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Polyoxometalate hybrid catalysts in epoxidation reactions. Study of the hydrophobic effect.

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

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TABLE OF CONTENTS

ACRONYMS, ABBREVIATIONS & SYMBOLS

Δf	Frequency shift
Δd	Dissipation shift
α	Ionization degree
δ	Chemical shift
ε_r	Relative permittivity (or dielectric constant)
k_1	Catalyst transformation rate constant
k_2	Epoxidation reaction rate constant
λ	Wavelength
ν	Infrared Frequency
μ	Dipole moment
θ	Scattering angle
A	pre-exponential factor of the Arrhenius equation
AFM	Atomic force microscopy
CA	Carboxylic acid
COO-	Carboxylate function
COOH	Carboxylic function
COPO	Copolymer
DSC	Differential scanning calorimetry
E_a	Apparent activation energy
EF	Electrostatic factor
EO	Ethylene oxide
E_T	Molar transition energy
FID	Flame ionization detector
FTIR	Fourier transform infrared spectroscopy
FWHM	Full width at half maximum
GC-MS	Gas chromatography - Mass spectrometry
HBA solvent	Hydrogen-bond donor solvent
HBD solvent	Hydrogen-bond acceptor solvent
HOMO	Homopolymer
HPA	Heteropolyacid

HPC	Heteropolycompound
ICP-AES	Inductively coupled plasma - Atomic emission spectroscopy
IUPAC	International Union of Pure and Applied Chemistry
JCPDS-ICDD	Joint Committee on Powder Diffraction Standards - International Center for Diffraction Data
LMCT	Ligand-to Metal charge-transfer
MAS NMR	Magic angle spinning Nuclear magnetic resonance
PEI	Polyethyleneimine
PO	Propylene oxide
POMs	Polyoxometalates
PW4	Ishii-Venturello $[PW_4O_{24}]^{3-}$ cluster
PW11	Lacunary Keggin $[PW_{11}O_{39}]^{7-}$ cluster
PW12	Keggin $[PW_{12}O_{40}]^{3-}$ cluster
QCM-D	Quartz crystal microbalance with dissipation monitoring
SEC	Surfactant-encapsulated clusters
SEM	Scanning electron microscopy
SEP	Surfactant-encapsulated POMs
TGA	Thermogravimetric analysis
THF	Tetrahydrofuran
TOF	Turnover frequency
UV-Vis	Ultraviolet visible
XRD	X-Ray diffraction

GENERAL INTRODUCTION:

THE POLYOXOMETALATES

The general introduction describes the context on which the thesis is established. A description of polyoxometalate chemistry and properties are then expressed. Details on the polyoxometalate application in epoxidation reactions are given and correlated with limitations of nowadays understanding. Current challenges and perspectives are exposed and compared with our objectives. Finally, the strategy followed during the research to address these issues is depicted.

1. CONTEXT

Depending on the field of research that you explore, some discoveries seem more remarkable and fascinating than others. Catalysis is not an exception to the rule. Since the term of catalysis has been coined in 1835 by Berzelius, some discoveries dictate the evolution of this science and the history of industrial chemistry. To mention just one example, for more than three decades, zeolite material is at the root of many petrochemical processes. The high tunability in composition, porosity and acidity makes of zeolite inescapable material in many areas as gas or liquid separation [1], ion-exchange process [2] and naturally, catalysis [3].

The story of zeolite can be expected for polyoxometalate compounds in a foreseeable future. Polyoxometalates (or POMs for convenience) are constituted by early transition metals in their highest oxidation state and form oxo anionic clusters. They were firstly reported in 1826 by again Berzelius [4]. The arrangement and the structure of these compounds were hard to determine and it is only in 1933 that Keggin reported the first structure of a POM [5]. The structure, bearing the name of its discoverer, is the most common structure in POM chemistry. Since this discovery, a wide range of polyoxometalate compounds have been synthesized and characterized. Actually, an extreme variability of POM exists owing to that most of the elements in the periodic table can be incorporated into the structural framework of these compounds [4]. This high degree of molecular tunability leads to a large range of remarkable 'value-adding properties' [6]. Their composition, structure, size, redox chemistry, charge versatility and solubility in various media are the numerous reasons that boost the POM chemistry at the forefront of fundamental research today such as in materials [6-7], medicine [8] and catalysis [9].

