by Fe, Mg, Ca, Ni and Zn among other elements [107, 110]. Moreover, the AlPO_4 acidity can be increased by treatment with SO_4^{2-} and F^- anions which generates stronger acid sites [111-112]. The latest research works have focused on AlPO_4 zeolite type often combined with silicates species forming solids called SAPO [26, 113-115].

Depending on the synthesis method and on the P/Al ratio used, the final solid is constituted by a mixture of oxides $\text{AlPO}_4\text{-Al}_2\text{O}_3$ [99-100] or an intimate mixture of aluminium and phosphate forming octahedral and tetrahedral species. When the P/Al molar ratio is close to 0, aluminium species are coordinated in tetrahedral and octahedral

structures that turn completely into a tetrahedral system, as soon as the amount of P increases [105]. The AlPOs structure can be considered to be similar to SiO₂ as both systems are based in oxygen tetrahedral coordination [100]. In addition, these structures follow also parallel polymorphic transformations [110]. The acidity of the surface varies with the P/Al ratio, being zero when P/Al = 2 and maximum when P/Al = 0.33 [104]. The acidity may be related to the presence of P-OH and Al-OH groups with protons attached to exposed oxygen (representing Brønsted acid sites) and to the presence of Al³⁺ cations and P atoms (Lewis acid sites) [112, 116-117]. In addition, aluminium can be linked to three types of hydroxyls [118].

The different performance of various aluminium phosphates and mixtures of AlPO₄, Al₂O₃ and SiO₂ have been studied in benzoic acid gas phase esterification with ethanol [119]. The authors concluded that the reaction mechanism can be explained via the Hougen-Watson model, where the rate-controlling step was the chemical reaction between the adsorbed benzoic acid and the ethanol in gas phase. Another study carried out over several substituted benzoic acids and ethanol under similar conditions validated this pathway [120]. Pure AlPO₄ and mixed oxides such as SiO₂-AlPO₄ and Al₂O₃-AlPO₄ have also been tested in esterification between acetic acid and amyl alcohol [121]. The best catalytic performance was reported for the Al₂O₃-AlPO₄ sample, due to its higher surface area. On the contrary, pure AlPO₄ showed high activity in the transesterification reaction. Better performances were obtained in liquid media where the formation of

by-products was avoided in comparison to the gas phase reaction [122-123]. More recently, AlPO and SAPO type zeolites have shown satisfactory performances in esterification of phthalic acid with 2-ethylhexanol and pentanoic acid with n-butanol [47]

In summary, many studies present the characteristics of AlPOs. However, to our knowledge, studies concerning the application of these solids for glycerol acetylation have not been published yet. As the textural and acidic properties of this type of solids are easily mouldable via the synthesis parameters, they offer very interesting possibilities which could be applied in our esterification reaction. That is the reason why three samples obtained by co-precipitation varying the P/Al molar ratio (1, 0.66 and 0.33) have been tested in glycerol acetylation.

3A.3.2. Solid characterisation

Aluminium phosphates are known for their high specific surface area. As it can be seen in Table 4, all the samples present a surface area greater than 350 m²/g. The obtained isotherms correspond to type IV characteristic of mesoporous materials (Figure 11). The hysteresis loop corresponds to type H2 as the adsorption branch presents a not so steep line while the desorption branch is nearly vertical which means that the presence of pores with narrow and wide section with interconnecting channels.

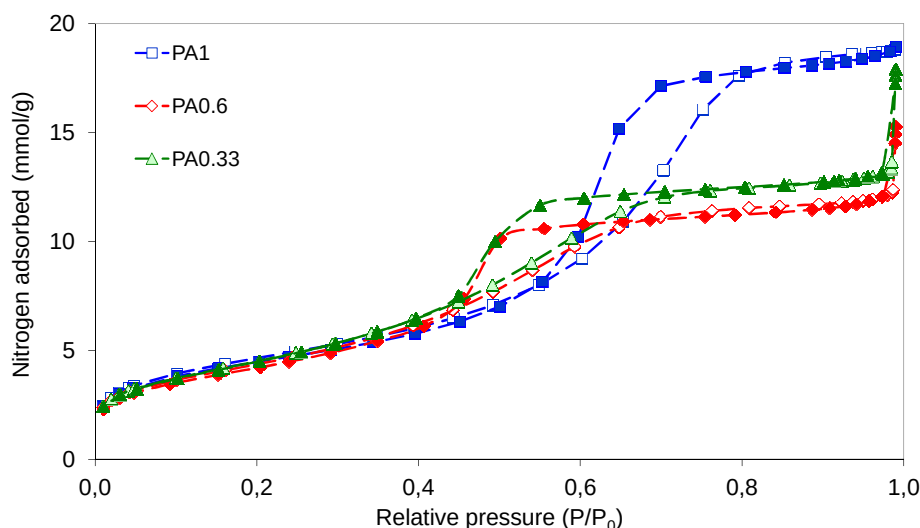


Figure 11. N₂-adsorption-desorption isotherms for AlPOs samples. Open symbols are used for adsorption isotherms and the corresponding filled symbols are used for desorption isotherms.

In Table 4, it can be seen that there is no clear influence of the P/Al molar ratio over the textural properties. However, in literature a surface area increase was reported for a diminution of the P/Al ratio value [100]. In our case, the values of surface area are quite similar and are included in the range of error of the apparatus. Moreover, they agree with values belonging to the solids synthesised by sol-gel [74, 105].

Table 4. Textural properties of the AlPOs samples.

Sample	A _{BET} (m ² /g)	Pore volume (cm ³ /g)	Average pore diameter (nm)
PA1	370.4	0.64	5.1
PA0.6	360.4	0.51	4.4
PA0.33	375.5	0.61	4.7

XRD analyses confirmed the amorphous structure of all samples.

The chemical composition of aluminium phosphate samples analysed by ICP-AES technique is equal to the nominal values as can be observed in Table 5. Thus, it can be concluded that the preparation method allows a good control of the final composition of the catalyst, and that there is no preferential leaching to the organic solvent during the washing step.

Table 5. Bulk chemical composition of AlPOs samples analysed by ICP-AES.

Sample	P loading (%_{wt})	Al loading (%_{wt})	P/Al molar ratio
PA1	21.5	18.6	1.00
PA0.6	16.7	23.9	0.61
PA0.33	11.7	30.6	0.33

3A.3.3. Catalytic activity

The variation of the P/Al molar ratio was used to modify the chemical properties of the solids and to study the influence of the obtained materials in the glycerol acetylation. However, it can be observed in Figure 12 that AlPOs performance in the esterification reaction are lower or equivalent to the reaction carried out in absence of solid. None of the solids achieved the acetylation yield shown by the pseudo-catalysed reaction. All the samples were amorphous and presented very similar texture; the only difference among them is the aluminium content. Thus, the chemical composition of the solid can be correlated to the esterification rate decrease: the higher the Al

content (the lower the P/Al molar ratio), the slower the esterification rate.

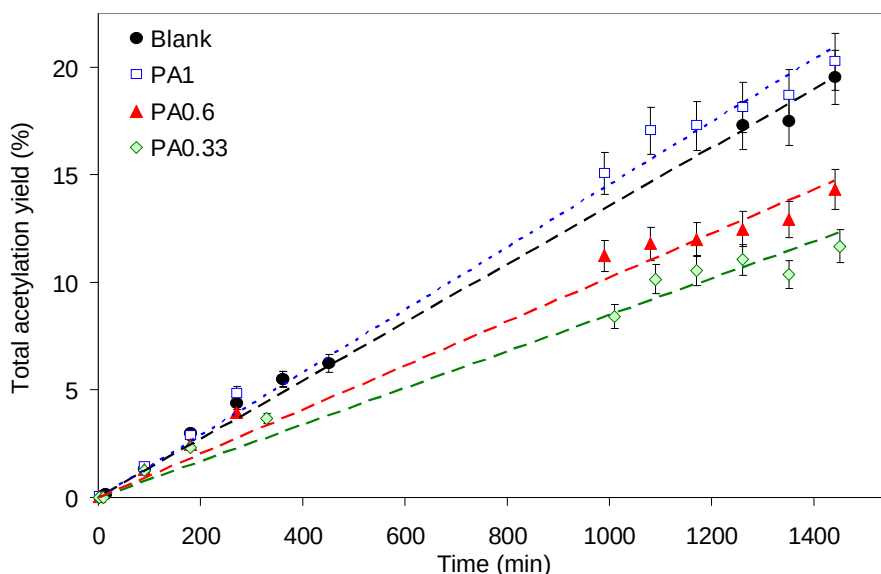


Figure 12. Acetylation yield in the esterification reaction conducted over AlPOs samples at 55 °C.

3A.4. Tungstated zirconia

3A.4.1. Introduction

Tungstated zirconia solids have been widely used for alkylation and isomerisation reactions of hydrocarbons due to their acidic character and properties as supports [124-130]. The characteristics of the final solids depend on the calcination atmosphere and temperature [38, 40, 131], the precursors used, and the preparation method: wet impregnation over zirconium hydroxide and zirconium oxide (the

Part III: Results

latter is obtained after calcination of zirconium hydroxide) [128, 132], equilibrium impregnation [133-134], co-precipitation [75] and sol-gel [135-136].

The structure of zirconia (amorphous, metastable tetragonal and metastable monoclinic) can be modulated by heat treatment [137-138]. The presence of a foreign element, such as W, on the surface or inside the matrix and its quantity can strongly influence the thermal stabilisation of the different structures of zirconia. The higher the thermal stabilisation, the higher the specific surface area of the final solid [38, 128, 139]. For example, tungstated zirconia synthesised by co-precipitation shows higher thermal stability, specific surface area and acidity properties than the same solid obtained by impregnation [140-141], which is mainly due to a larger number of interactions between W and zirconium hydroxyl groups [140].

Many authors agree that the optimal phase is a metastable tetragonal phase in the presence of polytungstates species, which allows a better catalytic performance. Thus, the monoclinic phase and the presence of WO_3 crystals are generally reported as inactive [40, 128]. However, these two phenomena were not studied separately, as generally they are held together at high calcination temperatures. It was found that the crystallinity of the support has no influence on the acidic properties of the catalyst and consequently the catalytic performance in hydrocarbon isomerisation [128]. The acidity and the amount of Brønsted and Lewis acid sites depend on the surface covering [132]. Moreover, even if the Lewis acid sites do not

participate directly in the reaction they can exert favourable inductive effects over Brønsted acid sites, increasing the acid strength of the latter [140, 142].

The correlation between the structure of zirconia, density surface of the W atoms of the solid with the acid and catalytic properties has been widely studied. Depending on the density surface of W atoms of various supports (Al_2O_3 , Nb_2O_5 , TiO_2 and ZrO_2) three types of tungsten species have been defined: monotungstates species WO_4 ; polytungstates WO_5/WO_6 ; microcrystals and crystals WO_3 [38, 132, 143]. The different W species formed by wet impregnation technique over amorphous $\text{ZrO}_x(\text{OH})_{4-2x}$ hydroxide [128] and commercial monoclinic zirconia [128, 130] were studied by XRD, Raman, XPS and TPR techniques resulting in very similar conclusions. For both supports, an evolution of the W surface species with the W loading was reported. For W loadings $< 9\%$ the tungsten atoms presented a tetrahedral coordination forming W^{6+} , W^{5+} monomeric or polymeric species. An increase in the loading led to the formation of polymeric octahedrally coordinated W^{4+} species. Above $15\%_{\text{wt}}$ loading of W, crystallites of WO_3 were detected [130]. The evolution of the W species structure was also correlated to a variation of the acidic properties of the samples [130]. In addition, some studies revealed a relationship between the reducibility of the species and the acidic properties [129, 134, 140]. Polytungstated species are more easily reducible than monomeric species, this result being explained by a stronger interaction between the monomeric species and the

Part III: Results

support [128]. Thus W^{6+} and W^{5+} species (W loading $<15\%_{wt}$) developed weak to moderate acidity, associated to Brønsted sites [129].

Concerning the esterification and transesterification reactions, tungsten oxides supported on zirconia have also exhibited good catalytic performances. Tungsten-based catalysts are less active than sulphated zirconia in the transesterification of triacetin with methanol. However, they showed higher recyclability properties [24]. Several esterification reactions reported in literature are the esterification of acetic, n-octanoic, and palmitic acid with low-molecular-weight alcohols [40, 144-145]. The study of the reaction kinetics of acetic acid esterification with methanol [57], leads to the conclusion that the mechanism is the same both in liquid and gas phase. This mechanism is based in a single-site mechanism, where the adsorbed protonated carboxylic acid reacts with the non adsorbed alcohol from the liquid or gas phase. Moreover, it was remarked that the presence of water created a competition with the reagents for the active sites. The influence of the calcination temperature has also been analysed on both triacetin transesterification and acetic acid esterification with methanol in gas and liquid phase [41]. The authors determined that the sample presenting the best catalytic properties for both reactions in both phases was the solid containing $16\%_{wt}$ of W and calcined at $800\text{ }^{\circ}\text{C}$. Even if Lewis and Brønsted acid sites were present on the solid, only Brønsted sites were active for the reaction. On the other side, the best catalytic performance for the palmitic acid esterification with

methanol was exhibited by a solid containing 5%_{wt} W calcined at 500 °C [40]. A linear correlation between the fraction of tetragonal phase present in the solid and the esterification rate was established. The presence of monoclinic crystals and tungsten oxide species resulted in an activity decrease also due to lower surface area. The influence of the calcination atmosphere (air or H₂) of ZrO₂ obtained by solvothermal method over the interaction between the Zr and the wet impregnate W species were studied for the esterification of acetic acid with methanol [131]. The studies showed that a better dispersion of monomeric tungstated species was obtained when the support was calcined under reductive atmosphere, resulting in a higher esterification rate than for the sample calcined in air. The same kind of solid was tested in the two-phase esterification of acetic acid and 1-heptanol [146]. In this case, zirconia obtained by solvothermal method calcined in reductive atmosphere or non-calcined was used as support for the W species. Conversion of acetic acid was higher for the non treated samples due to the presence of Zr-OH functions which provide Brønsted acid sites needed to accelerate the reaction. In the same reaction, zirconia modified with several elements (Bi, Si, Pb, and Al) was used as support. Nevertheless, the addition of these elements to the support promoted a decrease on the final solid acidity due to a strong interaction between the W species and the support, resulting in a decrease in the esterification rate versus the non modified sample [147]. Varying the solvent alkoxide molar ratio of the synthesis of ZrO₂, can also have very important effects over the acidity of the solids. It was demonstrated that a higher solvent/alkoxide ratio led to a

Part III: Results

higher amount of carbon residue on the support which induced a lower acidity on the samples. Therefore, the sample obtained with the lowest solvent/alkoxide ratio was the most active in acetic acid esterification with methanol.

In conclusion, various studies existing in literature showed that tungsten oxide supported on zirconia is an active catalyst in reactions that require an acid catalyst, such as alkenes isomerisation, transesterification and esterification. Despite its lower activity compared to other catalysts in the esterification reactions, it shows very favourable properties of recyclability which makes it an interesting solid to study in glycerol acetylation.

In this work, two synthesis methods were used: wet impregnation and co-precipitation method. Further details on the synthesis can be found in the preceding sections.

3A.4.2. Solid characterisation

N₂ adsorption desorption isotherms for the wet impregnated samples calcined at 500 °C and 700 °C are shown in Figure 13. Both calcination temperatures lead to solids presenting type IV isotherms with both adsorption and desorption sloping branches. The dried support presents a surface area equal to 248 m²/g with an average pore diameter of 25 Å. Even if the shape of the isotherms remains almost the same when increasing the calcination temperature, the measured

surface area diminished, which is a typical phenomenon for zirconia (Table 6).

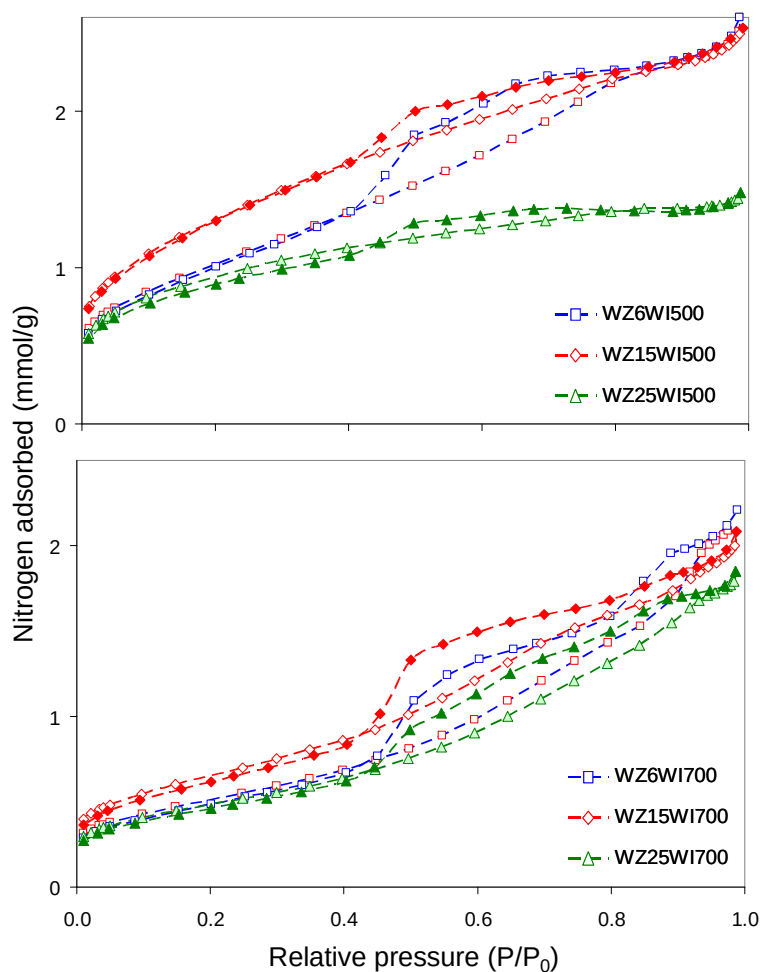


Figure 13. N₂-adsorption-desorption isotherms of WZ-WI samples. Open symbols are used for adsorption isotherms and the corresponding filled symbols are used for desorption isotherms.

Table 6. Textural properties of tungstated zirconia samples obtained by wet impregnation technique.

Sample	A_{BET} (m²/g)	Pore volume (cm³/g)	Average pore diameter (nm)
WZ6WI500	83.4	0.08	3.7
WZ6WI700	41.6	0.07	6.4
WZ15WI500	105.5	0.07	3.3
WZ15WI700	52.7	0.07	4.3
WZ25WI500	72.8	0.04	2.9
WZ25WI700	38.8	0.06	4.9

Comparing the results obtained for the wet impregnated samples with those corresponding to the WZ-CP samples it can be seen that except for one sample (WZ25CP-700), the co-precipitation leads to a higher specific surface for the same theoretical W loading. In addition, the pores are more numerous but smaller in size and the pore volume is higher. The obtained catalysts are mesoporous solids exhibiting type IV isotherms as reported in literature for the same preparation method [139]. As for the WZ-WI samples, increasing the calcination temperature decreases the surface area [38]. The type H2 hysteresis loop may indicate the presence of pores with narrow and wide section with interconnecting channels or ink pot pores.

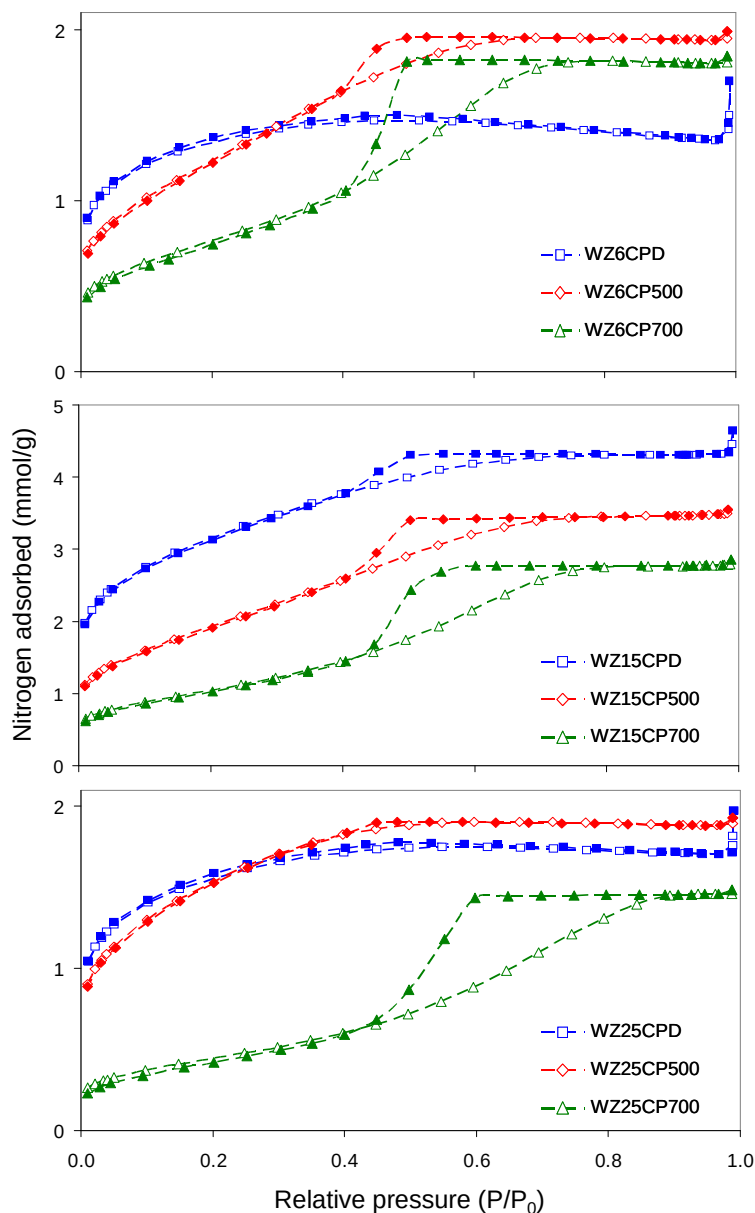


Figure 14. N_2 -adsorption-desorption isotherms for the WZ-CP samples. Open symbols are used for adsorption isotherms and the corresponding filled symbols are used for desorption isotherms.

Part III: Results

Table 7. Textural properties of tungstated zirconia samples obtained by co-precipitation method.

Sample	A_{BET} (m²/g)	Pore volume (cm³/g)	Pore average diameter (nm)
WZ6CPD	102	0.06	3.9
WZ6CP500	99	0.06	2.7
WZ6CP700	60	0.06	3.1
WZ15CPD	234	0.11	2.6
WZ15CP500	143	0.09	2.9
WZ15CP700	81	0.10	4.0
WZ25CPD	110	0.04	2.4
WZ25CP500	115	0.05	2.2
WZ25CP700	36	0.05	3.7

The XRD patterns of the WZ samples synthesised by wet-impregnation can be observed in Figure 15. As reported in literature, the apparition of a monoclinic phase from the transformation of the tetragonal phase is retarded when adding the tungsten species, leading to a thermal stabilisation of the support [38, 128]. The higher the amount of W added to the support, the lower the intensity of the peak related to the monoclinic phase of ZrO₂ (31.7 °). At similar loading, a higher calcination temperature leads to the transformation of tetragonal phase of zirconia to the monoclinic phase [38]. Calcination at 700 °C results in the formation of tungsten oxide crystals in the sample with 15%_{wt} of W. WO₃ crystals were always present for the loading equal to 25%_{wt} in W. The presence of the monoclinic phase can be correlated to the surface area decrease as can be seen in Table 6.

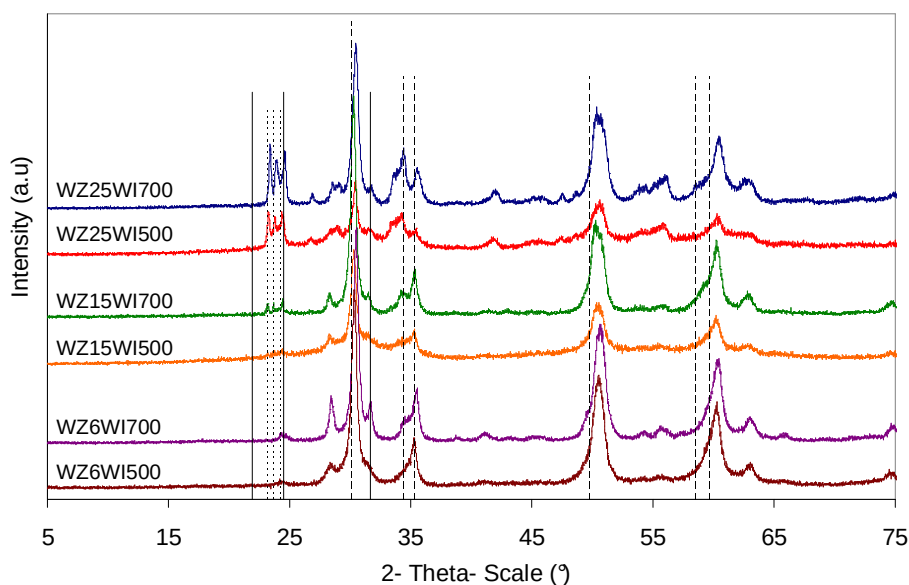


Figure 15. XRD patterns of tungstated zirconia obtained by wet impregnation method. Vertical lines indicate the positions of diffraction reflects corresponding to the tetragonal (---), monoclinic (—) phase of zirconia and WO_3 crystals (....).

The thermal stabilisation of zirconia is even more pronounced when the introduction of W species is conducted by co-precipitation (Figure 16). At calcination temperature equal to 500 °C, all the samples conserve the amorphous structure except for a W loading of 6%_{wt}, which is well stabilised in the tetragonal phase. For a calcination temperature equal to 700 °C, only the tetragonal phase is obtained, regardless of the content in W. The presence of crystals of WO_3 is observed only with the loading of 25%_{wt} in W calcined at 700 °C. The absence of monoclinic phase should be noted as compared to the same solids synthesised by wet impregnation (peak at 31.7 °).

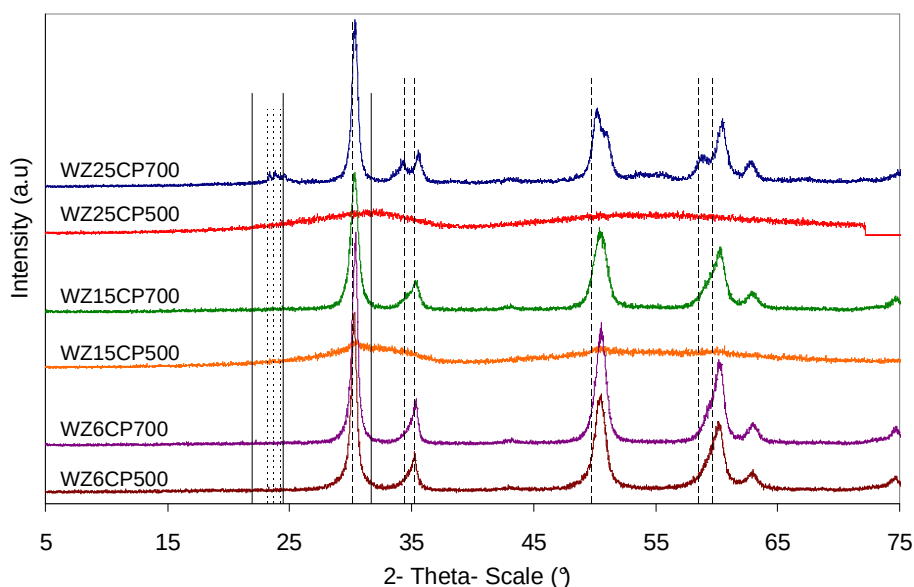


Figure 16. XRD patterns of tungstated zirconia obtained by co-precipitation. Vertical lines indicate the positions of diffraction reflects corresponding to the tetragonal (---), monoclinic (—) phase of zirconia and WO_3 crystals (....).

Regarding the chemical composition of the samples (Table 8), it can be concluded that wet impregnation provides a better control of the W loading in the final solid with an error lower than 4%. For the co-precipitated samples, the experimental composition differs slightly when the nominal loading increases. This could be due to losses related to the filtration step in the synthesis. The tungsten species possibly form WO_4^- anions which would remain dissolved in the liquid and which could thus not be retained in the matrix of the solid [135].

Table 8. Bulk chemical composition of the tungstated zirconia samples analysed by ICP-AES.

Sample	W (% _{wt})	Zr (% _{wt})	Sample	W (% _{wt})	Zr (% _{wt})
WZ6WI500	6.11	61.56	WZ6CP500	6.55	59.17
WZ6WI700	6.14	61.54	WZ6CP700	6.61	59.69
WZ15WI500	15.57	54.94	WZ15CP500	12.59	51.09
WZ15WI700	15.57	54.74	WZ15CP700	13.53	53.81
WZ25WI500	25.61	44.77	WZ25CP500	18.18	47.18
WZ25WI700	25.52	44.78	WZ25CP700	19.61	49.17

3A.4.3. Catalytic activity

Samples synthesised by the sol-gel method showed higher surface area and better structural features (absence of monoclinic phase and WO₃ crystals) than the wet impregnated samples. Moreover, it was reported in literature that they present higher acidity [140]. Insolubility tests (Annexe 1) confirmed that WZ-CP samples suffered lower leaching compared than WZ-WI samples. For these reasons, only the catalysts synthesised by co-precipitation were tested in glycerol acetylation. As can be seen in Figure 17, the catalytic activity of the tests performed in the presence of the solids is not higher than the blank reaction. Even more, some samples show a slower esterification rate than the blank reaction (catalyst with a W loading of 15%_{wt} calcined at 500 °C). The correlation of the physicochemical features of the solids to the behaviour observed in the esterification reaction cannot be established as they developed very similar esterification rates.

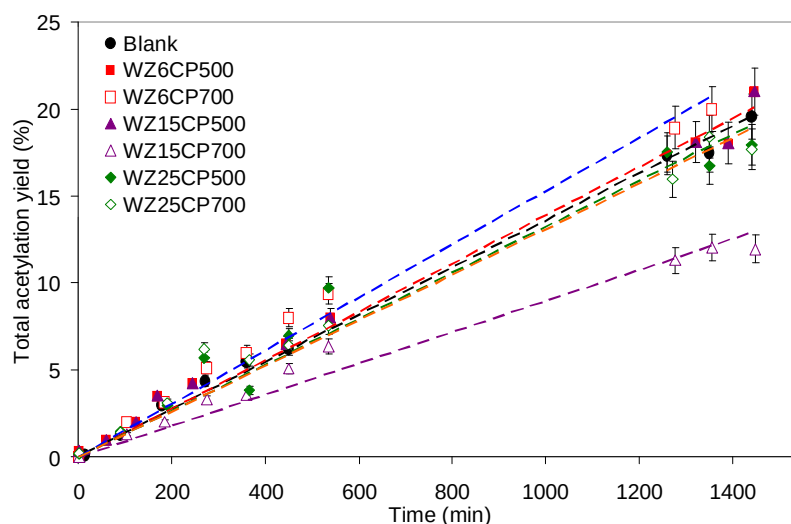


Figure 17. Acetylation yield for the esterification reaction conducted over the WZ-CP samples at 55 °C.

3A.5. Sulphated zirconia

3A.5.1. Introduction

Sulphated zirconias, SZ, are solids that find a large number of applications in industry because of their well-known high acidity [148]: selective isomerisation of hydrocarbons under mild conditions [149], dehydration [150], alkylation [151] or esterification [41], among others. Based on the use of Hammett indicators, these solids have been considered as superacids. However, some authors considered that the Hammett technique is only reliable for the characterisation of liquid substances [152].

The final properties of SZ can be modulated by the chosen synthesis method and the applied parameters. Two main methods are usually employed: impregnation technique and sol-gel method. The impregnation technique is divided in two steps [148], the first one is the synthesis of the zirconium hydroxide; and the second one is the sulphonation that can be conducted with a solution of sulphuric acid or with ammonium sulphate [24]. This synthetic route presents low reproducibility in terms of textural properties and, therefore, catalytic performances [153]. On the contrary, sol-gel synthesis is a one step method. The formation of zirconium hydroxide is performed in the presence of sulphate anions which are trapped in the matrix of the solid formed. Sol-gel materials present higher surface area and better control of the pore size distribution than wet impregnated samples due to the modulation of the synthesis parameters such as the chemical composition of the precursor medium (alkoxide/solvent/H₂SO₄/H₂O molar ratios), temperature, reactive addition rate and gel aging time [153-154].

Moreover, the calcination temperature is a critical parameter directly influencing the texture, structure and the acidic properties of the final solid [155-159]. An optimal calcination temperature has to be used in order to bind the sulphate groups onto the surface of the oxide [158]. In general, the amount of Brønsted sites decreases as the calcination temperature increases to the benefit of Lewis acid sites whose number increases [155].

Part III: Results

The nature of the sulphate species over zirconia is still a matter of debate. Several works proposed possible structures for the sulphated species [160-165]. Morterra and co-workers [166] suggested that both Brønsted and Lewis acid centres can exist at the surface of a sulphated zirconia [166]. In general, the Brønsted/Lewis acid sites ratio and strength are influenced by the hydration degree and the calcination temperature [156-159, 166-167]. Further details on these structures can be found in Chapter 4.

Various studies have tested sulphated zirconia in several esterification and transesterification reactions carried out in liquid phase [41-42, 44-46, 168-169]. These reactions were recurrently performed at temperatures higher than 100 °C and in the presence of an excess of carboxylic acid. Regarding the recyclability of the solids, studies differ, but in most cases the catalysts gradually lost their activity during the course of the reaction tests.

Therefore, given the significant activity of sulphated zirconia in the various esterification reactions in liquid phase presented above, this family of catalysts seems to be promising in the context of our research.

In this work, the sol-gel method was used instead of the classical two step method because of the better anchoring of sulphur species that sol-gel could provide which could avoid the leaching of sulphate groups and insure the recyclability of the solids.

3A.5.2. Solid characterisation

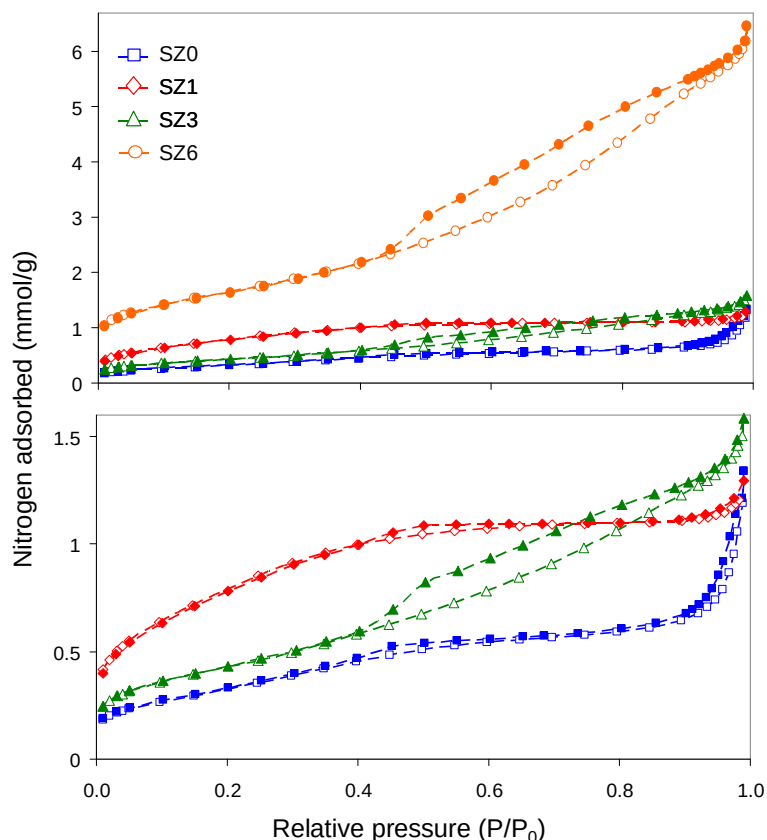


Figure 18. N₂-adsorption-desorption isotherms for the SZ samples. Open symbols are used for adsorption isotherms and the corresponding filled symbols are used for desorption isotherms.

N₂-adsorption-desorption isotherms for sulphated zirconia samples are presented in Figure 18. SZ0 sample exhibits an adsorption-desorption isotherm characteristic of a non porous or macroporous material (type II isotherm). SZ3 and SZ6 isotherms can be classified as type IV, characteristic of mesoporous materials, with sloping adsorption and desorption branches describing a H3 hysteresis loop,

Part III: Results

probably due to the presence of slit-like pores. SZ1 sample shows a very narrow hysteresis loop that can also be classified as H3 type.

The surface area, total pore volume and average pore diameter are given in Table 9. The SZ0 sample exhibited the lowest specific surface; instead, SZ6 surface area was the highest among the series. It can be observed that the textural properties of the samples cannot be linearly correlated with the hydrolysis ratio.

Table 9. Textural properties of sulphated zirconia samples obtained by sol-gel method.

Sample	A _{BET} (m ² /g)	Pore volume (cm ³ /g)	Average pore diameter (nm)
SZ0	9	0.03	6.0
SZ1	68	0.03	2.6
SZ3	31	0.05	4.8
SZ6	139	0.20	5.2

XRD patterns for the SZ samples are shown in Figure 19. The single peak observed at approximately 30°, between the position of the characteristic peaks of the monoclinic (31.5°) and the tetragonal (30.2°) phases, is solely attributed to the tetragonal phase. The characteristic peaks of the monoclinic phase are totally absent on the collected diffractograms. Thus, it can be concluded that all samples present amorphous or tetragonal crystalline phase. The SZ6 sample is almost completely composed of amorphous zirconia. However, the presence of a slight amount of tetragonal phase cannot be excluded as the diffractogram presents a broad band around 30°. The rise in the hydrolysis ratio (H) promotes a stabilisation of the amorphous phase

in regard to the tetragonal phase. SZ1 sample is totally crystallised in the tetragonal phase. The absence of a hydrolysis agent (SZ0 sample) results in a combination of tetragonal and amorphous phases.

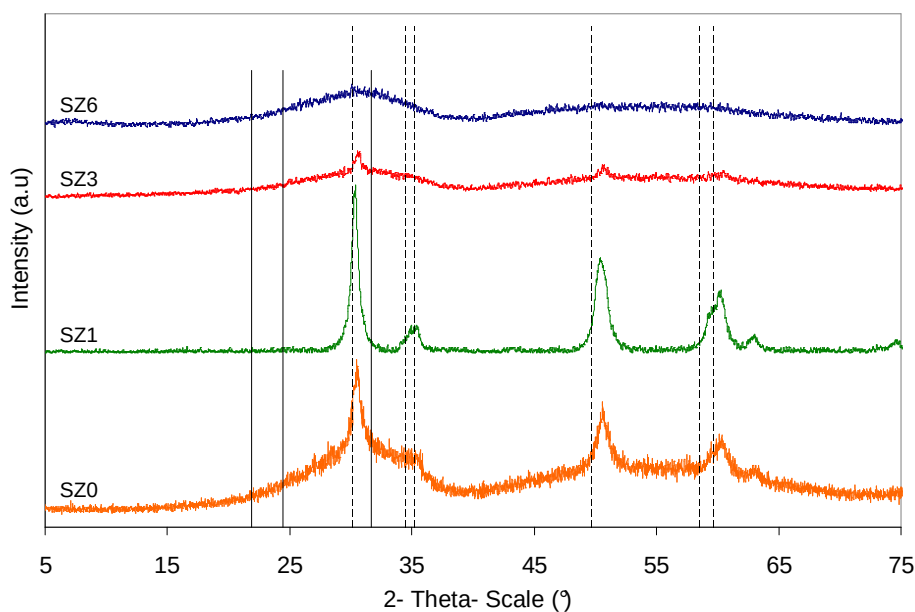


Figure 19. XRD patterns for sulphated zirconia. Vertical lines indicate the positions of diffraction reflects corresponding to the tetragonal (---), and monoclinic (—) phases of zirconia.

Results concerning the chemical composition of the SZ solids are presented in Table 10. All samples were prepared with an initial S/Zr molar ratio equal to 0.5 (8.6 %_{wt} S). This ratio was reported to lead to an optimal specific surface area/content of S and to allow a maximum effective concentration of sulphur in the final catalyst [170]. All calcined solids present a lower S/Zr molar ratio than the nominal one. This is due to sulphur losses, during the calcination step presumably as SO_x. Again, a correlation between the chemical

Part III: Results

composition of the solids and the hydrolysis ratio cannot be stabilised, the sulphur content of the samples being in the range 6.2 to 8.3 %wt.

Table 10. Bulk chemical composition analysed by ICP and S/Zr final molar ratio of SZ samples.

Sample	S content (%wt)	Zr content (% wt)	S/Zr final molar ratio
SZ0	8.30	51.26	0.46
SZ1	6.24	56.93	0.31
SZ3	7.69	50.80	0.43
SZ6	7.54	50.00	0.43

3A.5.3. Catalytic activity

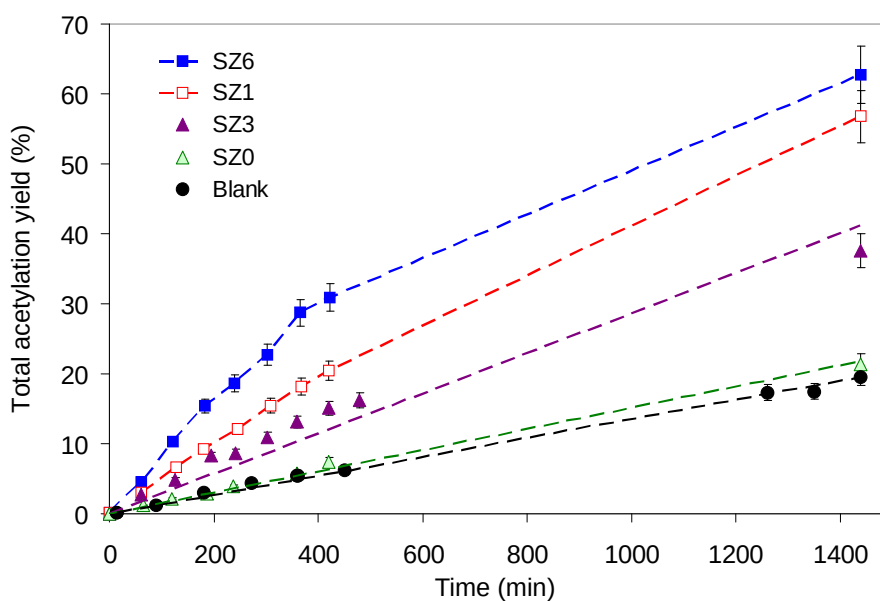


Figure 20. Acetylation yield for the esterification reaction conducted over the SZ samples at 55 °C.

The catalytic performance of SZ samples is compared to the blank reaction in Figure 20. This family of solids is active in the

esterification reaction, as they lead to an acceleration of the glycerol acetylation rate. SZ0 sample does not lead to any improvement, maybe due to the low surface area exhibited. The use of SZ3, SZ1 and SZ6 samples resulted in total acetylation yields of 38%, 57% and 63% respectively, after 24 hours of reaction.

Taking into account the previous characterisation results, we can clearly observe that the catalytic activity is independent of the structural properties of the solid: while SZ6 is amorphous and SZ1 is totally stabilised in the tetragonal phase of zirconia, both solids show comparable final acetylation yields, despite that the tetragonal phase is reported to be the active phase of sulphated zirconia [171]. All the catalysts showed a similar sulphur bulk content, so this parameter cannot be the main parameter influencing the catalytic performance in the esterification reaction.

Further studies trying to find a correlation between these catalytic performances and the physicochemical properties are presented in Chapter 4.

3A.6. Discussion of the results

In the previous section, the different characterisation results concerning the families of acid solids (Nb-SA, WZ, PA and SZ) have been presented and discussed. These solids were tested in the glycerol acetylation conducted with an excess of glycerol, but solely the solids

Part III: Results

belonging to the family of sulphated zirconia showed an interesting catalytic performance. This type of solids was hence considered catalytically active. Two other behaviours were observed for the other families (Nb-SA, WZ and PA): the «inert» behaviour exhibited by solids leading to a lack of catalytic activity; and the «inhibitory» one presented by solids inducing an esterification rate lower than the one presented by the blank reaction. The absence of catalytic properties of the solids (inert and inhibitor behaviours) cannot be solely attributed to an incorrect synthesis of the samples, as the characterisation results (texture, structure and chemical composition) are consistent with those reported in literature. All the solids were selected because they presented good catalytic activities in different carboxylic acid esterifications with monoalcohols and often using an excess of acid. Thus, the absence of activity in glycerol acetylation could initially be attributed to several complications related to the use of a polyalcohol molecule instead of a monoalcohol, and to the large excess of glycerol used in this work.

At this stage one question arises: **Why are these solids not active in glycerol acetylation?** Taking into account the steps of a heterogeneous catalytic process, two main reasons, presented in the next paragraph, could explain the absence of catalytic activity, the second one being divided in two issues closely related but approached separately:

1. Diffusion limitations.
2. Interaction reactive-solid.
 - 2.1. Influence of the reaction medium.
 - 2.2. Acidic properties of the sample.

3A.6.1. Diffusion limitations

Two types of diffusion limitations can be present under the employed reaction conditions: the external diffusion in the liquid medium and the internal diffusion in the pores.

External diffusion limitations induced by the high viscosity of glycerol were reduced by using the maximal stirring rate. The latter is limited mainly by the high viscosity of glycerol and the stirring method. Besides, the existence of slight diffusion problems in the reaction medium could not explain the esterification rates lower than the blank reaction. Thus in our case, limitations by external diffusion can be discarded as an explanation of the solids inactivity.

The diffusion limitations within the pores seem to have a more important effect over the reaction rate. Even if all the samples synthesised were mesoporous, the active sites could be located inside tortuous pores, thus being poorly inaccessible to the reactants resulting in steric hindrance effects. This could explain the absence of catalytic performances, the reaction being only catalysed by the existence of acetic acid in the reaction medium. The inhibitor behaviour could be explained similarly, supposing that acetic acid and glycerol can react

Part III: Results

in the pores but the ester formed is blocked in, so the concentration of ester in the liquid media is lower than for the blank reaction. However, there is no experimental data confirming the latter hypothesis which seems quite unlikely.

Even if the hypotheses proposed above were correct, it could be possible that the active sites present on the external surface of the catalyst would remain able to promote slightly the esterification rate, which is not the case. Thus the diffusion problem within the pores is not the sole reason explaining the different behaviours of solids.

3A.6.2. Interaction reactants-solid

Another approach to understand the behaviour of the solids is the study of the reaction system via the interactions between the solids and the reactants.

3A.6.2.1. Influence of the reaction medium

The esterification mechanism in heterogeneous systems has been widely discussed (see introduction). Depending on the nature of the solid, conditions and reactants used, the kinetic model applied to describe the reaction can be different. Generally, the most accepted model for esterification reactions between carboxylic acids and monoalcohols over solid acid catalysts is the Eley-Rideal, where the carboxylic acid is adsorbed over the active site and attacked by the alcohol molecule remaining in the liquid medium [49-54].

Assuming that glycerol acetylation is described by this mechanism, it could be possible that the presence of a large excess of glycerol impedes the carboxylic acid to adsorb on the acid sites by poisoning them. As a reminder, the acetic acid: glycerol molar ratio is $\sim 1:8$. Three types of behaviour have been identified in the glycerol acetylation system: active, inert and inhibitor. If we consider an Eley-Rideal mechanism where the acetic acid has to adsorb on the catalyst to improve its reactivity, we could explain these behaviours as follows:

- The active catalysts can accelerate the esterification reaction rate resulting in higher conversion and yield in the same interval of time. That could be explained by a facility of protonation of the acetic acid and thus, an easier nucleophilic attack by the alcohol molecule. Thus, a correct interaction between the acetic acid and the active site takes place.
- As the working conditions present a very high excess of glycerol, it could happen that the glycerol adsorbs preferentially at the surface of the solid. This preferential adsorption would result in a deactivation of the solid and the impediment of the acetic acid to be protonated by the solid. As there is enough glycerol available to react with acetic acid the esterification reaction would continue by the pseudo-catalysed mechanism, as if the solid was not in the reaction medium, thus leading to an esterification rate equal

to the blank reaction. This situation would correspond to the «inert» behaviour.

- Finally, inhibitor behaviour could be explained by an irreversible or strong adsorption of acetic acid over the solid catalyst leading to a reduction of the acidic nature of acetic acid. Unlike the previous case this would correspond to a stabilisation of the acetic acid over the surface of the solid, which would reduce the availability of protons which are also the catalyst of the pseudo-catalysed reaction. As the acetic acid is the limiting reactant and its protons the activator of the reaction, the diminution of the available protons would influence strongly the esterification rate resulting in a retarding effect.

Noticeably, the adsorption of the different molecules present in the reaction media depends on the nature of these compounds but also on the nature of the solid surface. That is the reason why in the next section the role of the active sites of the solids is discussed.

3A.6.2.2. Acidic properties of the samples

It must be noticed that, for some types of reactions, a sole combination of number, strength and type of acids sites could result in a satisfactory catalytic effect.

All the catalysts presented in this chapter were selected as they were reported to be active in esterification reactions with

monoalcohols, Brønsted and Lewis acid sites being reported as catalytically active. Nevertheless, in our reaction conditions, it was observed that the presence of Lewis acid sites (Nb-SA and PA samples) has a negative effect on the esterification rate. Furthermore, the number of acid sites, their strength and their density can strongly influence the catalytic performance of the solid.

One could think that conducting acidity measurements over all the samples could resolve the doubts about the absence of catalytic activity or about the inhibitory effect of some samples over the reaction rate. However, if we review the experimental methods used to determine the acidic properties of solids, we will see that any of the current techniques gives an absolute value of the acidic properties. Thus, the results obtained from these techniques are not so trivial to interpret and therefore to correlate with the catalytic performances in glycerol acetylation.

At first sight, liquid phase methods could meet better the requirements of our system.

The amine titration method using indicators, which is also called the Hammet method, consists in titrating an acid solid suspended in an organic solvent (benzene [172] or hexane [173]) with n-butylamine, in the presence of a coloured indicator. The colour change of the indicator in an interval of pH gives a measure of the acidity strength. The amount of acid sites on a solid surface can also be measured. Both the amounts of Brønsted and Lewis acid sites are measured, as the

Part III: Results

electron pair ($-N=$) of the indicator and that of the amine ($=N:$) react with both proton donors and electron pair acceptors on the surface of the solid [172]. However, this method presents some limitations as it is difficult to apply to coloured samples, even if data are available for several acid solids [174]. In addition, the results obtained with this technique do not give a truthfully representation of the acid strength of the solid [152]. The presence of narrow pores could lead to diffusion limitations of the indicators. Moreover, the change of colour is only representative of the species attached to the external surface of the solid, as colour changes in the meso and micro pores are not visible for the experimentator [26]. The use of a different solvent can have a strong influence on the behaviour of the systems due to solvation effects, nonspecific van der Waals and electrostatic acid-solvent interactions [173, 175]. Finally, this titration method is normally conducted at ambient temperature, thus acidic properties could be different in the reaction conditions where the temperature is much higher [26].

Potentiometric or conductometric titration methods are variations of the Hammett indicator method. The solid is put in a solvent (aqueous or non-aqueous such as acetonitrile) and titrated with a base (n-butylamine, aqueous salts or alkalis) while the pH variation is measured [173]. This technique allows to quantify the amount of acid sites and to determine their strength. The acid strength of the acid sites can be classified via the initial response of the apparatus. It has to be noted that protic solvents such as water are not an inert medium

and they can influence the acidity measurements by the creation of new Brønsted acid sites from Lewis sites by adsorption. Thus, the solute-solvent and solid-solvent interactions have to be taken into account in order to understand the effective acidity of the solids [77, 175]. Some solvent molecules can interact with acid sites of the solid preventing them to perform the catalytic reaction. In the same manner, the acid strength depends strongly on the solvent nature. Solvents can be classified in many ways according to their polarity, acidity, electron pair dielectric constant and proton-donating properties [26]. Generally, the proton donor character of a substance is higher when the solvent used presents a lower basic character [26]. For example, the number of sites of tungstophosphoric and molybdophosphoric acids measured by the potentiometric method was different depending on the solvent used (water or acetonitrile) [176]. The addition of dioxane in the solvent also modified the measured acid strength of the samples. Moreover, the quantity of solid used has to be optimised in order to obtain a good titration curve [176].

The calorimetric titration of a solid acid with amine is also available for the estimation of the number and the strength of acid sites in solution or in gas phase. This experimental technique is used to determine quantitatively the binding enthalpy of a molecule or molecular complex, by measuring the heat released or absorbed at constant pressure during a reaction designed specifically for the experience [152, 174-175]. Other technique used in liquid phase analysis in both aqueous and non-aqueous media is the measurement

Part III: Results

of the isoelectric point, which expresses the ability of an acidic surface to attract protons [77].

The acidic measurement depends also on the probe molecule used. Broadly, the number of acids sites titrated is higher when the basicity of the probe molecule is elevated. Nevertheless, the experimental results can also depend on the molecular dimension of the probe molecule, steric hindrance, and other chemical characteristics. The most used probe molecules are ammonia, aniline, pyridine and 2-phenyl-ethylamine [77]. Moreover, A. Corma wonders about the adequacy of using basic probe molecules to correlate the catalytic behaviour of the solids with very different molecules such as hydrocarbons, which may not act in the same manner as the basic probe molecule [152]. Thus, the correlation between the interaction of a probe basic molecule and the solid may not be the same as the interaction of a hydrocarbon with different nature, molecule size, dissociation constant, and thus affinity over the different types of acid sites. That is our case, as in the same medium acetic acid acts as an acid (proton donor, catalyst for the blank reaction) and as a base (proton acceptor, being a reactant).

When using gas phase techniques for the determination of the acidic characteristics of a solid, the measured intrinsic acidity may be totally different from the effective acidity displayed in the reaction media where the solid can interact with the solvent and the reactant molecules [77, 95, 177] . Moreover, it must be pointed out that acidic measurements are performed in gas phase, in aprotic media, in

absence of water and usually after a pre-treatment of the solid, which is not necessary the same as the one performed before the catalytic reaction. Further information concerning gas phase characterisation of solids acids can be found elsewhere [26, 29, 152, 172, 178].

In brief, the use of a liquid phase titration would be more adequate than gas-phase techniques to understand the interaction between the reaction media and the solid, as in our reaction medium water is continuously produced with the esters and the reaction is carried out in presence of a solvent such as glycerol. However, the obtained result could not be totally correlated to the esterification results. Moreover, would the results be useful when comparing samples presenting a very slight variation in the catalytic performances? In the case of the WZ-CP samples, almost every samples show an inert behaviour that could not be correlated with the possibly different acidic properties of the solids. Gas phase techniques could be useful for comparing the acidity of solids presenting the same nature, which is the case of the SZ samples whose acidity can be measured by the NH_3 -TPD technique described in the Chapter 1.

There is still an alternative technique to characterise indirectly the acidity of solids. Several works use a catalytic reaction where the mechanisms or the required acidic properties are known [152, 178-179]. Thus, the use of a reference reaction seems a good solution in order to state a final conclusion about the behaviour in glycerol acetylation of the solids.

Part III: Results

It should be remarked that the use of an excess of glycerol (highly viscous and with several alcohol groups) represents a poorly favourable condition to achieve a high esterification rate, which, in addition, to the best of our knowledge, has never been reported in literature. That is the reason why a representative sample of each family of solids was tested in propanol acetylation reaction conducted in a large excess of acetic acid.

Therefore, in the next subchapter the details concerning the propanol acetylation reaction will be presented.

CHAPTER 3B. PROPANOL ACETYLATION OVER CATALYSTS OF DIFFERENT NATURE

Is it possible to work in an excess of glycerol? The propanol acetylation is used as «standard reaction» to answer this question.

In the precedent subchapter, several different solid acids were tested in glycerol acetylation. Three different solid behaviours were arbitrarily defined: active, inert and inhibitory. In order to determine if these behaviours were dictated by the nature of the reaction medium (large glycerol excess) or by the different nature of the solids, a standard reaction was performed: propanol acetylation carried out in an excess of acetic acid as it would a priori constitute an “easier” system to catalyse.

In this section, the expected behaviour of the solids in propanol acetylation is compared to the results, trying to figure out the cause of the absence of catalytic activity of the different solids.

3B.1. Propanol acetylation

A further regard over the existing works reveals the absence of a «standard reaction» that could allow the comparison of the catalytic performances of the different acid solids. However, the use of an esterification reaction between acetic acid and a monoalcohol becomes indispensable for the comprehension of the solid behaviour in glycerol acetylation. In our case, this reference reaction was established by the use of n-propanol as its carbon chain is close to the glycerol. Nonetheless, esterification of acetic acid with this alcohol does not appear in the references of the selected catalysts but only using ion exchange resins [180].

A physical property that differs strongly between n-propanol and glycerol is the very high viscosity of the latter (0.002 Pa•s and 1.5 Pa•s respectively, as a reference the viscosity of water is 0.001 Pa•s). The use of propanol instead of glycerol and the use of an excess of acetic acid could then avoid problems related to external diffusion in the reaction medium. Moreover, the molecule of propanol is smaller than the glycerol one, resulting also in a better diffusion of the molecule within the pores of the solids (Table 11). The reaction conditions used here in terms of concentration are similar than those reported in literature, in particular an excess of acetic acid is used.

Table 11. Some properties of the compounds participating in the esterification reactions. Data were taken from references [181-182].

Molecule	Molecular diameter (Å)	pKa	Dipolar moment (D)	Dielectric constant (ε)
Acetic acid	4.42	4.76	1.74	6.2 at 25 °C
Water	3.43	14	1.85	80.4 at 20 °C
Propanol	5.15	16.01	1.68	20.8 at 20 °C
Glycerol	5.47	14.10	4.21	41.1 at 20 °C 42.5 at 25 °C

The dielectric constant of acetic acid is quite low, indicating that when used in excess it acts as a weak dissociating solvent. Solvents possessing a dielectric constant between 15 and 40 lead to a partial dissociation of ionic substances. Glycerol can thus be considered as a dissociating solvent as its dielectric constant is higher than 40 [182]. Therefore, working in excess of acetic acid or glycerol (acting as solvents) strongly influences the dissociation of the ionic compounds existing in the reaction medium.

3B.2. Experimental

For the propanol acetylation test, samples were dried before use (overnight, under vacuum, at 90 °C). The esterification reaction was performed with 30 mmol propanol, 100 mmol acetic acid 30 mmol toluene (internal standard GC) and 50 mg of solid at 90 °C. The reaction medium samples were diluted in acetonitrile before being analysed by GC on Finnigan Trace GC ultra (Thermo electro corporation) with an FID detector. The column (10 m) consists of 5% phenyl and 95% PDMS with an internal diameter of 0.1 mm. Helium

Part III: Results

was the carrier gas and the inlet temperature was fixed to 250 °C. Chromatograms were analysed with the Chromcard software. Amberlyst-15 in its wet form was purchased from Fluka and used as a reference catalyst after drying overnight at 90 °C.

3B.3. Results

In Figure 21, the catalytic performance of some selected solids in propanol acetylation are presented. Again, the only solids that are able to catalyse the reaction are Amberlyst-15 and SZ6. Solids belonging to the family of Nb-SA, PA and WZ-CP show a slightly inhibitory effect on the catalytic reaction. The main hypothesis to explain the lack of catalytic activity of the samples Nb-SA, WZ and PA in glycerol acetylation at 55 °C will be discussed and compared to the esterification of acetic acid with propanol similarly to the previous section.

Figure 22 displays the carbon balance for the glycerol acetylation tests expressed as the acetic acid transformed to esters versus the acetic acid conversion. It can be seen that the carbon balance is almost equal to 100% when using Amberlyst-15 and SZ6 catalysts. When the reaction is conducted in the absence of a catalyst the points are shifted towards a lower production of esters. These differences will be explained in more detail for each family of solids in the subchapter 3C.

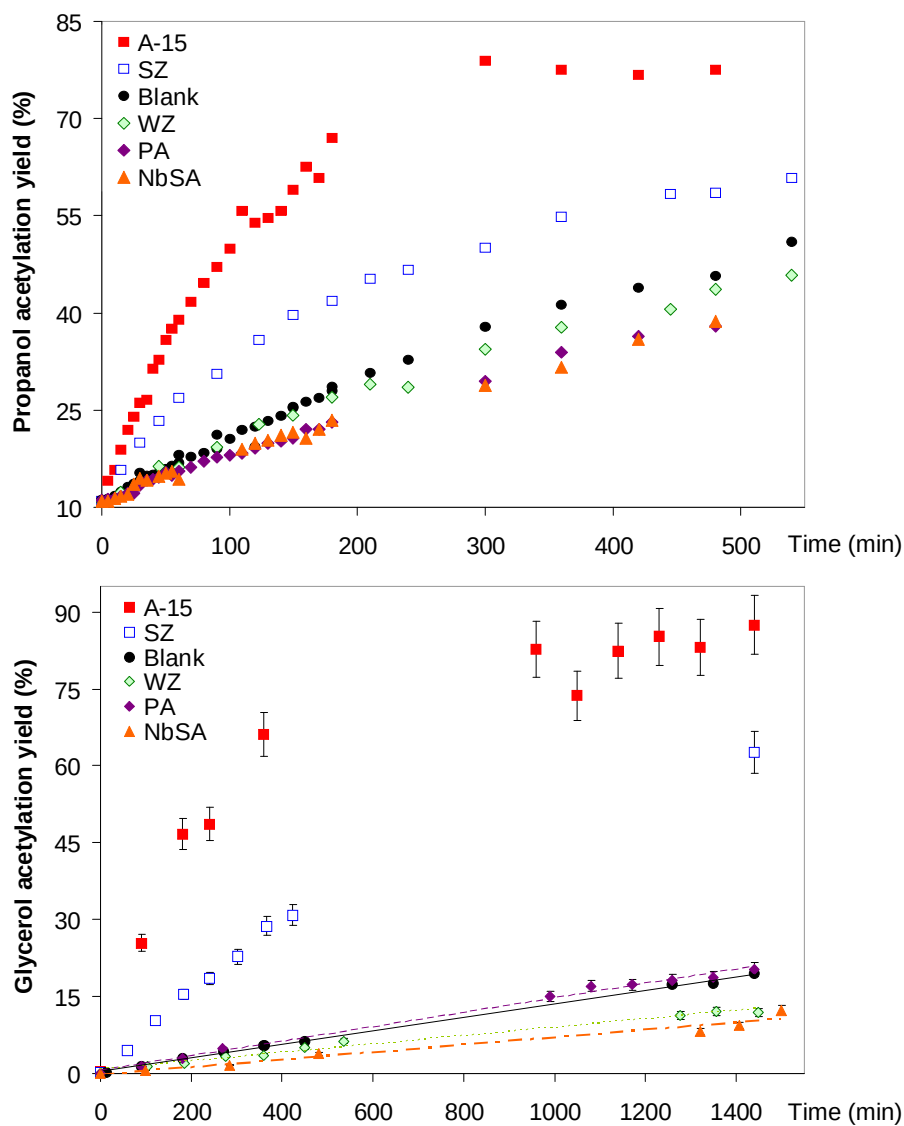


Figure 21. Esterification yield for propanol and glycerol acetylation respectively. «A-15»: Amberlyst-15; «SZ»: SZ6; «WZ»: WZ15CP500; «PA»: PA1 and «NbSA»:Nb15. Esterification reactions were conducted at 90 and 55 °C for propanol and glycerol acetylation, respectively.

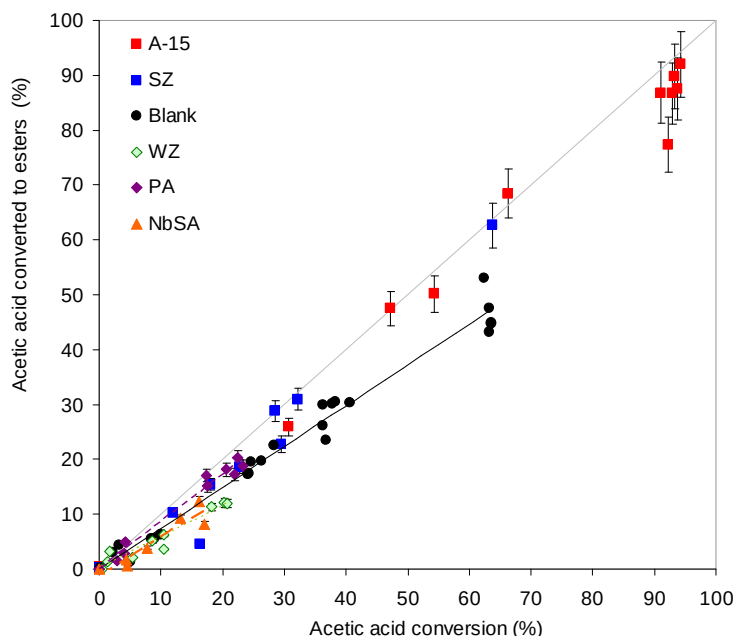


Figure 22. Carbon balance expressed as the acetic acid converted to esters (%) versus the acetic acid conversion (%) for the glycerol acetylation test conducted at 55 °C in the presence of several acid solids: «A-15»: Amberlyst-15; «SZ»: SZ6; «WZ»: WZ15CP500; «PA»: PA1 and «NbSA»:Nb15. The black line represents the blank reaction, included in order to compare the catalytic behaviour of the solids. The diagonal represents a carbon balance equal to 100%.

3B.4. Discussion of the results

3B.4.1. Diffusion limitations

In the previous analogous section concerning the acetylation conducted in an excess of glycerol, it has been discussed that the reaction medium could be too viscous and may present external diffusion problems. This supposition was theoretically discarded.

Now, it can be clearly seen that external diffusion problems are not the reason of the absence of a catalytic effect of the samples from the families Nb-SA, PA and WZ-CP, these families also presenting an inhibitor behaviour in propanol acetylation reaction.

The lower size of propanol versus glycerol and the lower number of OH functions could avoid the steric hindrance effect present in glycerol acetylation, and thus decreasing the internal diffusion limitations. If this hypothesis is correct, acetic acid and propanol could easily access the active sites and a catalytic effect would be observed in the esterification rate. Nevertheless, Nb-SA, PA and WZ-CP samples showed an inhibitory effect in the propanol acetylation decreasing the esterification rate as compared to the blank reaction. Consequently, the hypothesis of diffusion problems can be discarded as it could not explain the lack of catalytic activity of the solids.

3B.4.2 Interaction reactants-solid

3B.4.2.1. Influence of the reaction medium

Assuming that the esterification mechanism is explained by the Eley-Rideal model where the acetic acid is the adsorbed molecule, we could think that the large excess of glycerol with three OH functions could impede the correct adsorption of acetic acid. Then, if the esterification reaction is carried out with propanol presenting similar pKa as glycerol (Table 11) we could expect that propanol would

Part III: Results

interact with the solid in the same manner as glycerol even if the concentration of carboxylic acid and alcohol is inversed. Thus, the different behaviours of the solids in glycerol acetylation could be used to predict their catalytic performances in propanol acetylation. A representation of the predicted behaviour of the solids in propanol acetylation is therefore presented in Figure 23, supposing that the affinity of both alcohols (glycerol and propanol) is equivalent and independent of the acetic acid concentration. In propanol acetylation, the inert behaviour could be explained by an adsorption of acetic acid; and the inhibitor behaviour could be explained by the adsorption of propanol.

The results of both esterification reactions are summarised in Table 12. It can be seen that our hypothesis does not correlate with the experimental results. The composition of the reaction medium both excess of glycerol and excess of acetic acid do not influence the effect of the solid over the esterification rate. This phenomenon could then be explained only by the properties of the solids, namely their acidic properties.

↓ Glycerol acetylation Acetic acid: glycerol molar ratio=1:8 ↓	Correct interaction between the active sites and acetic acid		↓ Propanol acetylation. Acetic acid: propanol molar ratio=10:3 ↓
	Active solid		
	Preferential adsorption of alcohol molecules over the active sites		
	Inert solid. The excess of glycerol allows the reaction to continue as a pseudo catalysed reaction.	Inhibitor solid. As the limiting reactant is propanol, its adsorption could result in a lower reactivity.	
↓ Glycerol acetylation Acetic acid: glycerol molar ratio=10:3 ↓	Strong adsorption of acetic acid. Lower availability of protons.		
	Inhibitor solid. As the limit reactant is also acetic acid	Inert solid. There are enough molecules in the reaction medium to react with propanol	

Figure 23. Previous hypothesis and expected solid behaviour in the esterification reaction of acetic acid with propanol. Hypotheses are based in an Eley-Rideal model where the acetic acid is protonated by the active site and attacked by the alcohol molecule. A: acetic acid molecule; B: alcohol molecule, glycerol (left) and propanol (right), Rectangle: solid catalyst.

Part III: Results

Table 12. Summary of the different behaviours presented by the solid acid in glycerol and propanol systems.

Behaviour ➤ Solid ▼	Glycerol acetylation	Propanol acetylation		Conclusion
		Expected	Experimental	
Nb-SA	Inhibitor	Inert	Inhibitor	In propanol acetylation the solid showed the same behaviour as in glycerol acetylation.
PA	Inhibitor	Inert	Inhibitor	
WZ-CP	Inert	Inhibitor	Slight inhibitor	
SZ-H	Active	Active	Active	
Amberlyst-15	Active	Active	Active	

3B.4.2.2. Acidic properties of the samples

All indications lead us to think that the nature of the solid's surface may be the sole parameter explaining its behaviour in the esterification reaction. Nevertheless, a further analysis of the samples nature and the existence of secondary reactions has to be applied in order to understand the obtained results; which is presented in the section 3C.

CHAPTER 3C. GENERAL DISCUSSION AND CONCLUSIONS

Why several acid solids used in the initial screening are not active in the esterification reaction?

It has been shown that the only active solids in glycerol and propanol acetylation were sulphated zirconia and Amberlyst-15 (ion exchange resin). Tungstated zirconia did not show any catalytic activity, while niobium oxide supported on silica-alumina and aluminophosphate solids lead to an esterification rate slower than the pseudo-catalysed reaction conducted in the absence of a catalyst.

In this subsection, different hypotheses trying to elucidate what occurs in the reaction medium are presented.

3C.1. Different hypotheses to explain the catalytic behaviour of the solids

Hypothesis 1: Different synthesis method, different catalytic properties

The initial screening was based on solids that have been reported to promote the esterification reaction between carboxylic acids and monoalcohols. The solids synthesised in this work fail to present the same catalytic properties in glycerol acetylation except for the family of sulphated zirconia. Therefore, in order to discard problems related to the use of glycerol, a sample of each family of synthesised solids was tested in propanol acetylation conducted with an excess of acetic acid. Again the synthesised samples did not promote any catalytic effect except for sulphated zirconia. In consequence, it can be questioned if this discrepancy is due to differences in the catalyst preparation.

It is known that due to the presence of impurities, the study of a single catalyst cannot give reliable information [14]. Thus, for acid catalysts the most important factors of variability are the interconversion of Lewis to Brønsted centres and the presence of impurities such as anions or cations which are able to modify the number, strength and nature of the acid-base sites [14].

Busca states that the properties related to the morphology and purity/impurity of synthesised solids depend on the particular preparation method and the precursors used [183].

For example, a series of commercial alumina was tested in the n-butene skeletal isomerisation [184]. The solids possessed similar surface areas and morphologies (XRD) and are sold as highly “pure” gamma-aluminas. FT-IR analysis did not show any remarkable differences concerning the nature of the surface hydroxyl-groups and of the surface Lewis and basic sites. Nevertheless, when tested in the isomerisation reaction they show very different catalytic activities, namely due to their different sodium content as impurity which influences the stretching band of the surface hydroxyl groups and thus the medium-strong Brønsted acidity of the solids. Other works also reported the influence of sodium impurities on the number and strength of active sites [185-186].

In consequence, the synthesis methods and the precursors used are very important parameters that can influence the final properties of the solid and thus affect negatively the catalytic activity developed in the reaction. This will be discussed latter in the manuscript.

Hypothesis 2: the nature of the solids: amphoteric character

In Chapter 3, the influence of different solid acid catalysts based on metal oxides was tested. In general, solid oxides are constituted of

Part III: Results

metallic cations and oxygen anions. In the surface of these solids oxide species and metal or non-metal centres remain exposed and form acidic and basic sites as well as acid–base pair sites [183, 187].

Therefore, the surface of solid oxides can be constituted by unsaturated cationic centres, potentially acting as Lewis acid sites; lattice oxygen anions or exposed oxide species, potentially acting as basic sites; hydroxyl-groups, presenting an amphoteric character making that they can act as a Brønsted acid or a basic site; and other adsorbed substances arising from the environment, such as carbonate species or water [183]. Depending on the hydration degree of the surface, Lewis acid and basic sites can be transformed into a Brønsted acid and base sites, respectively [187-188]. Therefore, Lewis acid sites can react with water or acetic acid forming a Brønsted acid site whose strength depends on the initial characteristics of the Lewis site.

The amphoteric character of hydroxyl groups depends on the presence of acid or basic substances in the medium (Figure 24) [188]:

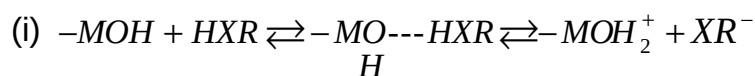


Figure 24. Surface hydroxyl interaction with an organic acid (i) and base (ii) where X represents an oxygen, sulphur or nitrogen atom [188].

If the interaction between the hydroxyl groups and the organic molecules is weak, water can replace these molecules as presented in Figure 25:

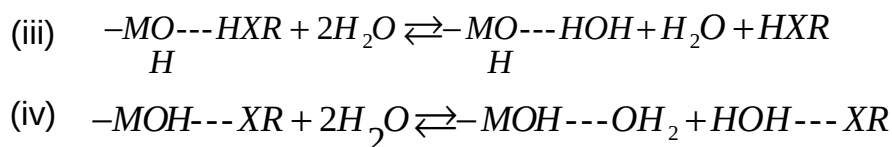


Figure 25. Surface hydroxyl interaction with water in the presence of an organic acid (iii) and base (iv). X represents an oxygen, a sulphur or a nitrogen atom [188].

Therefore, the presence of basic sites over the solid could favour a strong adsorption of acetic acid. This could be a reasonable explanation for the low activity observed if the sites are of low acid strength. Moreover, the hydroxyl groups of the solid could be influenced by the composition of the reaction medium. The inhibitory effect could be due to a strong adsorption of the limiting reagent (acetic acid) on the catalyst surface subtracting it from the pseudo-catalysed homogeneous reaction.

Hypothesis 3: Solubility of solids

Aluminium oxide exhibits amphoteric behaviour and is soluble in both acids and bases [189]. It can react with acids, producing their corresponding salts. In acid medium, it thus exists as a solvated aluminium ion, in which water molecules are hexacoordinated to trivalent Al^{3+} , as shown below [190]:



Moreover, it could be suggested that aluminum phosphates could also exhibit a tendency to solubilise in acid media and to react in the presence of acetic acid forming acetate species.

Therefore, amphoteric solids containing Al, such as niobium oxide supported on silica alumina and $AlPO_4$ samples, may suffer from Al leaching, consuming acetate species and thus negatively influencing the esterification rate.

Hypothesis 4: Secondary reactions in the reaction medium for glycerol acetylation

Glycerol oxidation

Glycerol in liquid phase can undergo oxidation due to the presence of molecular oxygen in the reactor thus producing dihydroxyacetone and glyceraldehydes (Figure 26). In consequence, several authors working with glycerol in liquid phase suggest conducting the experiment under an inert atmosphere such as that provided by nitrogen [191-193].

Trejda and coworkers studied the glycerol acetylation in liquid phase conducted under nitrogen atmosphere at 100, 125 and 150 °C [192]. Different glycerol:acetic acid ratios were applied 1:3, 1:6 and 1:9. The authors stated that working under inert atmosphere allowed

obtaining exclusively glyceryl acetates and a carbon balance close to 100% [192].

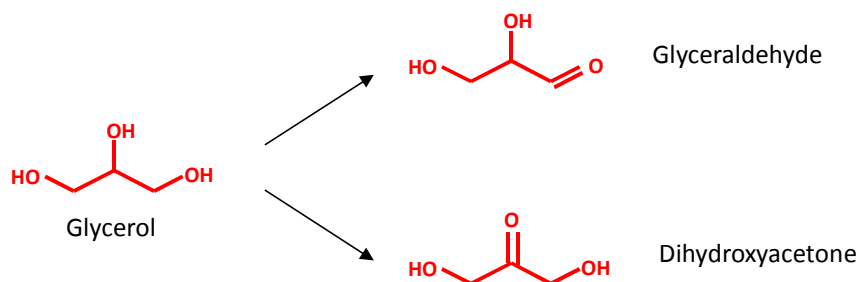


Figure 26. Glycerol oxidation products [194].

Glycerol dehydration

Gonçalves et al. reported the presence of glycerol dehydration as a secondary reaction in the glycerol acetylation reaction carried out with an excess of acetic acid at 110 °C [67]. The selectivity to the dehydration product α -hydroxy-acetone (acetol) was the lowest for Amberlyst-15 and the highest for niobic acid followed by zeolites, which may be due to the different acid strength of the solids.

The mechanism proposed for the dehydration of glycerol is presented in Figure 27. The authors remarked that the dehydration preferentially occurs on the terminal hydroxyl group and not on the central hydroxyl, which would lead to acrolein maybe due to problems related to steric hindrance and solvation effects.

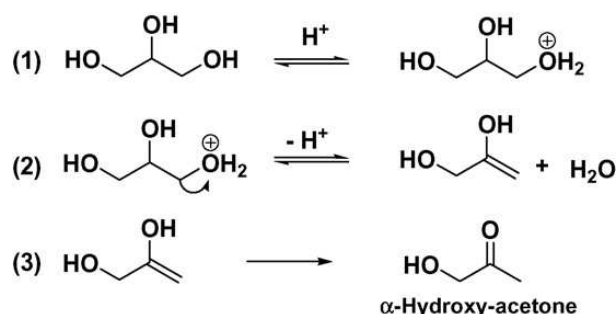


Figure 27. Mechanistic pathway for the formation of α -hydroxy-acetone upon glycerol dehydration over acidic catalysts [67].

Alhanash and co-workers proposed different mechanisms for glycerol dehydration in gas phase over Brønsted and Lewis acid sites [195].

The authors suggested that the presence of Lewis acid sites favoured the formation of acetol, whereas the production of 3-hydroxypropanal and acrolein may occur in the presence of strong Brønsted acid sites (Figure 28).

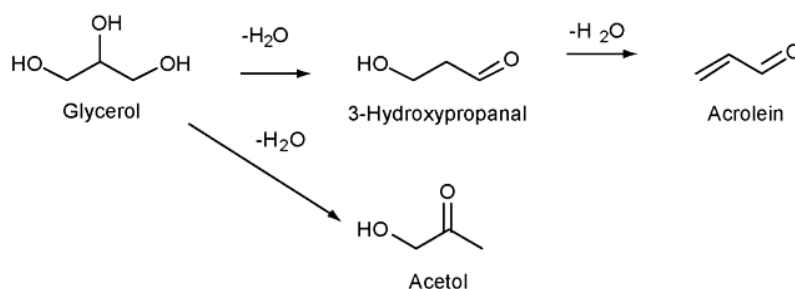


Figure 28. Dehydration of glycerol over acid catalysts [195].

The formation of acetol represented in Figure 29, was explained as follows: the glycerol molecule is protonated on the internal oxygen

which possesses a higher negative charge compared to the terminal oxygens. 1,3-dihydroxypropene was obtained after elimination of H_3O^+ . Finally 3-hydroxypropanal, formed by tautomerisation, was dehydrated to yield acrolein. The proton site is regenerated by an interaction of its conjugated base with H_3O^+ [195].

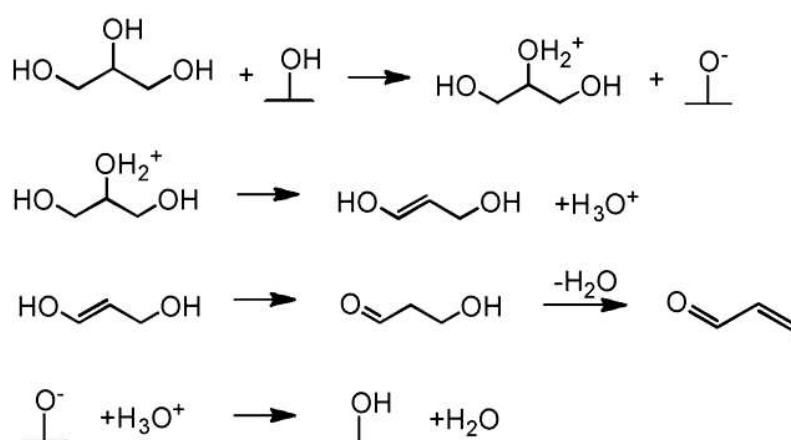


Figure 29. Mechanism of glycerol dehydration on Brønsted acid sites [195].

In contrast, the dehydration of glycerol over Lewis acid sites takes place differently due to steric constraints (Figure 30). The terminal OH group of glycerol rather than the internal one is more likely to interact with the Lewis acid sites. 2,3-Dihydroxypropene together with the hydrated active site of the catalyst is formed after a concerted transfer of the terminal OH group of glycerol to the metal and H^+ migration from the internal carbon atom to the bridging O atom of the oxide. Finally, the Lewis acid site is regenerated by dehydration of its hydrated form [195].

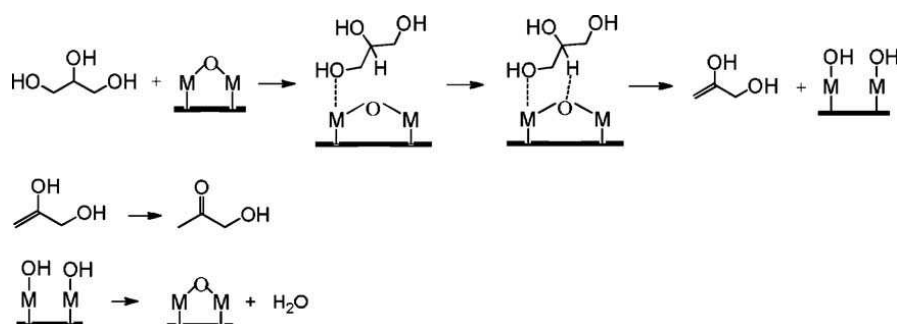


Figure 30. Mechanism of glycerol dehydration on Lewis acid sites [195]. The Lewis acid sites are represented by two oxo-bridged metal ions (M).

Etherification of glycerol

The etherification of glycerol can be performed in liquid phase by base catalysts, such as LiOH, NaOH, KOH and Na₂CO₃, working in an inert atmosphere and temperatures between 180–260 °C [193].

Silva et al. studied the etherification of glycerol with benzyl alcohol in liquid phase at 110 °C in presence of zeolite β, Amberlyst-35, K-10 montmorillonite and p-toluenesulphonic acid [196]. In all cases, self-etherification of benzyl alcohol was observed.

The etherification of glycerol with ethanol can be catalysed over different types of solid acids such as sulphonic resins, zeolites and grafted silicas [197]. Pariente and coworkers remarked that in this reaction a good compromise between the acidic properties and the polarity of the solid surface is needed [197].

Yuan and co-workers analysed the catalytic behaviour of acid (H-ZSM5, H-β, tungstophosphoric acid (HPW), FeCl₃, AlCl₃, and

H₂SO₄) and a base catalyst (MgO) in the etherification of biodiesel-based glycerol with bioethanol [191]. MgO was found to be inactive under the reaction conditions (5.0 g of glycerol combined with 15.0 g of ethanol and a constant loading of 1.0 g of solid catalyst at temperatures ranging from 80 to 160 °C under N₂ atmosphere). Both Brønsted and Lewis acids showed catalytic activity, nevertheless the SiO₂-supported HPW catalysts exhibited the highest activity. A recycling run performed on the latter catalyst showed that the HPW was leached during the tests.

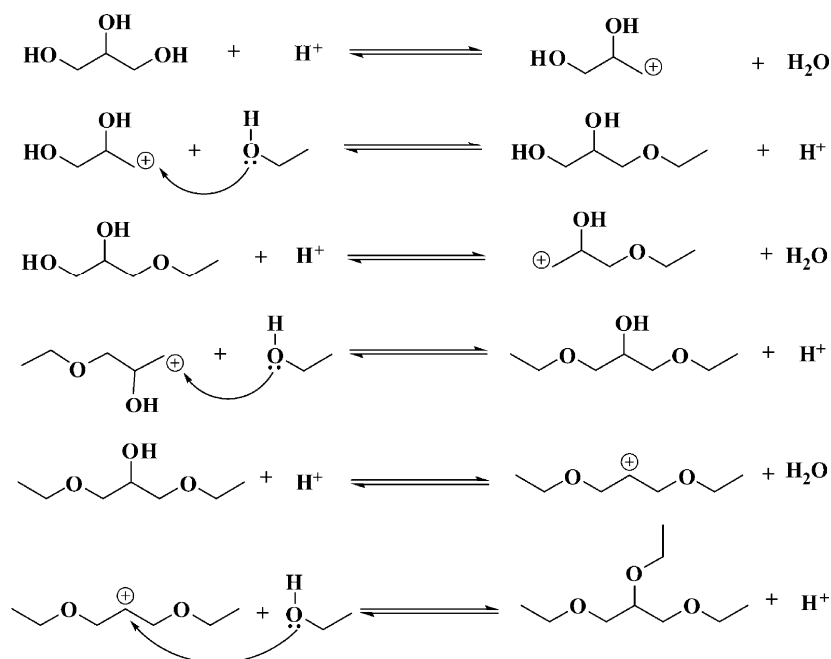


Figure 31. Scheme 2. Reaction Mechanism between glycerol and ethanol over Brønsted Acids [191].

The authors proposed the etherification mechanism presented in Figure 31. The protonated glycerol is attacked by ethanol to form 3-

Part III: Results

ethoxy-1,2-propanediol. This process is repeated with the remaining hydroxyl group of the C3 molecule.

In brief, several secondary reactions can take place in our reactor, mainly oxidation of glycerol but also dehydration and etherification, the latter being however less probable as it would take place between two identical molecules (glycerol) and needs more elevated temperatures [193]. All these reactions are glycerol consuming, nevertheless the intermediates or the final products can react with acetic acid due to the remaining hydroxyl groups, forming new molecules and thus consuming the carboxylic acid. However, the determination of the presence of these molecules by gas chromatography could be hindered mainly by the sampling protocol, based on the extraction of the interest products (acetic acid and glycerates) in heptanol.

3C.2. The catalytic behaviour of the synthesised solids

Taking into account the previous hypotheses, each family of solids will be reviewed in order to highlight their respective principal surface properties and their interaction with the reaction medium in an attempt to understand their behaviour.

From now on, all the discussion will be based on the results obtained with glycerol acetylation. This was due to the higher number

of data available for glycerol acetylation (both acetic acid conversion and esterification yield) than for propanol acetylation where only the formation of propyl acetate was measured.

In order to facilitate the comprehension of the catalytic behaviour the acetic acid converted to esters is plotted versus the acetic acid conversion. Therefore, if all the consumed acetic acid is converted to esters, the points will be situated in the diagonal (carbon balance = 100%). For the sake of clarity each figure is commented in the corresponding section.

3C.1.1 Niobium oxide supported on commercial silica-alumina

All Nb-SA samples resulted in inhibitory behaviour on the esterification reaction both in glycerol and propanol acetylations. It can be seen that in glycerol acetylation, an increase in the Nb loading results in a diminution of the inhibitor behaviour of the solid. However, the esterification rate still remained below the acetylation rate of the blank reaction. The esterification rate is the same for samples with a Nb loading lower than 7.5%wt. The Nb loading increase from 15% to 25%wt resulted in a reduction of the inhibitory effect.

These solids were synthesised by the procedure described by Braga and co-workers [37], therefore the absence of catalytic activity cannot be solely attributed to a different preparation procedure.

Part III: Results

A further analysis of the literature reveals that the use of niobium oxide as catalyst in esterification reaction is in several cases contradictory. Niobium oxide supported over silica-alumina has been reported as an active solid for the esterification reaction of acetic acid with ethanol, butanol and iso-pentanol [37] and suitable for reactions in presence of water [95]. However, bulk niobic acid presented lower catalytic performances than ion exchange resins and some zeolites in acetic acid esterification with butanol [42]. In addition, the use of $\text{Nb}_2\text{O}_5/\text{HNO}_3$ in the esterification of fatty acids with methanol resulted in a lower esterification rate than $\text{Nb}_2\text{O}_5\cdot\text{H}_2\text{O}$. The authors suggested that the higher acidity of $\text{Nb}_2\text{O}_5/\text{HNO}_3$ could result in a deactivation of the active sites by a strong interaction with water [97]. Other studies attributed the low activity of bulk niobium oxide to its low density of effective acid sites [198], to their weak acidic character and to the hydration of acidic OH groups which decreases the acid catalysis effect via water adsorption [20, 199]. Thus, a lower amount of acid sites, a weak acid strength or a probable deactivation of active sites by water adsorption could explain the absence of a catalytic effect of the Nb-SA samples in glycerol and propanol acetylations. Nevertheless, this argument cannot explain the inhibitory effect of the samples.