2. POLYOXOMETALATE CHEMISTRY IN SOLUTION

Polyoxometalate species are formed from the dissolution of metal ions M^{n+} in aqueous solution [9B, 9C, 10]. This dissolution then leads to the coordination of water molecules to the cations, the formation of M–O bonds and ionization of the OH bond. Ionization facilitates the proton dissociation, enhanced with higher charged metal ion which increases the proton acidity. The new formed monomeric complexes are not stable and tend to dimerize by formation of hydroxo bridges or oxo groups. Since the overall positive charge of the dimer is higher than the charge of the monomer, the dimer forms further hydroxo groups, and thus continues the polymerization process. This generates metal-oxo or metal-hydroxo polymers in solution, until the electrostatic repulsion developed in edge-sharing polyhedra is too strong. Metals in polyhedra can be connected via one or two M–O–M bridges, thus sharing corners and edges respectively of the coordination spheres. The nature of the ligand (water, hydroxo or oxo species) dictates the extent of the polymerization. The nature and the number of the ligands depend on the solution pH and on the metal M^{n+} charge value. For intermediate charges (5+ and 6+) and under favorable acidic conditions, the oligomerization of the hydroxo species forms polyoxoanions, or so-called isopolyanions. The growth of these anionic oligomers composed by the edge or corner-sharing of MO_6 octahedra (still for M^{5+} or M^{6+} metals as V^{5+}, Mo^{6+} or W^{6+}) depends on the electrostatic repulsion (coming from the M^{n+} ions), the M^{n+} concentration, the ion size, the ion π-acceptor properties and the solution pH.

The so-called heteropolyanions (or heteropolyoxometalates, or heteropolycompounds, HPC) are formed by the incorporation of other anions (referred to the heteroatoms) at the center of the polyanion under acidic conditions of Mo^{6+} or W^{6+} solutions. A large variety of atoms can be slotted as heteroatom as Be, B, Al, Si, Ge, Sn, P, Te and the whole first row of transition elements. The atomic ratio between the surrounding atoms (referred to the addenda atoms) and the central heteroatom (arranged in a tetrahedral or octahedral coordination) can be 6, 9, 11 or 12.

These ratios come from the most common heteropolycompound structures. The most well-known and studied structure is the so-called Keggin with the general formula $[X^{n+}M_{12}O_{40}]^{(8-n)-}$ (atomic ratio M/X = 12) (Fig. I-1a). These easily synthesized and highly stable compounds are generally formed with P^{5+} or Si^{4+} as heteroatom X and Mo^{6+} and W^{6+} as the addenda M atoms. Nevertheless, Keggin species can be synthesized with numerous different atoms. The Keggin anion results from the association of 12 edge and corner-sharing MO_6 octahedra surrounding the central XO_4 tetrahedron. MO_6 octahedra are arranged by edge-sharing in four trigonal M_3O_{13} groups, each sharing corners with neighboring groups and with the central tetrahedron. This spherical organization leads to distinguish four kinds of oxygen atoms as the terminal oxygen ($M=O_t$), the oxygen sharing the edge ($M–O_c–M$), the corner-sharing oxygen ($M–O_b–M$) and the oxygen bridging the central heteroatom ($X–O_a–M$). This Keggin species will be at the root of the major heteropolycompounds used in this work. Less stable skeletal isomers also exist. As a function of the solution pH, hydrolysis of the Keggin structure can occur. By raising the pH, lacunary Keggin compound is formed by the loss of one MO_6 octahedron (stoichiometrically one MO unit). The general formula is $[XM_{11}O_{39}]^{n-}$ (atomic ratio M/X = 11) (Fig. I-1b). Of course, stability of the Keggin structure is dependent on the constituting atoms. For Mo^{6+} addenda atoms, the stability of the Keggin structure as a function of the heteroatom is Si > Ti > Ge > P > As. This leads to the possibility to introduce guest metal ions and form mixed HPC by adding another oxoanion to the lacunary compound solution as Fe^{2+}, Ni^{2+} or Co^{2+} and noble metals [11].

The adjustment of the solution pH can induce the loss of three octahedra of the Keggin structure. Dimerization of two XM_9O_{34} moieties leads to a new class of HPC. From this fusion, it results the Wells-Dawson compound with the general formula $[X_2^{n+}M_{18}O_{62}]^{(2n-16)-}$ (atomic ratio W/P = 9) (Fig. I-1c). Finally, the latter common HPC described here is the Anderson structure with the general formula $[X^{n+}M_6O_{24}]^{(12-n)-}$ (atomic ratio W/P = 6). This planar structure is generally obtained from aqueous solutions at pH 4-5 (Fig. I-1d).

The different structures detailed hereabove and the influence of the pH on the stability of these structures based on W^{6+} and P^{5+} metal atoms are presented in Figure I-1 [12].

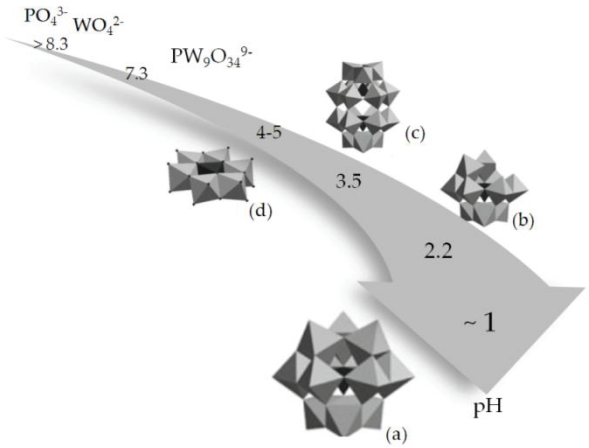

Figure I-1 – Structure and organization of the polyoxometalate species as a function of the aqueous solution pH. (a) Keggin, (b) lacunary Keggin, (c) Wells-Dawson and (d) Anderson structure.