According to Trombetta et al. [183] the Brønsted acid sites of silica alumina are due to terminal silanols, which are influenced by nearest Al cations. Datka and co-workers studied the nature of the acidic species present in niobium oxide supported over silica and over

alumina samples [92]. The supported samples presented Brønsted acid sites when overpassing a critical surface coverage. Below this limit (~ 0.5 monolayer), the solid only presents Lewis acid sites: those already present on the support and those created by the niobium oxide. The created Lewis sites were normally weaker than the Lewis acid sites of the support. Brønsted acid sites increased until a maximum when increasing the loading of niobium. Braga and co-workers determined that the theoretical monolayer of niobium pentoxide supported on silica-alumina ($475 \text{ m}^2/\text{g}$) based on the Nb_2O_5 crystal unit dimensions (0.32 nm^2) are close to 39.6%_{wt} of Nb_2O_5 . However, the experimental studies show that the monolayer is reached between values of Nb_2O_5 loading between 10 and 15%_{wt} [200].

Catalysts based on niobia supported on γ -alumina synthesised by impregnation with niobium pentaethoxide (Nb loading between 8 and 28%_{wt}) were tested in isopropanol dehydration, 1-butene isomerisation and cumene dealkylation. It was shown that the density and strength of the Lewis acid sites and of the basic sites decreases strongly with niobium addition, while the number of Brønsted acid sites increases [201].

These results could be applied to picture the nature of the surface species present on Nb-SA samples and to explain their inhibitory effect. Silica-alumina contains Al atoms; thus, it can be suggested that it also contains basic sites, which are modified after supporting the niobium oxide. The increase of the niobium loading

Part III: Results

and thus, the niobium oxide coverage lead to a diminution of basic sites, Lewis acid sites and to an increase in Brønsted acid sites.

Therefore, in our case, the deceleration of the esterification rate could result from a strong adsorption of acetic acid over the basic sites of the solid. The increase in Nb loading results in a decrease of basic sites and an increase in the number of Brønsted acid sites, which could explain the higher activity of samples whose loading is above 15%_{wt}. However, the amount of acetic acid molecules adsorbed may still be important, thus the number of available acetic acid molecules in the reaction medium is as high as in the blank reaction. Nevertheless, the possibility that Al^{3+} species could react with the acetic acid to form acetates and thus being unavailable for the esterification reaction cannot be supported by any experimental data.

When representing the acetic acid transformed in esters versus the acetic acid conversion (Figure 32), it can be seen that in the blank reaction there is an error between the acetic acid consumed and the acetic acid converted in esters (as the points are located below the diagonal). This error can be related to evaporation losses of acetic acid but also to the fact that the reaction takes place under ambient atmosphere that could lead to oxidation reactions. Thus giving the large reaction times, the oxidation of glycerol (reactant in excess) can lead to the formation of dihydroxyacetone and glyceraldehydes [191-193]. The acetic acid present in the reaction medium may react with these sub-products being also consumed, forming products other than mono, di or triacetins. As said before, the detection of these

substances in gas chromatography (GC) was not possible as these substances may remain in glycerol phase when extracting the acetic acid and glycerol esters with heptanol, which was the analysed phase.

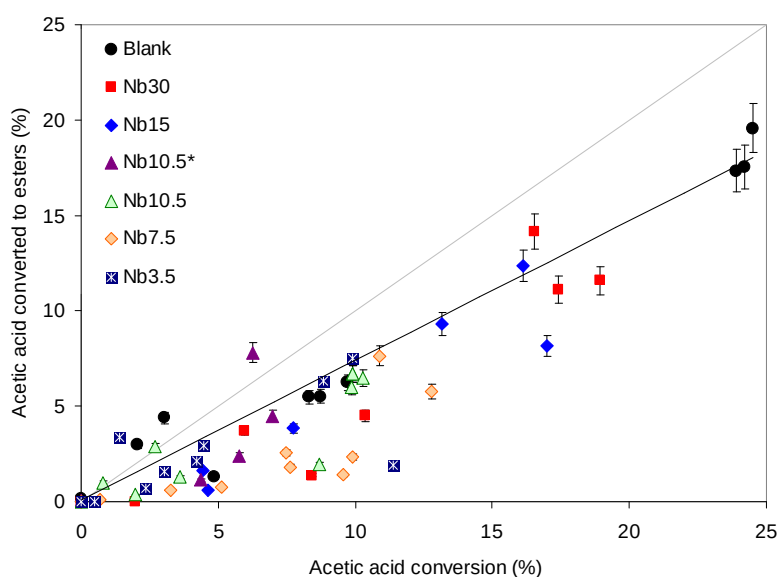


Figure 32. Carbon balance expressed as the acetic acid converted to esters (%) versus the acetic acid conversion (%) for the glycerol acetylation test conducted at 55 °C in presence of Nb-SA samples. The black line represents the blank reaction, provided in order to compare the catalytic behaviour of the solids. The diagonal represents the carbon balance equal to 100%.

Moreover, it can be seen that when comparing the acetic acid converted to esters for the tests conducted in presence of the solid samples, the points at low conversions present very low esters yield. It can be supposed that the acetic acid disappeared from the reaction medium being adsorbed over the solid or giving place to another secondary reaction.

Gonçalves et al. reported that niobic acid presented some selectivity to hydroxy-acetone in the esterification of acetic acid (reactive in excess) with glycerol [67]. In our case, the potential products obtained from the glycerol dehydration or oxidation may react with acetic acid to give another sub product not detected by GC explaining the unavailability of acetic acid for the glycerol acetylation reaction.

In conclusion, the inactivity of niobium oxides based samples may be due to the presence of basic sites on the surface of the support which adsorbs acetic acid molecules, and to the reaction produced between the acetic acid and the product of glycerol oxidation and/or dehydration.

3C.1.2. Amorphous aluminophosphates

In the introduction, aluminophosphates based solids were reported to be active in different esterification reactions [121-123]; however, this was not the case in the acetic acid esterification with glycerol and propanol. This divergence could be due to the different preparation methods used in both cases. In this work, aluminophosphate solids were prepared by a hydrogel method [73-74] in propylene oxide adding a dissolution of ammonia, while the group of Marina prepared the solids in an ethylene oxide medium [121-123]. Moreover, it is known that the rate of reagents addition, the temperature, and the stirring method can strongly influence the formation of the gel.

Amorphous aluminophosphates solids are amphoteric oxides [202], thus it is possible that basic sites are present on the surface of the synthesised PA samples. In the section 3.2.3 it was remarked that the composition of aluminium phosphates clearly influences the esterification rate of the reaction: the lower the P/Al ratio, the higher number of Al atoms and the stronger the inhibitory effect. It is known that an increase in the Al content of the solid leads to an increase in the number of Lewis acid sites present but also promotes the formation of basic sites [203]. In consequence it could be suggested that acetic acid could be strongly adsorbed over the solid surface.

When plotting the acetic acid converted to glyceryl esters versus the acetic acid conversion (Figure 33), a different behaviour can be seen as compared to the Nb-SA samples. The points of the esterification reaction conducted in presence of the PA samples are located quite close to the blank reaction line. This may suggest that some acetic acid is strongly adsorbed on the basic sites of PA0.33 and PA0.6 samples, as the points are slightly below the blank reaction. For the PA1 sample, the carbon balance presents a lower error (points close to the diagonal) thus it could be suggested that the secondary reaction (oxidation and dehydration of glycerol) are not so marked, thus, meaning that the acetic acid only reacts with pure glycerol to give monoesters and not with the glycerol sub-products.

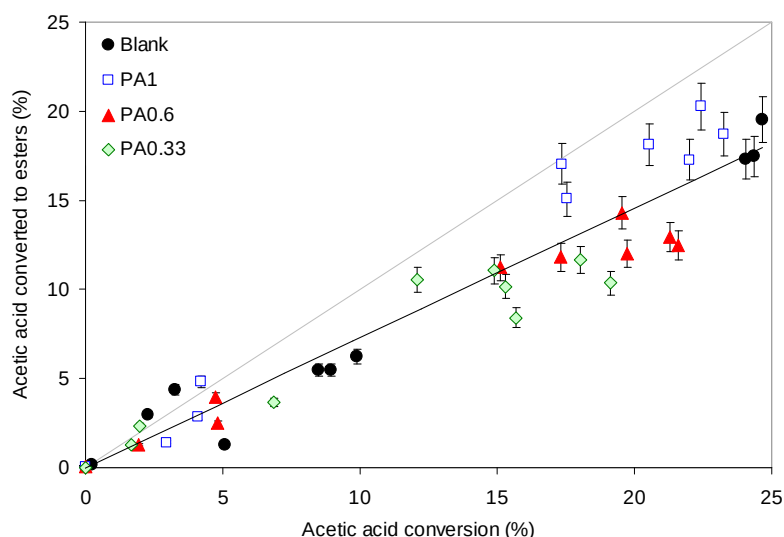


Figure 33. Carbon balance expressed as the acetic acid converted to esters (%) versus the acetic acid conversion (%) for the glycerol acetylation test conducted at 55 °C in presence of PA samples. The black line represents the blank reaction, included in order to compare the catalytic behaviour of the solids. The diagonal represent a carbon balance equal to 100%.

In summary, the inactivity of the PA samples may be due to several reasons concerning the different preparation procedures which could lead to different surface properties as compared to the solid tested in literature in esterification reactions, or to the presence of basic sites, where acetic acid can be strongly absorbed. The absence of secondary reaction could be suggested based on the carbon balance when conducting the test in the presence of the PA1 sample.

3C.1.3. Tungstated zirconia

Our work shows that WZ-WI samples were prone much more to leaching than co-precipitated ones. Moreover, they are reported to

have lower acidity features than samples obtained by co-precipitation. Therefore, they were not tested in glycerol acetylation. The WZ-CP samples did not show satisfactory acetylation yield in the reaction. Even if the variation of synthesis parameters (W loading and calcination temperature) resulted in very different textural and structural properties, different catalytic performances could not be observed in the reaction. Again, it can be seen that in literature the tungstated zirconia tested in esterification reaction were in most of the cases synthesised by wet impregnation. Thus, it could be suggested that co-precipitated samples present different species on their surface.

Zirconia presents an amphoteric character. However, the presence of tungstated species caused an almost full disappearance of the surface anions acting as basic sites, a little increase in the Lewis acid strength of the residual Lewis sites and the appearance of strong Brønsted acid sites [183]. Therefore, the lack of catalytic activity of these solids can be attributed to an inadequate acid strength of acid sites which could result in a strong adsorption of glycerol or water molecules present in the reaction medium which hinders the acetic acid to interact with the active sites.

In Figure 34, it can be seen that there is a large number of points located above the diagonal (carbon balance = 100%) indicating that the measurement of acetic acid in the reaction medium is often quite difficult as it is the limiting reagent. The evaporated acetic acid can return to the liquid medium in form of droplets thus strongly varying the measured concentration. Moreover, it can remain in the GC

Part III: Results

apparatus influencing the consecutive measurements. That is the reason why esters yield is used to follow the reaction rate.

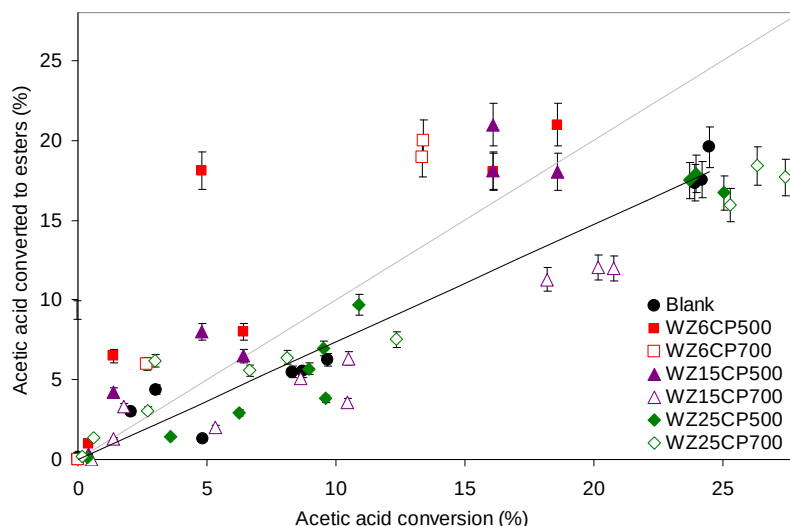


Figure 34. Carbon balance expressed as the acetic acid converted to esters (%) versus the acetic acid conversion (%) for the glycerol acetylation test conducted at 55 °C in presence of WZ-CP samples. The black line represents the blank reaction, included to compare the catalytic behaviour of the solids. The diagonal represent a carbon balance equal to 100%.

3C.1.4. Sulphated zirconia

SZ samples belong to the only series showing different catalytic performances. As cited in the section 3.4.1., sulphated zirconia samples can present very different natures of acid sites depending on the preparation conditions and on the calcination temperature. Nevertheless, sol-gel sulphated zirconia was active in acetic acid esterification as reported for other sulphated zirconia solids reported

in literature which in most cases were synthesised by impregnation method.

Even if zirconia presents an amphoteric character, sulphated zirconia does not present basic sites but only Lewis and Brønsted acid sites [183].

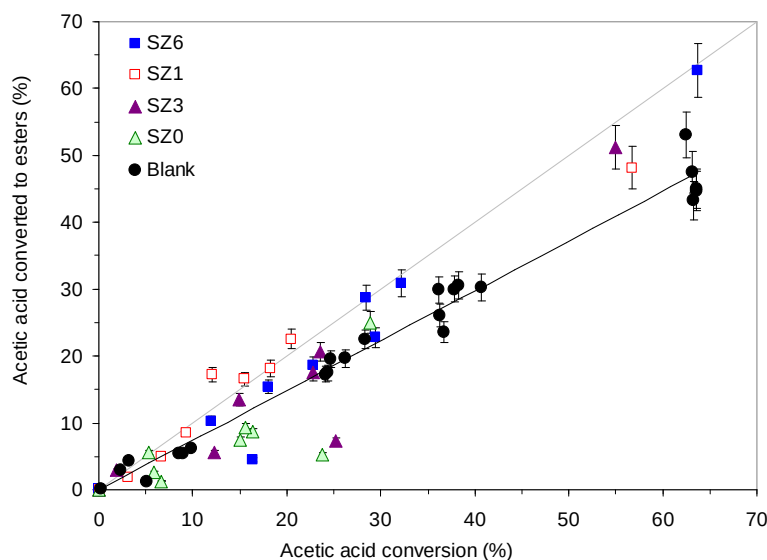


Figure 35. Carbon balance expressed as the acetic acid converted to esters (%) versus the acetic acid conversion (%) for the glycerol acetylation test conducted at 55 °C in presence of SZ samples. The black line represents the blank reaction, included to compare the catalytic behaviour of the solids. The diagonal represent a carbon balance equal to 100%.

In Figure 35, it can be seen that almost all of the points related to the SZ1 and 6 tests are located in the diagonal meaning that all the consumed acetic acid is converted to esters. Thus, the presence of secondary reactions consuming the carboxylic acid can be discarded from this figure.

In order to correlate the different catalytic performances of the series, the strength and the number of acid sites were measured by NH_3 -TPD as further presented in Chapter 4.

3C.3. Conclusions

In Chapter 3A, the screening of different solids belonging to the families of solid acid catalysts is presented. Surface, structure and chemical composition of samples were characterised. The results obtained matched with the data present in literature. Nevertheless, the expected catalytic performance of the synthesised solids did not agree with the experimental results obtained in glycerol acetylation, namely, they were less active than expected.

To verify if the inactivity of the solids was correlated to experimental conditions (used of a large excess of glycerol) or to the features solid (texture and acidic properties) the esterification of n-propanol was conducted in an excess of acetic acid. The results issued from this series of experiments revealed that the reaction medium was not the origin of the different behaviours of the solids in the esterification reaction but that the nature of the solids was responsible.

Several hypotheses were considered in order to elucidate the origin of the behaviour of the solids in the esterification reaction. Among them, the different preparation methods explaining the different catalytic activities obtained in this work from those

appearing in the literature, the presence of basic sites, the solubility of the samples and the presence of secondary reactions were evoked.

Due to the lack of additional experimental data, the carbon balance was used to compare the catalytic properties of the samples.

It can be seen that in the absence of a catalyst there is a consumption of acetic acid that is not converted to esters. It was suggested that the oxidation or dehydration of glycerol could lead to the formation of compound presenting hydroxyl groups which could react with acetic acid forming sub-products. These sub-products were not detected by gas chromatography, probably due to their low solubility in heptanol. Additional experiments would have to be conducted in order to verify this hypothesis.

Only the family of sulphated zirconia samples presented a good catalytic activity in the esterification of acetic acid with glycerol, which is the reactant in excess. The rest of the families showed an inert or inhibitory behaviour.

The inhibitory effect detected for aluminium containing samples was considered to be due to the amphoteric character of the alumina hydroxyl groups and the presence of basic sites. The acetic acid may be strongly adsorbed and therefore be unavailable to interact with glycerol. Moreover, in the case of the Nb-SA samples, the presence of a secondary reaction between acetic acid and the products of glycerol

Part III: Results

oxidation and/or dehydration could be evoked. This latter hypothesis could also be applied for the PA samples PA0.6 and PA0.33.

The inert behaviour of WZ-CP samples may be attributed to the strong adsorption of water or glycerol on the acid sites of the surface, deactivating the solid for further interaction with the acetic acid.

In the case of SZ samples, all the consumed acetic acid form esters. The secondary reactions consuming acetic acid were not detected.

A brief summary of the results obtained from the solids screening and the conclusions attained therein are presented in Table 13.

Table 13. Glycerol acetylation over catalysts of different nature.

Solids	Catalytic performances	Conclusion
Nb-SA: niobium oxide supported on commercial silica-alumina	Inhibitor	Presence of basic sites Secondary reactions consuming acetic acid
PA: amorphous aluminophosphate	Inhibitor	
WZ: tungstated zirconia	Inert	Acid sites poisoned by adsorption of water or glycerol
SZ: sulphated zirconia	Active	Absence of secondary reaction consuming acetic acid

I

CHAPTER 4: FURTHER STUDIES ON SULPHATED ZIRCONIA CATALYSTS

The origin of the catalytic performance and the recyclability properties.

This Chapter focuses on the role of the hydrolysis ratio over the physicochemical properties of sulphated zirconia (SZ) obtained by the sol-gel method. A correlation between the acidic properties of the SZ samples and their catalytic performances in the acetylation reaction is established. It is shown that the lower the acid site density the higher the catalytic activity. Finally, the recyclability properties of a representative sample of the series (SZ1) is also studied. The solid undergoes a progressive deactivation in successive tests due to sulphur leaching which induces a catalytic activity in the homogeneous phase and contamination of the products.

4.1. Introduction

In Chapter 3, it was noticed that only SZ samples increased the esterification rate when added to the reaction medium. More precisely, it has been observed that there are large differences in the surface area and structure of the solids but such differences cannot be directly correlated to the variation of the hydrolysis ratio. The solids obtained were mesoporous and presented different surface areas (29, 68, 31 and 139 m²/g for SZ0, 1, 3 and 6 respectively). Only amorphous and tetragonal phase were present in SZ0, 3 and 6 samples, SZ1 being considered as totally crystallised in the tetragonal phase of zirconia. Concerning the chemical composition, it was noticed that the sulphur content is slightly different for each sample with no correlation with the hydrolysis ratio. The interval of S composition in the bulk varied from 6.24 to 8.30 %_{wt} in S for SZ1 and SZ0 respectively. Moreover, it was not possible to correlate properly the physicochemical properties of the solids with the catalytic performances even if the higher the surface area the higher the catalytic activity. The structure of the samples does not seem to influence the catalytic performances, as both SZ1 (tetragonal structure) and SZ6 (amorphous structure) showed very comparable activities. The differences of catalytic performances between the samples, SZ0 sample being almost inert whereas SZ1 being very active, can neither be explained on the basis of the bulk chemical composition of the sample as SZ0 shows the highest sulphur content and SZ1 the lowest.

4.1.1. Main objectives of this chapter

In the present chapter, the origin of the catalytic performances shown by the different SZ samples is investigated. Moreover, the stability of the prepared solids in terms of recyclability was studied since some previous works suggested a possible deactivation due to leaching of sulphur species. The possibility that the sulphur species could leach away into the reaction medium is also considered. In addition the role of these leached species as a homogeneous catalyst in the reaction has been studied.

The questions discussed during this chapter are:

- (i) What is the role played by the hydrolysis ratio over the properties of the solid?
- (ii) Is there any correlation between the physicochemical properties and the catalytic behaviour? What is this correlation?
- (iii) Are these solids recyclable in this system?

To respond the first two questions, surface composition, acid properties, and the nature of the sulphate species of the solid were analysed by XPS, NH_3 -TPD and FTIR techniques respectively. The results issued from these experiments and the correlation of the physicochemical properties of the solid and their catalytic behaviour shown in the reaction system are presented in the next sections. The

last question related to the reuse of the solids was solved from solubility and recyclability tests.

4.1.2. The nature of sulphated zirconia species

The nature of the sulphate species over zirconia is still very debated and is highly dependent on the preparation method (precipitating agent, sulphating agent, precursors...), calcination temperature, pre-treatment, and storage [204-205]. Several works proposed possible structures for the sulphated species [160-165, 205-207].

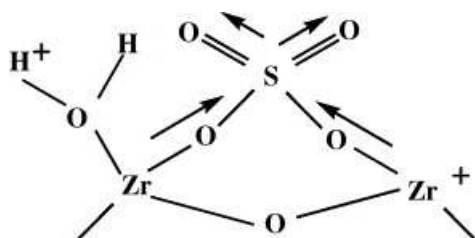


Figure 36. Model presented by Arata and co-workers [208]. Figure taken from reference [209].

Yamaguchi and co-workers proposed the presence of strong Lewis acid sites generated by the inductive effect of S=O double bond, which increases the electron deficiency of the atom attached to the zirconium sulphate group. A summary table collecting the S-O stretching frequencies of various sulphur oxides is presented in reference [210]. A similar model was proposed by Arata et al. [208] (Figure 36). From IR results, a model based on a surface structure of SO₄ species combined with Zr elements in the bridging bidentate

state, similarly to those found in sulphated titania, was proposed. They correlate the results presented by Yamaguchi and co-workers concerning the inductive effect of S=O leading to a strong Lewis acidity of Zr^{4+} [210]. Moreover, Lewis acid sites can be converted to Brønsted acid sites via proton transfer in the presence of water [208].

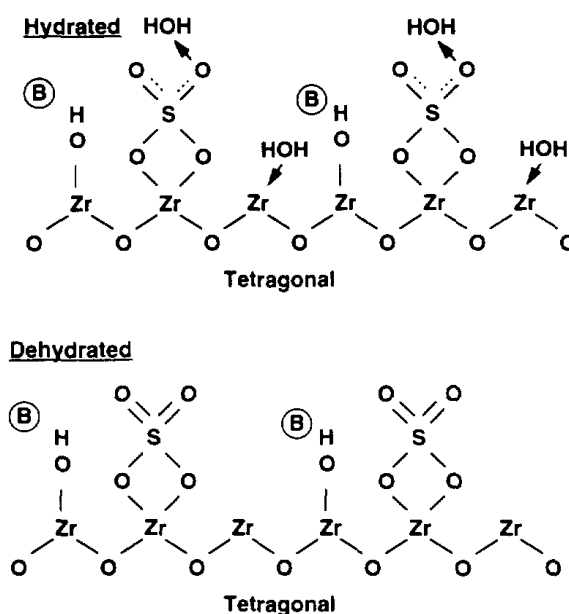


Figure 37. Model proposed by Ward and Ko [211]. (B): Brønsted acid site.

Tanabe and co-workers [212], also on the basis of a chelating bidentate model, proposed that Brønsted acid sites are generated by the interaction of hydrocarbons or water with Lewis acid sites. Ward and Ko [211] suggested a similar structure but added that the electron-inductive effect of two S=O bonds in the sulphate group could also influence the hydroxyl group bonded to a Zr atom adjacent to the chelated Zr (Figure 37).

Hino and et al. proposed a structural model composed by polysulphate species presenting mainly three or four S atoms with two ionic bonds of S-O-Zr, in addition to coordination bonds of S=O with Zr [209]. Figure 38 presents the monodentate, bisulphate and trisulphate species.

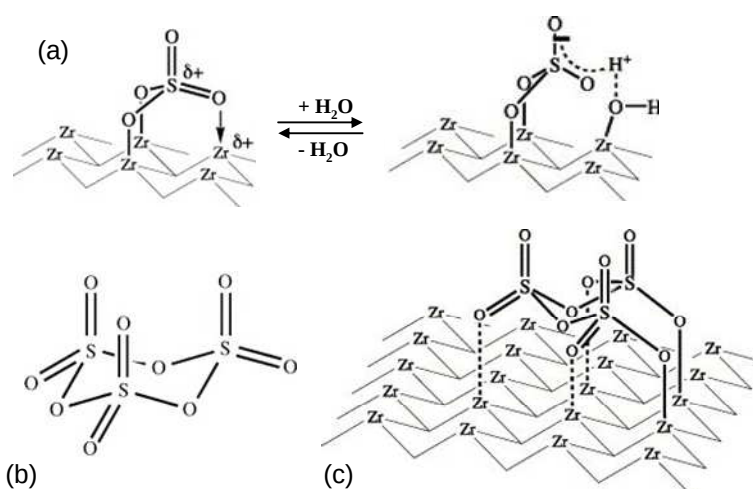


Figure 38. Models proposed by Hino et al [209]. (a) Mono-sulphate structure, (b) SO_3 cyclic trimer and (c) trimer structural model.

Laizet et al. suggested that sulphate ions can be distributed into three surface states of different densities: pyrosulphate, bidentate sulphate and thionyl tetraoxide [213]. The defined species would be presented at the same time on the zirconia surface regardless of the preparation method. The group of Vedrine studied the IR spectra of SZ samples with different hydration degrees [161]. The calcination of the samples led to a condensation of the hydroxyl groups of $\text{Zr}(\text{OH})_4$ resulting in a tetragonal crystallized sample without any change of the sulphated species. Models based on SO_3 species coordinated with

zirconia were proposed. Morterra and co-workers studied also the effect of support calcination temperature, sulphur content and the calcination temperature [166]. Based on the experimental results, it was suggested that both Brønsted and Lewis acidic centres can exist at the surface of a sulphated zirconia either isolated or, forming polynuclear units. The same authors stated that only structures presenting two S=O oscillators with an angle close to 90° are active in n-alkene isomerisation [214].

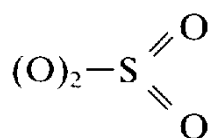


Figure 39. Model proposed by Morterra and co-workers [214].

Most of the works agree that the Brønsted/Lewis acid sites ratio and strength are influenced by the hydration degree and the calcination temperature [156-159, 166-167]. In general, the amount of Brønsted acid sites decreases as the calcination temperature increases, on the benefit of Lewis acid sites whose number increases [155]. Further details of these structures can be found in [204, 211, 215-216] and references therein.

4.2. Experimental

4.2.1. Preparation of the catalysts

SZ samples were prepared by sol-gel method starting from Zr propoxide and using H_2SO_4 both as the sulphating agent and as the initiator of the polycondensation of the gel (S/Zr initial atomic ratio= 0.5). The hydrolysis molar ratio ($\text{H}=\text{H}_2\text{O}/\text{Zr}$) was modified from 0 to 6. Calcination was performed in air at 560 °C. Catalysts are denoted SZH, where SZ stands for sulphated zirconia and H represents the hydrolysis ratio employed. Further details concerning the preparation of SZ samples are given in Chapter 1.

4.2.2. Further solid characterisation

N_2 -physisorption, X-ray diffraction ICP-AES and FTIR techniques were described in Chapter 1.

As a reminder, XPS analysis was performed on a Kratos Axis Ultra spectrometer. For SZ samples the sequence of spectra was recorded as follows: survey spectrum, C 1s, O 1s, S 2p, Zr 3d, and C 1s again, to check the stability of charge compensation as a function of time and the absence of degradation of the sample during the analyses. The C-(C,H) component of the C 1s peak of carbon was fixed to 284.8 eV to set the binding energies. Data treatment was executed with the CasaXPS program. The O 1s peak was split into two components (O-S and O-Zr) attributed to sulphate species and the

Zr-O network of zirconium oxide respectively, without any constraint imposed. The (S 2p_{3/2})/(S 2p_{1/2}) intensity ratio was fixed at 2 with an energy difference of 1.18 eV. The (Zr 3d_{5/2})/(Zr 3d_{3/2}) intensity ratio was fixed at 1.5, with an energy difference of 2.43 eV [217]. Molar fractions were calculated using normalized peak areas on the basis of acquisition parameters and sensitivity factors provided by the manufacturer.

Acidity properties of samples were evaluated by temperature programmed desorption of ammonia (NH₃-TPD), as described in Chapter 1. Prior to NH₃-TPD studies, samples were pre-treated at 560 °C for 1 hour in a flow of helium gas (Praxair, 60 ml/min).

4.2.3. Catalytic performances measurements

4.2.3.1. Esterification tests

Several additional tests were performed in order to compare the activity of SZ samples. Amberlyst-15 was used as a reference catalyst after drying under vacuum at 105 °C overnight. The role of the different species participating in the reaction was verified by conducting several tests in presence of zirconia (ZrO₂ monoclinic, Acros, 98,5 %, specific surface area: 64.3 m²/g), SO₄²⁻ anions as added in the reactor via dissolution in the reaction medium of (NH₄)₂SO₄ and H⁺ as added in the reactor via H₂SO₄. All these experiment were carried out with equivalent quantities of presumed active species as for the SZ1 sample (Zr and S).

Part III: Results

Moreover, to verify the role of acidic properties of the solids over the catalytic performances, an additional test was carried out in presence of SZ3 sample, but varying the mass of solid added (~0.35 g/run instead of 0.25 g/run), so that the reaction was conducted with the same number of acid sites as with the SZ1 sample. This test is named SZ3*.

4.2.3.2. Effect of glycerol excess

The esterification is an equilibrated reaction. Therefore, the use of an excess of one reagent is needed to lead the reaction towards the product formation. As the working conditions present an excess of glycerol, it would be useful to study if this excess has a buffering effect in the reaction system during a change in the concentration of reactants (acetic acid) or products (esters and water).

For this type of test, a mixture of MAG, DAG and TAG (Monoacetin, 40%, Acros) or distilled water is added in an amount equal to that which would be obtained if the acetic acid conversion was equal to 100%. These additions were conducted at reaction times equal to 0 and 16 hours. Similarly, the effect of acetic acid addition was studied: a quantity of 3.8 ml of acetic acid was added at 16 hours reaction time. The different kinetic curves of acetylation yield were fitted by linear regression.

4.2.3.3. Esters distribution

A specific test was carried out in order to elucidate whether the origin of the preferential formation of one product over another was thermodynamic or catalytic. The test was performed at the same temperature and pressure as the catalytic tests. 1.57 ml of a mixture of esters (Monoacetin, 40%, Acros) was added to 40 ml of glycerol, in the presence of 0.25 g of SZ1 catalyst. For comparison, the same test was performed in the absence of catalyst (blank reaction).

4.2.3.4. Leaching tests

The leaching tests were conducted in the same reactor as the catalytic tests with a catalyst concentration equal to 5 g/l of glycerol and a temperature equal to 65 °C. S and Zr contents of the liquid media filtered twice (1st filtration: filter paper Whatman 6 and 2nd filtration: PTFE filter syringe VWR, filtration thresholds 3µm and 0.45 µm respectively) were analysed by ICP-AES technique. The glycerol solution was placed in a beaker and submitted to evaporation in a hot plate. 1 ml of H₂O₂ (30%) was added to destroy organic matter and submitted at moderate temperature for evaporation. This step was repeated 5 times. The residue was dissolved with 2 ml of HCl (37%) and diluted to 20 ml with distilled water.

Two types of tests were carried out: one in the presence of glycerol and the other one in the presence of the reaction mixture (acetic acid and glycerol).

4.2.3.5. Homogeneous and recyclability tests

Homogeneous and recyclability tests were carried out in the same conditions as for the acetylation runs, but at 16 hours reaction time of a first acetylation run the catalyst was separated from the liquid medium by centrifugation and reused in a new run, this being achieved up to a fourth run. On the other side, the so recovered liquid medium was filtered (filter paper Whatman 6) and kept in the reaction conditions for detecting possible homogeneous catalysis induced by sulphur species potentially leached by the solid catalyst and quantified by ICP. As for the test related to the buffering effect of glycerol excess, the acetylation yield was modelled by linear regression.

4.3. Results and discussion

4.3.1. Further solid characterisation

XPS analyses were performed for all samples to verify the presence of sulphate species and determine the S/Zr final molar ratio at the surface. The results are presented in Table 14. No impurities were found, except the carbon contamination due to the analysis itself. All samples exhibit a lower S/Zr final molar ratio on the surface than in the bulk. This is a typical phenomenon obtained for all the samples synthesised by sol-gel and calcined [215].

All samples show the peak associated to the S 2p_{3/2} (Be = 169.4 eV), which confirms the presence of sulphur with an oxidation state +

VI, which is expected for sulphate groups at the solid surface. Moreover, any reduction reaction associated with the solvent (alcohol) and the alkoxide decomposition were avoided by the calcination step in air [165, 218].

Table 14. Molar ratios determined by XPS and binding energies (Be) of SZ samples.

		SZ0	SZ1	SZ3	SZ6
Molar ratio	S/Zr	ICP	0.46	0.31	0.43
		XPS	0.38	0.29	0.37
	C/Zr	1.170	0.928	0.878	0.771
	O _{ZrO2} /Zr	1.095	1.277	1.237	1.218
	O _{SO4} /Zr	2.006	1.490	1.727	2.039
Be (eV)	Zr 3d _{5/2}	182.9	182.9	182.9	182.9
	S 2p _{3/2}	169.4	169.4	169.4	169.4
	O 1s	O-Zr	530.3	530.3	530.3
		O-S	532.1	532.1	532.1

Regarding the 1s spectrum of the oxygen (Figure 40), two components can be distinguished: the first at 530.3 eV, corresponding to the oxygen in the network of zirconium oxide and the second, located at 532.1 eV, attributed to oxygen involved in sulphated species [219-220]. It can be noticed that the intensity of the peak located at 532.1 eV becomes more intense when the S/Zr final molar ratio of the surface increases, indicating that a larger number of oxygen atoms are bound to sulphur atoms. This is in agreement with the experimental data in Table 14, where the surface SO₄/Zr is seen to increase when the surface ratio S/Zr increases.

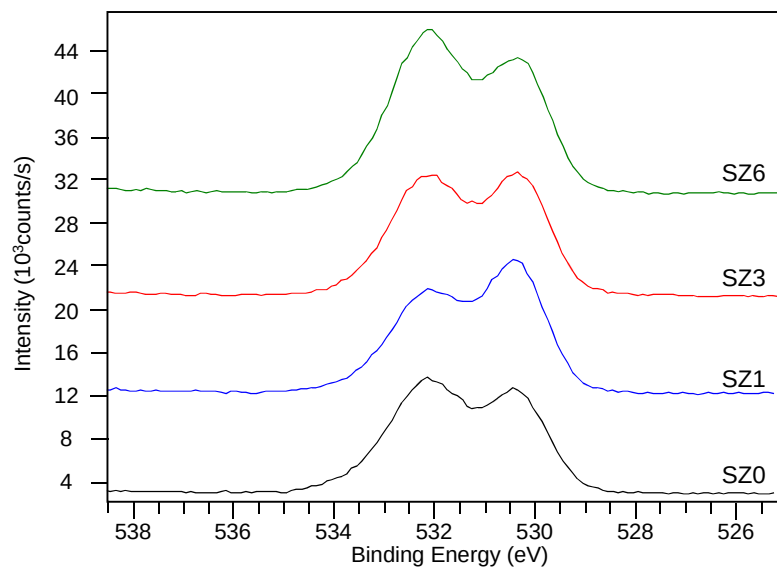


Figure 40. O 1s XPS spectra for the different SZ samples.

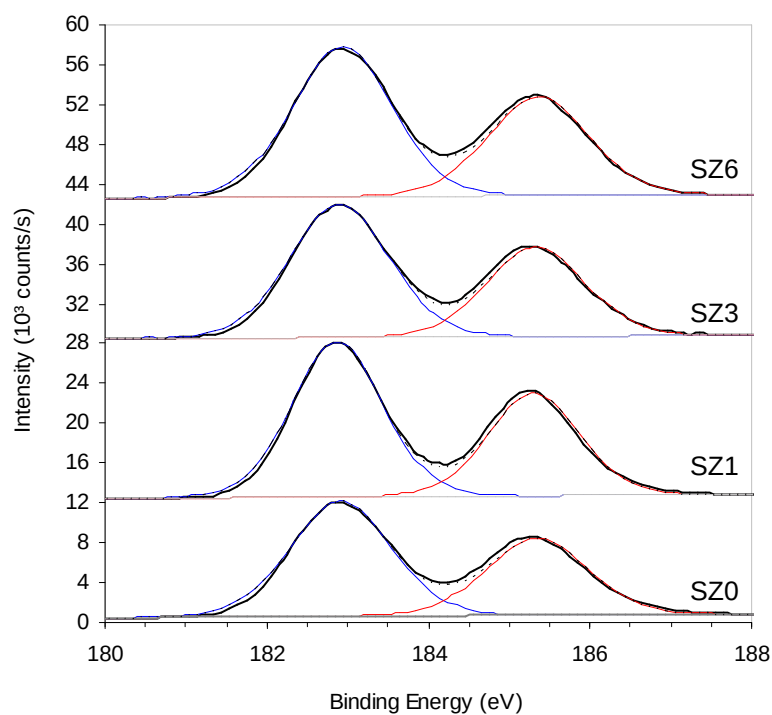


Figure 41. Zr 3d XPS spectra for the different SZ samples.

The binding energies of Zr peaks $3d_{3/2}$ and $3d_{5/2}$ of zirconium oxide are typically 182.2 eV and 184.6 eV [155, 219]. In the Figure 41, a shift of 0.7 eV to higher energies is observed for our samples, indicating the electron attracting effect of sulphate groups on the surface Zr species [155]

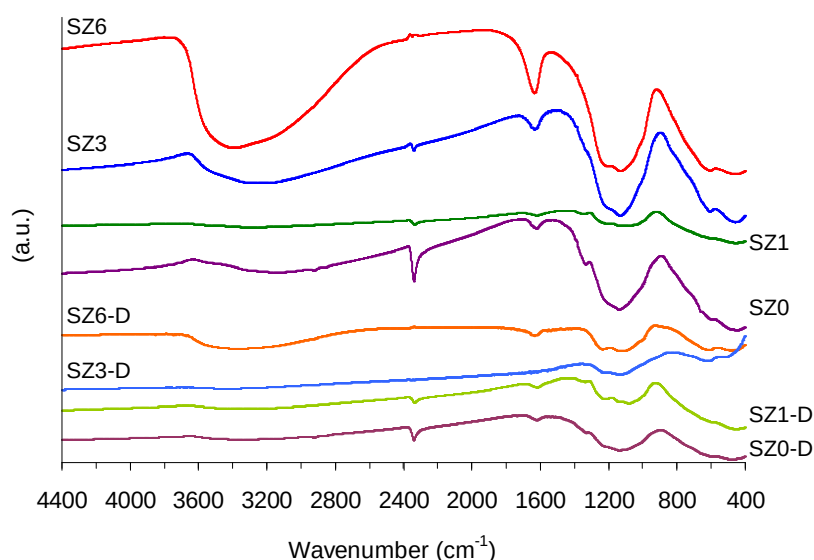


Figure 42. FTIR spectra for the SZ samples in the 400-4000 cm^{-1} region. Analysed as stored and after drying 24 hours in air at 120 °C (D).

In Figure 42, the FTIR spectra of SZ solid analysed without pre-treatment and after drying (24 hours in air at 120 °C) are presented. For the non pre-treated samples a broad and unresolved band is observed in the region 3600-3000 cm^{-1} which corresponds to the stretching vibration mode of hydroxyl groups assigned to physisorbed water [157, 161, 221]. Moreover, the band at 1630 cm^{-1} corresponds to the adsorbed water bending mode (δ_{HOH}) [157]. These bands

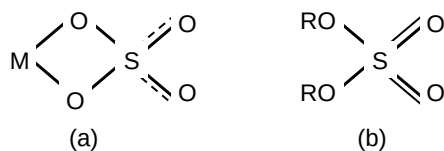
Part III: Results

disappeared almost completely for samples treated at 120 °C. Nevertheless, the SZ1 samples show the less marked modification of the bands related to adsorbed water, which could suggest the lower hydration degree of SZ1 in comparison with the other solids.

The FTIR bands are summarised in Table 15. All the samples show spectra with broad peaks having shoulders at the frequencies corresponding to the typical vibrations of a chelating bidentate sulphate ion SO_4^{2-} coordinated to metal elements (characteristic bands at 1090-1125 and 1210-1230 cm^{-1} [160, 208]). This structure is reported to present an inductive effect of sulphur-oxygen bonds, resulting in an increase in the Lewis acidity of the Zr^{4+} cation [215]. It is quite probable that the hydroxyl groups formed on the surface act as Brønsted acid sites. [215]. Moreover, in Figure 43 it can be seen that some spectra present a slight band at 1325-1310 cm^{-1} which could correspond to S species with a similar structure to the organic sulphates (characteristic bands at 1350-1460 cm^{-1} [160]) due to the remaining fragments of precursor of the sol-gel synthesis. That can also be correlated to XPS results, showing that the content of C was higher for SZ0 and SZ1 samples than for SZ3 and SZ6. Taking into account the XPS and FTIR results it can be suggested that the nature of sulphur species was chelating bidentate SO_4^{2-} species in mono and polysulphate structures.

Table 15. FTIR absorption bands for the SZ samples in cm^{-1} .

	Characteristic bands (cm^{-1})				Corresponding to
	SZ0	SZ1	SZ3	SZ6	
Non pre-treated	569	451	436	420	Crystallised ZrO_2 , characteristic bands : 415 and 557 cm^{-1} [161]
	586	586	594	594	
	1121	1119	1115	1110	Chelating bidentate SO_4^{2-} species [160, 208]
	1207	1213	1215	1213	
	1325	1326	-	-	Organic sulphate [160]
Dried	440	476	460	451	Crystallised ZrO_2 [161]
	592	596	586	586	
	1126	1100	1096	997-1088	Chelating bidentate SO_4^{2-} species [160, 208]
	1231	1221	1213	1205	
	1315	1308	-	-	Organic sulphate [160]

Figure 43. Structure of (a) Chelating bidentate SO_4^{2-} and (b) organic sulphates [160].

NH_3 -TPD technique was used to examine the distribution of acid sites strength and to quantify the total acidity of the samples. The maximal desorption temperature is quite similar for all the samples (Table 16). In addition, it can be seen that the distribution of acid strength differs slightly among the solids. Nevertheless, SZ6 sample exhibits the largest proportion of stronger acid sites (16.3%) in spite of its lowest proportion of weak acid sites (35.6%), based on the distribution of strength stated in Chapter 2: weak (35 to 150 $^\circ\text{C}$);

Part III: Results

medium (150 to 350 °C) and strong (350 to 600 °C). It can be noticed that the hydrolysis ratio, H, slightly influences the proportion of weak acid sites in the following way: the higher the H, the lower the proportion of weak acid sites. Regarding the total acidity, samples can be sorted as follows SZ6, SZ1, SZ3 and SZ0, SZ6 being the most acidic catalyst. If the acid site density ($\mu\text{mol NH}_3/\text{m}^2$) is plotted versus the total number of acid sites (Figure 44), it clearly turns out that values of H=1 and H=6, presenting the highest total number of acid sites, also show the lowest acid site density. In brief, solids with higher number of acid sites are those whose acid site density is lower.

Table 16. Acid properties of SZ samples measured by NH_3 -TPD. (Max. Des.T): Maximal desorption temperature; (Tot. AS): Total acid sites; Distribution of acid sites strength: (W) weak, (M) medium and (S) strong.

Sample	Max. Des.T (°C)	Tot. AS ($\mu\text{mol NH}_3/\text{g}$)	Distribution of acid sites strength			$\mu\text{mol SO}_4^{2-}$ (XPS)/ μmol NH_3 (TPD)
			W (%)	M (%)	S (%)	
SZ0	126	621	41.9	47.4	10.6	3.70
SZ1	133	1450	41.5	47.6	10.9	1.27
SZ3	132	1046	37.2	50.7	12.0	2.17
SZ6	107	1896	35.6	48.1	16.3	1.35

Data presented in the last column of Table 16 represent the sulphur content of the surface measured by XPS reported to the number of acid sites, considering that each molecule of NH_3 corresponds to one acid site as said in Chapter 1. The values of $\text{SO}_4^{2-}/\text{NH}_3$ are closer to 1 for samples SZ1 and SZ6 than for SZ0 and SZ3. This can be interpreted as follows: the polynuclear sulphate groups represent a single acid site. Consequently it can be claimed that a

higher specific surface area favours the spacing of the sulphate groups, leading to a larger number of total acid sites presenting lower density and thus higher accessibility.