At the solid state, these anionic structures are associated to counter-ions to form their secondary structures. If water molecules crystallize with POMs, heteropolyacid compounds are formed. Other counter-ions as Na^+, NH_4^+, K^+, Cs^+ can be found and change the solubility and the surface area of the resulting salts.

The brief and basic description developed here on the polyoxometalate chemistry must not hide the huge adjustable possibilities brought by these compounds. More than just create a large variety of mixed HPC, these discrete and well-defined structures are building blocks for infinity of functional nanoscale systems [10a]. Polyoxometalate clusters can be assembled by physical blending, electrostatic or covalent bonding in such a way to form incredible architectures for different applications (Fig. I-2).

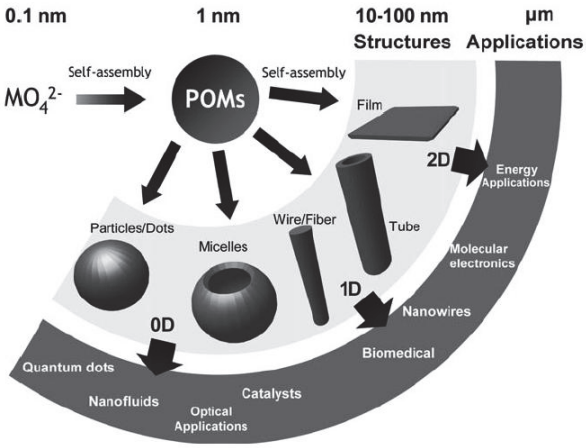

Figure I-2 – Polyoxometalate clusters (ca. 1-5 nm size) can be assembled by electrostatic self-assembly, template-mediated or covalent bonding in zero-dimensional particles and micelles, one-dimensional tube and wire architectures or to two-dimensional thin films [10a].

3. SCOPE OF APPLICATIONS

The value-adding properties of polyoxometalates were listing by Kastoulis [6] and are displayed in Table I-1. Based on these numerous properties, plenty of opportunities of POM applications emerge.

Table I-1 – Value-adding properties of POM [6-7]

Metal oxide like
Stable
Large size diameter (6 – 50 Å)
Discrete size/structure
Anions (charge from -3 to -14)
High ionic weight (10^3 – 10^4 g/mol)
Fully oxidized compounds/reducible
Variable oxidation numbers for the addenda atoms
Variable color as a function of the oxidation state
Photoreducible
Arrhenius acids ($pK_a < 0$)
Incorporate over 70 elements and form large number of structures
Acid forms very soluble in H_2O & other oxygen carrying solvents; also soluble or transferable into nonpolar solvents
Hydrolysable to form deficient structures

The possibility to undergo reversible redox processes under mild conditions, their high ionic conductivity and their capability to form salts with almost any cations make of POM precursors to build membrane-based devices and sensors. Applications of these devices and membranes are selective electrodes, gas detection equipments and liquid and solid electrolytic cells [6-7]. This ability to undergo highly reversible multi-electron redox processes makes of POM potential precursors as redox active centers for aqueous batteries [7d, 13]. Also, polyoxometalates exhibit significant photo- and electrochromism [7c]. These properties allow to make them suitable as nanocomposite molecular devices and as models for probing the physical properties of infinite metal oxides. In medicine, some polyoxometalates exhibit biological activity *in vitro* as well as *in vivo*, including anticancer, antibiotic, antiviral, antiprotozoal and antidiabetic effects [8, 14]. In addition to applications in nanomagnetism [15], electronics [7d], analysis and cations separation [6], and as electron-dense imaging agents in medicine [16], POMs possess remarkable properties and applications in catalysis. Presently, more than 80-85 % of the patent applications concerning with polyoxometalates are related to catalysis [17]. According to Misono, in 1993, some large-scale industrial processes were operating with POMs, all commercialized by Japanese chemical companies [18]. Nowadays, except this example, no other industrial process operating with POMs was found in the literature. In the next points, an overview of POM application as homogeneous or heterogeneous catalysts is presented.

4. APPLICATION AS HOMOGENEOUS CATALYSTS

The numerous catalysts known today can be classified according to various criteria: structure, composition, area of application, or state of aggregation. Two large groups of classification of the catalysts according to the state of aggregation are commonly distinguished: homogeneous catalysts and heterogeneous catalysts (solid-state catalysts). Intermediate forms also exist such as homogeneous catalysts attached to solids (supported catalysts), also known as immobilized or heterogenized catalysts and finally, biocatalysts. Nowadays, biocatalyst chemistry becomes one of the trendy promising subjects in catalysis [19].

Homogeneous catalysts are generally well-defined chemical compounds or coordination complexes. They are molecularly dispersed in the reaction medium. Both the reactants and the catalyst are in the same phase [20]. Heterogeneous catalysis takes place between several phases. Generally the catalyst is a solid, and the reactants are gases or liquids. Catalytic reactions occur at the surface of the solid catalyst [20-21].

(i) POM catalyst properties

Solid POMs form ionic crystals composed of heteropolyanions, counter-cations and hydration water. When counter-cations are protons, heteropolyacids (HPA) are formed with strong acidity, much stronger than mineral acids. In aqueous solution, HPA are completely dissociated while they are partly dissociated in organic solvents. The large size of POM allows a delocalization of the surface charge density throughout the polyanion, leading to a weak interaction between H^+ and the anion. This explains their high acidity. Therefore, like many HPA, acidity of $H_3PW_{12}O_{40}$ species is considered as superacid [9e]. The order of acidity strength in solution is the same as that observed at the solid state and decreases in the order: $H_3PW_{12}O_{40} > H_4SiW_{12}O_{40} > H_3PMo_{12}O_{40} > H_4SiMo_{12}O_{40}$. At the solid state, the acidity of HPA is stronger than conventional solid acids, such as SiO_2-Al_2O_3 or HY zeolites.

This high Brønsted acidity makes them alternative catalysts for acid-catalyzed transformations such as alkylation and acylation reactions based on unfriendly homogeneous liquid acids (HF, $AlCl_3$ or H_2SO_4). Their high acidic property gives the opportunity to realize the catalytic process at lower catalyst concentration or at lower temperature. In terms of safety, HPA are relatively nontoxic crystalline substances and easy to handle [9b]. As acid homogeneous catalysts, HPA show activity in condensation [22], acetonation [23], esterification [24], alkylation reactions [25] and hydration of olefins [9b].

In addition to high Brønsted acidity, POMs display efficient redox behavior allowing fast transformations under soft conditions. This makes of POM highly efficient catalysts in oxidation reactions [9d, 26]. Both dioxygen and hydrogen peroxide can be used as oxidant. The mechanism is a redox-

type which means that the substrate is firstly oxidized by the POM followed by a re-oxidation of the POM by O_2 or H_2O_2. The reduction of POM in solution is accomplished by a protonation to maintain the charge of the polyanion. The two redox steps can be done in a same reactor, in monophasic or biphasic conditions, or separately in a second reactor for O_2 [9c]. In biphasic conditions, a phase-transfer catalyst is needed. Unfortunately, the large variety of pH-dependent polyanions in solution complicates the knowledge of the mechanisms of oxidation reactions catalyzed by POMs [9b].

Again, a large range of oxidation reactions can be accomplished by polyoxometalates as alcohol [27], aldehyde [9c], amine [28], or sulfide oxidation [29] and as alkene epoxidation [30].

(ii) The epoxidation reaction

In this work, we will focus on the epoxidation reaction by polyoxometalates. Epoxidation of olefins is an important reaction in the laboratory as well as in the chemical industry because epoxides are widely used as raw materials for epoxy resins, paints, surfactants, and intermediates in organic syntheses. The epoxide constitutes indeed one of the most important intermediates in synthetic organic chemistry and biochemistry [30b, 31]. Formerly based on a non-catalytic chlorohydrin-based process, catalytic oxidation of alkenes with different oxidants as O_2, H_2O_2, organic peroxides or peracids is now largely developed [30a].

The largest commercial epoxidation process is the direct oxidation of ethylene to ethylene oxide (EO). All EO production occurs by air-based processes over silver-based catalysts at temperatures between 220 and 300°C. The only other epoxide manufactured on an industrial scale is propylene oxide (PO). Some companies still produce PO using a chlorohydrin-based process, which is a liquid-phase non catalytic process. The second commercial route is a hydroperoxide-based process. The hydroperoxide-based processes are liquid-phase, carried out between 100 and 130°C, and use either homogeneous Mo-based catalysts or heterogeneous Ti-based catalysts [32]. In addition to Mo(VI), epoxidation with alkyl hydroperoxides can be proceeded with early transition elements in

high oxidation states, e.g., W(VI), V(V), and Ti(IV) [33]. Yet, in addition to the multistep and complex facilities, the production of coproducts which need to be sold separately or recycled, is the major drawback associated to these hydroperoxides processes. To overcome these constraints, the epoxidation with hydrogen peroxide is becoming an emerging technology in the PO production and more widely, in alkene epoxidation [34]. Yet, when hydrogen peroxide is used as the oxygen donor, neither the homogeneous Mo nor the heterogeneous Ti/SiO_2 catalysts are effective. In this case, titanium silicalite catalysts like TS-1 are used to run the reaction in methanol as solvent [31]. However, despite its high activity, a serious limitation of the TS-1 catalyst is the low accessibility to their catalytic sites by bulky molecules, limiting thereby its application in organic synthesis [34]. Development of new heterogeneous catalysts based on W [35], Re [36], Ru [37], Mn [38], Fe [39] or formed by hydrotalcite [40] and alumina [41] systems was then carried out and is still abundantly studied. Figure I-3 compiles some data of homogeneous and heterogeneous catalytic systems in epoxidation reaction which can be gathered in three regions: the biological and biomimetic systems, the industrial systems and the homogeneous and heterogeneous systems [31]. As presented in Figure I-3, W-based polyoxometalate catalysts seem promising homogeneous catalysts in epoxidation reaction.