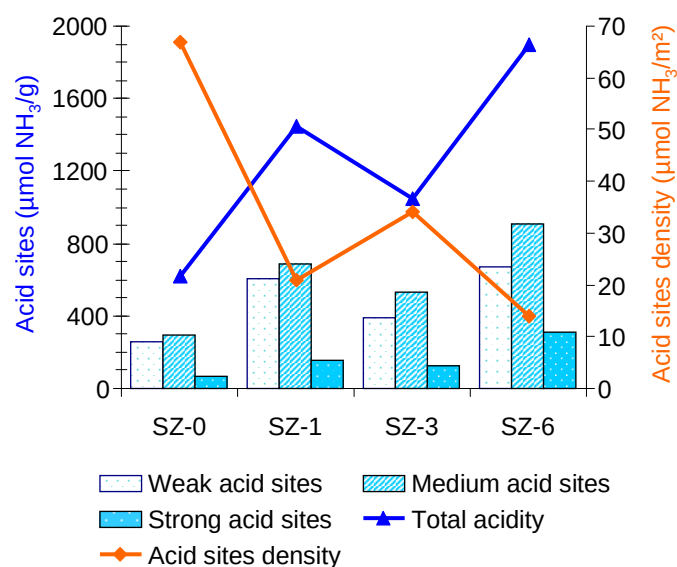


Figure 44. Acidic properties for the SZ samples. Left axis: total number of acid sites, right axis: acid sites density. Bars: acid strength distribution.

4.3.2. Catalytic performances

4.3.2.1. Esterification tests

In Chapter 3, the catalytic performances of sulphated zirconia catalysts have been reported. In Table 17 the distribution of esters obtained in the blank reaction, in presence of SZ samples and with Amberlyst-15 is presented. The total acetylation yield obtained with Amberlyst-15 could be considered as corresponding to the equilibrium of the reaction.

Part III: Results

Table 17. Conversion of acetic acid and acetylation yield of the glycerol acetylation experiments conducted at 55 °C. The relative standard deviation of the total acetylation yield is approximately 6.5%.

Test/Sample	Acetic acid conversion (%)	Total acetylation yield (%)	Esters molar distribution (%)	
			MAG	DAG
Blank (24 h)	24.7	19.5	99.8	0.2
Blank (120 h)	63.2	46.8	98.4	1.6
SZ0	28.9	23.2	99.4	0.7
SZ1	48.2	54.0	98.9	1.2
SZ3	44.2	36.5	99.0	1.0
SZ6	63.6	62.1	98.3	1.7
Amberlyst-15	93.8	~ 80	98.0	2.0

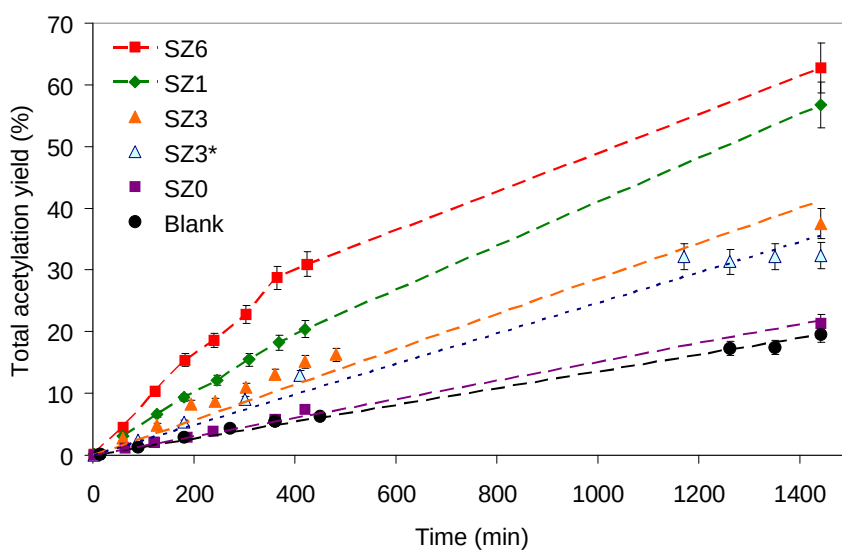


Figure 45. Total yield in esters profiles of SZ samples during glycerol acetylation conducted at 55 °C.

Taking into account the previous characterisation results, a correlation between the physicochemical properties of the solid and their behaviour in the esterification reaction can be established.

As said in the precedent section, it is clearly observed from Figure 45 that the catalytic activity is independent on the structural properties of the solid: while SZ6 is amorphous and SZ1 is totally stabilised in the tetragonal phase of zirconia, both solids evidence comparable final acetylation yields. All the catalysts showed a similar sulphur bulk content, so this parameter can neither be the main parameter influencing the catalytic performances developed in the esterification reaction.

In Figure 46 the total number of acid sites is plotted (taking into account the acid sites strength) versus the final esterification yield at 24 hours reaction time. It can be seen that although having the at same number of total acid sites and strong acid sites, SZ1 and SZ3* did not present the same esterification yield. Thus neither the total number of acid sites or the number of strong acid sites influences the glycerol acetylation yield.

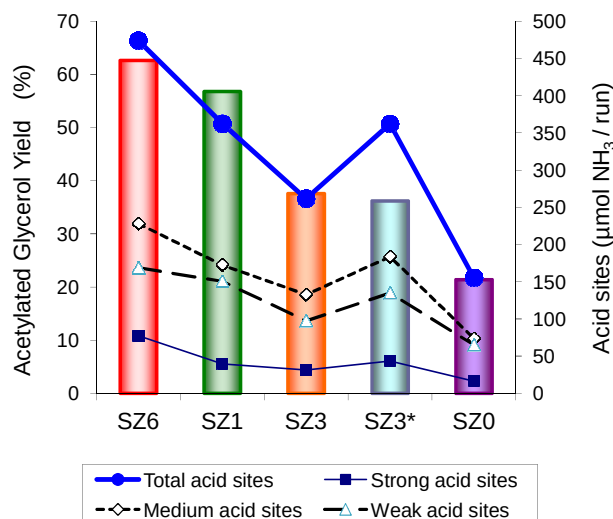


Figure 46. Acetylated glycerol yield (bar graph, left axis) at 24 hours reaction time (reaction temperature=55 °C) vs the number of acid sites of SZ samples (rhombus line, right axis).

On the contrary, while comparing the final acetylation yield of the reaction with the density of acid sites (Figure 47) a clear relation is observed: the lower the acid site density, the higher the catalytic activity. Assuming that the rate determining step in the esterification reaction is the nucleophilic attack by hydroxyl group of the alcohol onto the acetic acid adsorbed over the surface of the catalyst [53, 222], this phenomenon could be explained as follows. The acetic acid molecules adsorbed on the isolated acid sites could present a lower steric hindrance for the approach of glycerol than the acetic acid molecules adsorbed on very close acid sites. Therefore, the solid presenting the lower density of acid sites could facilitate the nucleophilic attack of protonated acetic acid by glycerol molecules.

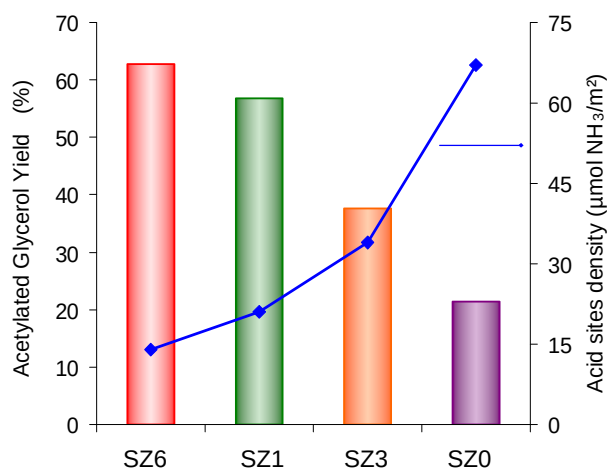


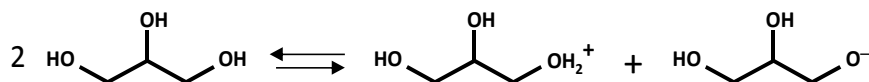
Figure 47. Acetylated glycerol yield (bar graph, left axis) at 24 hours reaction time (reaction temperature=55 °C) vs acid site density of SZ samples (rhombus line, right axis).

In order to verify the influence of the different compounds present in the reaction medium a series of catalytic tests were conducted in presence of ZrO_2 , sulphuric acid and $(\text{NH}_4)_2\text{SO}_4$ (0.1 mmol/run). The final acetylation yield of a 24 hours reaction test carried with monoclinic ZrO_2 was equal to 20% indicating that non-sulphated zirconia is inactive in this reaction. The use of SO_4^{2-} anion resulted in a total acetylation yield only equal to 10% mainly due to the presence of NH_4^+ cation. While H_2SO_4 is used with an equivalent quantity of S species as when SZ1 is used, the equilibrium point of the reaction is achieved in 5 hours.

Every solvent containing hydrogen can undergo autoprotolysis, that is to say the proton transfer between two identical molecules. Given that glycerol is used in large excess, it can be considered as the

Part III: Results

solvent of the reaction. Therefore, the following equation can be written:

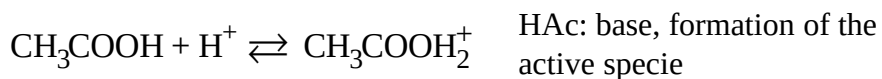
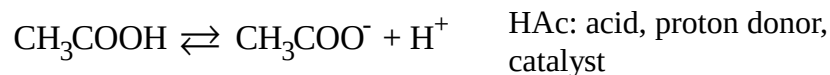


Where the autoprotolysis constant is equal to:

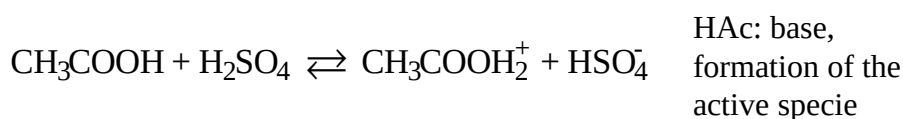
$$K_s = \frac{[H_2S^+][S^-]}{[HS]^2}$$

The dissociation of the different compounds in the glycerol (acetic acid, $(\text{NH}_4)_2\text{SO}_4$ and sulphuric acid) depends on the autoprotolysis constant of glycerol, and can strongly differ versus the dissociation in other solvents such as water.

It can be suggested that in the pseudo-catalysed, acetic acid, HAc, acts as a Brønsted acid (proton donor) and as a base (accepting the proton) forming the active species $\text{CH}_3\text{COOH}_2^+$ necessary to the nucleophilic attack of the alcohol:



Likely, when a strong Brønsted acid as sulphuric acid is used as catalyst, the acetic acid acts only as a base, thus forming the active species:



The $(\text{NH}_4)_2\text{SO}_4$ can be considered as totally dissociated in glycerol (dielectric constant = 40.2, making it a dissociative solvent [182]). However, without experimental data it is difficult to determine the interaction with the dissociated species of acetic acid. Therefore, no further conclusions can be made to explain the inhibitory behaviour of ammonium sulphate salt.

4.3.2.2. Effect of glycerol excess

The study of the buffering effect of glycerol was addressed in two ways: by testing the influence of the addition of products: esters or water (1), and of acetic acid (2). The results for these tests are shown in Figure 48. For the sake of clarity the values of the slopes of the esterification rate and the linear regression coefficients are shown in Table 18. The initial esterification rates of tests relative to the product addition at time equal to 16 hours are not represented, only the standard catalytic test is shown. When adding a product of the reaction (water or esters) at 16 hours reaction time, the slope of the esterification rate decreases by half, regardless of the type of product added. Similarly, the same addition at reaction time equal to 0 resulted

Part III: Results

in a decrease of the esterification rate. Addition of a mix of esters has the same impact, whatever the moment at which the addition was executed, 0 or 16 hours. Nonetheless, it is not the case with the addition of water at 16 hours which caused a sharp decrease in the esterification rate in comparison with the addition at time 0. This is likely due to the hydrolysis of the esters present in the reaction medium.

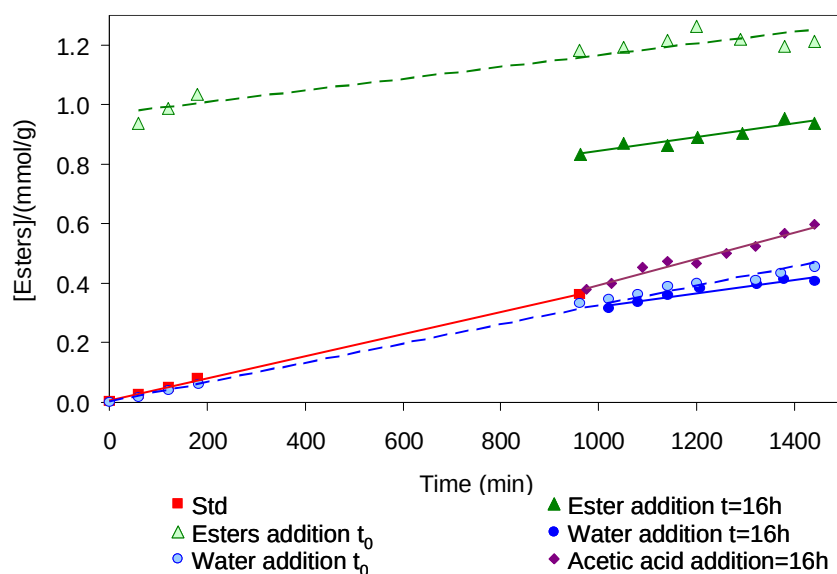


Figure 48. Effect of the addition of reactant (acetic acid) and products (esters and water) on the esterification rate. «Std»: standard test. Temperature=55 °C.

When the addition of acetic acid is carried out after 16 hours of reaction, there is an increased production of esters. This is quite logical because the acetic acid itself is able to catalyse the reaction, so more acetic acid means more protons available to catalyse the reaction. In summary, these findings show that despite the large

excess of glycerol present, the reaction system evolution towards the equilibrium can be modified by a slight variation of the amounts of compounds participating in the reaction.

Table 18. Linear regressions parameters established for investigating the influence of reactant or products addition on the esterification rate.

Evolution of the esters concentration versus time	Slope x 10 ⁻⁴ (mol esters/ g min)	R ² (%)
Standard test	3.9	99.50
Ester addition t = 16 hours	2.3	91.36
Esters addition t ₀	2.0	90.10
Water addition t = 16 hours	2.2	92.40
Water addition t ₀	3.2	99.46
Acetic acid addition t = 16 hours	4.4	96.92

4.3.2.3. Esters distribution

Regarding the distribution of esters developed by each catalyst, presented in Table 17, no remarkable difference is noticed. This is because the distribution of esters is determined by the equilibrium of the reaction, which depends only on the reactants concentrations and the temperature, being not influenced by the catalyst used. Thus, it can be claimed that the only role of the catalyst is to accelerate the reaction toward the equilibrium. In the conditions applied, the major product of the reaction was the MAG (with 90% 1-MAG and 10% 2-MAG). The yield to DAG was always lower than 2% (with 70% 1-3DAG and 30% 1-2DAG). In these conditions the formation of TAG was never observed.

Part III: Results

Nevertheless, in order to verify that the catalyst does not influence the distribution of esters obtained in the reaction, a test in presence of a mix of esters was conducted. As shown in Figure 49, when starting from the acetin mixture, the concentration of esters other than 1-MAG progressively decreases, while that of 1-MAG increases. This tendency is more pronounced for 2-MAG. When a catalyst (SZ1) was added to the mixture, this rearrangement was accomplished faster. This demonstrates that the most stable ester in our reaction conditions is 1-MAG, and that the catalyst does not influence the distribution of produced esters.

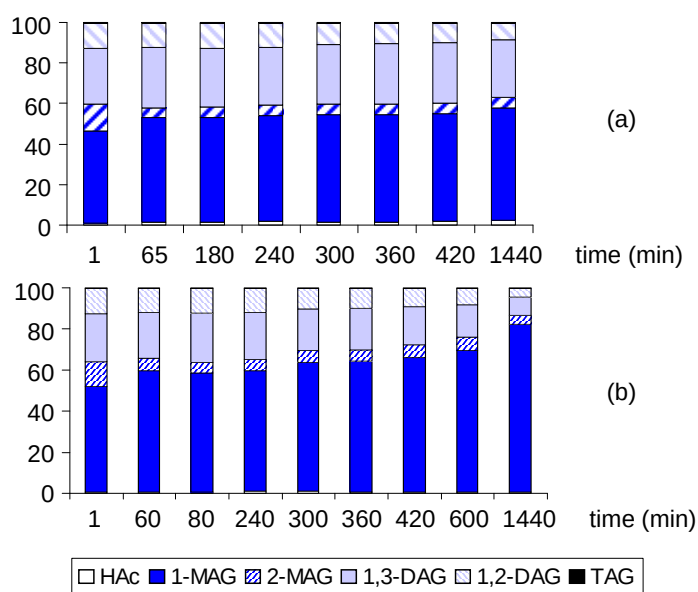


Figure 49. Distribution of esters test expressed in percent. (a) Blank, (b) test carried out with SZ1. Reaction temperature=55 °C.

4.3.2.4. Leaching tests

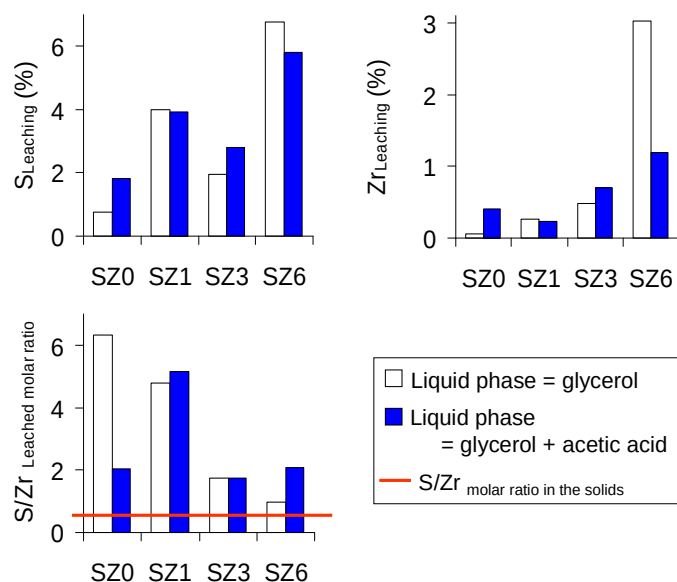


Figure 50. S and Zr leached expressed in relative percentages: (Element analysed in the liquid medium/ initial content of the element on the solid) $\times 100$. **S/Zr_{Leached} molar ratio:** S/Zr molar ratio in the treated liquid medium compared to the nominal bulk S/Zr molar ratio (horizontal line). Liquid media were filtered with a filtration threshold of 0.45 μm .

The results of the leaching tests are shown in Figure 50 which represents the losses of S and Zr in %_{wt} of the initial sulphur and zirconium present in the solid. The S/Zr molar ratio determined for the liquid medium is compared with the S/Zr nominal molar ratio of the solids. All samples, except SZ6, show losses lower than 5% for each element. However, the S/Zr molar ratios calculated for the liquid medium indicate a significant preference of sulphur leaching. In the case of SZ6 sample, the leaching values are the highest but the S/Zr molar ratio calculated for the liquids remains quite low. The presence

Part III: Results

of solid particles in suspension was suspected and verified by means of optical microscopy.

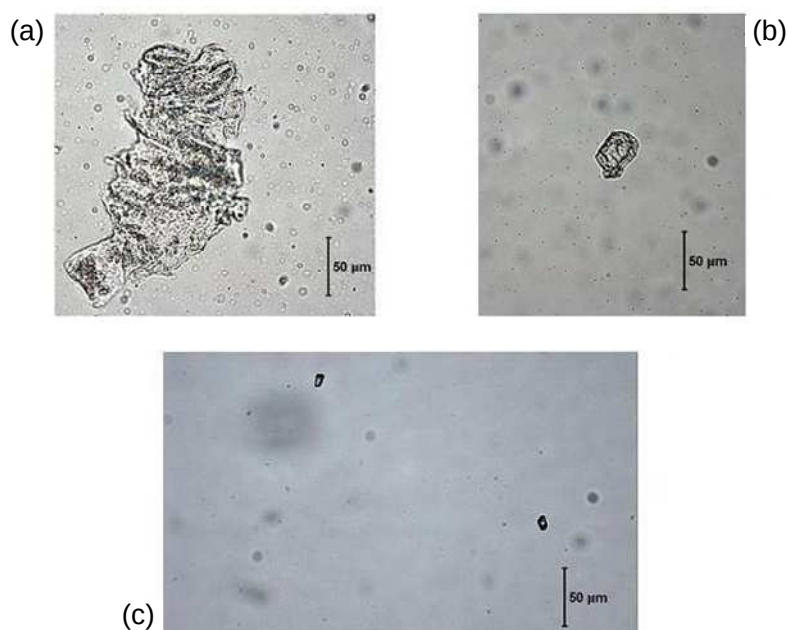


Figure 51. Optical microscope images of the liquid medium issued from leaching tests with SZ6. (a, b) after vacuum filtration on Whatman No.6 filter paper and (c) after filtration on PTFE filter syringe.

The presence of solid particles in the filtrated liquid medium issued from the leaching test of SZ6 was verified by an optical microscope. Few particles larger than 200 microns (Figure 51 (a)) were found; particles with a size of about 50 microns (Figure 51 (b)) were present in higher concentration. These particles were not exclusive to this catalyst, as they are also present in all other liquid media recovered from leaching tests. Nevertheless, the presence of particles for SZ0, SZ1 and SZ3 were lower. The liquid medium was

thus submitted to an additional filtration with PTFE filter syringe (filtration threshold = 0.45 μm). The images revealed the presence of fine particles remaining in the filtered liquid medium for the SZ6 sample (Figure 51 (c)).

Therefore, it can be concluded that SZ6 exhibited a low mechanical resistance and it was divided in fine particles smaller than the filter threshold during the leaching test.

4.3.2.5. Homogeneous catalysis and catalyst recyclability tests

The existence of sulphur leaching was detected in the previous section. Thus, the role of these leached species as catalysts in homogeneous phase and as the origin of the possible deactivation of the solid is questioned.

Both SZ1 and SZ6 presented good performances in the catalytic reaction but only the SZ1 sample underwent additional studies in homogeneous and recyclability tests. This sample was chosen because of its high activity, and its better mechanical resistance compared to SZ6. SZ6 sample was divided in fine particles during the catalytic test which complexified the filtration and consequently precluded an efficient recuperation process.

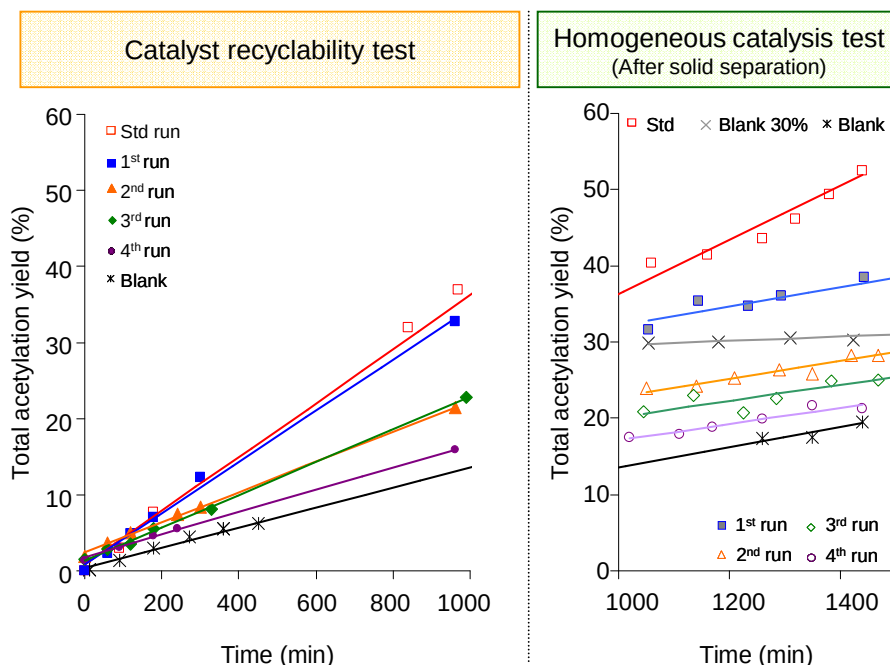


Figure 52. (Left) recyclability test performed over SZ1 sample at 55 °C. Reference lines: the activity of one standard test «Std run» and the blank reaction «Blank». «N-run» stands for the tests carried out in presence of the solid. (Right) Reference lines: «Std run» (carried out in presence of the SZ-1 sample), «Blank» and «Blank 30%» which correspond to the activity of the non catalysed reaction after achieving an acetic acid conversion close to 30%. « N-run » stands for the activity shown by the liquid phase after its separation from the solid.

The results regarding the recyclability tests carried out over the reused SZ1 solid are shown in Figure 52 (left). It can be observed that in the first run the total acetylation yield of the solid is very close to the standard test which confirms the repeatability of the tests. The activity developed in the second use of the sample is lower but still remains higher than for the blank reaction. In the successive runs, the activity drops at every reuse of the catalyst. The latter is totally deactivated at the 4th esterification run since the slope of the catalysed

reaction is the same as for the reaction carried out without adding a catalyst. This deactivation is interpreted to be a consequence of sulphur leaching from the surface of the solid which was quantified by ICP-AES analysis of the recovered and filtered liquid media. In Table 19, it can be observed that there is a preferential leaching of sulphur species as the S/Zr molar ratio measured in the filtered liquid media is higher than 0.5. The quantity of sulphur leached is the highest at the first run and corresponds to a loss of 2.9%_{wt} of the sulphur initially present (corresponding to 100%_{wt} of S). This value is lower than the one corresponding to the solubility test due to the lower temperature applied. However, this leaching does not bring a total loss of activity. The solid is indeed still active during the second run, indicating the persistence of sulphates attached to the surface. Unfortunately, these remaining species are not more resistant to leaching than those leached in the 1st run as they also got removed from the solid in the successive runs, leading to impoverishment of the sulphur content at the surface of the catalyst and to the deactivation of the latter.

Table 19. Concentration of leached species in the filtered liquid medium after the recyclability tests.

	[S] (ppm)	[Zr] (ppm)	S/Zr
1 st run	7.9	9.7	2.30
2 nd run	3.1	6.1	1.45
3 rd run	1.5	3.3	1.26
4 th run	1.7	6.5	0.74

Part III: Results

Table 20. Separated liquid media activity compared to blank reaction. Slope expressed in total glycerol acetylation yield (%) /min. R²: linear regression coefficient. Slope ratio: coefficient between the activity of the separated liquid media with its corresponding blank (1st run vs. Blank 30% and 2nd-4th run vs. Blank).

	Slope (Total glycerol acetylation yield, %/min) · 10³	R² (%)	Slope ratio
1 st run	12.8	85.3	4.7
Blank 30%	2.7	72.7	-
2 nd run	11.5	92.7	0.9
3 rd run	10.6	77.5	0.9
4 th run	10.7	92.6	1.0
Blank	12.4	81.2	-

In order to verify if the sulphur species leached at each run of the recyclability test, could act as a catalyst in homogeneous phase, the activity of the filtered liquid medium has been studied. As we can see in Figure 52 (right) and in Table 20, the liquid medium filtered from the first use of the solid (1st run) exhibits a lower activity than that obtained if the catalyst is maintained in the reaction, (Std run). Regarding the slope ratio, it can be observed that this activity is almost 5 times higher than the blank test (Blank 30%). In the successive tests, the slope of the evolution of the acetylation yield measured for the liquid medium decreases, reaching values close to those obtained for the blank reaction. If the slope of the acetylation yield of the homogeneous catalysis reaction is plotted versus the concentration of sulphur in the liquid medium (Figure 53), it can be seen that the higher the sulphur concentration the higher the catalytic effect in homogeneous phase.

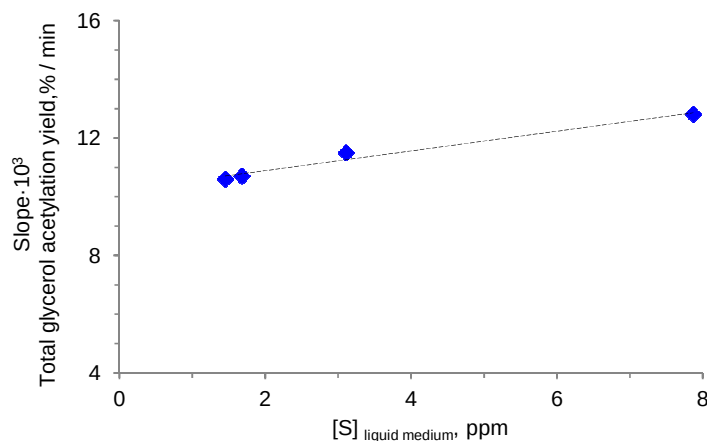


Figure 53. Total glycerol acetylation yield by unit of time of the different runs of homogeneous catalysis tests (after catalyst separation) plotted versus the sulphur concentration in the liquid medium.

In the first test, the sulphur concentration is the highest, as it is generated by the catalyst still very rich in sulphur and leads to an activity in homogeneous phase. In the next runs, the concentration of sulphur in the liquid decreases as generated by the solid already impoverished. The catalytic effect of sulphur species in the liquid is thus lower and does not lead to a remarkable improvement of the yield compared to the blank. We suspect that these sulphur species removed from the solid to the liquid act as sulphuric acid as it has been proposed by Suwannakarn et al. [45].

4.4. Conclusions

The objectives of this chapter were to answer the different questions summarised here:

(i) What is the role played by the hydrolysis ratio over the properties of the solids?

This study confirms that the physicochemical properties of sulphated zirconia obtained by sol-gel method can be modified by varying the hydrolysis ratio applied. Nevertheless, no correlation between the textural and structural properties and the hydrolysis ratio could be found. Concerning the content of sulphur of the samples the S/Zr molar ratio of the solid surface was always lower than the bulk content, this being attributed to sulphur losses during calcination step. Lower H ratio (0 and 1) leads to slightly higher content of remaining carbon species in the solid (verified by XPS and FTIR techniques). The acidic properties of the samples could neither be correlated to the hydrolysis ratio. The samples which exhibited the higher number of acid sites were also the samples presenting the lower acid site density.

(ii) Is there any correlation between the physicochemical properties and the catalytic behaviour? What is this correlation?

Taking into account the previous characterisation results, it was observed that the catalytic activity is independent on the structural properties of the solid: while SZ6 is amorphous and SZ1 is totally stabilised in the tetragonal phase of zirconia, both solids show comparable final acetylation yields. The sole difference found for these samples was the mechanical resistance to attrition during the test: crystallisation of zirconia in the tetragonal phase enhances the mechanical resistance of the samples. Thus, the mechanical resistance

was higher for the SZ1 sample than for SZ6. However, it was also observed that tetragonal samples showed a preferential leaching of sulphur occurs during the tests, this leaching being higher than the totally amorphous sample SZ6. Independently on H, the catalysts showed approximately the same strength distribution of acid sites. The combination of the results obtained with XPS, FTIR and NH_3 -TPD allowed correlating the acidic properties of the solids with their catalytic performances: the lower the acid sites density, the higher the catalytic activity exhibited in the esterification reaction. It could be suggested that isolated bidentated SO_4^{2-} species lead to a higher accessibility to acid sites than polysulphate species.

Moreover, additional tests showed that the distribution of esters obtained is solely influenced by the reaction conditions; the solids did not present a preferential selectivity toward one of the products. Despite the large excess of glycerol used, a modification in the acid, ester or water concentrations has an important effect over the esterification rate.

(iii) Are these solids recyclable in this system?

For homogeneous catalysis and catalyst recyclability tests SZ1 sample was used even if it exhibited a higher preferential leaching of sulphur species than SZ6 sample. This choice was based in the impossibility to separate the fine particles of SZ6 sample from the liquid media which would have lead to ambiguous results concerning the activity of the separated liquid medium. It was concluded that SZ1

Part III: Results

catalyst is fully deactivated after four esterification runs and cannot be directly reused even in mild conditions. The deactivation of the samples is apparently due to the continuous leaching of sulphur species in each run until the complete impoverishment of the solid. Depending on their concentration, these leached species were able to catalyse the esterification reaction in homogeneous phase.

CHAPTER 5: IMMOBILISED HETEROPOLYACIDS IN SILICA AND ZIRCONIA MATRIX BY SOL-GEL AND WET IMPREGNATION TECHNIQUES FOR GLYCEROL ACETYLATION

From homogeneous to heterogeneous catalysts...

This chapter focuses on the use of heteropolyacids as homogeneous catalysts (pure form) and as heterogeneous catalysts (tungstophosphoric acid immobilised over silica and zirconia via wet impregnation and sol-gel techniques).

Heteropolyacids immobilised in silica and zirconia synthesis, characterisation (nitrogen adsorption desorption, XRD, ICP-AES, XPS and FTIR) and catalytic activity are presented. The physicochemical features of these solids are correlated to their behaviour in glycerol acetylation tests both in homogeneous and heterogeneous phase.

5.1. Introduction

From Chapter 3, it was revealed that Brønsted acid sites are needed in order to accelerate the glycerol acetylation reaction.

Heteropolyacids present strong acid sites and high solubility in polar media. However, their immobilisation over a support is required in order to avoid the drawback of homogeneous catalysts. This immobilisation is made via interaction between the heteropolyacid units and the support. A strong interaction would result in a solid highly resistant to leaching but likely exhibiting a lower acid strength. Thus, a compromise is needed in order to obtain a satisfactory catalyst.

5.1.1. Keggin heteropolyacids

Keggin heteropolycompounds are well defined structures formed by a polyanion $[XM_{12}O_{40}]$ and a cation [223-224]. This chapter is focused on Keggin heteropolyacids (HPAs) where the cation is a proton H^+ , thus HPAs are Brønsted type substances [178]. Solid heteropolyacids absorb easily polar molecules such as water, which can penetrate the bulk of their crystallites, so forming protonated monomers or oligomeric clusters [225-227] (Figure 54).

Moreover, heteropolyacids exhibit three different hierarchical structures which are presented in Figure 55. The primary structure

consists in the heteropolyanion, that is to say, the oxide cluster molecule. The secondary structure consists in the assembly of heteropolyanions, counter cations and additional molecules like for example crystallization water. The tertiary structure is the arrangement of secondary units into solid particles and defines the properties such as particle size, surface area and pore structure [228].

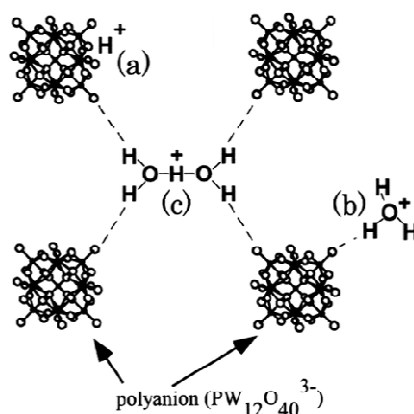


Figure 54. Protonic species formed by Keggin heteropolyacids in presence of water. a) Isolated proton, b) H_3O^+ and c) H_5O_2^+ [226].

The structure of the heteropolyacid and the different elements participating in their formulation determine the solid properties as the acidity and the chemical and thermal stabilities. Taking into account the acid strength, Keggin type heteropolyacids can be ranked from the most acidic to the less acidic as follows: $\text{H}_3\text{PW}_{12}\text{O}_{40}$, (HPW) > $\text{H}_4\text{SiW}_{12}\text{O}_{40}$, (HSiW) > $\text{H}_3\text{P}_2\text{Mo}_{12}\text{O}_{40}$ (HPMo) > $\text{H}_4\text{SiMo}_{12}\text{O}_{40}$ (HSiMo) [229]. As there is almost no charge localization, the protons are very mobile resulting in strong Brønsted acidity [230]. Nevertheless, the acidity developed by the HPAs depends also on the polarity of the solvent [176]. As previously said, heteropolyacids are

soluble in polar solvents. Thus, they can be used in acid catalysed reactions as an alternative to H_2SO_4 , as they are less toxic, volatile, corrosive and more active than conventional mineral acids [31, 223, 230-232].

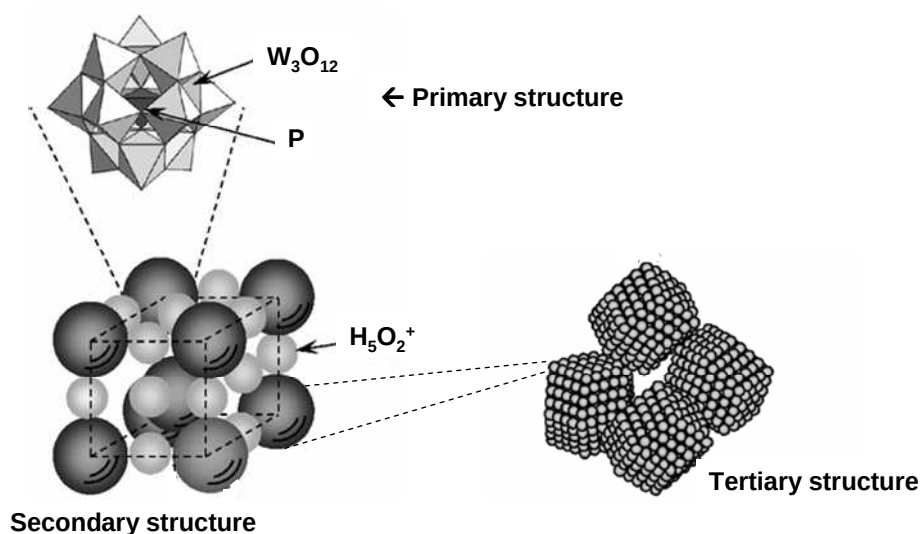


Figure 55. Hierarchical structures of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ [228].

Heteropolyacids can be applied to a large number of catalytic processes due to their acidic and redox properties, in pure form or immobilised on a support or in a matrix, both in gas or liquid phase: hydration of olefins including propene, butene, and isobutene [228, 230, 233], oxidation of methacrolein to methacrylic acid [225], production of ethyl acetate from ethylene and acetic acid [228], oxidation of ethylene and styrene [228, 234], dehydration of glycerol to acrolein [235-236] ether cleavage, transesterification and esterification [233, 237-242], polymerization of tetrahydrofurane

[225] and the reaction of o-phenylenediamine with ketones under solvent free conditions [243] are some examples.

5.1.2. From homogeneous to heterogeneous systems

The immobilisation of HPAs results in an increase of the surface area comparing to the bulk HPA and facilitates the recovery process which makes them suitable for heterogeneous catalysis avoiding contamination of final products, corrosion of the equipment and low recyclability [244]. Other properties of HPA, such as the thermal stability, are improved when immobilised. The decomposition of supported HPA on TiO_2 , SiO_2 and ZrO_2 was retarded with respect to the bulk HPW due to the interaction with the surface at temperatures close to 400-500 °C [238-239, 244].

Different types of solids can be used in order to immobilise the HPAs. They must have a neutral or acidic nature, as the use of supports presenting some basic character such as alumina can induce the destruction of the Keggin units [223-224, 245-247]. In general, the most employed supports are molecular sieves [248-249], zeolites [250], activated carbon and oxides such as TiO_2 , SiO_2 , and ZrO_2 [233, 243-244, 246, 251-253].

Both wet impregnation and sol-gel techniques are employed in several works in order to immobilise the different heteropolyacids [253-260]. Sol-gel technique provides a better immobilisation of the HPAs than wet impregnation technique. The HPA can be incorporated

in different matrixes such as silica, titanium and zirconia [251, 259-261]. Different works have focused on the immobilisation of heteropolyacids by sol gel technique in silica involving hydrolysis of tetraethyl orthosilicate [76, 254, 256, 258, 261-262] in order to obtain a high resistance to leaching in polar media. Moreover, some of these solids have been tested in esterification reactions and will be discussed latter in this section [70, 76, 263-264].

5.1.2.1. Matrix interactions

The chemical interactions between the HPA and the support are a matter of great interest because a strong interaction could fix the HPA to the carrier, avoiding the leaching of HPA in liquid-phase [224]. However, these interactions can also cause a decrease in the acidity strength compared to the bulk HPA (see section 5.1.2.2.).

Newman et al. focused on the evolution of surface species present at low and high loadings in the solids obtained by impregnation of HPW over silica, monolayer and multilayer regimes, respectively [223]. The surface and structure were characterised by XPS and XRD techniques. When the heteropolyacid was impregnated at low loading over silica, HPA units reacted with a hydroxylated silica surface to form an ionic pair with one or more silanol groups via simple proton transfer, possibly involving dehydration as following $(\equiv\text{SiOH}_2)^+(\text{H}_2\text{PW}_{12}\text{O}_{40})^-$ or $(\equiv\text{Si})_m^+(\text{H}_{3-m}\text{PW}_{12}\text{O}_{40})^{m-} + \text{H}_2\text{O}$. Therefore, it was suggested that the $\text{H}_3\text{PW}_{12}\text{O}_{40}$ units close to the silica surface coordinate to silica through three terminal $\text{W}=\text{O}$ linkages. Kamiya and

co-workers stated that the heteropolyacids very close to the silica surface (below the monolayer) decompose or are much distorted due to strong interactions between HPAs units and SiO₂ surface, resulting in the reduction of the acid strength. Nevertheless, at higher loadings, the HPA is preserved and thus the acidity exhibited by the solid is quite similar to the bulk Keggin HPA [228].

It can be observed that the use of zirconia as a support in wet impregnation technique is preferred to silica. This is due to the stronger interaction existing between the zirconia and the HPA compared to silica [224]. This phenomenon can be explained by the presence of a large amount of hydroxyl groups on the surface of zirconia which are capable of stabilising the HPA [239]. The Keggin units of heteropolyacids interact with hydrated zirconia via chemical interaction with the hydroxyl groups forming $(\text{Zr}(\text{OH}_2)_n^+)(\text{H}_{3-n}\text{W}_{12}\text{O}_{40})$ like species [56, 265]. López-Salinas et al. immobilised tungstophosphoric acid in a freshly precipitated zirconia with different loadings (0–25%_{wt} HPW) in order to examine the effect of the calcination temperature (100–800 °C) over the structural integrity of the HPW and the possible interactions between HPW and ZrO₂ [224]. It was observed that below 400 °C, Keggin species were distorted due to the interactions with $\equiv\text{Zr}-\text{OH}$ or $\equiv\text{Zr}^+$ groups. The nature of the species can be explained as either $(\equiv\text{Zr}-\text{OH}_2)_n^+ [\text{H}_{3-n}\text{W}_{12}\text{PO}_{40}]^{n-3}$ or $(\equiv\text{Zr}-\text{O})_n-[\text{H}_{3-n}\text{W}_{12}\text{PO}_{40-n}]$ which was also proposed by Oliviera and co-workers based on solid state nuclear magnetic

resonance (^{31}P MAS NMR) spectra [266]. Above 500 °C, the Keggin structure was destroyed forming WO_3 and phosphorous oxides [224].

5.1.2.2. Change in acidity strength

As it was remarked before, the interaction of the Keggin units with the support or the matrix can improve the resistance to leaching but can also cause a decrease of the HPA acid strength [176, 267-268].

In addition, several works reported the presence of both Brønsted and Lewis acid sites for supported heteropolyacids [243, 265] in contrast to the bulk HPA whose acidity is only Brønsted type.

The total acidity of supported samples can also fluctuate with the loading of HPA. The total number of acid sites in silicotungstic acid impregnated on zirconia increases gradually up to a loading of 15%_{wt} thereafter it decreases [56]. The same trend is also observed for Brønsted acid sites. Similarly, the total acidity of tin oxide-supported 12-tungstophosphoric acid increases with the rise of HPW content up to 20%_{wt} (monolayer coverage) and decreases thereafter [241].

Pizzio and co-workers observed that the acidity of supported catalysts depended on the interaction existing between the heteropolyacid and the support [246]. Generally, the acidity strength decreases when this interaction is stronger. Moreover, it was remarked that the interaction when using carbon as support is stronger than when using TiO_2 and SiO_2 . This was also confirmed by Alsalmé et al. who studied the interaction of HPW with different supports calcined at

300 °C [269]. The acid strength was established based on NH₃-TPD measurements and isopropanol dehydration as follows from the most to the less acidic: SiO₂>TiO₂>Nb₂O₅>ZrO₂, thus the interaction of HPW species with the support was the strongest for the zirconia sample.

Commeli and co-workers [244] supported HPW on TiO₂, SiO₂ and ZrO₂. The interaction strength between the HPW and the support decreased in the order ZrO₂>TiO₂>SiO₂. This phenomenon was also observed by the formation of HPW crystals on SiO₂ even if this support showed higher surface area than the others. The Keggin structure was maintained when supported on zirconia and silica, but TiO₂ support led to a deformation in lacunar species of the polyoxometalate anion. FTIR performed over the samples with adsorbed ammonia revealed that the Brønsted acid sites were almost negligible for ZrO₂ samples. Moreover, this sample was the less acidic in terms of number of acid sites measured by NH₃-TPD leading to a lower catalytic activity in the isomerisation of alpha pinene.

When supporting HPW in silica the number of acid sites of the obtained solid (10%_{wt} HPW) measured by NH₃-TPD was higher than that from silica but lower than that of the bulk HPA : 0.41 < 1.12 < 1.7 mmol/g NH₃, (silica, HPW on silica and bulk HPW respectively) [233]. The acid strength was also reduced due to the interaction of HPW units with the silanol groups of the silica surface [233].

Part III: Results

The stabilisation of Keggin unit over the hydroxyl groups of zirconia can lead to a neutralisation of the Brønsted acidic character of the heteropolyacid due to the formation of $(\text{Zr}(\text{OH}_2)_n)^+(\text{H}_{3-n}\text{W}_{12}\text{O}_{40})$ like species [265]. At low calcination temperatures, the Lewis acidity is mainly due to the support. At higher calcination temperatures, dehydration-dehydroxylation occurs and the interaction of HPA with the support increases creating strong Zr-O-W bond and new Brønsted acid sites [265]. This phenomenon can be explained by the formation of larger polyanions that can effectively delocalize the negative charge required for the formation of Brønsted acid centres [265-266]. López-Salinas and co-workers showed that HPW supported on hydrated zirconia and calcined at 400 °C exhibit predominantly Lewis acid sites, contrary to HPW supported on a previously calcined ZrO_2 at 500 °C where both Brønsted and Lewis acid sites were detected. [26]. Tungstophosphoric acid immobilised in zirconia by sol-gel presented strong acidic Lewis sites when calcined, due to the interaction of the hydroxyls liberated with the protons associated to the HPA [259].

Thus, for each reaction system, it is essential to find a solid presenting a good compromise between the resistance to leaching (requiring a strong interaction with the support) and maintenance of acidic properties (requiring not too strong interaction) needed for the esterification reaction.

5.1.3. Immobilised heteropolyacids in esterification reactions

Even if immobilised heteropolyacids can be used in both gas [263, 268, 270] and liquid phase esterification, this chapter will focus exclusively on the liquid phase reaction.

Kovalchuk et al. immobilised a series of heteropolyacids (HPMo, HPW, HSiMo and HSiW) on functionalised silica as their onium (propylpyridinium and alkylimidazolium) salts. Among the heteropolyacids studied, HSiW displayed the best catalytic performances per anion unit in acetic acid esterification with ethanol [263]. The interaction between HPA and the surface-grafted onium cations provide monoanionic dispersions of HPA on the surface and high resistance to leaching in polar media. Nevertheless, some leaching was detected after two consecutive esterification tests. Tetraprotic acids, HSiW and HSiMo, gave better surface exchange yields and resulted in solids with higher number and strength of acid sites per anion [263]. The synthesis of isoamyl acetate can be catalysed by heteropolyacid supported on amine-functionalised silica and SiMCM-41 which also presented low leachability [270]. Kumar and co-workers studied the esterification of acetic acid with primary (n-), secondary (sec-) and tertiary (tert-) butanol in presence of HPW, HSiW and HPMo acids supported on activated Bentonite (AT-GMB) [271]. The reusability study showed that after regeneration (washing with water for several times followed by drying at 120 °C in air), the catalysts remained stable and active. Mesoporous sol–gel derived 12-

Part III: Results

phosphotungstic acid SBA-15 was active and reusable in the esterification of acetic acid with ethanol [242].

Tungstophosphoric acid catalysts supported over SiO_2 , ZrO_2 and carbon were tested in the esterification of acetic acid with butanol [272]. The supported HPA presented higher activity per acid site than Amberlyst-35. However, silica and zirconia supported solids suffered from leaching in the reaction medium. Carbon-supported HPA catalysts exhibited lower activity but presented very high recyclability due to a strong electrostatic adsorption between the heteropolyacid and the support.

Alsalmé and co-workers performed hexanoic acid esterification, and transesterification of ethyl propanoate and ethyl hexanoate with methanol, in presence of several acid catalysts both in homogeneous and heterogeneous phase [240]. It was observed that the turnover frequency (TOF) decreases with decreasing catalyst acid strength in the order: bulk HPW $\approx \text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40} > \text{HSiW} > \text{HPW}$ supported on Nb_2O_5 (15%_{wt} HPW), HPW supported on ZrO_2 (15%_{wt} HPW), HPW supported on TiO_2 (15%_{wt} HPW) $> \text{H}_2\text{SO}_4 > \text{HY}$, H-Beta $> \text{Amberlyst-15}$. Nevertheless, the activity per unit of catalyst weight falls in a different order: $\text{H}_2\text{SO}_4 > \text{HPW} \approx \text{HSiW} > \text{Amberlyst-15} \geq \text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40} > \text{supported HPW} > \text{HY}$, H-Beta. Further studies concerning the leachability of supported samples showed that leaching is larger in water than in ethanol due to the higher reflux temperature and greater solubilisation power of water. Therefore, the authors remarked that the activity of supported samples was mainly due to

leached HPA species. In contrast, CsPW heteropolyacid salt exhibited high catalytic activity despite its very low leaching.

Tin oxide-supported 12-tungstophosphoric, exhibiting both Brønsted and Lewis acid sites, showed high activity and recyclability after regeneration at 400 °C under N₂ in the esterification of acetic acid with amyl alcohol carried out at 150-250 °C [241].

Izumi and co-workers studied the catalytic properties of silica-included HPW in the hydrolysis of ethyl acetate in the liquid phase and production of methyl, ethyl, n-butyl, benzyl and n-octyl acetates [76, 256]. The catalyst (11%_{wt} HPW) was compared to H-ZSM-5 zeolite, Amberlyst-15, sulphuric acid and bulk HPW. Even if Amberlyst-15 was the most effective catalyst per weight unit, silica-included HPW showed the highest activity per unit of acid site compared to the resin and the zeolite, this being probably due to its higher acidity strength in alcohol ($+1.5 \leq H_0 \leq 3.3$) compared to H-ZSM-5 ($+6.8 \leq H_0$) [76]. The immobilised HPW in silica was used three times after recovering and washing with 1-butanol for the acetic acid esterification with butanol, showing similar catalytic activity at each (re)use.

For the esterification of palmitic acid with methanol, it was observed that the catalytic activity decreases in the series: HPW, HSiW and HPMo acids immobilised by sol–gel method in silica [264]. The solid based on HPW immobilised in silica showed a stabilisation of the catalytic activity after the second use. Moreover,

Part III: Results

this catalyst exhibited good performances in the esterification of oleic and stearic acids.

HPA supported on zirconium hydroxide are suitable, active and recyclable solids for the esterification reaction between formic, acetic and propenoic acids and n-butanol, iso-butanol, sec-butyl alcohol and cyclohexanol [56, 238-239, 273-274].

A series of HPW supported onto hydrous zirconia was tested after calcination at 300 and 500 °C in the esterification of cyclohexanol to cyclohexyl acetate [273]. The solid with 30%_{wt} HPW and calcined at 300 °C showed the best catalytic properties. The catalyst, regenerated by washing with water several times and dried at 100 °C, showed a stable activity after the second use, the yield decreasing only of 5% between the first and the second run. Similarly, the same catalyst was tested in the esterification of primary (n-butanol, iso-butanol) and secondary (2-butanol, cyclohexanol) alcohols using different molar ratios of acid to alcohol [239, 274]. Again, the catalyst showing the best catalytic performances is the one with 30%_{wt} of HPW calcined at 300 °C. Repeated use of the solid after regeneration (washed with water till filtrate is free from acid, dried at 100 °C for 5 hours) showed that the initial esterification yield decreases by 5%, thereafter remaining stable.

Phosphomolybdic acid supported on hydrous zirconia and calcined in air at 500 °C exhibited good catalytic and recyclability properties in the esterification of acetic acid with n-butanol [238].

Silicotungstic acid (15%_{wt}) supported on hydrous zirconia acts as an efficient and stable solid acid catalyst for esterification of formic, acetic, propionic and n-butyric acids with n-butyl, iso-butyl and sec-butyl alcohols. The catalyst can be regenerated easily and reused at least five times [56].

Oliveira et al. studied the esterification of oleic acid with ethanol over 12-tungstophosphoric acid supported on commercial monoclinic zirconia and calcined at 200 °C [266]. The reaction was conducted at 100 °C using an acid: ethanol molar ratio equal to 1:6. The best catalytic performances were achieved with the solid presenting 20%_{wt} loading. However, a leaching equal to 8%_{wt} of the initial mass of this catalyst was detected at the end of the reaction. The catalyst achieved the stability in the reaction after a regeneration step (washing with n-hexane, drying at 100 °C and calcination at 300 °C for 4 hours). When regenerated, the final conversion of the acid changed from 88% in the first run to 70% in the second run.

5.1.3.1. Glycerol acetylation

Concerning the glycerol acetylation in presence of a large excess of acetic acid, Ferreira and co-workers performed successfully catalytic reactions over molybdophosphoric acid immobilised in USY zeolites [69] and tungstophosphoric acid immobilised on silica [70] and activated carbon [71].

Part III: Results

The immobilisation of HPW into silica was performed both by wet impregnation and sol-gel techniques. The esterification tests were carried with a glycerol: acetic acid molar ratio equal to 1:6, 1:11 and 1:16. The effects of the temperature and amount of catalyst used were also tested. The catalytic stability of the immobilised HPW was evaluated by performing consecutive batch runs with the regenerated catalyst (washed with water and dried at 120 °C overnight). It was observed a slight decrease of the catalytic activity in the second run. However, similar catalytic activity was observed after the third use [70]. The sample obtained by wet impregnation was not recyclable due to HPW losses via leaching.

When impregnated over activated carbon (HPW loading varying from 3.5 to 6.5%wt), it was shown that the sample with 4.9%_{wt} loading was the most active in glycerol acetylation conducted in an excess of acetic acid [71]. An increase in the loading resulted in lower esterification rate probably due to some hindrance in the activated carbon porous system. The samples showed a stable catalytic activity after the third run.

5.1.4. Main objectives of this chapter

To the best of our knowledge, there is a lack of studies comparing the performances of immobilised HPA by sol-gel technique in different matrixes in the glycerol acetylation reaction performed in an excess of glycerol. Therefore, this chapter focuses on the synthesis, characterisation and determination of catalytic activity

of heteropolyacids (HPA) immobilised in zirconia and silica by wet impregnation and sol-gel methods.

The main objectives are:

- (i) To compare the activity of different Keggin heteropolyacids and heterocompounds (NH_4^+) in glycerol acetylation.
- (ii) To immobilise satisfactorily the most active HPA in silica and zirconia by wet impregnation (WI) and sol-gel (SG) techniques.
- (iii) To compare the properties of the immobilised samples.
- (iv) To test them in glycerol acetylation carried out in an excess of glycerol.

5.2. Experimental

5.2.1. Preparation of the catalysts

Both the immobilisation of tungstophosphoric acid in silica and zirconia by sol-gel (SG) technique and the immobilisation by wet impregnation technique (WI) are described in Chapter 1, section 1.1.5.

The samples obtained were named as: Nn-xx-Mm-tt-S, where «Nn» is the matrix (Zr for zirconia and Si for silica), «xx» is the nominal loading of HPW expressed in %_{wt}, «Mm» is the synthesis method, «SG» for sol-gel and «WI» for wet impregnation method, «tt» stands for the thermal treatment applied («D» for samples dried at

120 °C in air and «C» for samples calcined at 200 °C in air) and «S» stands for samples being submitted to a Soxhlet extraction.

5.2.1.1. Soxhlet washing



Figure 56. Diagram of a Soxhlet apparatus.

The washing step by Soxhlet method consists in a continuous solid-liquid extraction. The Soxhlet apparatus is equipped with a condenser, the Soxhlet extractor and a round bottomed flask (Figure 56). The powder to be treated, containing substances soluble in the solvent selected, is placed in a cellulose cartridge, which is introduced into the extractor. The flask containing the solvent is heated in order to achieve the boiling point. The produced vapour is condensed and then collected in the Soxhlet extractor where the solid is placed. When the level of liquid reaches the top of the tube, the liquid returns to the flask enriched in the soluble substance contained in the solid. In this manner, the solid is always in contact with pure solvent (condensed)

and the extraction is conducted in mild temperatures lower than the boiling point of the solvent. The cycle is repeated several times.

The use of this washing step in the synthesis of the immobilised heteropolyacids is of great interest as it can be used to simultaneously remove the solvents used in the synthesis and to check the resistance to leaching. In this manner, molecules weakly attached to the support will be leached into the solvent during the washing step avoiding contamination of the esterification medium.

5.2.2. Characterisation

The catalysts are characterised by nitrogen adsorption, XRD, ICP-AES, FTIR and ammonia chemisorption at 50 °C as described in Chapter 1.

For nitrogen adsorption and desorption isotherms, the outgassing of the samples was performed during minimum 3 days and at 120 °C in order to evacuate the water present in the sample that could impede the correct adsorption of nitrogen and negatively affect the measurement of surface area and texture of the samples. The micropore volume was estimated using t-plot analysis in the P/P_0 range 0.25 – 0.5, which was in some case slightly adjusted in order to find the best fit.

The XPS analyses were performed in a Kratos Axis Ultra spectrometer. The sequence of spectra was recorded as follows:

survey spectrum, C 1s, O 1s, W 4f, P 2p, Zr 3d or Si 2p, and C 1s again, to check the stability of charge compensation as a function of time and the absence of degradation of the sample during the analyses. The C-(C,H) component of the C 1s peak of carbon was fixed to 284.8 eV to set the binding energies. Data treatment was executed with the CasaXPS program.

5.2.3. Catalytic performances measurements

5.2.3.1. Esterification tests

The esterification reactions were performed as described in Chapter 2, in liquid phase with a concentration of acetic acid equal to 100 g/l of glycerol. The temperature was changed from 55 °C to 105 °C. The objective of this change was to reduce the viscosity of glycerol and reduce the reaction time as the kinetic of the reaction was accelerated. The behaviour of the catalytic properties of the solids remained unchanged.

Glycerol acetylation catalysed in homogeneous phase by bulk heteropolyacids was conducted in presence of several HPA: tungstophosphoric acid HPW ($\text{H}_3\text{P}(\text{W}_3\text{O}_{10})_4 \cdot x\text{H}_2\text{O}$) purchased from Fluka, silicotungstic acid HSiW, (p. a. reag. $\text{SiO}_2 \cdot 12\text{WO}_3 \cdot x\text{H}_2\text{O}$) purchased from UCB; silicomolybdic acid hydrate HSiMo ($\text{H}_4\text{SiMo}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$) from Sigma-Aldrich and HPMo ($\text{H}_3\text{PMo}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$) obtained by a method described elsewhere [275-276]. The concentration of Keggin HPA was equal to 75 mg/40 ml of

glycerol. Moreover the effect of a Keggin heteropolycompound (NH_4PMo , $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$ synthesised at the laboratory [275-276]) was also checked. The concentration of the NH_4PMo used was 77 mg per run (equivalent to 0.116 mmol of NH_4^+) in order to have the same amount of Keggin anion than in the previous cases. 250 mg per run of immobilised HPW, (SG or WI). The glycerol volume used in each reaction was equal to 40 ml.

5.3. Results

5.3.1. Solid characterisation

5.3.1.1. Textural properties

Table 21. Textural properties of Si-PW and Zr-PW samples.

Sample	A_{Langmuir} (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)	Micropore Area $t\text{-Plot}$ (m^2/g)
Si-D	453	0.74	9.9	216
Si-11-SG-DS	484	0.06	2.1	304
Si-30-SG-DS	465	0.18	2.1	455
Si-30-WI-D	311	0.50	10.2	203
Si-30-WI-DS	460	0.88	10.1	232
Zr-D	197	0.01	5.8	192
Zr-30-SG-DS	152	0.01	3.6	144
Zr-30-WI-D	113	0.01	6.1	108
Zr-30-WI-DS	187	0.01	6.0	181

It is clearly observed in Figure 57, that silica samples containing tungstophosphoric acid and obtained by sol-gel technique presented a

Part III: Results

type I isotherm, suggesting the presence of micropores [70, 254, 258, 264]. Nevertheless, pure silica and the samples obtained by wet impregnation method present a type IV isotherm, characteristic of mesoporous solids [264]. Wet impregnated silica showed lower surface area than the base support, indicating pore blockage or filling by HPW which is also reported in the literature [223, 244-245]. This phenomenon was also observed for the sample supported on zirconia [56]. All the zirconia samples presented microporosity (Figure 58). Zirconia samples developed lower surface area than silica ones (Table 21).

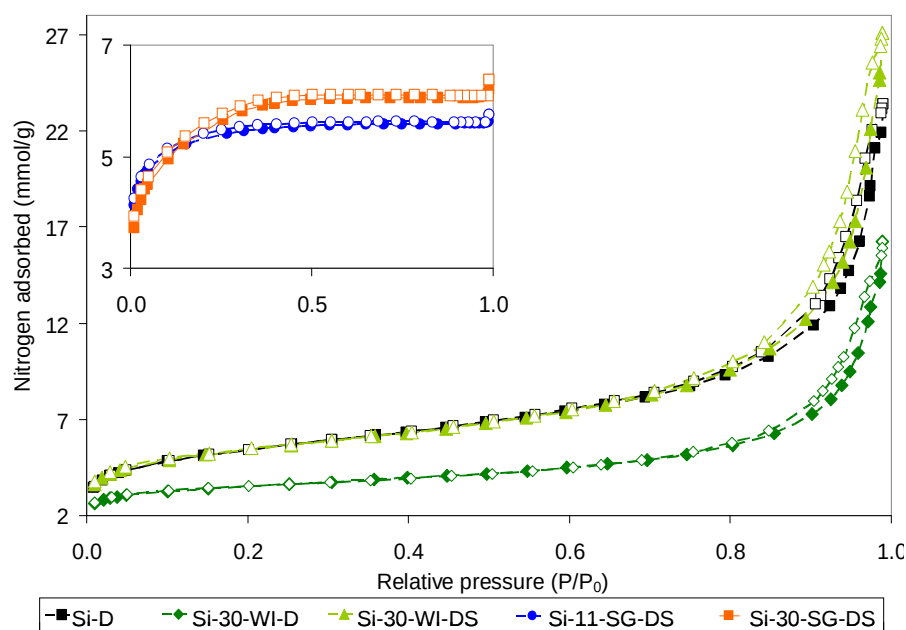


Figure 57. N_2 -adsorption-desorption isotherms of Si-PW samples. Filled symbols are used for adsorption isotherms and the corresponding open symbols are used for desorption isotherms.

The leaching of HPW species can be observed in wet impregnated samples, whose surface area increases after Soxhlet extraction presenting a value very close to the support both for silica and zirconia based samples. The surface area of all the samples is calculated by Langmuir model as BET calculation resulted in negative values of C , which could suggest that the adsorption of nitrogen over these samples was performed by monolayer and not by multilayer.

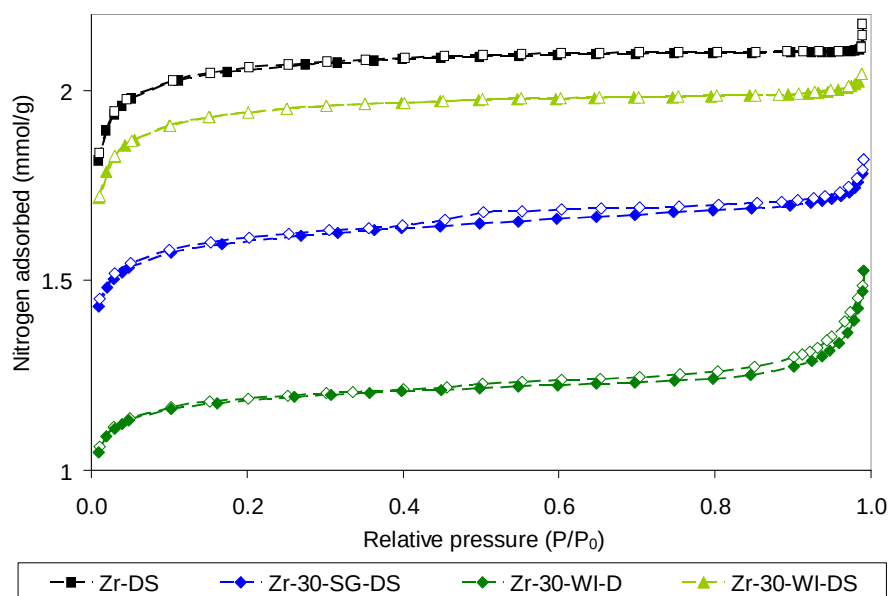


Figure 58. N_2 -adsorption-desorption isotherms of Zr-PW samples. Filled symbols are used for adsorption isotherms and the corresponding open symbols are used for desorption isotherms.

5.3.1.2. Structure

The XRD patterns of silica samples are shown in Figure 59. HPW immobilised in zirconia showed the same pattern (not presented here). The matrixes were amorphous in both cases. Solids synthesised

Part III: Results

by sol-gel method present a high dispersion of the heteropolyacid as the XRD pattern of pure HPW was absent. This result agree with those present in the literature [258] and reference therein, However, the solid synthesised by wet impregnation presented a well defined pattern of HPW crystals, which disappears after a washing step by Soxhlet extraction. This indicated that the HPW crystals are soluble in water and thus they present a high tendency to leaching in polar medium as glycerol. This behaviour was observed for both silica and zirconia samples.

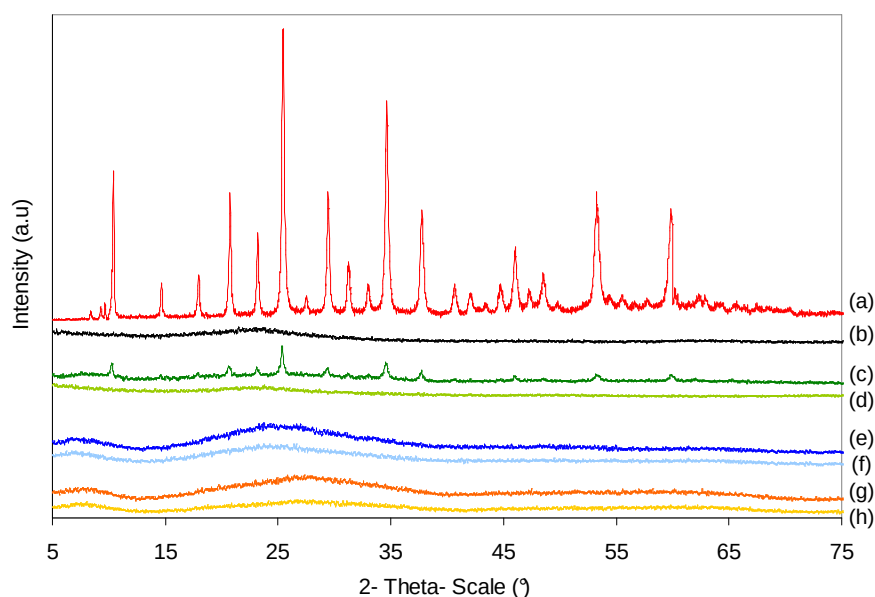


Figure 59. XRD patterns of HPW immobilised in silica. (a) HPW; (b) Si-D; (c) Si-30-WI-D; (d) Si-30-WI-DS; (e) Si-11-SG-D; (f) Si-11-SG-DS; (g) Si-30-SG-D and (h) Si-30-SG-DS.

5.3.1.3. Immobilisation yield

Regarding the tungstophosphoric content at the surface of the solid (Figure 60 and Table 22), it can be observed that in zirconia matrix, the content of HPW is higher after a Soxhlet extraction. This can be explained by the loss of Zr^{+} weakly anchored to the matrix, which are leached during the Soxhlet step. For silica matrix, the HPW content at the surface of the samples after Soxhlet extraction is the same, approximately 2%_{wt}, independently on the HPW content before the extraction.

Table 22. Chemical composition of tungstophosphoric acid immobilised in zirconia and silica samples.

Sample	Bulk composition				Surface composition
	P (% wt)	W (% wt)	W/P molaire	HPW (%wt)	HPW (%wt)
Zr-30-SG-D	0.25	18.0	12.2	23.54	18.1
Zr-30-SG-DS	0.26	18.6	12.2	24.27	24.2
Si-30-SG-D	0.28	19.0	11.4	24.76	12.3
Si-30-SG-DS	0.15	10.3	11.5	13.46	2.0
Si-11-SG-D	0.10	6.8	11.6	8.84	3.3
Si-11-SG-DS	0.10	6.9	11.7	8.99	2.1
HPW	1.02	66.9	11.1	-	-

Figure 60 displays the loading of tungstophosphoric acid before and after the Soxhlet extraction. The ICP-AES analysis demonstrated that the content of heteropolyacid in the solids synthesised by sol-gel technique remained constant after Soxhlet extraction, except for the sample Si-30-SG whose HPW bulk content varied from 24.8 to 13.5 %_{wt} after Soxhlet extraction.

Part III: Results

Therefore, it can be concluded that zirconia matrix retains a higher quantity of HPW than silica matrix. The content of tungstophosphoric acid at the surface of silica after Soxhlet extraction is constant and close to 2%_{wt}.

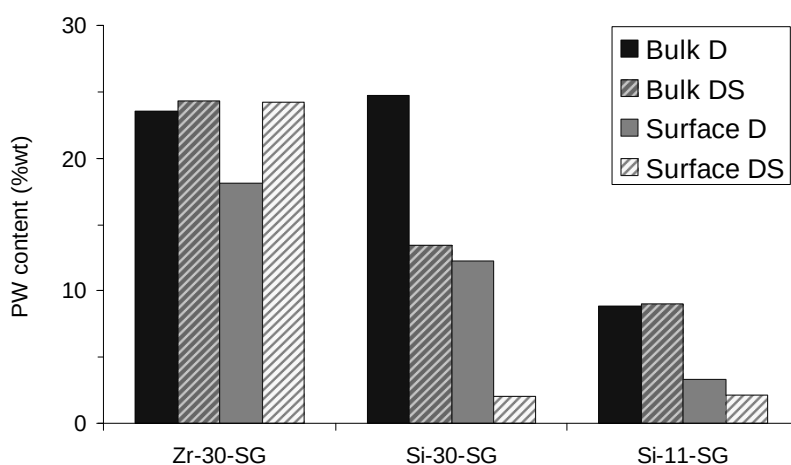


Figure 60. Tungstophosphoric acid immobilised in the samples. « Bulk » total loading calculated from W measured by ICP; « Surface » loading at the surface calculated from W measured by XPS; « D » dried samples; « DS » samples after Soxhlet extraction.

The XPS spectra of samples based on tungstophosphoric acid immobilised on silica or zirconia show a broad doublet between 33 and 42 eV, corresponding to 4f signal of tungsten. This doublet is also present in pure tungstophosphoric acid. In the case of zirconia, this doublet is very well defined (Figure 61, left), confirming that the oxidation state of W is +6. Thus, it can be said that the surface of ZrO₂ immobilised HPW is composed of unchanged heteropolyanion species which agrees with the literature [277].

In the case of silica, a shoulder can be observed around 35 eV (Figure 61, right). The presence of this shoulder may be due to W atoms interactions with the Si present in the surface as following: $(\equiv\text{SiOH}_2)^+(\text{H}_2\text{PW}_{12}\text{O}_{40})^-$ or $(\equiv\text{Si})_m^+(\text{H}_{3-m}\text{PW}_{12}\text{O}_{40})^{m-} + \text{H}_2\text{O}$ [223].

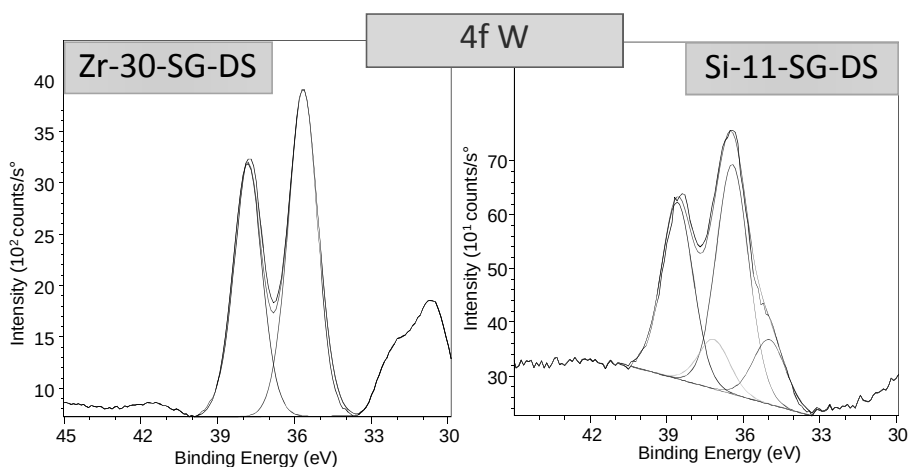


Figure 61. 4f W XPS spectra of immobilised HPW by sol-gel technique in zirconia (left) and silica (right). In the left figure, the peak at 31 eV corresponds to the 4p Zr XPS spectra.

5.3.1.4. Stability of the Keggin units

The stability of the Keggin units of HPW after the synthesis was verified by FTIR. The structure of Keggin heteropolyacids, $[\text{XM}_{12}\text{O}_{40}]^{n-}$, is composed of a central tetrahedron XO_4 (where X is the heteroatom) surrounded by four groups of three MO_6 octahedra (edge-sharing) where M is the additional atom. In this structure there are four different types of oxygen atoms marked with signs depending on where they occur in the unit: a, internal oxygen linking the central atom X to additional atom (X-Oa-M); b, corner-sharing oxygen linking two trimetallic groups (M-Ob-M); c, edge-sharing oxygen

Part III: Results

linking two atoms inside of a trimetallic group (M-Oc-M) and d, terminal oxygen, which is a vertex of an octahedron (M=Od) [278]. In the FTIR spectrum of tungstophosphoric acid, the band at 1080 cm^{-1} is attributed to the stretching vibration of the tetrahedron PO_4 (P-Oa), while the one at 982 cm^{-1} is due to the stretching vibration of W-Od (terminal oxygen). The band at 893 cm^{-1} is due to the stretching vibration, W-Ob-W, and the band at 810-790 cm^{-1} is due to W-Oc-W bond [70, 242, 244, 246, 258, 262]. (See Table 23).

Table 23. FTIR bands of HPW immobilised samples. Bb: broad band.

	P-Oa	W-Od	W-Ob-W	W-Oc-W
Bibliography	1083-1081	982	893-889	811-798
HPW $[\text{PW}_{12}\text{O}_{40}]^{3-}$	1080	981	840	793
Si-11-SG-D	1080	-		Bb
Si-11-SG-DS	1080	-	-	Bb
Si-30-SG-D	1080	973	890	Bb
Si-30-SG-DS	1080	972	890	Bb
Si-30-WI-D	1080	977	890	Bb
Si-30-WI-DS	1080	-	-	Slightly Bb
Zr-30-SG-D	1043	933	835	Bb
Zr-30-SG-DS	1043	937	835	Bb
Zr-30-SG-C	1080 Bb	937	835	Bb
Zr-30-SG-CS	1080 Bb	937	835	Bb
Zr-30-WI-D	1080	982	890	812
Zr-30-WI-DS	-	-	-	-

Figure 62 shows the FTIR spectra of tungstophosphoric acid samples immobilised in silica (left) and zirconia (right). For silica samples, the characteristic bands of the heteropolyacid (1080, 980,

840 and 793 cm^{-1}) are overlapped with the bands of the silica matrix, only slight spikes are observed for the wet impregnated sample (Si-30-WI-D). This phenomenon was also reported in literature [258]. Nevertheless, the existence of broad bands at 1070-1050 cm^{-1} reveal that the structure of the Keggin anions is conserved during the synthesis [70, 254, 258, 278]. The sample Si-30-WI-DS presents a spectrum almost identical to the support, meaning that the HPW is entirely leached in the Soxhlet extraction.

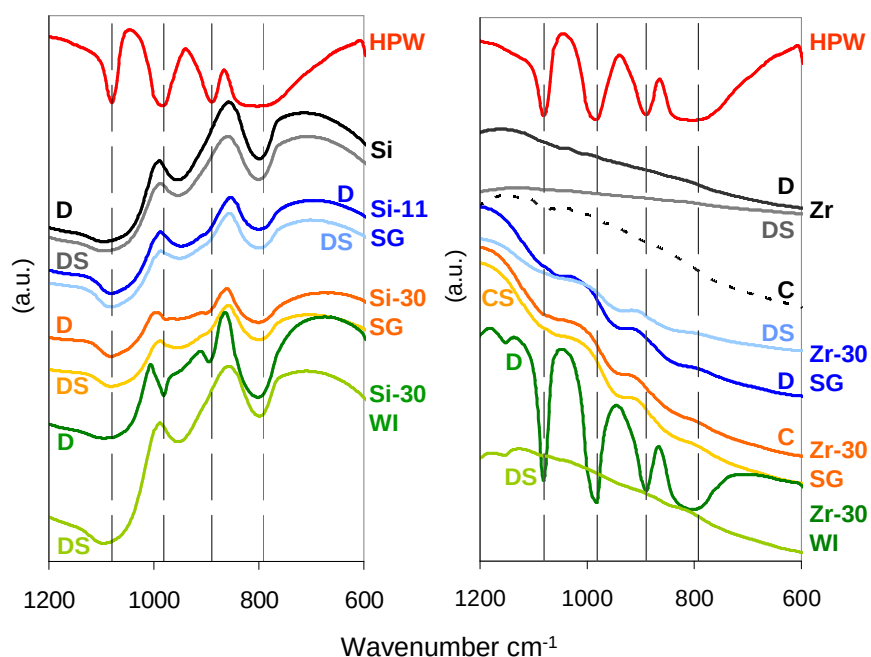


Figure 62 FTIR spectra of HPW immobilised in silica (left) and zirconia (right) matrix. The vertical lines indicate the FTIR bands corresponding to pure HPW (1080, 981, 890, and 793 cm^{-1}).

When tungstophosphoric acid is immobilised on zirconia by sol-gel, the band located at 1081 cm^{-1} is slightly shifted towards 1040 cm^{-1} suggesting a decrease in the geometry of the tetrahedron PO_4 ,

Part III: Results

probably due to a strong interaction between zirconia and the Keggin unit. A shift towards lower wavelengths is also observed for the band at 980 cm^{-1} corresponding to terminal oxygen. This indicates a distortion in the structure of the Keggin unit due to a lower cohesion within the anion. The presence of a broad band at 835 cm^{-1} indicates that the Keggin unit is preserved [224, 244, 273].

The spectrum of solid tungstophosphoric acid immobilised on zirconia by wet impregnation exhibits well defined bands corresponding to characteristic bands of the Keggin unit. However, after Soxhlet extraction and drying, these bands disappear which indicates that the tungstophosphoric acid is not resistant to leaching when immobilised by wet impregnation.

In conclusion, the FTIR spectra of prepared samples exhibited the characteristic bands of the Keggin structure despite the overlapping with the characteristic bands of the matrix. Therefore, the Keggin unit is preserved. However, in the case of zirconia based samples, some geometric distortions were detected as some positions of the characteristic bands were shifted from the pure HPW spectrum. This phenomenon could be due to a strong interaction between the HPW and the matrix. The FTIR spectra of the solids prepared by wet impregnation technique, and washed with distilled water did not show the existence of Keggin HPA units, which indicates occurrence of a leaching phenomenon in polar solvents. This result is in accordance with the results obtained with the previous characterisation techniques.

5.3.1.5. Number of acid sites

Table 24 shows the results of the acidity measurements by ammonia chemisorption at 50 °C. It can be seen that the immobilisation of tungstophosphoric acid by sol-gel in silica and zirconia clearly promotes and increases the number of acid sites in solids comparing to the supports. This result agrees with those reported in the literature [233, 247, 277] where the addition of the HPA to the support clearly increases the number of acid sites expressed per gram of solid.

Table 24. Acidity of tungstophosphoric acid immobilised by sol-gel in silica and zirconia, compared to the matrixes.

Sample	Number of acid sites	Acid sites density
	($\mu\text{mol NH}_3/\text{g}$)	($\mu\text{mol NH}_3/\text{m}^2$)
Si-11-SG-DS	720	1.5
Si-DS	222	0.5
Zr-30-SG-DS	590	3.9
Zr-DS	295	1.5

5.3.2. Catalytic performances

5.3.2.1. Esterification tests in homogeneous phase

Glycerol acetylation tests in homogeneous phase were performed with pure HPA. Figure 63 demonstrates that HPW and HSiW exhibit the same acceleration of acetic acid conversion.

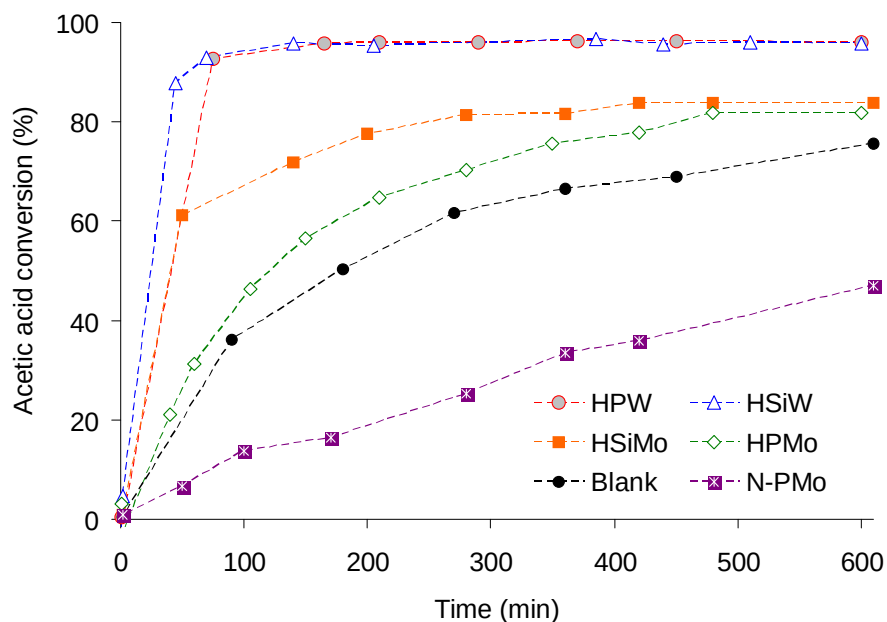


Figure 63. Catalytic performances of pure HPA in glycerol acetylation conducted at 105 °C.

If this conversion is reported to the quantity of theoretical H^+ loaded in the reaction (Figure 64), it can be observed that the acceleration of the reaction is performed according to the ranking of acidity presented before ($H_3PW_{12}O_{40}$, (HPW)> $H_4SiW_{12}O_{40}$, (HSiW)> $H_3P_2Mo_{12}O_{40}$ (HPMo)> $H_4SiMo_{12}O_{40}$ (HSiMo)). In addition, working with an equivalent quantity of PMo anion with a NH_4^+ cation, leads to an esterification rate lower than the blank reaction.

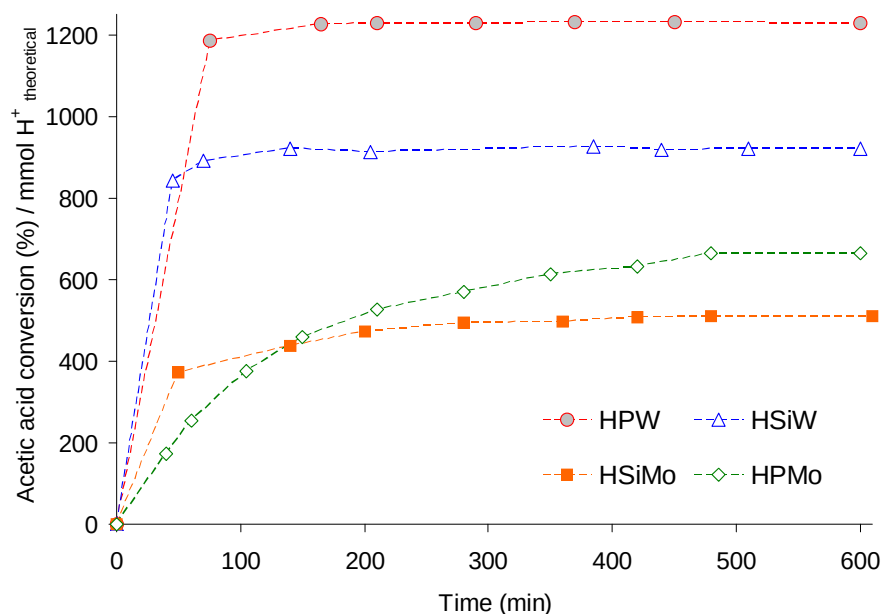


Figure 64. Catalytic performances of pure HPA in glycerol acetylation conducted at 105 °C. Activity normalised by unit of protons.

5.3.2.2. Esterification tests with immobilised HPW

The results concerning the esterification carried out in presence of entrapped or supported HPW are shown in Figure 65. For comparison, the activity of pure HPW is also presented.

It can be observed that HPW immobilised by wet impregnation exhibited a catalytic activity very similar to the one obtained for the corresponding pure heteropolyacid. When the same test was performed after Soxhlet extraction, the solid did not achieve the same activity. Moreover, the characterisation of the wet impregnated samples before and after washing showed that after the Soxhlet step the HPW was removed from the solid. Therefore, the large difference

Part III: Results

of activity of the solid before and after the Soxhlet step is due to the leaching of the HPW. The leached species act as homogeneous catalyst, which was also observed in other works [70, 240, 262, 265].

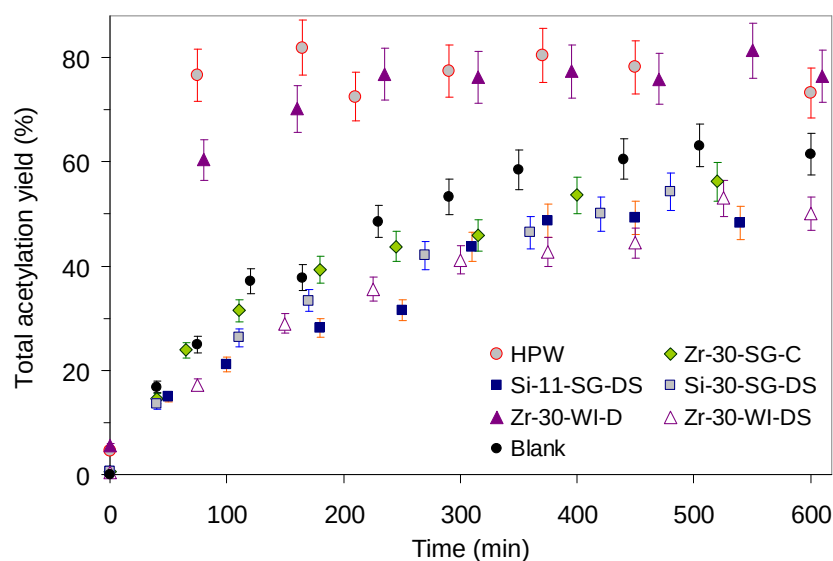


Figure 65. Catalytic performances of HPW immobilised by wet impregnation technique and sol-gel method in zirconia and silica in glycerol acetylation conducted at 105 °C.

On the other hand, solids synthesised by sol-gel present a slight inhibitory effect over the esterification reaction. This could be related to the interaction of Keggin units with the solid matrix, which could result in a decrease of acidity strength for the immobilised samples compared to the pure heteropolyacids, and to the existence of basic sites. When representing the carbon balance (Figure 66), it can be seen that in presence of the synthesised samples the consumed acetic acid is not totally converted in esters, as the points are located below the blank reaction line. Therefore, it could be suggested that the secondary

reactions related to the oxidation or dehydration of glycerol and the subsequent reaction with acetic acid are favoured in presence of tungstophosphoric acid immobilised in silica and zirconia.