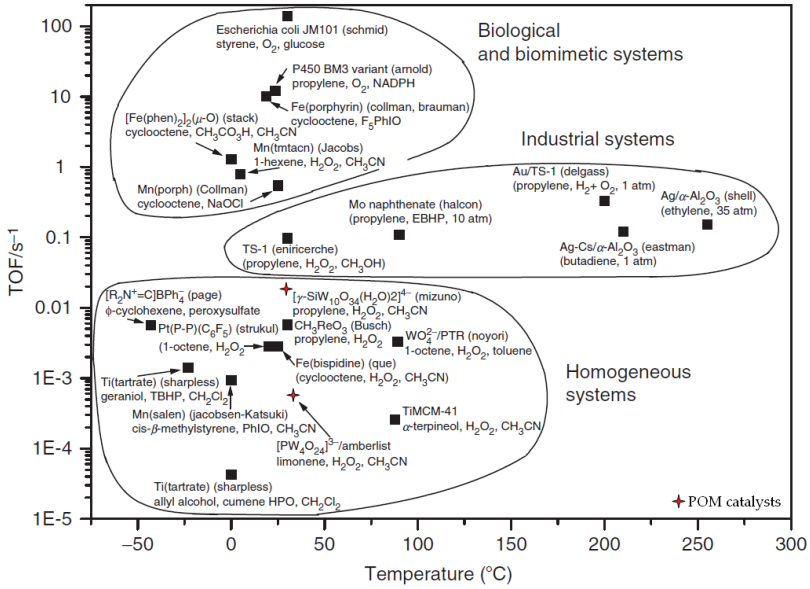

Figure I-3 Comparison of rate in alkene epoxidation for different catalytic systems[31]

(iii) Homogeneous POMs in epoxidation reaction

The activity of POMs in epoxidation reaction was firstly reported simultaneously by Venturello and Ishii groups in the 80s. In 1983, Venturello and coworkers showed the direct epoxidation of olefins by hydrogen peroxide with Na_2WO_4 and H_3PO_4 in biphasic conditions [42]. Two years later, the group managed to crystallize the active anionic complex $[(C_6H_{13})_4N^+]_3\{PO_4[W(O)(O_2)_2]_4\}^{3-}$ [43]. It consists in the central PO_4 tetrahedron linked with oxygen atoms to two $[W_2O_2(O_2)_4]$ species composed of edge-sharing distorted pentagonal bipyramids. Each tungsten atom is linked to two peroxo groups, one nonbridging and the other bridging, located in the equatorial plane of the pentagonal bipyramid (Fig. I-4).

In 1988, after further studies and applications of the complex to oxidation reactions and epoxidation of various olefins by the Venturello group [44], Ishii demonstrated the activity of $H_3PW_{12}O_{40}$, $H_3PMo_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ species in oxidation reactions, directly used in a $H_2O_2/CHCl_3$ biphasic system [45]. Tungstophosphate species were the most active species. In both Venturello and Ishii biphasic systems, a phase-transfer catalyst is needed.

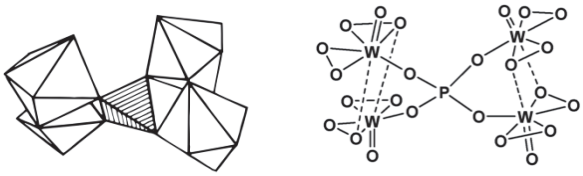

Figure I-4 – The structure of the Ishii-Venturello anion $\{PO_4[W(O)(O_2)_2]_4\}^{3-}$ [30b, 46]

Since this discovery in 1983, a large number of studies attempted to characterize the active species or to develop new polyoxometalate active species in epoxidation reactions. Brégeault's group investigated the Ishii and Venturello systems and suggested the presence of the same peroxo species $\{PO_4[W(O)(O_2)_2]_4\}^{3-}$ in both studies (hereafter called PW4) [46-47]. Under the influence of hydrogen peroxide, the Keggin compounds would form less condensed peroxo structures identical to the Venturello species. By NMR, Salles' group proved that the $H_3PW_{12}O_{40}$ compound is degraded in an excess of H_2O_2 to a mixture of mono-, bi-, tri- and tetranuclear anions with the general formula $[PW_xO_y]^{w-}$ [30c, 48]. A step forward in the knowledge of the

active species was brought by Duncan *et al.*, who mentioned the need of an excess of hydrogen peroxide (at least 50-fold) to form the most active species PW4 from PW12 clusters. In addition, they observed the formation of subsequent peroxo species after the catalytic reaction of PW4 with the substrate. These subsequent peroxo species are rapidly converted back to regenerate the PW4 with hydrogen peroxide [49]. Furthermore, it was proven that tungsten-based catalysts were the most active polyoxometalate species in epoxidation reaction, and two times more active than the peroxotungstate $\{[WO(O_2)_2(H_2O)]_2O\}^{2-}$ species. Finally, drawbacks of these systems were highlighted. In addition to the use of toxic and carcinogenic chlorocarbon solvents, a rapid deactivation of the Ishii-Venturello system was observed. This deactivation would be due to an over-adsorption of epoxide and diol on the catalytic species and would irreversibly decompose the catalyst [49-50].