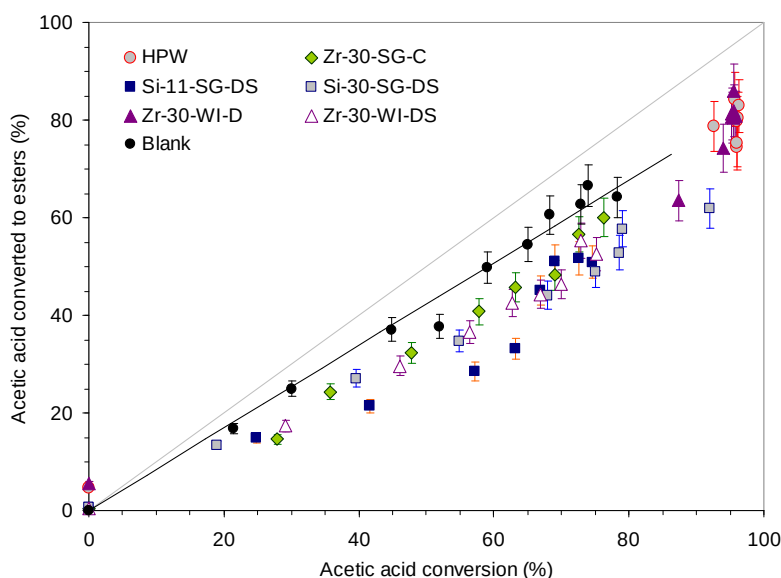


Figure 66. Carbon balance expressed as the acetic acid converted to esters (%) versus the acetic acid conversion (%) for the glycerol acetylation test conducted at 105 °C in presence of tungstophosphoric acid immobilised on and in silica and zirconia samples. The black line represents the blank reaction, in order to compare the catalytic behaviour of the solids. The diagonal represent the carbon balance equal to 100%.

5.4. Discussion of the results

In Chapter 3, it was pointed out that strong acid catalyst as sulphated zirconia is needed for developing a satisfactory catalytic behaviour, however, these solids suffered from S leaching and were not recyclable. Consequently, the research was directed towards the

Part III: Results

study of solids presenting strong Brønsted acidity such as heteropolyacids. The heteropolyacids are soluble in the reaction medium and catalyse the reaction according to their strength of acid sites: the stronger the acidity, the higher is the acceleration of the esterification reaction. To avoid problems of homogeneous catalysis (not recyclable and contamination of final products), the immobilisation of the tungstophosphoric acid was performed over two different matrixes ZrO_2 and SiO_2 by two different methods, wet impregnation and sol-gel synthesis.

Concerning the textural characterisation, it was observed that silica samples developed higher surface areas than zirconia samples. Pure silica used as support showed mesoporosity that was conserved when the heteropolyacid was supported. However, the HPW immobilised in silica by sol-gel sample exhibited microporosity. In the case of zirconia based samples, the introduction of the Keggin units in the matrix causes a slightly reduction of surface area. Both zirconia and HPW immobilised in/on zirconia exhibited microporosity.

Immobilisation by wet impregnation techniques produced a sharp decrease in the surface area compared with the matrix, may be due to the blockage of pores by tungstophosphoric acid. Nevertheless, after submission to a Soxhlet extraction the values of surface area are roughly the same as the supports. This was a clear signal than Keggin units deposited at the surface of the solid were not resistant to leaching in water.

Regarding the crystal structure of the samples, it can be seen that the matrix structures were amorphous in all cases. Independently of the matrix used, the tungstophosphoric acid was highly dispersed in the matrixes when synthesised by sol-gel method, as the characteristic peaks of pure HPW crystals were not observed in the XRD diffractograms. Wet impregnated samples presented the formation of HPW crystal after the drying step; however, after Soxhlet extraction these crystals disappeared completely. Consequently, it can be concluded that leaching of supported species can also be observed by XRD technique.

The stability of the Keggin unit was verified by the FTIR technique. The Keggin unit is maintained both in zirconia and silica samples. Nevertheless, some geometrical distortions were detected in the zirconia based samples synthesised by sol-gel, probably due to a strong interaction between the heteropolyacid and the zirconia matrix.

The immobilisation of the tungstophosphoric acid in the bulk and in the surface was studied with ICP and XPS techniques. It was found that zirconia retains larger amount of heteropolyacid ($\sim 24\%_{\text{wt}}$) both in bulk and at the surface than silica. Moreover, the surface content of tungstophosphoric acid in zirconia matrix remains roughly constant after Soxhlet extraction. However, the silica matrix only retained $2\%_{\text{wt}}$ HPW at the surface after Soxhlet extraction. The analysis of XPS W 4f spectra showed that the heteropolyacid interacts with the hydroxyl groups of the silica matrix, but remains at the oxidation state +6 when immobilised in zirconia.

Part III: Results

In our case, the solid supported by wet impregnation on silica or zirconia were not resistant to leaching in contrast to other several works cited in the introduction. Leaching was verified by several characterisation techniques (nitrogen adsorption-desorption, XRD, FTIR, XPS) and catalytic tests performed before and after washing. It was clearly observed that the samples became totally inert after a washing by Soxhlet, while before washing they exhibited an activity close to the pure heteropolyacid. Therefore, the heteropolyacid was leached towards the reaction medium and then acted as a catalyst in homogeneous phase.

From homogeneous esterification tests, it can be seen that HPMo acid shows a very low catalytic effect, may be due to the fact that it presents the lower acid strength of the series. Reddy and co-workers measured the acidity constants of 12-tungstophosphoric and 12-molybdophosphoric acid both in aqueous solution (0.1 M) and as a solid suspension in acetonitrile using a potentiometric titration method [176]. The pKa values obtained were 1.6, 3.54, and 7.16 for HPW and 2.4, 4.31, and 5.46 for HPMo. HPMo presents lower acid strength than HPW; as the first dissociation constant of HPMo is lower than the one of HPW. Taking into account that the pKa of acetic acid is equal to 4.76 in aqueous solution [181], it can be suggested that the Brønsted acid sites required for the reaction must exhibit a stronger acid strength than the one from acetic acid. Therefore, the use of a solid developing a large number of acid sites but with low acid strength will not have an impact over the esterification reaction. A

solid with higher acid strength than acetic acid is needed in order to catalyse the esterification of the carboxylic acid with glycerol.

Regardless of the solid matrix (zirconia or silica), samples synthesised by sol-gel method under inert atmosphere remained inactive in the esterification reaction, despite the high number of acid sites measured by ammonia chemisorption at 50 °C. The lack of activity could be explained by the decrease in acid strength of heteropolyacid. The interaction between the HPW and the matrix could effectively lower the acid strength of the immobilised heteropolyacid. Therefore, despite the large number of acid sites present in the immobilised HPW, the absence of catalytic activity could be explained also by an inadequate acid strength, too weak to catalyse the glycerol acetylation.

5.5. Conclusions

In this chapter, the synthesis and characterisation of HPW incorporated in silica and zirconia by different methods, namely sol-gel and wet impregnation techniques, were performed. The properties of the solids were tested in the glycerol acetylation carried out in an excess of glycerol.

The objectives of this chapter and the conclusions are summarised here:

(i) To compare the catalytic activity of pure heteropolyacids (HPA) in the glycerol acetylation.

Homogeneous tests in presence of pure heteropolyacids showed that the catalytic activity normalised by proton unit decreases in the following order: HPW>HSiW>HPMo>HSiMo which agrees with the decrease of acid strength of the pure HPA. The HPMo solid only catalyse slightly the reaction, indicating that a stronger acid than the carboxylic acid is needed to have a catalytic effect over the reaction. The use of NH_4^+ salt resulted in a lower esterification rate.

(ii)-(iii) To immobilise the most active HPA in two different supports, zirconia and silica, by two different methods (wet impregnation and sol-gel techniques); and to compare the properties of the final solids, depending on the matrix and the synthesis method used.

The tungstophosphoric acid immobilisation by sol-gel was carried out under an inert atmosphere with controlled temperature by hydrolysis using zirconium propoxide and tetraethyl orthosilicate. Similarly, two samples were synthesised without adding the heteropolyacid in order to obtain pure ZrO_2 and SiO_2 which were used as supports for the wet impregnation samples.

Silica prepared by sol-gel and HPW impregnated in silica exhibited mesopores. However, sol-gel immobilised HPW samples

were mainly microporous. Zirconia samples exhibited only micropores.

High dispersion of the HPW was obtained for the samples obtained by sol-gel, independently of the matrix used. Nevertheless, HPW crystals were detected both in zirconia and silica impregnated samples. Both silica and zirconia matrixes were amorphous.

Keggin HPA unit was maintained in the final powders, although some geometric distortions were detected by FTIR, probably due to a strong interaction between the HPW and the matrix.

The solids synthesised by sol-gel presented a very high resistance to leaching as the HPW content remains constant after extraction with distilled water in Soxhlet apparatus. Zirconia matrix allows the immobilisation of a larger amount of HPW both in bulk and at the surface respect the silica samples. In silica, the quantity of HPW retained at the surface was independent of the initial amount of HPW loaded. On the contrary, solids prepared by wet impregnation presented a low resistance to leaching. The leachability of wet impregnated solids was detected by several techniques due to marked changes (texture, structure, FTIR spectra) observed in the washed samples.

XPS measurements showed that an interaction exist between the HPW and the Si present at the surface ($\equiv\text{SiOH}_2$)⁺(H₂PW₁₂O₄₀)⁻ or

Part III: Results

$(\equiv\text{Si})_m^+ (\text{H}_{3-m}\text{PW}_{12}\text{O}_{40})^{m-} + \text{H}_2\text{O}$. In zirconia such interaction was not detected.

The number of acid sites of samples obtained by sol-gel technique was compared to the matrixes. It was clearly observed that the introduction of HPW in the matrixes improved the number of acid sites.

(iv) To test these solids in the glycerol acetylation.

The samples obtained by wet impregnation showed high activity in the glycerol acetylation due to the leaching of HPW species which acted as homogeneous catalysts. When the samples were washed by Soxhlet extraction, no activity was detected, due to the absence of remaining HPW on the surface of the solids.

The HPW immobilised by sol-gel could not accelerate the glycerol acetylation reaction despite its large number of acid sites measured by NH_3 -chemisorption. The absence of activity could be explained by the modification of acidic properties of HPA when immobilised as their structure is modified due to interactions with the matrix lowering the acid strength of the HPW species compared to the pure HPW. Moreover the presence of secondary reactions between the product of glycerol oxidation or dehydration and acetic acid were favoured in presence of the synthesised solids.

CHAPTER 6: GLYCEROL ACETYLATION CATALYSED BY ION EXCHANGE RESINS

Ion exchange resins and their optimisation in glycerol acetylation.

In this chapter, the catalytic performances of ion exchange resins in glycerol acetylation are presented. Two types of resins were selected for our study, Amberlyst and Dowex (macroreticular and gel type, respectively). The effects of catalyst loading and the pre-treatment are also studied for the most active resin of each family. Recyclability tests show that these solids are directly reusable up to 4-5 esterification tests. No homogeneous catalysis is detected in the filtered liquid media obtained after contact with the solids. Resins are not deactivated in presence of water in the reaction medium.

6.1. Introduction: ion exchange resins as catalysts

Ion exchange resins consist in a styrene and di-vinylbenzene copolymeric matrix functionalised with sulphonic groups and present an elevated protons donor character. The difference between Amberlyst and Dowex resins is their crosslinkage, defined as the percentage of di-vinylbenzene in the resin, which influences the porosity of the materials, their swelling properties and thus their catalytic activity.

Common uses of ion-exchange resins include water softening, environmental remediation, wastewater treatment, hydrometallurgy, chromatography, biomolecular separations, biomass conversion, metal recovery and separation, ion substitution, acid–base catalysis, removal of impurities from aqueous and non aqueous media, as sensors or as solid electrolytes in chemical, food, and beverage industries, and in power, nuclear, semiconductor, and pharmaceutical industries [279-281].

In catalysis, the ion exchange resins can participate in numerous reactions both in slurry and fixed bed reactors. They can effectively enhance the selectivity and reaction rate of acetal formation, alkylation, condensation, epoxidation, esterification of olefins [282-283], esterification of alcohols [180, 284-289], etherification [7], hydration, hydrolysis [285], isomerisation, transesterification, separation of close-boiling compounds through catalysed reactions

[281, 290]. Moreover, ion exchange resins can also be used as support [279].

The main disadvantages of ion exchange resins are their low thermal stability and their deactivation by adsorption of metals and cations [291]. Working temperatures higher than 125-150 °C can indeed cause desulphonation and thus, the breakdown of the active sites [290]. The ion exchange resins can be deactivated by metals as iron or cations as Na^+ , basic molecules as ammonia, amines, nitriles and amides present in the reaction medium and also by a strong adsorption of products of the reaction (alkylation reaction of o-xylene with styrene) or blocking of the pores [290, 292].

Further details on ion exchange resins are presented in the section below.

6.1.1. Ion exchange definition and classification

An ion exchange resin can be defined as an insoluble polymeric matrix containing labile ions, capable of exchanging these ions with others present in the surrounding medium [285, 290]. As said before, ion exchange resins are usually composed by polystyrene-divinylbenzene copolymers bearing ion-exchanging functional groups as shown in Figure 67.

The catalytic performances of ion exchange resins depend on the acidity and the accessibility of their active sites. Acidity is determined

by the type and number of acid sites, divinylbenzene content and reaction medium. In addition, the crosslinkage, particle size, porosity and diffusivity of the reactants influence the accessibility [290].

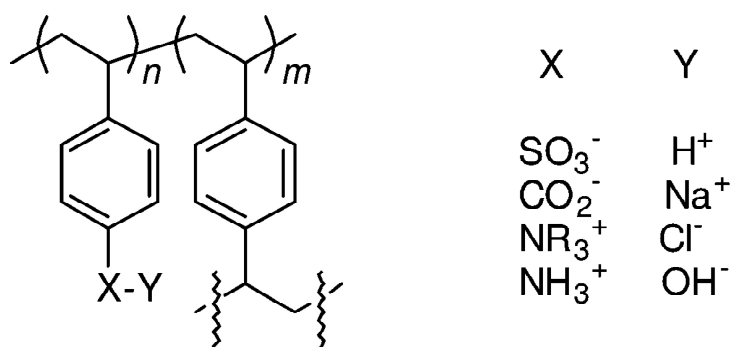


Figure 67. Scheme of ion exchange resins [279].

Depending on the crosslinkage, defined as the percentage of divinylbenzene in the resin, ion exchange resins can be classified in gel or macroreticular type. Gel-type copolymers are characterised by divinylbenzene content generally below 12% and present a homogeneous microporous structure with no discontinuities in the pore system [279, 282, 290]. Gelular resins are rigid, transparent, not deformable and exhibit a spherical shape which can be tailored during the synthesis [282]. The polymeric matrix of gel resins collapses when the gel beads are dried, the polystyrene chains then being as close as atomic forces allow [282, 290]. Therefore, the dried gel-type resins are completely ineffective in non-polar media because of the little number of acid sites accessible to the reactants present on the beads surface [283, 290]. Thus, this type of solid is only catalytically active

in reaction media where the solvent or the reactants are capable of inducing the swelling of the matrix [282, 290].

Macroreticular or macroporous resins consist of agglomerates of very small microspheres interspersed with macropores exhibiting crosslinkage degrees higher than 12% [290]. The permanent porosity, involving channels between agglomerates of spherical gel particles, allows these solids to be effective in polar as well as in non-polar solvents [279, 283, 290].

The efficiency of macroreticular resins in both swelling and non-swelling conditions due to a fixed porosity even in dry conditions and their higher resistance to attrition make their use broadly expanded [282]. Nevertheless, in some cases the enhanced mass transfer inside the polymer beads leading to a higher accessibility of the active sites makes the gel type resins preferable to macroporous ones in polar media [279].

6.1.2. Swelling of ion exchange resins

The swelling properties of the resins are directly influenced by their bulk properties, namely the crosslinkage degree. Moreover, the swelling properties and the porosity of the resin can determine the different catalytic applications. Generally, the lower the crosslinking percentage, the higher the swelling, the moisture content, the equilibration rate of the exchange, the loading capacity and the ability to accommodate larger ions [279, 282].

Part III: Results

Several authors have studied the swelling properties of ion exchange resins in different solvents. The swelling depends on the polarity of the solvent, which can be evaluated via its dielectric constant [7, 293]. In general in the presence of a polar component the swelling increases with the temperature [286]. In addition, the lower crosslinking, the higher the swelling capacity [286, 293].

Resins can develop selective catalysis of the reactant (i.e. the pore size can impede the passage of larger molecules allowing only the small molecules to access to the active sites and react) and similarly selectivity towards the product depending on the matrix nature, fixed ionic groups, the type of polymer, the swelling properties, and reaction conditions (liquid phase composition and temperature) [281, 290]. In some cases, the selective swelling of the polymer matrix leads to values of the reaction equilibrium higher from those typically achieved in homogeneous catalytic systems under similar conditions due to preferential adsorption of one compound [281, 294]. This is because, the concentration of the reactants inside the catalyst (where the reaction takes place) may be different from that in the bulk solution [290]. This phenomenon can be applied to several organic reactions as alkylation, esterification and etherification [281, 290-291, 295] and the references therein.

Highly crosslinked ion-exchange resins catalysts Amberlyst-15 and 35 were compared to low and medium crosslinked resins Amberlyst-36 and 39 in tert-butylation of glycerol [7]. Amberlyst-15 and 35 appeared as a very active catalysts both in wet and dry forms

due to larger pore size compared to Amberlyst-36 and 39 which were inactive in the wet form. The authors suggested that the water molecules occupying the pores of the polymer hinder the glycerol molecules to access the inner surface of the catalyst preventing the formation of voluminous ethers and slowing the diffusion of glycerol. The authors remarked also that the swelling in water was faster than in glycerol, due to the smaller volume of water molecule compared to glycerol, and to the dielectric constant of water which is higher than that of glycerol [7].

Ali and co-workers agreed that the gel type Dowex50Wx8 adsorption behaviour of the system's components (water, benzyl alcohol, acetic acid, benzyl acetate) is appreciably higher from that of macroreticular catalysts Amberlyst-15 and microreticular Amberlite IR 120 for the esterification and hydrolysis of benzyl acetate, resulting in a faster initial esterification rate for the Dowex resin [285].

Liu and Tan focused on the esterification of propionic acid with n-butanol in liquid phase [296]. The results showed that due to the swelling nature of Amberlyst-15, 35 and 39 ion exchange resins, the equilibrium of the reaction was shifted toward a higher conversion of propionic acid compared to the equilibrium achieved in homogeneous reaction with sulphuric acid [296].

Therefore, it can be seen that the resin crosslinkages have a very important effect in the catalytic behaviour of the resin, the latter

depending also on the polarity of the different substances participating in the reaction.

6.1.3. Esterification mechanism over ion exchange resins

Tesser et al. presented a reaction mechanism for fatty acid esterification with methanol over ion exchange resins based on the Eley-Rideal model where the protonated carboxylic acid is attacked by a free molecule of alcohol [295]. Nevertheless, they proposed the adsorption equilibrium of the alcohol as the first step of the mechanism followed by successive protonic exchange equilibrium (Figure 68). The first hypothesis proposed was that all the active sites of the resin are occupied; the major part of them being occupied by methanol in a protonated form, as the methanol/ fatty acid molar ratio is equal to 6.5:1. The second hypothesis proposed was that all the components (fatty acid, water and methylesters) undergo a protonic exchange equilibrium with the protonated methanol adsorbed onto the active sites.

According to the work of Tesser et al., it can be suggested that in our reaction the adsorption glycerol (the reactant in excess) over the active sites of the resin would not involve the deactivation of the latters. Thus, the excess of glycerol would not affect negatively the catalytic performances of the resin.

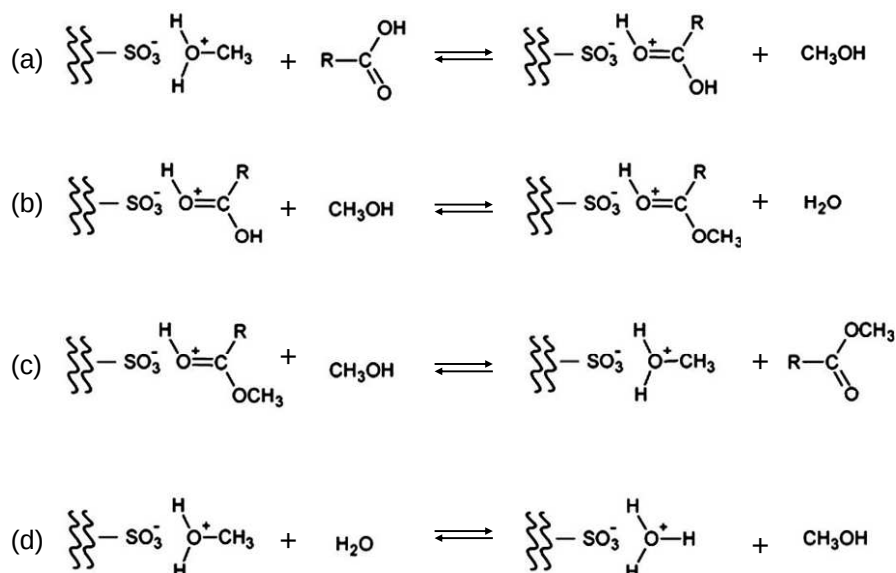


Figure 68. Scheme of exchange and reaction steps. Figure taken from reference [295]. (a) Protonation of the fatty acid by means of methanol. (b) Nucleophilic attack of free methanol molecule over the protonated fatty acid. (c) Regeneration of the active site by desorption of the formed ester. (d) Deactivation of acid sites by water adsorption.

6.1.4. Influence of water

Water can have a detrimental effect over the catalytic performances of ion exchange resins [290]. This is because water competes with the reactant for the active sites and can attach itself on four sulphonic groups leading to a reduction in the number of the effective active sites [180, 290, 295]. Water can be present in the system as the moisture content of the resin used wet and as being a by-product of the reaction (dehydration of alcohols and esterification).

6.1.4.1. Effect of catalyst moisture content

In general, gel and macroporous resins present very different catalytic performances before and after drying even if the mass of dry sample used in each reaction test remains constant [283].

In esterification reactions, the moisture content of the solid ion-exchange resins has a retarding effect on the conversion of acid [180] and references within. Nevertheless, Erdem and co-workers studied the esterification of propionic acid with n-amyl alcohol in the presence of Dowex 50W-x8 and x2, Amberlyst-15 and 35 and Amberlite IR-120. The authors performed experiments with wet and dry catalysts, using in both cases the same dry mass. It was found that wet Amberlyst-15 was most effective than in the dry form [283]. In dry conditions, it was observed that the propionic acid conversion decreased as the divinylbenzene content in the resin was increased [283].

For this reason, in this chapter, the moisture effect over the glycerol acetylation was examined by testing a representative sample in dry and wet form of each family of ion exchange resins (Amberlyt-36 and Dowex-2).

6.1.4.2. Effect of water adding

Several works have focused on the effect of water addition on the catalytic performances of ion exchange resins and their deactivation by water adsorption. In esterification reactions, both

water as well as ester additions decrease the esterification rate. However, the presence of water rather than ester in the feed exerts a more detrimental effect because water can promote ester hydrolysis and adversely affect catalytic activity as cited before [180, 285].

Depending on the reactant and the pore size, the detrimental effect of water can be more marked over a determined type of resins [180]. In the esterification of free fatty acids, Amberlyst BD20 (non porous) shows better recycling properties compared to Amberlyst 15 (porous) due to the deactivation of the latter by water adsorption in the inner pores avoiding the oil to react [297].

The effect of water addition in oleic acid and other fatty acids esterification with methanol in the presence of Amberlyst-15 and sulphuric acid as homogeneous catalyst was compared by Park and co-workers [298]. It was observed that the activity of Amberlyst-15 decreased more rapidly than that of sulphuric acid, due to the direct poisoning of acid sites by water. The strong affinity of water for cation exchange resins seems to be the reason for this behaviour [285].

Accordingly, it is very important to verify that the catalytic activity of resins remains still higher even in presence of water in the reaction medium. That is the reason why in this chapter, two different volume ratios of acetic acid: water were tested in our conditions 2:1 and 1:2.

6.1.5. Main objectives of the chapter

In this chapter, the influence of the crosslinkage degree over the esterification rate of acetic acid with glycerol was studied by performing the standard catalytic test with different resins: Amberlyst and Dowex.

Moreover, the optimal amount of resin used in each run of glycerol acetylation was determined. Generally, the higher the amount of catalyst loaded the higher the esterification rate with which the reaction equilibrium is achieved. This phenomenon is explained by the higher availability of active sites which allows the simultaneous protonation of more numerous acetic acid molecules. The use of lower quantities of catalyst would lead to longer reaction times. Nevertheless, an overloading of catalyst results in a waste of solid which would not promote an increase in the reaction rate. These are the reasons why it is very important to determine the optimal amount of solid to employ in our reaction conditions, maximising the esterification rate but avoiding solid waste.

The effect of different pre-treatment of the resins before reaction were also studied by testing the solids as received, in dry form and after washing with water. The goal of these procedures is to study the different behaviours of the solids as function on their pre-treatments and to determine if the latters are advantageous for the esterification reaction. For example, if the catalytic performances of the non dried samples are similar to those of the dried resins, it can be suggested

that avoiding the drying step will lead to a gain of energy and time in the process applied to the industrial scale. Moreover, the reason that led to analyse the effect of a washing step are twofold: the first one is to remove impurities that may be present in the wet solid and could not be eliminated by the drying step; the second one is to verify that the sulphonic groups are resistant to leaching in a polar medium as water. Furthermore, it could be useful to determine the effect of the washing step over the resin in order to employ this procedure for the resin recyclability tests. Resin can be deactivated by saturation of reaction compounds, in our case, glycerol, and esters. Thus, a possible option to regenerate the solid and to recover the initial activity could be a washing step with water followed by drying.

As said in the previous section, the adsorption of water over the active sites of the resin can deactivate the latter and thus reduce its catalytic behaviour [180, 290, 295]. Therefore, the influence of the water content in the reactants over the catalytic performances of ion exchange resins Amberlyst-36 and Dowex-2 was also analysed.

Finally, the recyclability of the solids and the possibility of leaching were studied.

In brief, the main objectives of this chapter are:

- (i) To determine which type of solid is the most active of each family of resins (macreticular and gel type).

- (ii) To study which are the optimal conditions of use of the resins, concerning the amount of solid used in each run and the best pretreatment.
- (iii) To verify if the ion exchange resins are deactivated by the presence of water.
- (iv) To analyse the recyclability of this type of solids in the conditions studied.

6.2. Experimental

6.2.1. Ion exchange resins

For our study, two Amberlyst resins were chosen, Amberlyst-15 and Amberlyst-36 (A-15 and A-36 respectively). Amberlyst resins are co-polymeric ion exchange consisting primarily of styrene and di-vinylbenzene produced exclusively by Rohm and Haas. These resins are in the form of small macro-reticular bead (mm) with a brown and gelatinous appearance. The principal properties of these solids are presented in Table 25.

In addition, three Dowex type resins were also selected to participate in the esterification of acetic acid with glycerol (Dowex 50Wx2, D-2; Dowex 50Wx4, D-4; and Dowex 50Wx8, D-8, with respective crosslinkage equal to 2, 4 and 8%). Similarly, Dowex resins are constituted of styrene and di-vinylbenzene copolymers functionalised with sulphonic groups forming gel beads (mm). Dowex

is a registered trademark of Dow Chemical Co. Dowex type resins were purchased from Sigma-Aldrich. Specifications supplied by the manufacturer are listed in Table 25.

Table 25. Main properties of sulphonic acid functionalised resins. A-15: Amberlyst-15, A-36: Amberlyst-36, D-2: Dowex 50Wx2, D-4: Dowex 50Wx4, D-8; and Dowex 50Wx8. Max.Op Temp: Maximal operational temperature. Data were taken from supplier except specified otherwise. Moisture (%) ^{*1}: water content determined after drying the resin overnight at 105 °C under vacuum. Capacity H⁺*²: calculated dividing the capacity expressed in eq/L by density of the wet resin measured experimentally. ^{*3}Data taken from reference [293].

Sample		A- 15	A-36	D-2	D-4	D-8
Max. Op. Temp (°C)		120	150	150	-	-
Moisture (%)		~48	52.4* ¹	76.7* ¹	65.6* ¹	50.8* ¹
Texture	Surface area (m ² /g)	53	33	-	-	-
	Average pore diameter (nm)	30	24	-	-	-
	Total pore volume (cm ³ /g)	0.4	0.2	-	-	-
Capacity H ⁺	eq/L	1.70	1.95	0.6	1.1	1.7
	eq/kg	4.7	5.4	4.8	4.6* ²	4.7* ²
Particle size	(mesh)	20-50	-	50-100	20-50	100-200
	µm	841-297	600-850	297-149	841-297	149-74
Crosslinkage (%)		20* ³	12* ³	2	4	8
Polymer type		Macro-reticular			Gel-type	

6.2.2. Esterification tests

The esterification test procedure was made as described in Chapter 2. The catalyst dried overnight at 105 °C under vacuum was

put in the reactor together with the glycerol and the mixture was brought to the reaction temperature. When the temperature was reached, acetic acid was injected. One minute after the injection, a sample was taken and analysed. This result was considered as the initial chemical composition of the medium.

6.2.3. Catalyst loading optimisation

The influence of the mass of the resin used was checked by varying the mass of solid pre-dried at 105 °C under vacuum overnight from 0.1 to 0.3 g/run. These tests were performed with the most active catalyst of each family of resins (Amberlyst-36 and Dowex-2).

6.2.4. Catalysts pre-treatment optimisation

The influence of different pre-treatments was also analysed. Solids were used as received, dried overnight at 105 °C under vacuum, or after being submitted to a Soxhlet extraction with distilled water and subsequent drying overnight at 105 °C under vacuum. Similarly to the previous section, these tests were performed only with Amberlyst-36 and Dowex-2.

6.2.5. Effect of water addition

The aim of these tests was to check the influence of the water content in the reactants over the catalytic performances of ion exchange resins Amberlyst-36 and Dowex-2. The volume ratios acetic

acid: water used were 2:1 and 1:2. These experiments were carried out similarly to standard tests; the addition of water was achieved immediately after the addition of acetic acid. The first sample was then taken after 1 minute of stirring and its composition was considered as the initial chemical composition of the medium at $t=0$.

6.2.6. Homogeneous catalysis and catalyst recyclability tests

The homogenous and recyclability tests were carried out in the same conditions as the catalytic tests: after an adequate period of time to achieve a total acetylation yield of approximately 50-60% the catalyst was separated from the liquid medium by centrifugation and then put in a fresh reaction medium without further pre-treatment. Homogeneous catalysis of the liquid medium was also analysed. Therefore, the used liquid medium was filtered (paper filter Whatman No 6, filtration threshold=0.3 μm) and kept under reaction conditions.

Homogeneous catalysis tests aim at verifying if the catalytic activity is the result of the presence of active sites on the solid surface (heterogeneous catalysis), or of the species leached from the solid toward the reaction medium (homogeneous catalysis). Homogeneous catalysis is an undesirable phenomenon as it leads to the contamination of reaction product and disables the reuse of the solid.

To compare the activity rate from the liquid media separated and the fresh liquid medium (blank), the initial reaction mixture of both

Part III: Results

systems should have the same composition of reactants and products. The reconstruction of the starting point of the homogeneous catalysis test is quite laborious as pure monoacetin is only available as a mix of several compounds (diacetin, triacetin and glycerol), making that the reconstituted mixture is much more rich in diacetin and triacetin than the actual reaction mixture, where the proportion of these esters is quite low. Therefore, the comparison of the activity rate between the liquid media separated and the fresh liquid medium (blank) is performed by shifting the first point of the curve in homogeneous catalysis reaction to the point of the blank reaction presenting similar composition.

Recyclability tests were conducted in conjunction with homogeneous catalysis tests. For this, the solids recovered by centrifugation and still wet (no further treatment was applied) were employed in a new esterification run. The recyclability tests have as main objective to analyse the possibility to use the resins in a series of successive catalytic tests or eventually to use them in continuous processes over long periods. Amberlyst-36 and Dowex-2 were submitted to these experiments.

6.3. Results and Discussion

6.3.1. Esterification tests

Figure 69 shows the catalytic activity expressed in terms of acetic acid conversion for each resin. In addition, in Figure 70 it can be seen that in presence of ion exchange resins the carbon balance is close to 100%.

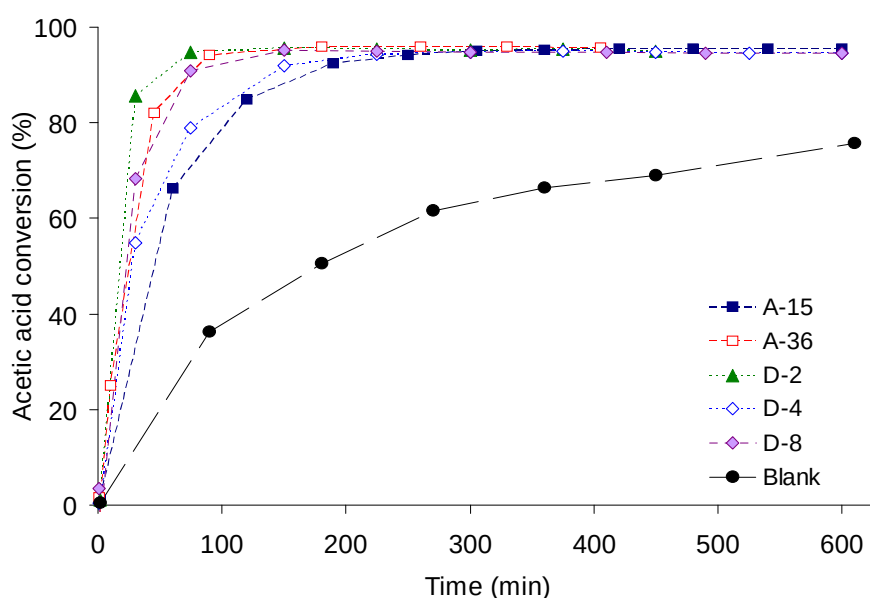


Figure 69. Catalytic performances of ion exchange resins in glycerol acetylation conducted at 105 °C.

In presence of the resins, the reaction equilibrium is achieved in less than 5 hours compared with the blank reaction where the acetylation conversion was approximately 85% at 10 hours reaction and the equilibrium achieved after more than 24 hours. The yield to the different esters is presented in Table 26. It can be seen that the

Part III: Results

esterification rate increases in the following order: A-15<D-4<A36<D-8<D-2. Taking into account the crosslinkage of the resins it could be suggested that lower crosslinkage promotes higher esterification except for D-4 probably due to the larger particle size used compared to the others Dowex resins (0.8-0.2 mm). The difference between the catalytic activity of Amberlyst-15 and 36 may also be related to the number of acid sites loaded, which is higher for the Amberlyst-36.

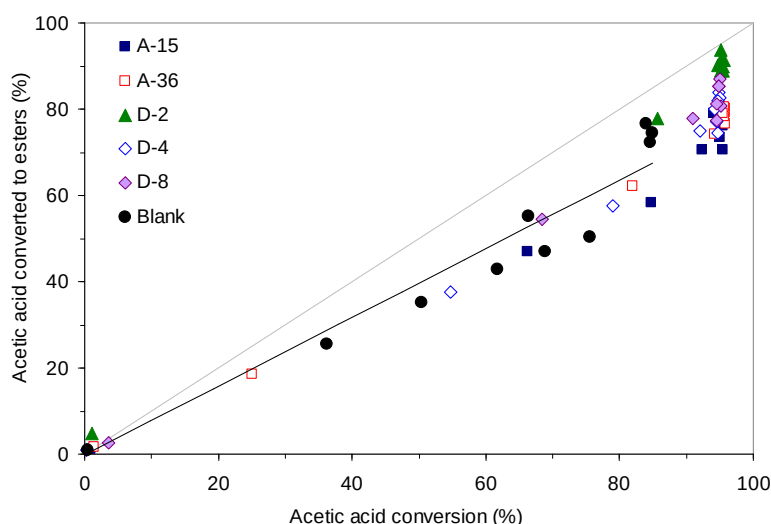


Figure 70. Carbon balance expressed as the acetic acid converted to esters (%) versus the acetic acid conversion (%) for the glycerol acetylation test conducted at 105 °C in presence of ion exchange resins. The black line represents the blank reaction, in order to compare the catalytic behaviour of the solids. The diagonal represent the carbon balance equal to 100%.

No remarkable difference was noticed in the conversion of acetic acid developed by each catalyst. However, a slightly higher esterification yield was observed for lower crosslinkages (Dowex-2). Gels resins have higher affinity for glycerol than for water, thus,

favouring the production of esters. Ours observations agree with those reported by Ali and co-workers [285] and Erdem group [283] for the esterification and hydrolysis of benzyl acetate and for esterification of propionic acid with n-amyl alcohol, respectively.

Table 26. Conversion of acetic acid and acetylation yield of the glycerol acetylation experiments conduted at 105 °C. The relative standard deviation of the total acetylation yield is approximately 6.5%.

Sample	Acetic acid conversion (%)	Acetylation yield (%)						
		1-MAG	2-MAG	MAG	1,3-DAG	1,2-DAG	DAG	Total
A-36	95.6	62.5	7.8	70.3	3.0	1.5	4.5	74.8
A-15	95.3	63.4	7.0	70.3	2.0	0.5	2.5	73.0
D-2	95.2	71.9	8.8	80.8	3.3	1.7	5.1	85.9
D-4	94.8	63.7	7.8	71.6	2.8	1.4	4.2	75.9
D-8	94.7	64.9	8.1	72.9	3.1	1.5	4.7	77.7
Blank (10 h)	75.7	52.8	5.9	58.7	1.7	1.1	2.7	61.5
Blank (24 h)	84.5	60.0	7.7	67.7	2.2	1.1	3.4	71.1

In the conditions applied in glycerol acetylation carried out in an excess of glycerol at 105 °C, the molar distribution of esters was as follows: 94% MAG (where 89% was 1-MAG and 11% was 2-MAG). The distribution of DAG was approximately 6 % (with 68% of them being 1,3-DAG and 32% being 1,2-DAG). The formation of TAG was never observed, likely due to the large excess of glycerol present. The maximal production of water is 1.2 g/run.

6.3.2. Catalyst loading optimisation

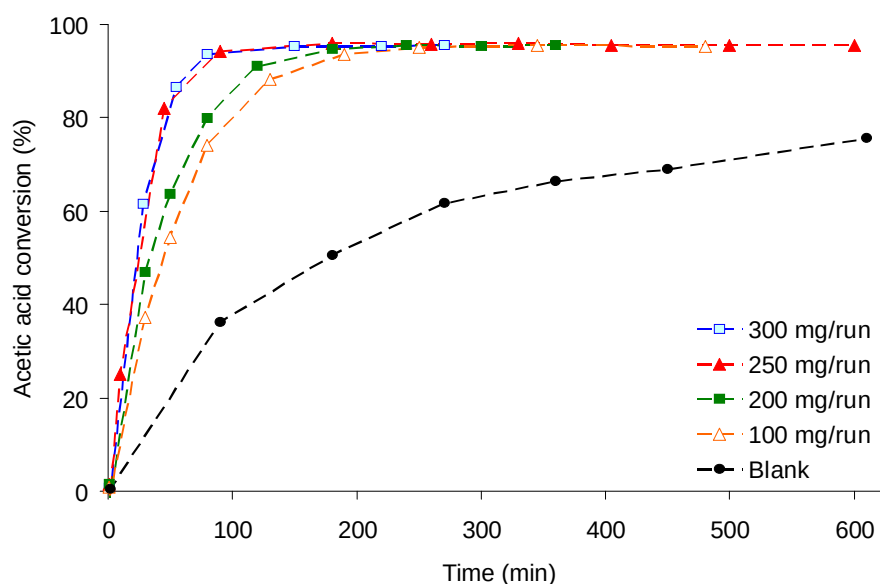


Figure 71. Influence of the commercial Amberlyst-36 resin loading in the esterification reaction conducted at 105 °C. The units of the mass loading are given in mg of catalyst per run. (Glycerol volume=40 ml). «Blank»: pseudo-catalysed reaction.

As it can be seen in Figure 71, the increase in Amberlyst-36 loading from 0.1 to 0.25 g/run has a considerable effect on the conversion of acetic acid. Similar results were obtained with ion exchange resins in esterification reactions with monoalcohols [180] and references therein. When the amount of resin increases from 0.25 to 0.3 g/run a slight increase in conversion is observed but the glycerol acetylation yield remained constant.

Therefore, it can be concluded that increasing the amount of Amberlyst-36 to 0.25 g/run improves the initial velocity of the

reaction, due to the increase of the number of total acid sites available. However, when the amount of catalyst is bigger than 0.25 g/run no influence on the reaction kinetic was observed.

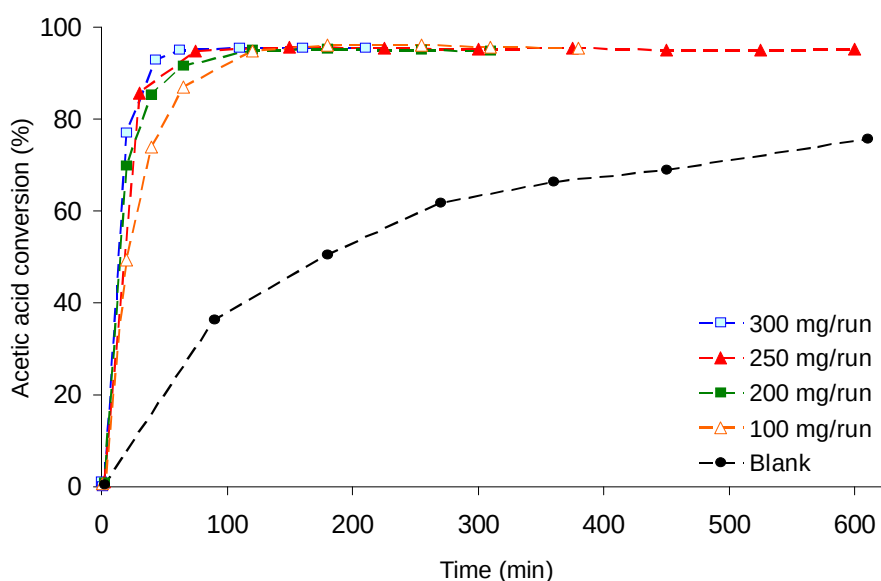


Figure 72. Influence of the commercial Dowex-2 resin loading in the esterification reaction conducted at 105 °C. The units of the mass loading are given in mg of catalyst per run. (Glycerol volume=40 ml). «Blank»: pseudo-catalysed reaction.

In the case of the ion exchange resin Dowex-2, the same behaviour is observed (Figure 72). The acetic acid conversion rate increases when accruing the catalyst loading from 0.1 to 0.25 g/run but remains constant when the amount of solid increases from 0.25 to 0.3 g/run.

In summary, for both solids (Amberlyst-36 and Dowex-2) the increase of the catalyst loading from 0.1 to 0.25 g/run had a considerable effect on the conversion of acetic acid, this tendency

being more remarkable for the Amberlyst-36. This phenomenon is mainly due to the higher number of acid sites available. However, the conversion remains approximately constant when the amount of resin increases from 0.25 to 0.3 g/run.

6.3.3. Catalysts pre-treatment optimisation

Figure 73 shows that, in the case of Amberlyst-36, a drying step before its use promotes the catalytic performance developed in the esterification reaction. The presence of water in the resin results in a slower esterification rate, probably due to the lower availability of acid sites occupied by water molecules, which hinders glycerol to enter in the pores of the resin [180]. Water has indeed more affinity than glycerol for the macroreticular resins [7]. Moreover, water can also lead to an eventual hydrolysis of the formed esters. Washing the resin and the successive drying step do not result in a different catalytic performance as compared to the resins only dried. This means that there is no leaching of sulphonic groups in water at mild temperatures (70 °C) and that the washing steps could be used for the regeneration of the resin if needed without modifying its properties.

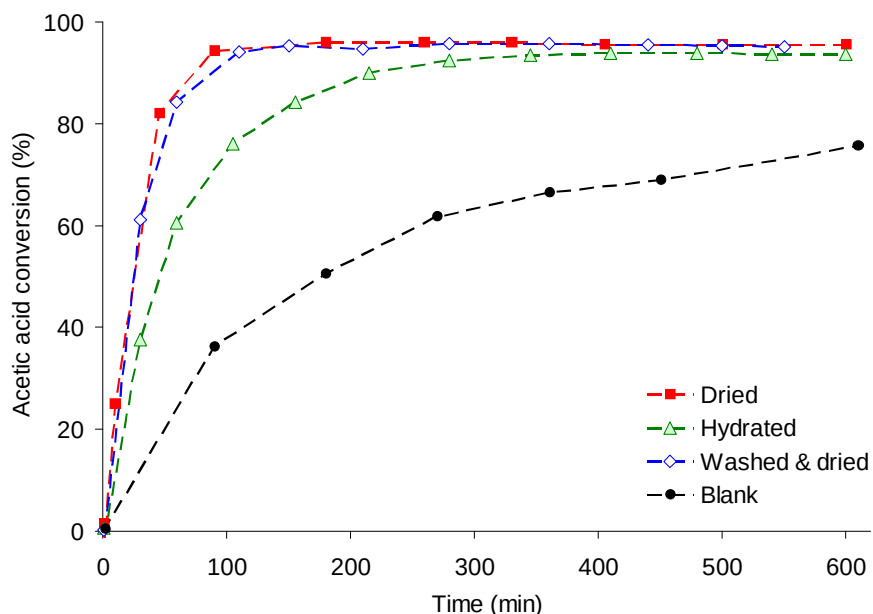


Figure 73. Influence of pre-treatment over Amberlyst-36 in glycerol acetylation reaction performed at 105 °C.

Figure 74 shows the esterification rate of experiments conducted in the presence of Dowex-2 being submitted to different pre-treatments. It can be seen that the different pre-treatments have little influence over the catalytic performances. In particular they are less marked than in the case of Amberlyst-36. Dowex-2 presented an excellent catalytic performance even without undergoing any pre-treatment before testing. Thus, it could be suggested that the affinity for the resin is quite similar for glycerol and for water. However, a drying step is desirable and avoids hydrolysis of formed esters [180, 285]. The use of a Soxhlet step before the catalytic reaction does not have a significant influence on the catalytic performance. This suggests that the sulphonic species of Dowex-2 are resistant to

Part III: Results

washing in a polar medium as water and can therefore be regarded as insoluble in the reaction medium.

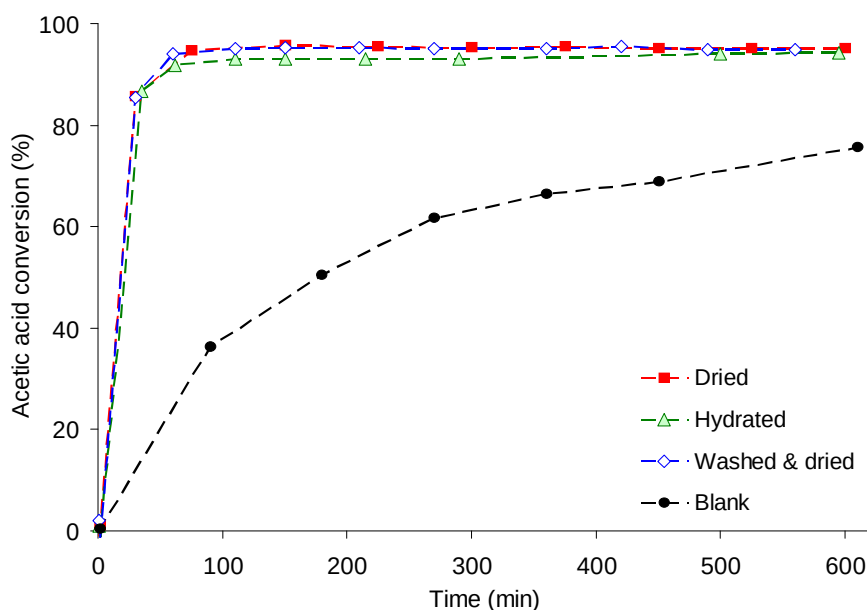


Figure 74. Influence of pre-treatment over Dowex-2 in glycerol acetylation reaction performed at 105 °C.

In conclusion, the catalytic tests carried out by varying the treatment of the resins allow optimising the performance achieved during the catalytic reaction. Drying the resin is necessary in the case on Amberlyst-36 and preferable for Dowex-2 in order to avoid hydrolysis of ester and/or slow esterification rate. Using a washing step by Soxhlet extraction before the catalytic reaction did not alter the catalytic performances of the resins. This suggests that sulphonic species remain unaltered after washing and that they are resistant to leaching. Thus, the resins can unambiguously be regarded as insoluble in the reaction medium.

6.3.4. Effect of water addition

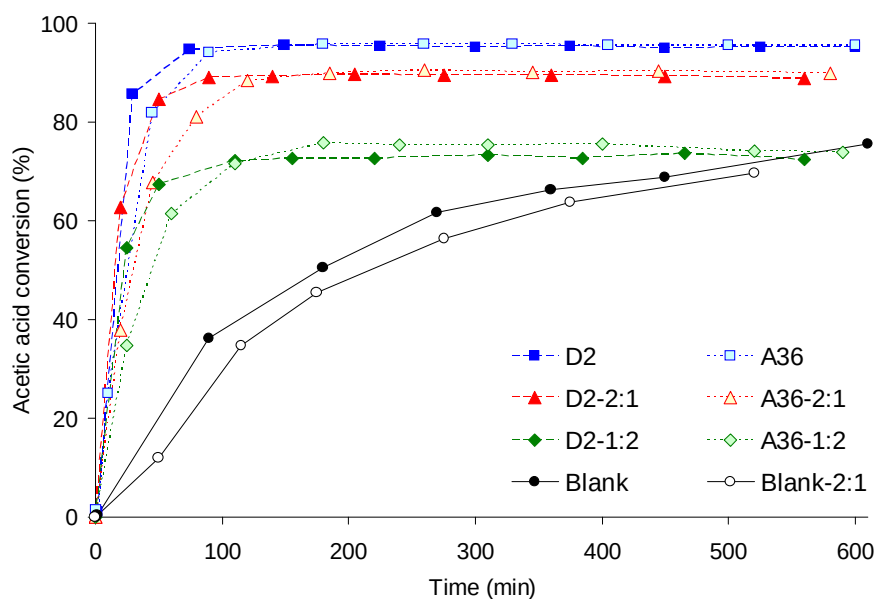


Figure 75. Effect of initial water addition over the esterification reaction. «D2»: Dowex-2, «A36»: Amberlyst-36, Acetic acid: water volume ratio «2:1» and «1:2». «Blank»: reaction conducted in absence of catalyst. Temperature=105 °C.

Figure 75 shows that the addition of water negatively affects the esterification rate and the equilibrium of the reaction. It can be observed that in both cases the initial esterification rate of Dowex-2 is higher than the one obtained with Amberlyst-36. As said before, this could be related to a lower affinity of water to Dowex resin and its low crosslinkage. Nevertheless, the resins remained catalytically active even in presence of water. Our results agree with those reported in literature [285, 287].

6.3.5. Homogeneous catalysis and catalyst recyclability tests

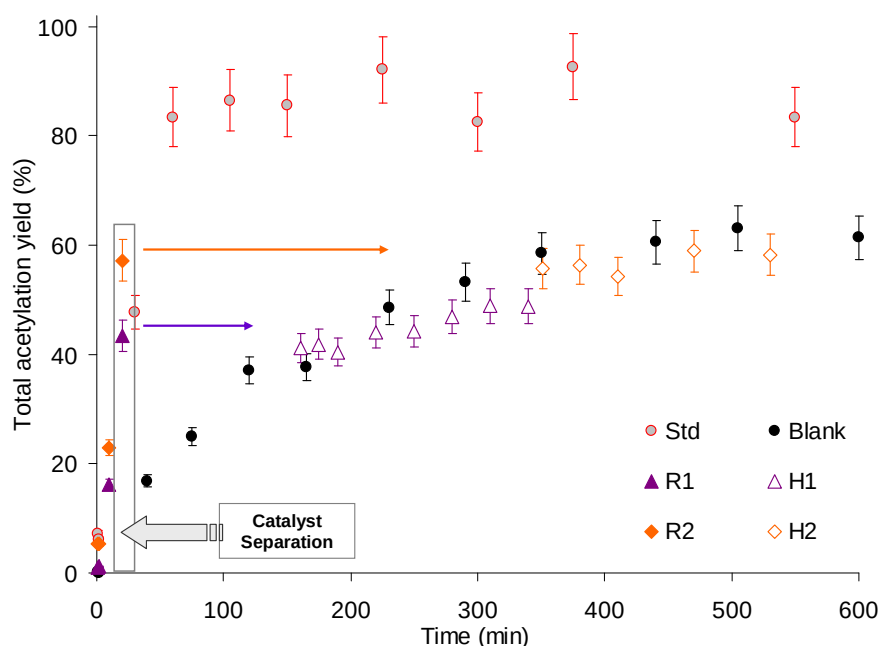


Figure 76. Homogeneous catalysis test for Amberlyst-36. Reference lines: «Std»: standard reaction; «Blank»: reaction conducted in absence of catalyst; «Rn»: tests carried out in presence of solid; «Hn»: activity shown by the liquid phase after its separation from the solid and «n»: number of runs. Temperature=105 °C.

Figure 76 displays the results of the homogeneous tests for Amberlyst-36. Once the solid was removed from the reaction medium (reaction time=40 min), the esterification rate of the liquid medium followed a curve very similar to the blank reaction. Thus, a stop in the activity is observed (horizontal arrows). This process being repeated twice, it can be seen that in the second esterification test there is no homogeneous activity when the solid is removed from the liquid

medium. Therefore, it can be concluded that Amberlyst-36 does not result in catalytic homogeneous activity due to leached species.

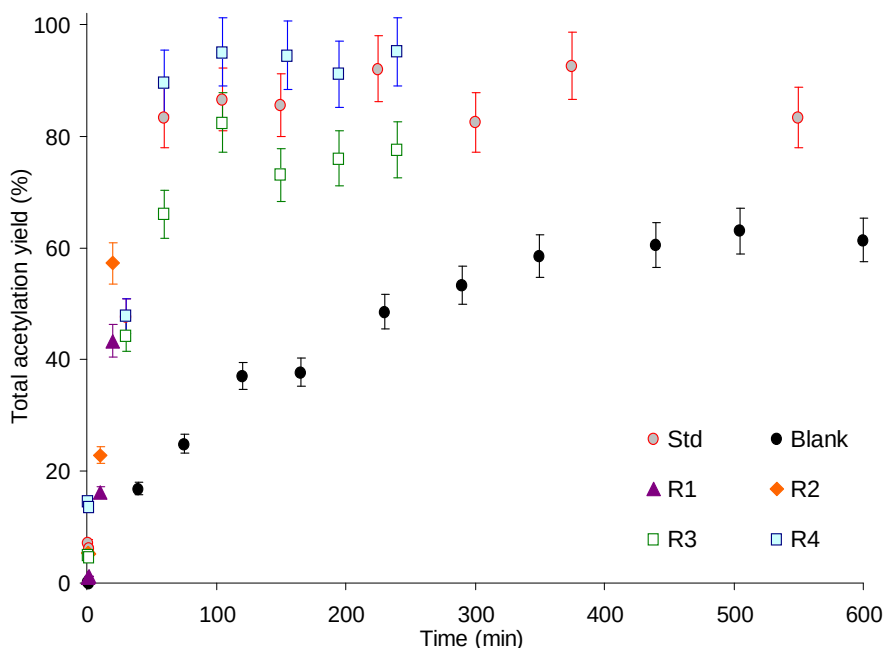


Figure 77. Recyclability test for Amberlyst-36. Reference lines: «Std»: standard reaction; «Blank»: reaction conducted in absence of catalyst; «Rn»: tests carried out in presence of solid; and «n»: number of runs. (R1 and R2, reaction time=40 min; R3-R4 reaction time=4 hours). Temperature=105 °C.

Concerning the recyclability test for Amberlyst-36, Figure 77 shows that the catalytic performances of the solid stayed unchanged after four esterification tests using a fresh liquid medium (R1 and R2, reaction time=40 minutes and R3-R4 reaction time=4 hours). The differences in yield from one run to another can be explained by the presence of remaining compounds from the previous liquid medium in the wet solid.

Part III: Results

Therefore, from the data presented in Figure 76 and Figure 77, it can be concluded that Amberlyst-36 is a suitable catalyst for the esterification of acetic acid and glycerol in the reaction conditions imposed.

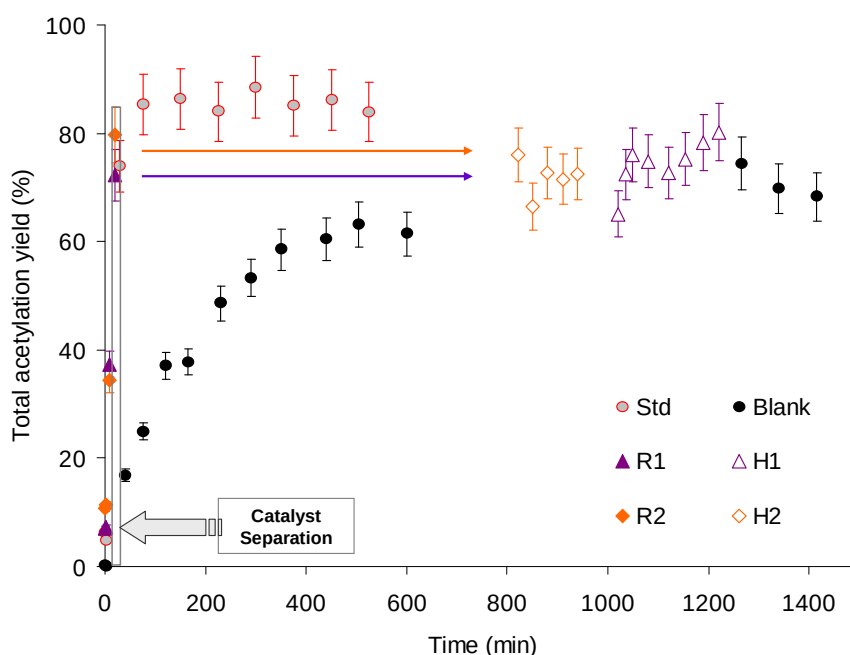


Figure 78. Homogeneous catalysis test for Dowex-2. Reference lines: «Std»: standard reaction; «Blank»: reaction conducted in absence of catalyst; «Rn»: tests carried out in presence of solid; «Hn»: activity shown by the liquid phase after its separation from the solid and «n»: number of runs. Temperature=105 °C.

Similar results were obtained when Dowex-2 was reused in different tests (R1 and R2, reaction time=20 minutes and R3-R5, reaction time=4 hours), the catalytic activity is approximately the same in all cases (Figure 79). Moreover, homogeneous catalysis tests showed that there was no leaching of sulphonic species (Figure 78)

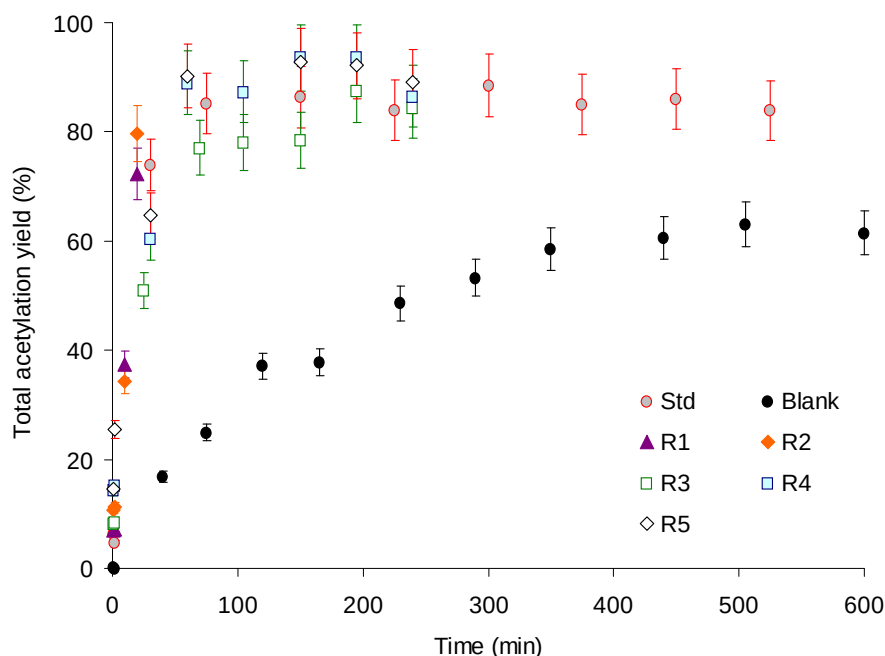


Figure 79. Recyclability test for Dowex-2. Reference lines: «Std»: standard reaction; «Blank»: reaction conducted in absence of catalyst; «Rn»: tests carried out in presence of solid; and «n»: number of runs. (R1 and R2, reaction time=20 min; R3-R5 reaction time=4 hours). Temperature=105 °C.

6.4. Conclusions

Amberlyst and Dowex ion exchange resins have shown very satisfactory catalytic performances on the glycerol acetylation carried out in an excess of glycerol. The different catalytic activities are related to the amount of acid sites of the resins but also to their compositions and crosslinkages, precisely, the lower the crosslinkage the higher the esterification rate.

Part III: Results

Among all the catalysts analysed, Amberlyst-36 and Dowex-2 were the most active of each family of resins and then were chosen for further tests aiming to determine the optimal pre-treatment steps and catalyst loading.

In our reaction conditions, the optimal loading of dry catalyst was fixed to 0.25 g/run for both resins (Amberlyst-36 and Dowex-2) since the use of a higher mass did not result in an acceleration of the esterification rate.

Amberlyst-36 presented better performance when dried overnight at 105 °C in vacuum. The use of wet catalyst resulted in a slightly lower reaction rate mainly because the presence of water may prevent the adsorption of acetic acid and the glycerol access to the pores. Moreover, water can also promote the hydrolysis of esters formed. In the case of Dowex-2, the drying before use is preferred, even if the wet catalyst showed almost the same activity than the dried one. The catalytic performances of both catalysts remained unchanged when washing with distilled water and dried overnight at 105 °C in vacuum. This observation suggests that the sulphonic groups are resistant to leaching in polar media.

Water initial addition causes a lower acetic acid conversion at the equilibrium of the reaction; nevertheless resin remained catalytically active presenting higher initial esterification rate than the blank reaction. For Dowex-2 resin, the decrease in the esterification rate when adding water was lower than for Amberlyst-36. This could

be due to a lower competition of water and glycerol in the core of the Dowex resin beads.

The experimental results of the recyclability tests showed that both solids are directly reusable without any loss of their catalytic performances. Concerning the homogeneous catalysis, once the solid is separated from the liquid medium, the esterification reaction presented the same esterification rate as the blank reaction, confirming the absence of active species leaching.

**PART IV: GENERAL DISCUSSION
CONCLUSIONS AND PERSPECTIVES**

GENERAL DISCUSSION

The principal purposes of this work were to determine if glycerol acetylation could be performed in excess of glycerol and to find out which was the maximum yield that could be obtained. To the best of our knowledge these experiments were not present in open literature.

Moreover, there is a lack of works analysing carefully the possibility that eventual leached species from solid catalysts can catalyse the reaction in homogeneous phase. In this work, a thorough methodology has been implemented in order to discard the contribution of the solid to homogeneous catalysis that is often neglected.

The catalytic performances of the solid in non favourable conditions have also been studied: reaction in presence of water and recyclability test without intermediate treatment. Compared to other works, this type of experiments is rarely presented.

Therefore, in order to reply to these issues, the main objectives of this research were summarised in two principal axes: one concerning the glycerol acetylation itself and the other one concerning the nature and properties of the catalyst used to accelerate this reaction. Therefore, they will be discussed separately.

Glycerol acetylation reaction conducted in excess of glycerol

In this work, glycerol was used in large excess (molar ratio acetic acid: glycerol $\sim 1:8$). The expectation was to shift the equilibrium of the esterification reaction towards the formation of products and to maximise the quantity of glycerol converted to high value molecules (monoacetin, diacetin and triacetin). To our knowledge, these reaction conditions have not been employed in previous works existing in the literature, where glycerol acetylation is generally conducted in presence of an excess of acetic acid in order to exclusively obtain triacetin. Thus, only one molecule of glycerol is revaluated consuming three molecules of acetic acid.

In the introduction, the main objectives of the thesis were presented as several questions that are answered in the following paragraphs.

- (i) Is it possible to carry out the glycerol acetylation reaction in the presence of a large excess of glycerol in order to consume the latter which is the low value molecule?**
- (ii) Otherwise, could the equilibrium of the reaction be shifted towards the products by using an excess of glycerol, instead of an excess of carboxylic acid?**

It was observed that the glycerol acetylation carried in absence of catalyst was a very slow reaction (both at 55 and 105 °C). The carbon balance presented an error of 20% which could be attributed to acetic acid losses by evaporation, but also to its consumption in secondary reactions. It was suggested that oxidation and/or dehydration of glycerol can occur in the conditions applied; therefore the consumption of acetic acid was explained by the reaction between the later and the sub-products of glycerol. Nevertheless these molecules could not be detected maybe due to the experimental protocol applied to analyse the liquid samples collected from the reaction medium.

In the applied conditions the main product was monoacetin with traces of diacetin (Table 27), in any case triacetin was produced.

Table 27. Conversion of acetic acid and acetylation yield of the glycerol acetylation experiments. The relative standard deviation of the total acetylation yield is approximately 6.5%.

Sample	T (°C)	Acetic acid conversion (%)	Total acetylation yield (%)	Esters molar distribution (%)	
				MAG	DAG
Blank (24 h)	55	24.7	19.5	99.8	0.2
Blank (120 h)		63.2	46.8	98.4	1.6
Blank (10 h)	105	75.7	61.5	95.4	4.6
Blank (24 h)		84.5	71.1	95.2	4.8

- (iii) Is it possible to modify the selectivity of the product under the defined reaction conditions by using different catalysts?**

In presence of sulphated zirconia and ion exchange resins the esterification rate was accelerated. However, the selectivity toward the different esters (monoacetin, diacetin and triacetin) was determined by the initial concentration of acetic acid and glycerol and the reaction temperature. Thus, in the working conditions selected, the only role of the catalyst is to accelerate the reaction in order to achieve the equilibrium more rapidly.

Table 28. Conversion of acetic acid and acetylation yield of the glycerol acetylation experiments. The relative standard deviation of the total acetylation yield is approximately 6.5%.

Sample	T (°C)	Acetic acid conversion (%)	Total acetylation yield (%)	Esters molar distribution (%)	
				MAG	DAG
SZ6 (24 h)	55	63.66	62.7	99.8	0.2
A-15 (16 h)		93.8	85.3	98.4	1.6
A-36 (5 h)		95.6	74.8	94.0	6.0
A-15 (5 h)	105	95.3	73	96.5	3.5
D-2 (5 h)		95.2	85.9	94.1	5.9
D-4 (5 h)		94.8	75.9	94.3	5.7
D-8 (5 h)		94.7	77.7	93.8	6.2

In presence of active catalyst the carbon balance showed an error lower than 10%. Thus, it may be suggested that the formation of compounds obtained via secondary reactions is less favoured than in absence of catalyst.

Nevertheless, at the final point of the reaction, a mixture of monoacetin and diacetin in glycerol is obtained. The separation of the

valuable ester from the remaining glycerol is a difficult process to accomplish. Therefore, it can be concluded that even if the esterification reaction between acetic acid and glycerol conducted in excess of the latter is possible, the recovering of glycerol and the esters obtained is from the experimental point of view quite a demanding process.

Heterogeneous catalysts for glycerol acetylation

In order to accelerate the esterification reaction, heterogeneous acid catalysts were preferred to homogeneous ones, avoiding the drawbacks of the latter concerning the contamination of the final products and their low recyclability.

The synthesis, development and characterisation of acid solids developing high catalytic activity in glycerol acetylation was the second axis of the main objectives of this work. This axis was divided in three parts:

- (i) To identify and synthesise solid acid catalysts having suitable properties (texture, structure and acidity) for glycerol acetylation leading to a satisfactory acetylation yield.**

A large scope of solid acids presenting very different natures has been tested in glycerol acetylation (Table 29). A first initial screening was based on a bibliographic research. Four families of solids of

different nature were selected: niobium oxide supported on commercial silica-alumina, aluminium phosphate, tungstated and sulphated zirconias.

The synthesised solids were analysed by N₂ adsorption-desorption, XDR and ICP techniques and tested in glycerol acetylation reaction conducted at 55 °C. In addition, representative samples of each family of catalysts studied in the initial screening were tested in the esterification of acetic acid with propanol in presence of an excess of acid. These tests allowed to avoid the problems related with the use of glycerol excess (large molecule, highly viscous, polyalcohol molecule). The catalytic activity of the solids developed in propanol acetylation tests were very similar to those obtained working with glycerol. Subsequently, it can be concluded that the behaviour of the solids is independent of the reaction conditions: acidity of the reaction system, viscosity and polarity.

Several hypotheses were proposed to describe the different solid behaviours obtained in glycerol acetylation test. The inhibitor effect of Al containing solids may be attributed to the presence of basic and amphoteric sites in the surface of the solids, where the acetic acid may be strongly adsorbed and therefore be unavailable to interact with glycerol. Moreover, the presence of secondary reactions consuming glycerol and acetic acid to form product other than glycerylacetates was suspected. However, the lack of further experimental data (measurement of the basicity of the solids, analysis of the dissolved species in glycerol by ICP after catalytic test and the analysis of the

glycerol samples taken from the reaction medium by another protocol or technique such as high-performance liquid chromatography, HPLC) did not allow to corroborate this hypothesis.

Among all the synthesised solids, only sulphated zirconia synthesised by sol-gel method varying the hydrolysis ratio showed good catalytic activity. It was shown that a correlation between the textural properties, structural, chemical composition, the hydrolysis ratio and the catalytic activity could not be performed. Nevertheless, the density of acid sites was correctly correlated with the catalytic activity in the esterification reaction: the lower the density of acid sites, the higher the catalytic activity.

Pure heteropolyacids also improve the esterification rate in homogenous phase according to their acid strength: the stronger the acidity, the higher the acceleration of the esterification reaction. In consequence, the most active heteropolyacid (tungstophosphoric acid, HPW) was selected with the purpose of obtaining a heterogeneous catalyst. In an attempt to immobilise HPW but keeping its catalytic activity, two types of synthesis were used: sol-gel and wet impregnation. Moreover, two matrixes were selected: silica and zirconia, in order to find a good compromise between the acidity developed and the resistance to leaching: the higher the interaction between the HPW and the matrix, the lower the acid strength but the higher the resistance to leaching. Regardless of the solid matrix (zirconia or silica), samples synthesised by sol-gel remained inactive in the esterification reaction, despite the high number of acid sites

Part IV

measured by ammonia chemisorption. The wet impregnated samples showed no resistance to leaching and thus led to catalysis in homogeneous phase.

Table 29. Glycerol acetylation over substances of different nature.

Solids		Catalytic performances	Conclusions
Nb-SA		Inhibitor	Presence of basic sites and secondary reactions consuming the acetic acid
PA		Inhibitor	
WZ		Inert	Acid sites poisoned by adsorption of water or glycerol
SZ		Active	The lower the acid site density the higher the catalytic activity
Pure HPA		Active (Homogeneous phase)	Absence of secondary reaction consuming the acetic acid. The higher the acid strength the higher the catalytic activity
Si-PW	WI	Active (Leaching)	The supported HPW is not resistant to leaching → Homogeneous catalysis
Zr-PW	SG	Slightly inhibitor	
Ion exchange resins		Active	Materials highly functionalised with sulphonic groups: large number of strong Brønsted acid sites. The lower the crosslinkage the higher the swelling properties, thus the access to reactants to the active sites.

Commercial ion exchange resins have also exhibited very high catalytic performances, mainly due to their large number of strong Brønsted acid sites (sulphonic groups). Nevertheless, for this type of solids another parameter has a very important role over the catalytic performances exhibited in the reaction: the crosslinkage. It was observed that the lower the degree of crosslinking, the higher capacity of the resin to swell in the reaction medium, and thus the higher the catalytic activity.

- (ii) To analyse the solids recyclability during several successive esterification runs, namely, the leachability of active species and the presence of eventual homogeneous catalysis and to test the deactivation of solid due to the presence of water in the reaction medium.

The results of these experiments and the conclusions are presented in Table 30.

Table 30. Recyclability of active samples and deactivation with water. (*1) The resistance to leaching was verified by submitting the solid to a soxlet extraction with water. (*2) The deactivation with water has not been performed due to the absence of recyclability.

Solids	Resistance to leaching	Comments
	Recyclability Water deactivation	
PW-WI	No resistant to leaching (* ¹)	Leaching of HPW species detected by characterisation techniques and by testing the solids before and after Soxhlet extraction
PW-SG	Resistant to leaching (* ¹)	Absence of leaching verified by characterisation techniques. The solids were inactive in the glycerol acetylation reaction
SZ: sulphated zirconia	No recyclable (* ²)	Leaching of sulphur species detected by homogeneous catalysis and ICP measurements. Sulphur contamination in the final products, not applicable for biodiesel.
Ion exchange resins	Recyclable	The solids are active after a washing step with distilled in a Soxhlet apparatus. No homogeneous catalysis: when the solid is recovered from the liquid medium before achieving the equilibrium, the catalytic activity stops.
	Not deactivated by water	The equilibrium of the reaction is achieved even in presence of water.

Concerning the HPW immobilised samples, the resistance to leaching (closely related to the recyclability properties) was tested by submission to a Soxhlet extraction with water. It was observed that impregnated samples suffered from leaching. This was verified by using several characterisation techniques and performing different catalytic tests before and after the washing step. Whereas, sol-gel samples presented a good immobilisation yield.

Only representative samples from the two active families of solids (sulphated zirconia and ion exchange resins) have been submitted to the recyclability tests and to tests in presence of water.

For the family of sulphated zirconia, analyses of filtered liquid medium revealed the occurrence of a sulphur preferential leaching during each esterification reaction. When used in consecutive tests, the solid is impoverished in S, influencing negatively its recyclability. Even in mild conditions, the sample was totally deactivated after four esterification runs. In addition, the sulphur leaching contributes to the acceleration of the esterification reaction in homogeneous phase and in the contamination of the final products of the reaction.

The recyclability tests performed for ion exchange resins showed that both these solids were directly reusable without any loss of catalytic performances namely due to the absence of leaching of active species. This was also verified by conducting catalytic tests before and after washing in a Soxhlet apparatus with distilled water. Despite the presence of water in the reaction medium, the resins

remained active, even if the esterification rate was decreased and the conversion of acetic acid at the equilibrium was lower than the tests conducted in absence of water.

(iii) To understand the phenomena occurring in the esterification reaction (reaction mechanism, effect of acidity in the reaction, identification of active sites etc.).

It was remarked that in presence of acid solids the reaction proceeded differently than when it was conducted as a pseudo catalysed reaction. Several solid as Nb-SA, PA and immobilised HPW presented an esterification yield lower than the blank reaction. By plotting the amount of acetic acid transformed to esters versus the amount of acetic acid consumed (both expressed in %) it was seen that an additional secondary reactions could take place in the reactor. It was suggested that secondary reactions could consist in the removal of hydroxyl groups of the glycerol (dehydration) and/or its oxidation and/or the reaction of the latters with acetic acid. This phenomenon was observed when using Al-containing solids such as Nb-SA and PA, and HPW containing samples. Another hypothesis, attempting to explain this difference, was also the strong adsorption of acetic acid over basic sites present in the surface of some solids. Nevertheless, this hypothesis remained unclear due to the absence of additional experimental data, as explained in the previous section.

It was also mentioned that the acid sites must be accessible. This is the case of ion exchange resins, which exhibit a large number of strong acid sites and an easy access to reactant due to the swelling properties (gel resins) or macroporosity (macroreticular resins).

Moreover, it was shown that the concentrations of the different compounds at the equilibrium are thermodynamically determined by the initial concentration of reactants and the reaction temperature. Therefore, the only role of the catalyst is to accelerate the progress of the reaction until the achievement of the equilibrium conditions.

CONCLUSIONS

The manufacture of first generation biodiesels (fatty acid alkyl esters) by transesterification processes has been growing continuously during the last years. This is principally due to the benefits of the biodiesel in comparison with the conventional fuels derived from petroleum. Consequently a large amount of glycerol is produced which has to be revaluated in order to make the bio-fuel industry economically and environmentally viable. In the present work, we focused on the esterification of acetic acid with glycerol in order to form new molecules or species which could be used as bio-fuels or raw materials for the production of biodegradable polyesters, mainly glyceryl monoacetate (MAG), glyceryl diacetate (DAG), and glyceryl triacetate (TAG). Heterogeneous catalysts are selected for our study in order to avoid the drawbacks of homogeneous catalysis (contamination of final products, corrosion of the equipment, low recyclability).

This work provided a comparative study of the catalytic performances of a large scope of acid solids in glycerol acetylation conducted in an excess of glycerol.

In the initial screening, selected solids which have been reported in the literature as active in esterification reactions between carboxylic acids and monoalcohols have been synthesised. Niobium oxide supported on silica (Nb-SA), aluminium phosphate (PA), tungstated and sulphated zirconias (WZ and SZ) are the selected families for the

initial screening. Their chemical composition, structure and texture were characterised.

When aluminium containing solids (Nb-SA and PA) were added to the reaction medium, a decrease in the esterification rate was observed. This phenomenon was attributed to the amphoteric character of aluminium-bonded hydroxyl groups and the presence of basic sites, where, the acetic acid may be strongly adsorbed and therefore be unavailable to interact with glycerol. In addition, the inhibitory effect was also related to the presence of potential secondary reactions which may take place between the acetic acid and glycerol oxidation and/or dehydration sub-products.

WZ samples were inactive, probably due to the deactivation of the acid sites by a strong adsorption of glycerol or water present in the liquid medium, preventing the protonation of acetic acid.

Only sulphated zirconia catalysts showed a satisfactory catalytic activity in the reaction. Further studies allowed to conclude that the lower the acid sites density, the higher the accessibility to acid sites and thus the higher the catalytic activity. Tests conducted in the presence of sulphated zirconia also led to the conclusion that the role of the catalyst is to accelerate the reaction to equilibrium. Despite their good catalytic performances, these solids can unfortunately not be recycled due to their sulphur leaching in the reaction conditions.

Conclusions

The immobilisation of tungstophosphoric acid has been conducted by sol-gel and wet impregnation methods in two different matrixes: silica and zirconia. The tungstophosphoric acid immobilised by sol-gel could not accelerate the glycerol acetylation reaction despite the good catalytic performance shown in homogeneous phase. The absence of activity was explained by the modification of the acidic properties of HPW when immobilised. The strong interaction existing between the heteropolyacid unit and the matrix indeed leads to a high resistance to leaching but to a weakening of the acid strength.

Ion exchange resins concluded this work. These materials showed interesting catalytic properties in the glycerol acetylation, which have been correlated to the presence of a large number of strong Brønsted acid sites and to a low crosslinkage degree. The amount of solid used in our reaction conditions and the pre-treatment have been optimised in order to obtain the best esterification rate. These solids have shown satisfactory recyclability properties in the presence of acetic acid. Moreover, their resistance to deactivation by the presence of water has been proven, showing that these solids are not deactivated in the conditions studied.

PERSPECTIVES

Some of the issues related to the explanation of the different behaviours developed by the acid solids tested in the glycerol acetylation reaction remained unclear. Performing basicity measurements, ICP analysis in order to verify the presence of soluble species and improving the analysis of the reaction medium samples could help to elucidate and go into further discussions concerning this complex reaction.

Taking into account that the separation of the final products from the remaining glycerol is a quite complicate process, some improvements could be introduced in order to increase the conversion of glycerol, maybe by changing the initial concentration acetic acid or by adding the acetic acid at determined intervals during the esterification.

Moreover, it has been shown that dehydration of glycerol in gas phase could be conducted in presence of acid catalysts such as tungstated and sulphated zirconia, zirconium and niobium mixed oxides, phosphated alumina and heteropolyacids among other acid solids [195, 299-302]. Therefore, the synthesised samples could be applied to promote other catalytic reaction as dehydration of glycerol to acrolein and to hydroxyacetone which can proceed in gas, liquid, or supercritical phase [303]. Generally, this reaction occurs at temperatures near 250-340 °C [299, 304]. For the liquid phase dehydration, zeolites and silica-niobia based solids and

heteropolyacids can also be used as catalyst [301, 303]. Both acrolein and hydroxyacetone obtained from glycerol can be an important intermediate in chemical and polymer industries [67, 195, 299, 301, 303].

REFERENCES

- [1] F. Ma, M.A. Hanna, *Bioresource Technology* 70 (1999) 1-15.
- [2] R. Sims, M. Taylor, J. Saddler, W. Mabey, IEA Bioenergy November (2008).
- [3] P.S. Nigam, A. Singh, *Progress in Energy and Combustion Science* 37 (2011) 52-68.
- [4] A. Eisentraut, International Energy Agency February (2010).
- [5] X. Liao, Y. Zhu, S.-G. Wang, Y. Li, *Fuel Processing Technology* 90 (2009) 988-993.
- [6] K. Klepáčová, D. Mravec, A. Kaszonyi, M. Bajus, *Applied Catalysis A: General* 328 (2007) 1-13.
- [7] K. Klepáčová, D. Mravec, M. Bajus, *Applied Catalysis A: General* 294 (2005) 141-147.
- [8] H. Nouredini, W.R. Daily, B.A. Hunt, *Chem Biomol Eng Res* 13 (1998) 121–129.
- [9] B. Delfort, I. Durand, A. Jaecker, T. Lacome, X. Montagne, F. Paille, Diesel fuel compounds containing glycerol acetals, in: Institut Francais du Petrole, (Ed.), United States, 2005.
- [10] J. Delgado Puche, Procedure to obtain biodiesel fuel with improved properties at low temperature, in: I.M. S.A., (Ed.), United States, 2009.
- [11] X. Liao, Y. Zhu, S.-G. Wang, Y. Li, *Fuel Processing Technology* 90 988-993.
- [12] R.L. McCormick, T.L. Alleman, M. Ratcliff, L. Moens, R. Lawrence, Survey of the quality and stability of biodiesel and biodiesel blends in the United States in 2004, Oct. 2005.
- [13] K. Yamane, K. Kawasaki, K. Sone, T. Hara, T. Prakoso, *International Journal of Engine Research* 8 (2007) 307-319.
- [14] J. Andrew Waynick, Technical Literature Review - The Coordinating Research Council (2005).
- [15] A. Corma, S. Iborra, A. Velty, *ChemInform* 38 (2007).

-
- [16] M.O. Guerrero-Perez, J. M Rosas, J. Bedia, J. Rodriguez-Mirasol, T. Cordero, Recent Patents on Chemical Engineering 2 (2009) 11-21.
 - [17] D.T. Johnson, K.A. Taconi, Environmental Progress 26 (2007) 338-348.
 - [18] I. Chorkendorff, J.W. Niemantsverdriet, Concepts of Modern Catalysis and Kinetics, Weinheim, 2003.
 - [19] O. Deutschmann, H. Knözinger, K. Kochloefl, T. Turek, Heterogeneous Catalysis and Solid Catalysts, Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH Verlag GmbH & Co. KGaA, 2000.
 - [20] M. Di Serio, M. Cozzolino, M. Giordano, R. Tesser, P. Patrono, E. Santacesaria, Ind. Eng. Chem. Res. 46 (2007) 6379-6384.
 - [21] K.J. Laidler, 68 (1996) 149-192.
 - [22] A.D. McNaught, A. Wilkinson, IUPAC. Compendium of Chemical Terminology, 2nd ed. (the "Gold Book"), XML on-line corrected version: <http://goldbook.iupac.org> (2006-) created by M. Nic, J. Jirat, B. Kosata; updates compiled by A. Jenkins. ISBN 0-9678550-9-8., Blackwell Scientific Publications, Oxford, 1997, pp. 77.
 - [23] J.F. Le Page, Catalyse de contact: conception, préparation et mise en œuvre des catalyseurs industriels, Technip, 1978.
 - [24] D.E. López, J.J.G. Goodwin, D.A. Bruce, E. Lotero, Applied Catalysis A: General 295 (2005) 97-105.
 - [25] A. Corma, H. Garcia, Catalysis Today 38 (1997) 257-308.
 - [26] C. Marcilly, Catalyse acido-basique. Application au raffinage et à la pétrochimie. Vol 1., Paris, 2003.
 - [27] E. Huheey, E.A. Keiter, R.L. Keiter, Chimie inorganique, 1996.
 - [28] G. Busca, Industrial & Engineering Chemistry Research 48 (2009) 6486-6511.
 - [29] G. Busca, Acid Catalysts in Industrial Hydrocarbon Chemistry, American Chemical Society, Washington, DC, ETATS-UNIS, 2007.
 - [30] T. Okuhara, ChemInform 34 (2003).
 - [31] M.N. Timofeeva, Applied Catalysis A: General 256 (2003) 19-35.
 - [32] M.P. Kapoor, S. Inagaki, ChemInform 38 (2007).

References

- [33] P. Van Der Voort, Advances in PMO (Periodic Mesoporous Organosilica) and OMP (Ordered Mesoporous Polymers), I-SUP-Brugge-2008, 2008.
- [34] O.M. Yaghi, L. Qiaowei, Reticular Chemistry and Metal-Organic Frameworks for Clean Energy, Materials Research Society, Warrendale, PA, ETATS-UNIS, 2009.
- [35] H. Hart, J.M. Conia, Introduction à la chimie organique., Paris, 1995.
- [36] Z.-H. Chen, T. Iizuka, K. Tanabe, Chemistry letters (1984) 1085-1088.
- [37] V.S. Braga, I.C.L. Barros, F.A.C. Garcia, S.C.L. Dias, J.A. Dias, Catalysis Today 133-135 (2008) 106-112.
- [38] D.E. López, K. Suwannakarn, D.A. Bruce, J.G. Goodwin Jr, Journal of Catalysis 247 (2007) 43-50.
- [39] D.E. López, K. Suwannakarn, J.G. Goodwin, D.A. Bruce, Industrial & engineering chemistry research 47 (2008) 2221-2230.
- [40] S. Ramu, N. Lingaiah, B.L.A. Prabhavathi Devi, R.B.N. Prasad, I. Suryanarayana, P.S. Sai Prasad, Applied Catalysis A: General 276 (2004) 163-168.
- [41] D.E. López, J.G. Goodwin Jr, D.A. Bruce, S. Furuta, Applied Catalysis A: General 339 (2008) 76-83.
- [42] T.A. Peters, N.E. Benes, A. Holmen, J.T.F. Keurentjes, Applied Catalysis A: General 297 (2006) 182-188.
- [43] A.A. Kiss, A.C. Dimian, G. Rothenberg, Advanced synthesis & catalysis 348 (2006) 75-81.
- [44] J. Ni, F.C. Meunier, Applied Catalysis A: General 333 (2007) 122-130.
- [45] K. Suwannakarn, E. Lotero, J.G. Goodwin Jr, C. Lu, Journal of Catalysis 255 (2008) 279-286.
- [46] J. Jitputti, B. Kitiyanan, P. Rangsunvigit, K. Bunyakiat, L. Attanatho, P. Jenvanitpanjakul, Chemical Engineering Journal 116 (2006) 61-66.
- [47] Z.H. Zhao, Journal of Molecular Catalysis A: Chemical 168 (2001) 147-152.
- [48] I. Mochida, Y. Anju, A. Kato, T. Seiyama, Journal of Catalysis 21 (1971) 263-269.
- [49] Y. Liu, E. Lotero, J.J.G. Goodwin, Journal of Catalysis 242 (2006) 278-286.

-
- [50] T.A. Nijhuis, A.E.W. Beers, F. Kapteijn, J.A. Moulijn, *Chemical Engineering Science* 57 (2002) 1627-1632.
- [51] J. Lilja, D.Y. Murzin, T. Salmi, J. Aumo, P. Mäki-Arvela, M. Sundell, *Journal of Molecular Catalysis A: Chemical* 182-183 (2002) 555-563.
- [52] J. Lilja, J. Aumo, T. Salmi, D.Y. Murzin, P. Mäki-Arvela, M. Sundell, K. Ekman, R. Peltonen, H. Vainio, *Applied Catalysis A: General* 228 (2002) 253-267.
- [53] J. Lilja, J. Wärnå, T. Salmi, L.J. Pettersson, J. Ahlqvist, H. Grénman, M. Rönnholm, D.Y. Murzin, *Chemical Engineering Journal* 115 (2005) 1-12.
- [54] J. Gangadwala, S. Mankar, S. Mahajani, A. Kienle, E. Stein, *Industrial & Engineering Chemistry Research* 42 (2003) 2146-2155.
- [55] M.R. Altiokka, A. Çitak, *Applied Catalysis A: General* 239 (2003) 141-148.
- [56] K.M. Parida, S. Mallick, *Journal of Molecular Catalysis A: Chemical* 275 (2007) 77-83.
- [57] D.E. Lopez, K. Suwannakarn, J.G. Goodwin, D.A. Bruce, *Industrial & Engineering Chemistry Research* 47 (2008) 2221-2230.
- [58] H.T.R. Teo, B. Saha, *Journal of Catalysis* 228 (2004) 174-182.
- [59] M.-J. Lee, H.-T. Wu, H.-m. Lin, *Industrial & Engineering Chemistry Research* 39 (2000) 4094-4099.
- [60] S.L. Barbosa, M.J. Dabdoub, G.R. Hurtado, S.I. Klein, A.C.M. Baroni, C. Cunha, *Applied Catalysis A: General* 313 (2006) 146-150.
- [61] V.M. Mello, G.P.A.G. Pousa, M.S.C. Pereira, I.M. Dias, P.A.Z. Suarez, *Fuel Processing Technology* 92 (2011) 53-57.
- [62] G.W. Parshall, S.D. Ittel, *Homogeneous Catalysis—The Applications and Chemistry of Catalysis by Soluble Transition Metal Complexes*, 1992.
- [63] J.A. Melero, R. van Grieken, G. Morales, M. Paniagua, *Energy & Fuels* 21 (2007) 1782-1791.
- [64] I. Díaz, C. Márquez-Alvarez, F. Mohino, J. Pérez-Pariente, E. Sastre, *Journal of Catalysis* 193 (2000) 295-302.
- [65] I. Díaz, F. Mohino, J. Pérez-Pariente, E. Sastre, *Applied Catalysis A: General* 242 (2003) 161-169.