Nowadays, the Ishii-Venturello system is still largely studied in epoxidation reaction [30a, 30c, 46-47, 50b, 51] but also in other oxidation systems [28, 30b, 52]. Although this is not an exhaustive list, a same observation comes from the majority of these studies: these systems are homogeneous systems and share common drawbacks. As the catalyst is in the same phase as the substrates and products, the catalyst separation and catalyst reuse are difficult. The immobilization (or heterogenization) of these catalytic active species onto solid supports can solve the catalyst recovery and recycling problems. Strategies of polyoxometalate species immobilization and heterogenization are presented in the next point.

5. APPLICATION AS HETEROGENEOUS CATALYSTS

The aim of homogeneous catalyst heterogenization is to combine in a same material, the inherent properties of a homogeneous catalyst with the properties of a solid heterogeneous catalyst. Development of efficient heterogeneous catalysts with POMs for liquid-phase oxidation reactions has been already attempted and the strategies can be classified into the following two main groups: POM immobilization on solid support and POM solidification (Fig. I-5). The first category refers to the immobilization of POMs through adsorption, encapsulation, covalent linkage or ion-exchange processes onto insoluble particles. The second strategy plays on

the selection of appropriate counter-cations to form insoluble solid ionic materials.

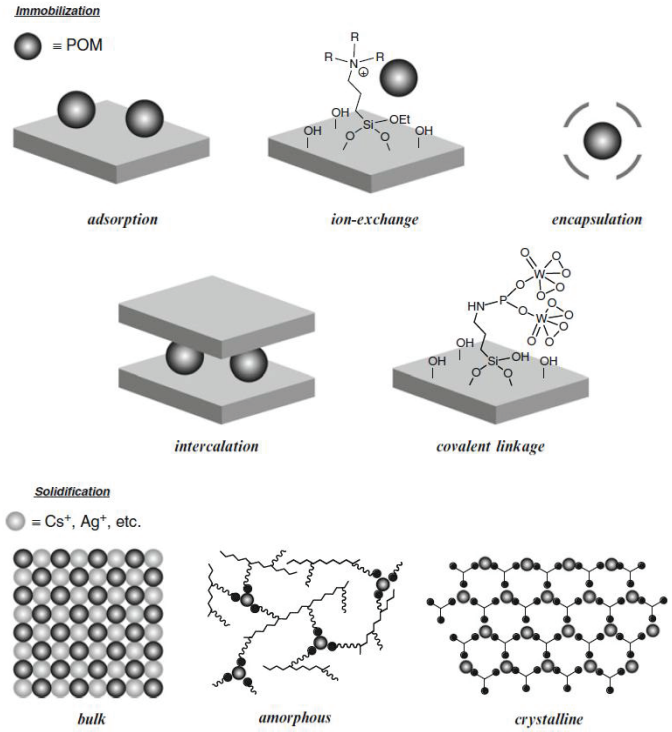

Figure I-5 – Strategies of polyoxometalate species heterogenization [53].

All these strategies were attempted and applied with more or less success to oxidation or epoxidation reactions. On the one hand, immobilization by adsorption onto inert supports is the simplest way to form solid catalysts [54]. Moreover it helps to increase the low surface area of unsupported POM catalysts (< 10 m^2/g). Unfortunately, decomposition or leaching of POMs often occur with this method [52c]. Encapsulation into silica matrix [52i, 52k, 55] or intercalation into layered double hydroxide for instance [56], could solve the leaching problem. In this case, low accessibility of organic substrates, because of the hydrophilicity and/or the low surface area of the catalyst, is the major problem associated to these approaches [57]. On the other hand, formation of insoluble solid ionic materials can reduce the solubility of the POMs in aqueous or organic solvents. The selection of appropriate counter-cations could increase the POM insolubility and could develop the surface area of the catalyst [58]. Introduction of magnetic particles into bulk materials of POMs was also carried out to enhance and facilitate the catalyst

separation [59]. Nevertheless, bulk materials limit the accessibility and decrease the intrinsic activity of POMs. In a biphasic medium, a phase-transfer catalyst is needed to allow the activation of soluble POMs in the aqueous H_2O_2 phase and their reactivity toward the substrate located in the organic phase. By a suitable selection of the surfactant, generally an alkylammonium ion, the formation of insoluble materials shared between the two phases was accomplished [52a, 60]. More remarkably, some surfactants allow the solubility of the catalyst during the reaction but when the hydrogen peroxide is consumed or temperature drops, catalyst precipitation occurs and allows its easy recovery. Nevertheless, the uncontrolled precipitation could lead to a difficult particle recovery [51o, 61]. Besides, immobilization by anion-exchange [9d, 62] or ionic crosslinking of POMs with polymers was successfully achieved to form hybrid catalysts [51l, 52b, 52d, 63]. Ikegami and coworkers prepared a novel insoluble catalyst of a crosslinked complex consisting of $[PW_{12}O_{40}]^{3-}$ and N-isopropylacrylamide with ammonium cations. This hybrid material catalyzes the oxidation of various substrates including allylic alcohols, amines, and sulfides with 30% aqueous H_2O_2 under mild reaction conditions without organic solvents [28, 52d, 63c]. Neumann and coworkers applied this strategy to the development of an alkylated polyethyleneimine/POM system [52b, 63d].