References

- [66] I. Diaz, F. Mohino, T. Blasco, E. Sastre, J. Pérez-Pariente, *Microporous and Mesoporous Materials* 80 (2005) 33-42.
- [67] V.L.C. Gonçalves, B.P. Pinto, J.C. Silva, C.J.A. Mota, *Catalysis Today* 133-135 (2008) 673-677.
- [68] R. Luque, V. Budarin, J.H. Clark, D.J. Macquarrie, *Applied Catalysis B: Environmental* 82 (2008) 157-162.
- [69] P. Ferreira, I.M. Fonseca, A.M. Ramos, J. Vital, J.E. Castanheiro, *Catalysis Communications* 10 (2009) 481-484.
- [70] P. Ferreira, I.M. Fonseca, A.M. Ramos, J. Vital, J.E. Castanheiro, *Applied Catalysis B: Environmental* 91 (2009) 416-422.
- [71] P. Ferreira, I.M. Fonseca, A.M. Ramos, J. Vital, J.E. Castanheiro, *Catalysis Communications* 12 (2011) 573-576.
- [72] V.S. Braga, I.C.L. Barros, F.A.C. Garcia, S.C.L. Dias, J.A. Dias, *Catalysis Today* 133-135 106-112.
- [73] K. Kearby., *Proceedings 2nd International Congress on Catalysis, Technip,, Paris, 1961, pp. 2567.*
- [74] M.A. Soria, *Etude des paramètres gouvernant les performances catalytiques d'AlPO, AlGaPO et GaPO purs et en présence de vanadium dans l'ammoxydation du propane, Université catholique de Louvain, 2008.*
- [75] M.A. Cortés-Jácome, J.A. Toledo-Antonio, H. Armendáriz, I. Hernández, X. Bokhimi, *Journal of Solid State Chemistry* 164 (2002) 339-344.
- [76] Y. Izumi, K. Hisano, T. Hida, *Applied Catalysis A: General* 181 (1999) 277-282.
- [77] P. Carniti, A. Gervasini, S. Biella, A. Auroux, *Chemistry of Materials* 17 (2005) 6128-6136.
- [78] K. Tanabe, S. Okazaki, *Applied Catalysis A: General* 133 (1995) 191-218.
- [79] K. Tanabe, *ChemInform* 35 (2004).
- [80] M. Ziolek, *Catalysis Today* 78 (2003) 47-64.
- [81] M. Trejda, K. Stawicka, M. Ziolek, *Applied Catalysis B: Environmental* 103 (2011) 404-412.
- [82] I. Nowak, M. Ziolek, *Chem. Rev.* 99 (1999) 3603-3624.
- [83] S. Okazaki, N. Wada, *Catalysis Today* 16 (1993) 349-359.
- [84] J.C. Védrine, G. Coudurier, A. Ouqour, P.G. Pries de Oliveira, J.C. Volta, *Catalysis Today* 28 (1996) 3-15.
- [85] I.E. Wachs, *Catalysis Today* 27 (1996) 437-455.

-
- [86] I.E. Wachs, J.M. Jehng, G. Deo, H. Hu, N. Arora, *Catalysis Today* 28 (1996) 199-205.
 - [87] T. Tanaka, T. Yoshida, H. Yoshida, H. Aritani, T. Funabiki, S. Yoshida, J.-M. Jehng, I.E. Wachs, *Catalysis Today* 28 (1996) 71-78.
 - [88] P.A. Burke, E.I. Ko, *Journal of Catalysis* 129 (1991) 38-46.
 - [89] H. Yoshida, T. Tanaka, T. Yoshida, T. Funabiki, S. Yoshida, *Catalysis Today* 28 (1996) 79-89.
 - [90] N. Ichikuni, M. Shirai, Y. Iwasawa, *Catalysis Today* 28 (1996) 49-58.
 - [91] S.M. Maurer, E.I. Ko, *Journal of Catalysis* 135 (1992) 125-134.
 - [92] J. Datka, A.M. Turek, J.M. Jehng, I.E. Wachs, *Journal of Catalysis* 135 (1992) 186-199.
 - [93] J.-M. Jehng, I.E. Wachs, *Catalysis Today* 8 (1990) 37-55.
 - [94] A. Aronne, M. Turco, G. Bagnasco, G. Ramis, E. Santacesaria, M. Di Serio, E. Marenga, M. Bevilacqua, C. Cammarano, E. Fanelli, *Applied Catalysis A: General* 347 (2008) 179-185.
 - [95] P. Carniti, A. Gervasini, M. Marzo, *Catalysis Today* 152 (2010) 42-47.
 - [96] M. Hiyoshi, B. Lee, D. Lu, M. Hara, J.N. Kondo, K. Domen, *Catalysis Letters* 98 (2004) 181-186.
 - [97] R.F. Brandão, R.L. Quirino, V.M. Mello, A.P. Tavares, A.C. Peres, F. Guinhos, J.C. Rubim, P.A.Z. Suarez, *Journal of the Brazilian Chemical Society* 20 (2009) 954-966.
 - [98] C.A.R. Melo Júnior, C.E.R. Albuquerque, J.S.A. Carneiro, C. Dariva, M. Fortuny, A.F. Santos, S.M.S. Egues, A.L.D. Ramos, *Industrial & Engineering Chemistry Research* 49 (2010) 12135-12139.
 - [99] R.F. Vogel, G. Marcelin, *Journal of Catalysis* 80 (1983) 492-493.
 - [100] G. Marcelin, R.F. Vogel, H.E. Swift, *Journal of Catalysis* 83 (1983) 42-49.
 - [101] M. Martín Pérez, *Síntesis y caracterización del fosfato de aluminio nitrurado (AlPON) y su aplicación en la síntesis de metal isobutyl cetona a partir de acetone en una sola etapa.*, Universidad del País Vasco, San Sebastián, 1998.
 - [102] K. Kearby, *Proc. 2nd Int. Congr. Catal.* (1961) 2567.

References

- [103] J.M. Campelo, J.M. Marinas, S. Mendioroz, J.A. Pajares, *Journal of Catalysis* 101 (1986) 484-495.
- [104] A. Massinon, Study of a new family of catalysts with acid-base properties : the aluminophosphate oxynitrides or «ALPONs», Université Catholique de Louvain, Louvain-la-Neuve, 1999.
- [105] R. Conanec, Synthèse et caractérisations physicochimiques de nouveaux metallophosphates azotés- Catalyseurs basiques «ALPON» phases cubiques de type $\text{Na}_3\text{AlP}_3\text{O}_3\text{N}_x$, Université de Rennes, 1994.
- [106] J.B. Moffat, *Catalysis Reviews* 18 (1978) 199-258.
- [107] F.M. Bautista, J.M. Campelo, D. Luna, J.M. Marinas, R.A. Quirós, A.A. Romero, *Applied Catalysis B: Environmental* 70 (2007) 611-620.
- [108] F.M. Bautista, J.M. Campelo, A. Garcia, D. Luna, J.M. Marinas, A.A. Romero, G. Colon, J.A. Navio, M. Macias, *Journal of Catalysis* 179 (1998) 483-494.
- [109] F.M. Bautista, J.M. Campelo, A. Garcia, D. Luna, J.M. Marinas, M.C. Moreno, A.A. Romero, *Applied Catalysis A: General* 170 (1998) 159-168.
- [110] F.M. Bautista, J.M. Campelo, A. García, D. Luna, J.M. Marinas, R.A. Quirós, A.A. Romero, *Applied Catalysis A: General* 243 (2003) 93-107.
- [111] F.M. Bautista, J.M. Campelo, A. Garcia, D. Luna, J.M. Marinas, A.A. Romero, J.A. Navio, M. Macias, *Journal of Catalysis* 145 (1994) 107-125.
- [112] J.M. Campelo, A. García, D. Luna, J.M. Marinas, *Journal of Catalysis* 102 (1986) 299-308.
- [113] V. Durgakumari, S. Narayanan, L. Guzzi, *Catalysis Letters* 5 (1990) 377-384.
- [114] L. Marchese, A. Frache, E. Gianotti, G. Martra, M. Causà, S. Coluccia, *Microporous and Mesoporous Materials* 30 (1999) 145-153.
- [115] L. Travalloni, A.C.L. Gomes, A.B. Gaspar, M.A.P. da Silva, *Catalysis Today* 133-135 406-412.
- [116] S. Delsarte, In-depth study of the generation of basic sites and of the catalytic properties of mixed phosphorus, aluminium and gallium oxynitrides "AlGaPON", Université catholique de Louvain, Louvain-la-Neuve, 2000.

-
- [117] S. Delsarte, V. Peltier, Y. Laurent, P. Grange, Synthesis of mixed galloaluminophosphate oxynitrides: the influence of nitridation on the «AlGaPON acido-basic properties, in: P.A.J.R.M.J.A.M.P.G. B. Delmon, G. Poncelet, (Eds.), *Studies in Surface Science and Catalysis*, Elsevier, 1998, pp. 869-878.
 - [118] B. Rebenstorf, T. Lindblad, S.L.T. Andersson, *Journal of Catalysis* 128 (1991) 293-302.
 - [119] A. Llobera, J.V. Sinisterra, *Reaction kinetics and catalysis letters* 23 (1983) 413-418.
 - [120] A. Llobera, J.V. Sinisterra, *Reaction kinetics and catalysis letters* 25 (1984) 181-186.
 - [121] C. Fernández-Sánchez, M.T. Gandasegui, J.M. Marinas, J.V. Sinisterra, *Bulletin Des Societes Chimiques Belges* 103 (1994) 641-645.
 - [122] C. Fernandez, J.M. Marinas, J.V. Sinisterra, *Reaction kinetics and catalysis letters* 36 (1988) 165-171.
 - [123] C. Fernandez, J.M. Marinas, J.V. Sinisterra, *Reaction kinetics and catalysis letters* 36 (1988) 313-318.
 - [124] S. Kuba, P. Lukinskas, R.K. Grasselli, B.C. Gates, H. Knözinger, *Journal of Catalysis* 216 353-361.
 - [125] A.V. Ivanov, T.V. Vasina, O.V. Masloboishchikova, E.G. Khelkovskaya-Sergeeva, L.M. Kustov, J.I. Houzvicka, *Catalysis Today* 73 (2002) 95-103.
 - [126] G. Larsen, E. Lotero, S. Raghavan, R.D. Parra, C.A. Querini, *Applied Catalysis A: General* 139 (1996) 201-211.
 - [127] T.N. Vu, J. van Gestel, J.P. Gilson, C. Collet, J.P. Dath, J.C. Duchet, *Journal of Catalysis* 231 (2005) 453-467.
 - [128] F. Di Gregorio, V. Keller, *Journal of Catalysis* 225 (2004) 45-55.
 - [129] F. Di Gregorio, N. Keller, V. Keller, *Journal of Catalysis* 256 (2008) 159-171.
 - [130] N. Vaidyanathan, D. Hercules, M. Houalla, *Analytical and Bioanalytical Chemistry* 373 (2002) 547-554.
 - [131] P. Wongmaneevil, B. Jongsomjit, P. Praserttham, *Catalysis Communications* 10 (2009) 1079-1084.
 - [132] I.E. Wachs, T. Kim, E.I. Ross, *Catalysis Today* 116 (2006) 162-168.

References

- [133] M. Valigi, D. Gazzoli, I. Pettiti, G. Mattei, S. Colonna, S. De Rossi, G. Ferraris, *Applied Catalysis A: General* 231 (2002) 159-172.
- [134] M. Occhiuzzi, D. Cordischi, D. Gazzoli, M. Valigi, P.C. Heydorn, *Applied Catalysis A: General* 269 (2004) 169-177.
- [135] M.A. Cortés-Jácome, C. Angeles-Chavez, X. Bokhimi, J.A. Toledo-Antonio, *Journal of Solid State Chemistry* 179 (2006) 2663-2673.
- [136] M.G. Falco, S.A. Canavese, N.S. Fígoli, *Catalysis Today* 107-108 (2005) 778-784.
- [137] M.A. Aramendia, V. Boráu, C. Jiménez, J.M. Marinas, A. Marinas, A. Porras, F.J. Urbano, *Journal of Catalysis* 183 (1999) 240-250.
- [138] R.A. Comelli, C.R. Vera, J.M. Parera, *Journal of Catalysis* 151 (1995) 96-101.
- [139] M.A. Cortés-Jácome, C. Angeles-Chavez, E. López-Salinas, J. Navarrete, P. Toribio, J.A. Toledo, *Applied Catalysis A: General* 318 (2007) 178-189.
- [140] J.G. Santiesteban, J.C. Vartuli, S. Han, R.D. Bastian, C.D. Chang, *Journal of Catalysis* 168 (1997) 431-441.
- [141] J.C. Vartuli, J.G. Santiesteban, P. Traverso, N. Cardona-Martínez, C.D. Chang, S.A. Stevenson, *Journal of Catalysis* 187 (1999) 131-138.
- [142] J. Macht, C.D. Baertsch, M. May-Lozano, S.L. Soled, Y. Wang, E. Iglesia, *Journal of Catalysis* 227 (2004) 479-491.
- [143] D.S. Kim, M. Ostromecki, I.E. Wachs, *Journal of Molecular Catalysis A: Chemical* 106 (1996) 93-102.
- [144] K. Suwannakarn, E. Lotero, J. Goodwin, *Catalysis Letters* 114 (2007) 122-128.
- [145] S. Furuta, H. Matsushashi, K. Arata, *Catalysis Communications* 5 (2004) 721-723.
- [146] K. Ngaosuwarn, B. Jongsomjit, P. Praserthdam, *Catalysis Letters* 136 (2010) 134-140.
- [147] S. Praserthdam, P. Wongmaneevil, B. Jongsomjit, *Journal of Industrial and Engineering Chemistry* 16 (2010) 935-940.
- [148] G.D. Yadav, J.J. Nair, *Microporous and Mesoporous Materials* 33 (1999) 1-48.
- [149] A. Sassi, J. Sommer, *Applied Catalysis A: General* 188 (1999) 155-162.

-
- [150] S. Chokkaram, B.H. Davis, *Journal of Molecular Catalysis A: Chemical* 118 (1997) 89-99.
- [151] R.B. Gore, W.J. Thomson, *Applied Catalysis A: General* 168 (1998) 23-32.
- [152] A. Corma, *Current Opinion in Solid State and Materials Science* 2 (1997) 63-75.
- [153] S. Melada, S.A. Ardizzzone, C.L. Bianchi, *Microporous and Mesoporous Materials* 73 (2004) 203-209.
- [154] L.B. Hamouda, A. Ghorbel, F. Figueras, Study of acidic and catalytic properties of sulfated zirconia prepared by sol-gel process: Influence of preparation conditions, in: Avelino Corma, F.V. Melo, S. Mendioroz, G.F. José Luis, (Eds.), *Studies in Surface Science and Catalysis*, Elsevier, 2000, pp. 971-976.
- [155] J.A. Moreno Lopera, Improvement of sulfated zirconia catalysts for n-butane isomerization by Al- and Ga-promotion, Université catholique de Louvain, Louvain-la-Neuve, 2002.
- [156] C.L. Bianchi, S. Ardizzzone, G. Cappelletti, *Surface and Interface Analysis* 36 (2004) 745-748.
- [157] S. Ardizzzone, C.L. Bianchi, G. Cappelletti, F. Porta, *Journal of Catalysis* 227 (2004) 470-478.
- [158] C.R. Vera, J.M. Parera, *Journal of Catalysis* 166 (1997) 254-262.
- [159] B.M. Reddy, P.M. Sreekanth, P. Lakshmanan, *Journal of Molecular Catalysis A: Chemical* 237 (2005) 93-100.
- [160] T. Yamaguchi, *Applied Catalysis* 61 (1990) 1-25.
- [161] F. Babou, G. Coudurier, J.C. Vedrine, *Journal of Catalysis* 152 (1995) 341-349.
- [162] A. Clearfield, G.P.D. Serrette, A.H. Khazi-Syed, *Catalysis Today* 20 (1994) 295-312.
- [163] D. Fărcașiu, J.Q. Li, *Applied Catalysis A: General* 175 (1998) 1-9.
- [164] D. Farcasiu, J.Q. Li, S. Cameron, *Applied Catalysis A: General* 154 (1997) 173-184.
- [165] D. Farcasiu, J.Q. Li, *Applied Catalysis A: General* 128 (1995) 97-105.
- [166] C. Morterra, G. Cerrato, V. Bolis, *Catalysis Today* 17 (1993) 505-515.

References

- [167] F. Pinna, M. Signoretto, G. Strukul, G. Cerrato, C. Morterra, *Catalysis Letters* 26 (1994) 339-344.
- [168] C.M. Garcia, S. Teixeira, L.L. Marciniuk, U. Schuchardt, *Bioresource Technology* 99 (2008) 6608-6613.
- [169] A.A. Kiss, A.C. Dimian, G. Rothenberg, *Advanced Synthesis & Catalysis* 348 (2006) 75-81.
- [170] B.L. Hammouda, *Relation entre paramètres de préparation, structure et réactivité de la zircone sulfatée, élaborée par voie sol-gel.*, Université de Tunis El Manar, 2003.
- [171] D.J. Zalewski, S. Alerasool, P.K. Doolin, *Catalysis Today* 53 (1999) 419-432.
- [172] K. Tanabe, *Solid Acids and Bases - Their Catalytic Properties.*, Kodansha, Academic Press, 1970.
- [173] T. Glazneva, N. Kotsarenko, E. Paukshtis, *Kinetics and Catalysis* 49 (2008) 859-867.
- [174] G. Busca, *Chemical Reviews* 107 (2007) 5366-5410.
- [175] R.J. Gorte, *Catalysis Letters* 62 (1999) 1-13.
- [176] K. Reddy, N. Lingaiah, P. Sai Prasad, I. Suryanarayana, *Journal of Solution Chemistry* 35 (2006) 407-423.
- [177] R. Weingarten, G.A. Tompsett, W.C. Conner Jr, G.W. Huber, *Journal of Catalysis* 279 (2011) 174-182.
- [178] K. Tanabe, M. Misono, Y. Ono, H. Hattori, *New Solid Acids and Bases - Their Catalytic Properties.*, Elsevier, 1989.
- [179] J. Lercher, A. Jentys, A. Brait, *Catalytic Test Reactions for Probing the Acidity and Basicity of Zeolites Acidity and Basicity*, Springer Berlin / Heidelberg, 2008, pp. 153-212.
- [180] S.H. Ali, A. Tarakmah, S.Q. Merchant, T. Al-Sahhaf, *Chemical Engineering Science* 62 (2007) 3197-3217.
- [181] Y. Marcus, *The properties of solvents*, Wiley Series in Solutions Chemistry, 1998.
- [182] G. Charlot, B. Trémillon, *Les réaction chimiques dans les solvants et sel fondus*, Paris, 1936.
- [183] G. Busca, *The Surface Acidity and Basicity of Solid Oxides and Zeolites, Metal Oxides*, CRC Press, 2005, pp. 247-318.
- [184] M. Trombetta, G. Busca, S.A. Rossini, V. Piccoli, U. Cornaro, *Journal of Catalysis* 168 (1997) 334-348.
- [185] L. Lietti, P. Forzatti, G. Ramis, G. Busca, F. Bregani, *Applied Catalysis B: Environmental* 3 (1993) 13-35.

-
- [186] A.B.M. Saad, V.A. Ivanov, J.C. Lavalley, P. Nortier, F. Luck, *Applied Catalysis A: General* 94 (1993) 71-83.
- [187] R. Benjaram, *Redox Properties of Metal Oxides*, Metal Oxides, CRC Press, 2005, pp. 215-246.
- [188] G.W. Simmons, B.C. Beard, *The Journal of Physical Chemistry* 91 (1987) 1143-1148.
- [189] P. Patnaik, *Handbook of inorganic chemicals*, 2003.
- [190] C.L. Rollinson, *Aluminum Compounds*, 3rd ed., Wiley Interscience, 1978.
- [191] Z. Yuan, S. Xia, P. Chen, Z. Hou, X. Zheng, *Energy & Fuels* 25 (2011) 3186-3191.
- [192] M. Trejda, K. Stawicka, M. Ziolek, *Applied Catalysis B: Environmental* 103 (2011) 404-412.
- [193] M. Ayoub, M.S. Khayoon, A.Z. Abdullah, *Bioresource Technology*.
- [194] W. Hu, D. Knight, B. Lowry, A. Varma, *Industrial & Engineering Chemistry Research* 49 (2010) 10876-10882.
- [195] A. Alhanash, E.F. Kozhevnikova, I.V. Kozhevnikov, *Applied Catalysis A: General* 378 (2010) 11-18.
- [196] C.R.B.d. Silva, V.L.C. Gonçalves, E.R. Lachter, C.J.A. Mota, *Journal of the Brazilian Chemical Society* 20 (2009) 201-204.
- [197] S. Pariente, N. Tanchoux, F. Fajula, *Green Chemistry* 11 (2009) 1256-1261.
- [198] M. Okamura, A. Takagaki, M. Toda, J.N. Kondo, K. Domen, T. Tatsumi, M. Hara, S. Hayashi, *Chemistry of Materials* 18 (2006) 3039-3045.
- [199] M. Kitano, D. Yamaguchi, S. Suganuma, K. Nakajima, H. Kato, S. Hayashi, M. Hara, *Langmuir* 25 (2009) 5068-5075.
- [200] V.S. Braga, F.A.C. García, J.A. Dias, C.L. Silvia, *Journal of Thermal Analysis and Calorimetry* 92 (2008) 5.
- [201] M.A. Abdel-Rehim, A.C.B. dos Santos, V.L.L. Camorim, A. da Costa Faro Jr, *Applied Catalysis A: General* 305 (2006) 211-218.
- [202] K.M. Dooley, *Catalysis of acid/aldehyde/alcohol condensations to ketones*, in: J.J. Spivey, G.W. Roberts, (Eds.), *Catalysis*, The Royal Society of Chemistry, 2004, pp. 293-319.
- [203] F.M. Bautista, J.M. Campelo, A. García, D. Luna, J.M. Marinas, R.A. Quirós, A.A. Romero, *Applied Catalysis A: General* 243 (2003) 93-107.

References

- [204] B.M. Reddy, M.K. Patil, *Chemical Reviews* 109 (2009) 2185-2208.
- [205] M. Bensitel, O. Saur, J.C. Lavalley, B.A. Morrow, *Materials Chemistry and Physics* 19 (1988) 147-156.
- [206] L.M. Kustov, V.B. Kazansky, F. Figueras, D. Tichit, *Journal of Catalysis* 150 (1994) 143-149.
- [207] F. Heshmatpour, R.B. Aghakhanpour, *Advanced Powder Technology* 23 (2012) 80-87.
- [208] K. Arata, *Advances in Catalysis* 37 (1990) 165-211.
- [209] M. Hino, M. Kurashige, H. Matsushashi, K. Arata, *Thermochimica Acta* 441 (2006) 35-41.
- [210] T. Jin, T. Yamaguchi, K. Tanabe, *The Journal of Physical Chemistry* 90 (1986) 4794-4796.
- [211] D.A. Ward, E.I. Ko, *Journal of Catalysis* 150 (1994) 18-33.
- [212] K. Tanabe, H. Hattori, T. Yamaguchi, *Critical Reviews in Surface Chemistry* 1 (1990) 1-25.
- [213] J.B. Laizet, A.K. Søliland, J. Leglise, J.C. Duchet, *Topics in Catalysis* 10 (2000) 89-97.
- [214] C. Morterra, G. Cerrato, F. Pinna, M. Signoretto, *Journal of Catalysis* 157 (1995) 109-123.
- [215] D.Y. Ganapati, J.N. Jayesh, *Microporous and Mesoporous Materials* 33 (1999) 1-48.
- [216] S. Ardizzone, C.L. Bianchi, E. Grassi, *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 135 (1998) 41-51.
- [217] J.F. Moulder, W. Stickle, P. Sobel, K. Bomben, *Handbook of X-Ray Photoelectron Spectroscopy*, 1992.
- [218] S. Melada, S.A. Ardizzone, C.L. Bianchi, *Microporous and Mesoporous Materials* 73 (2004) 203-209.
- [219] C.L. Bianchi, S. Ardizzone, G. Cappelletti, *Surface and Interface Analysis* 36 (2004) 745-748.
- [220] S. Ardizzone, C.L. Bianchi, G. Cappelletti, F. Porta, *Journal of Catalysis* 227 (2004) 470-478.
- [221] T. Yamaguchi, T. Jin, T. Ishida, K. Tanabe, *Materials Chemistry and Physics* 17 (1987) 3-19.
- [222] M. Di Serio, R. Tesser, L. Pengmei, E. Santacesaria, *Energy & Fuels* 22 (2008) 207-217.
- [223] A.D. Newman, A.F. Lee, K. Wilson, N.A. Young, *Catalysis Letters* 102 (2005) 45-50.

-
- [224] E. López-Salinas, J.G. Hernández-Cortéz, I. Schifter, E. Torres-García, J. Navarrete, A. Gutiérrez-Carrillo, T. López, P.P. Lottici, D. Bersani, *Applied Catalysis A: General* 193 (2000) 215-225.
- [225] A. Micek-Ilnicka, *Journal of Molecular Catalysis A: Chemical* 308 (2009) 1-14.
- [226] S. Uchida, K. Inumaru, M. Misono, *The Journal of Physical Chemistry B* 104 (2000) 8108-8115.
- [227] C. Pazé, S. Bordiga, A. Zecchina, *Langmuir* 16 (2000) 8139-8144.
- [228] Y. Kamiya, T. Okuhara, M. Misono, A. Miyaji, K. Tsuji, T. Nakajo, *Catalysis Surveys from Asia* 12 (2008) 101-113.
- [229] B.B. Bardin, S.V. Bordawekar, M. Neurock, R.J. Davis, *The Journal of Physical Chemistry B* 102 (1998) 10817-10825.
- [230] Y. Wu, X. Ye, X. Yang, X. Wang, W. Chu, Y. Hu, *Industrial & Engineering Chemistry Research* 35 (1996) 2546-2560.
- [231] Y. Wu, X. Ye, X. Yang, X. Wang, W. Chu, Y. Hu, *Industrial and Engineering Chemistry Research* 35 (1996) 2546-2560.
- [232] A.S. Dias, M. Pillinger, A.A. Valente, *Applied Catalysis A: General* 285 (2005) 126-131.
- [233] M.H. Bhure, I. Kumar, A.D. Natu, R.C. Chikate, C.V. Rode, *Catalysis Communications* 9 (2008) 1863-1868.
- [234] P. Sharma, A. Patel, *Applied Surface Science* 255 (2009) 7635-7641.
- [235] E. Tsukuda, S. Sato, R. Takahashi, T. Sodesawa, *Catalysis Communications* 8 (2007) 1349-1353.
- [236] S.-H. Chai, H.-P. Wang, Y. Liang, B.-Q. Xu, *Applied Catalysis A: General* 353 (2009) 213-222.
- [237] G. Sunita, B.M. Devassy, A. Vinu, D.P. Sawant, V.V. Balasubramanian, S.B. Halligudi, *Catalysis Communications* 9 (2008) 696-702.
- [238] S. Mallik, S.S. Dash, K.M. Parida, B.K. Mohapatra, *Journal of Colloid and Interface Science* 300 (2006) 237-243.
- [239] N. Bhatt, A. Patel, *Journal of Molecular Catalysis A: Chemical* 238 (2005) 223-228.
- [240] A. Alsalme, E.F. Kozhevnikova, I.V. Kozhevnikov, *Applied Catalysis A: General* 349 (2008) 170-176.
- [241] K. Abd El Rahman S, *Applied Catalysis A: General* 343 (2008) 109-116.

References

- [242] L. Yang, Y. Qi, X. Yuan, J. Shen, J. Kim, *Journal of Molecular Catalysis A: Chemical* 229 (2005) 199-205.
- [243] M. Abdollahi-Alibeik, I. Mohammadpoor-Baltork, Z. Zaghaghi, B.H. Yousefi, *Catalysis Communications* 9 (2008) 2496-2502.
- [244] N.A. Comelli, L.M. Grzona, O. Masini, E.N. Ponzi, M.I. Ponzi, *Journal of the Chilean Chemical Society* 49 (2004) 245-250.
- [245] W. Kuang, A. Rives, M. Fournier, R. Hubaut, *Applied Catalysis A: General* 250 (2003) 221-229.
- [246] L.R. Pizzio, C.V. Cáceres, M.N. Blanco, *Applied Catalysis A: General* 167 (1998) 283-294.
- [247] E. Lopez-Salinas, J.G. Hernandez-Cortez, M.A. Cortes-Jacome, J. Navarrete, M.E. Llanos, A. Vazquez, H. Armendariz, T. Lopez, *Applied Catalysis A: General* 175 (1998) 43-53.
- [248] I.V. Kozhevnikov, K.R. Kloetstra, A. Sinnema, H.W. Zandbergen, H. van Bekkum, *Journal of Molecular Catalysis A: Chemical* 114 (1996) 287-298.
- [249] L. Pizzio, G. Romanelli, P. Vázquez, J. Autino, M. Blanco, C. Cáceres, *Applied Catalysis A: General* 308 (2006) 153-160.
- [250] S.S. Rayalu, N. Dubey, R.V. Chatti, M.V. Joshi, N.K. Labhsetwar, S. Devotta, *Current Science* 93 (2007) 1376-1382.
- [251] E. Ortiz-Islas, T. López, R. Gómez, J. Navarrete, D.H. Aguilar, P. Quintana, M. Picquart, *Applied Surface Science* 252 (2005) 839-846.
- [252] Y. Izumi, K. Urabe, *Chemistry Letters* 10 (1981) 663-666.
- [253] T. López, E. Ortiz, R. Gómez, M. Picquart, *Journal of Sol-Gel Science and Technology* 37 (2006) 189-193.
- [254] X. Zhao, Y. Han, X. Sun, Y. Wang, *Chinese Journal of Catalysis* 28 (2007) 91-95.
- [255] J.G. Hernández-Cortéz, T. López, M.E. Manríquez, R. Gómez, J. Navarrete, *Journal of Sol-Gel Science and Technology* 26 (2003) 213-216.
- [256] Y. Izumi, M. Ono, M. Kitagawa, M. Yoshida, K. Urabe, *Microporous Materials* 5 (1995) 255-262.
- [257] Á. Kukovecz, Z. Kónya, I. Kiricsi, *Journal of Molecular Structure* 565-566 (2001) 121-124.

-
- [258] P. Ferreira, I.M. Fonseca, A.M. Ramos, J. Vital, J.E. Castanheiro, *Applied Catalysis B: Environmental* 98 (2010) 94-99.
- [259] T. López, R. Gómez, J.G. Hernández, E. López-Salinas, X. Bokhimi, A. Morales, J.L. Boldú, E. Muñoz, O. Novaro, *Langmuir* 15 (1999) 5820-5824.
- [260] V. Fuchs, L. Méndez, M. Blanco, L. Pizzio, *Applied Catalysis A: General* 358 (2009) 73-78.
- [261] A. Popa, V. Sasca, E.E. Kiss, R. Marinkovic-Neducin, M.T. Bokorov, I. Holclajtner-Antunović, *Materials Chemistry and Physics* 119 (2010) 465-470.
- [262] Á. Kukovecz, Z. Balogi, Z. Kónya, M. Toba, P. Lentz, S.I. Niwa, F. Mizukami, Á. Molnár, J.B. Nagy, I. Kiricsi, *Applied Catalysis A: General* 228 (2002) 83-94.
- [263] T.V. Kovalchuk, J.N. Kochkin, H. Sfihi, V.N. Zaitsev, J. Fraissard, *Journal of Catalysis* 263 (2009) 247-257.
- [264] C.S. Caetano, I.M. Fonseca, A.M. Ramos, J. Vital, J.E. Castanheiro, *Catalysis Communications* 9 (2008) 1996-1999.
- [265] B.M. Devassy, S.B. Halligudi, *Journal of Molecular Catalysis A: Chemical* 253 (2006) 8-15.
- [266] C.F. Oliveira, L.M. Dezaneti, F.A.C. Garcia, J.L. de Macedo, J.A. Dias, S.C.L. Dias, K.S.P. Alvim, *Applied Catalysis A: General* 372 (2010) 153-161.
- [267] E.F. Kozhevnikova, I.V. Kozhevnikov, *Journal of Catalysis* 224 (2004) 164-169.
- [268] L. Pizzio, P. Vázquez, C. Cáceres, M. Blanco, *Catalysis Letters* 77 (2001) 233-239.
- [269] A.M. Alsalme, P.V. Wiper, Y.Z. Khimyak, E.F. Kozhevnikova, I.V. Kozhevnikov, *Journal of Catalysis* 276 (2010) 181-189.
- [270] L.R. Pizzio, P.G. Vázquez, C.V. Cáceres, M.N. Blanco, *Applied Catalysis A: General* 256 (2003) 125-139.
- [271] S.K. Bhorodwaj, D.K. Dutta, *Applied Clay Science* 53 (2011) 347-352.
- [272] J.H. Sepúlveda, J.C. Yori, C.R. Vera, *Applied Catalysis A: General* 288 (2005) 18-24.
- [273] S. Patel, N. Purohit, A. Patel, *Journal of Molecular Catalysis A: Chemical* 192 (2003) 195-202.
- [274] P. Sharma, A. Patel, *Bull. Mater. Sci.* 29 (2006) 439-447.

References

- [275] E. Arendt, S. Ghislain, E.M. Gaigneaux, *Catalysis Today* 155 (2010) 227-240.
- [276] E. Arendt, K.M. McEvoy, E.M. Gaigneaux, *Applied Catalysis A: General* 357 (2009) 115-124.
- [277] N. Bhatt, P. Sharma, A. Patel, P. Selvam, *Catalysis Communications* 9 (2008) 1545-1550.
- [278] P. Vázquez, L. Pizzio, C. Cáceres, M. Blanco, H. Thomas, E. Alesso, L. Finkielstein, B. Lantaño, G. Moltrasio, J. Aguirre, *Journal of Molecular Catalysis A: Chemical* 161 (2000) 223-232.
- [279] P. Barbaro, F. Liguori, *Chem. Rev.* 109 (2009) 515-529.
- [280] S.D. Alexandratos, *Industrial & Engineering Chemistry Research* 48 (2008) 388-398.
- [281] M. Mazzotti, B. Neri, D. Gelosa, A. Kruglov, M. Morbidelli, *Industrial & Engineering Chemistry Research* 36 (1997) 3-10.
- [282] B. Saha, M. Sreat, *Catalysis Letters* 51 (1998) 121-127.
- [283] B. Erdem, M. Cebe, *Korean Journal of Chemical Engineering* 23 (2006) 896-901.
- [284] I.B. Ju, H.-W. Lim, W. Jeon, D.J. Suh, M.-J. Park, Y.-W. Suh, *Chemical Engineering Journal* 168 (2011) 293-302.
- [285] S.H. Ali, S.Q. Merchant, *Industrial & Engineering Chemistry Research* 48 (2009) 2519-2532.
- [286] N. Özbay, N. Oktar, N.A. Tapan, *Fuel* 87 (2008) 1789-1798.
- [287] S.H. Ali, S.Q. Merchant, *International Journal of Chemical Kinetics* 38 (2006) 593-612.
- [288] B. Schmid, M. Doker, J. Gmehling, *Industrial & Engineering Chemistry Research* 47 (2008) 698-703.
- [289] S.I. Kirbalasar, Z.B. Baykal, U. Dramur, *Turk J Engin Environ Sci* 25 (2001) 569-577.
- [290] A. Chakrabarti, M.M. Sharma, *Reactive Polymers* 20 (1993) 1-45.
- [291] R. Tesser, M. Di Serio, L. Casale, L. Sannino, M. Ledda, E. Santacesaria, *Chemical Engineering Journal* 161 (2010) 212-222.
- [292] Y. Liu, E. Lotero, J.G. Goodwin Jr, *Journal of Catalysis* 243 (2006) 221-228.
- [293] C. Casas, R. Bringué, E. Ramírez, M. Iborra, J. Tejero, *Applied Catalysis A: General* 396 (2011) 129-139.

-
- [294] A.R. Pitochelli, Ion Exchange Catalysis Matrix Effects, Philadelphia, 1980.
- [295] R. Tesser, L. Casale, D. Verde, M. Di Serio, E. Santacesaria, Chemical Engineering Journal 157 (2010) 539-550.
- [296] W.-T. Liu, C.-S. Tan, Industrial & Engineering Chemistry Research 40 (2001) 3281-3286.
- [297] J.-Y. Park, D.-K. Kim, J.-S. Lee, Bioresource Technology 101 (2010) S62-S65.
- [298] J.-Y. Park, Z.-M. Wang, D.-K. Kim, J.-S. Lee, Renewable Energy 35 (2010) 614-618.
- [299] P. Lauriol-Garbey, J.M.M. Millet, S. Loridant, V. Bellière-Baca, P. Rey, Journal of Catalysis 281 (2011) 362-370.
- [300] J.-I.M. Dubois, FR), Method for producing acrolein by means of dehydration of glycerol, ARKEMA FRANCE (Colombes Cedex, FR), United States, 2011.
- [301] A. Martin, U. Armbruster, H. Atia, European Journal of Lipid Science and Technology 114 (2012) 10-23.
- [302] H. Atia, U. Armbruster, A. Martin, Journal of Catalysis 258 (2008) 71-82.
- [303] L. Shen, H. Yin, A. Wang, Y. Feng, Y. Shen, Z. Wu, T. Jiang, Chemical Engineering Journal 180 (2012) 277-283.
- [304] M. Pagliaro, M. Rossi, The Future of Glycerol: New Uses of a Versatile Raw Material, The Royal Society of Chemistry, 2008.

PUBLICATIONS

Published articles

Glycerol acetylation on sulphated zirconia in mild conditions.

I.Dosuna-Rodríguez, C. Adrianly and E.M. Gaigneaux.

Catalysis Today, 2011. 167(1): p. 56-63.

Submitted articles

Glycerol acetylation catalysed by ion exchange resins

I.Dosuna-Rodríguez and E.M. Gaigneaux.

Catalysis Today.

CONFERENCE ABSTRACTS

Oral communications

1. *Synthèse, caractérisation et développement de zircons sulfatés dans le cadre de l'estérification des acides carboxyliques avec et dans le glycérol.* I.Dosuna-Rodríguez, C. Adrianly and E.M. Gaigneaux. Journée de rencontre Etudiant-Chercheur, UCL, (Belgium), 17th March 2010.
2. *Sulphated zirconia catalysts for the acetylation of glycerol in mild conditions.* I. Dosuna-Rodríguez, C. Adrianly and E.M. Gaigneaux. One-day scientific meeting-WP3-INANOMAT, UCL (Belgium), 16th April 2010.
3. *Sulphated zirconia catalyst for the glycerol acetylation in mild conditions.* I. Dosuna-Rodríguez, C. Adrianly and E.M. Gaigneaux. 6th International Conference on Environmental Catalysis (ICEC 2010) Beijing (China), 13th September 2010.
4. *Comparison of different ion exchange resins for glycerol acetylation.* I. Dosuna-Rodríguez and E.M. Gaigneaux. Ph.D. Students' Day UCL (Belgium), 27th May 2011.

-
5. *Glycerol acetylation catalyzed by ion exchange resins.* I. Dosuna-Rodríguez and E.M. Gaigneaux. Catbior 2011 - 1st International Congress on Catalysis for Biorefineries-Torremolinos (Spain) 3rd October 2011.

Poster communications

1. *Sulphated zirconia catalysts for the acetylation of glycerol in soft conditions.* I. Dosuna-Rodríguez, C. Adrianly and E.M. Gaigneaux. Ecole doctorale thématique du F.R.S.-FNRS MAIN, UCL (Belgium), 6th November 2009.
2. *Glycerol Acetylation on sulphated zirconia in mild conditions.* I. Dosuna-Rodríguez, C. Adrianly and E.M. Gaigneaux. COST ACTION CM0903 (UBIOCHEM) 1st workshop, Córdoba, (Spain), 13th-15th May, 2010.
3. *Immobilised heteropolyacids in zirconia and silica matrix by sol gel and wet impregnation techniques for glycerol acetylation.* I. Dosuna-Rodríguez and E.M. Gaigneaux. Catbior 2011-1st International Congress on Catalysis for Biorefineries-Torremolinos (Espagne) 3rd-5th October 2011.

PART V: ANNEXE

ANNEXE 1

Solubility tests concerning the tungstated zirconia samples.

Wet-impregnation vs co-precipitation.

1. Objectives

The goal of insolubility tests is to check the stability of the catalyst in contact with the reaction medium. The matrix of the solid and the active species must be insoluble in the reaction media. The presence of leaching implies a low recyclability of the solid and the contamination of the reaction final products.

2. Experimental

The insolubility tests were carried out at 65 °C and at atmospheric pressure in a round bottom flask reactor equipped with a magnetic stirrer (~300rpm) and a refrigerator in order to minimize the losses of carboxylic acid as in the esterification tests. The temperature was maintained constant ($\pm 1^\circ\text{C}$) using an oil bath. The catalyst (0.2 g) is put into a reactor with 40 ml of glycerol (puriss. pa, ACS reagent, anhydrous, dist., $\geq 99.5\%$ Fluka). After 24 hours the solid is removed from the liquid medium by means of a filter (Whatman 6, filtration threshold: 3 μm). The presence of tungsten species in the recovered liquid medium were analysed by ICP method

The equation used for calculation is as follows:

$$W_{\text{losses}} = \frac{[W]_{\text{LM}} \times m_{\text{LM}}}{[W]_{\text{solid}} \times m_{\text{solid}}}$$

Where $[W]_{\text{LM}}$ is the concentration of W in the liquid medium (LM) analysed by ICP (mg / kg); m_{LM} is the mass of the liquid media (kg); $[W]_{\text{solid}}$ is the loading of W in the solid mg/ kg and m_{solid} is the amount of catalyst used in the test

3. Results

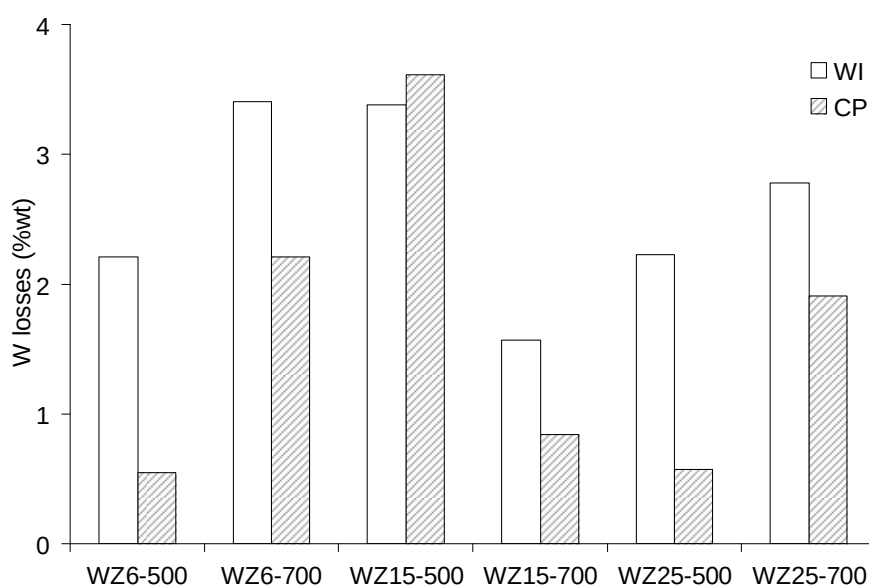


Figure 80. Solubility tests. W losses in the liquid medium WI: WZ-WI samples in glycerol and CP: WZ-CP samples in glycerol.

From Figure 80 it can be seen that in presence of glycerol the W losses of wet impregnated samples (A) are higher than those corresponding to the samples prepared by co-precipitation (B). This could be due to a lower interaction between the matrix and the tungstated species for the wet impregnated samples.

4. Conclusions

In presence of glycerol the samples obtained by wet impregnation technique were less resistant to leaching than for co-precipitated samples. The presence of leaching implies the low recyclability of the samples (as they are impoverished in the active species) and the contamination of the final products. In consequence, only co-precipitates samples were tested in the esterification reaction.