Utilization of ion-exchange resins highlighted the benefits of these catalysts based on electrostatic interactions with high activity and without leaching [50b, 51l, 62a]. Finally, a drastic solution to avoid leaching of POM species is to attach them onto a support by a covalent bond [62a, 64]. The chemistry behind this strategy is more complicated and a risk of catalyst deactivation by the covalent linkage exists.

6. TOWARD THE OBJECTIVES OF THE THESIS

Heterogenization is thus nowadays still a challenge. Various strategies of POM immobilization were looked over as described in the previous paragraph. It appears that heterogenization by hybridization would maintain the high activity of homogeneous catalysts while at the same time it would exploit the advantages of an easier catalyst separation without

active species leaching. But we claim that further improvements and more valuable effects can be expected by this method.

In heterogeneous catalysis, substrate adsorption or product desorption are crucial steps in the catalytic mechanism. Indeed, the competition between the kinetics for surface reaction and adsorption or desorption steps leads to the Sabatier principle which indicates that the overall catalytic reaction rate is maximized for an optimal interaction between the substrate molecules and the catalyst surface [65]. Optimization of these adsorption steps could allow a specific control of adsorption properties and modulate both the catalyst activity and selectivity. Besides, some studies reported the importance of the catalyst surface hydrophobicity to enhance the activity and selectivity in catalysis [66] and precisely in alkene epoxidation reaction [51m, 67]. It was claimed that the hydrophilic/hydrophobic properties of the catalyst surface was just as important as the number of active sites. This would be especially true in epoxidation reactions where the epoxide has a higher polarity than the substrate. Over-adsorption of epoxide could lead to ring-opening and hydrolysis to diols which have a poisoning effect on the catalyst activity.

The control of reactivity or selectivity achieved by the catalyst physicochemical properties is sometimes referred to catalyst specificity. Yet, the definition of catalyst specificity varies from authors and field of study. In enzymology, this term refers to the ability of enzymes to both discriminate between substrates and control a reaction outcome. Specificity arises from the three-dimensional structure of the enzyme active site [68]. In the catalysis field, catalytic specificity refers to the particular ability of a substance to catalyze a given type of chemical transformation [69]. For instance, from a mixture of CO/H_2, using different catalysts, it is possible to obtain methane [70], a mixture of liquid hydrocarbons [71], high-molecular-weigth solid hydrocarbons [72], mixtures of oxygen-containing compounds [73], and methyl or isobutyl alcohols [74]. Thus, based on this definition, specificity refers to the ability of a catalyst to realize a specific chemical reaction. But, according to other authors, catalytic specificity refers to the ability of a catalyst to recognize three-dimensionally a specific substrate, as performed by enzymes [75]. In this confused context, the definition of catalyst specificity applied in

this thesis is the ability of a catalyst to recognize a specific substrate. The definition of catalyst selectivity applied in this thesis is the ability of a catalyst to realize a specific chemical reaction and control a reaction outcome. Here, the specific chemical reaction is the alkene epoxidation reaction.

In addition to the catalyst adsorption properties, the catalyst specificity and selectivity can be modulated by the catalyst morphology. For instance, in zeolite catalysis, it is characterized by one or any combination of three primary mechanisms: (i) reactant shape-specificity whereby molecules are sterically discriminated based on their ability or inability to enter the restricted pores of the zeolite and diffuse in it, (ii) product shape-selectivity whereby bulkier molecules are sterically hindered from leaving the zeolite, and (iii) spatioselectivity whereby the formation of molecular transition states is restricted by the confinement of the zeolite channels, intersections, or cages [76]. Yet, inverse or reverse shape-selectivity was also reported with zeolite materials [77]. This is especially true for branched-chain alkanes. Generally, the specificity and selectivity effects on a molecule depend in a subtle way on the molecule size and shape, the molecule functional groups, the catalyst pore size and geometry, the presence of solvents and so on. Notice that shape-specificity or selectivity is just as important in fine chemistry as in petrochemical industry [78]. Specificity is currently met with natural catalysts as enzymes where the adsorption and the three-dimensional structure of the enzyme active site are really specific for one or a family of molecules [68]. To the best of our knowledge, no artificial heterogeneous catalysts can be considered as totally specific. To obtain shape-specificity and shape-selectivity properties with heterogenized species, encapsulation is one of the most often and effective methods used for homogeneous catalyst immobilization. This method does not change the chemical properties of the immobilized catalyst except for the steric confinement into the porous supports [79]. For instance, homogeneous species encapsulated in nanocages of zeolites may lose some of their degrees of freedom and accept exclusive geometries which may differ from homogeneous counterparts. Therefore, special characteristics such as size/shape specificity or selectivity can be attained [80]. For polyoxometalate

compounds, shape-selectivity was reported by forming microporous materials with adequate counter-cations [30b, 58].

Conclusions from a review of Mizuno *et al.* [30b] on homogeneous polyoxometalates summarize perfectly the interest of this thesis: *"Heterogeneous catalysts are more desirable than the homogeneous catalysts. To synthesize heterogeneous catalysts based on polyoxometalates for the liquid-phase oxidation, the following items (1) and (2) are important.*

(1) Supporting polyoxometalates on an appropriate support without loss of the intrinsic activity and selectivity is interesting.

(2) Complexation of polyoxometalates with appropriate cations to form micro/meso structures would lead to the appearance of shape-selectivity."

In the present work, we argue that hybridization is the heterogenization strategy which can lead to the incorporation of these two properties into a solid catalyst. The organization of the organic part is assumed to confer new specificity and selectivity properties to the solid POM-based catalyst. This could for instance occur via the organization of a polymeric support around the active sites to mimic the enzyme protein arm function. This organization would impose geometrical constraints to control the reaction of the catalytic inorganic partner. This tuned behavior of the physicochemical properties could lead to produce highly specific and selective heterogeneous catalysts.

Furthermore, after the heterogenization and specificity properties, a third interest with the use of an organic environment is the expectation of the induction of specific adsorption properties of reagents to the hybrid catalyst. In fact, adsorption and desorption control is another way to modulate the catalyst specificity, activity and selectivity. The specific adsorption capability of polymers was already observed in gas phase as in liquid phase [81] and finally, their application as support in catalysis was already proven [82].

7. OBJECTIVES

As exposed in the previous section, the feasibility of polyoxometalate hybridization applied in catalysis has already been proven. Yet, in the present work, in addition to an efficient heterogenization route of homogeneous species, we will tend to demonstrate that hybridization of polyoxometalate species can lead to remarkable properties in catalysis. The objectives of the thesis can be summarized in the following three points.

(i) Polyoxometalate heterogenization via hybridization

The first objective will be to find an ideal organic support for the hybridization of polyoxometalate species. These species and thus the hybrid catalysts formed must be active in epoxidation reactions in liquid phase. They should answer for all of the beneficial characteristics of heterogeneous catalysts: active with easy recovery and recyclability without deactivation.

(ii) Modulate catalyst activity via hybrid polarity

In catalysis, the main goal of a support is 'simply' to support and disperse the active phase onto its surface. This point of view could be judged as archaic. Indeed, the support is still sometimes wrongly considered as inert in the reaction whereas it in reality plays an important role on the catalyst activity and can take part in the reaction mechanism [83]. In alkene epoxidation reaction, the support polarity would impact on the specific alkene adsorption and epoxide desorption. Such a specificity could be induced through the presence of hydrophilic/hydrophobic organic environment around the active polyoxometalate species. In this work, the influence of the organic support polarity, namely that of the polymer host matrix, on the catalyst adsorption properties will be studied in epoxidation reactions in liquid phase.

(iii) Induce shape-specificity

Finally, the use of heterogeneous catalysis in liquid phase becomes more and more common. But the main drawback of these catalysts is still the control of the specificity of the reaction [21]. Heterogenization of highly specific homogeneous catalysts is thus clearly justified. Unfortunately, polyoxometalates possess poor specificity properties. To induce specificity properties, the morphology of the catalyst could play a crucial role. The last objective of this work will be focused on the impact and valorization of catalyst structuration and organization to confer shape-specificity properties on the catalyst.

8. STRATEGY

Three objectives were set in the previous paragraph. Logically, to reach the first objective, the most determinant choices are the selection of the active polyoxometalate species in oxidation reaction, and the selection of an appropriate organic support to immobilize these inorganic species. Hybridization of polyoxometalates is well documented in the literature and is obviously not only limited to catalytic applications [84]. Two classes of organic-inorganic hybrid composites can be defined according to the nature of the interaction between the organic and inorganic components [84a, 85]. The first class (class I) assembles all of the systems where no covalent bonds are shared between the organic and the inorganic parts. Thus, only electrostatic interactions, hydrogen bonds, or van der Waals interactions are involved. The second class (class II) gathers the organic and inorganic species held together via covalent bonds. The second class is an elegant way to form heterogeneous catalysts. Nevertheless, to achieve a hybridization by covalent bonding without modifying the intrinsic activity of the catalyst species is not evident. Therefore, class I appears the most appropriate strategy to immobilize the anionic POM clusters inside an organic matrix without perturbation of the catalyst performance. The best organic support for these nanometric anionic inorganic clusters is thus a polycationic polymer. According to the literature [52d], the strength of the electrostatic interactions would be enough to avoid the leaching of the species in the reaction medium.

The use of cationic surfactants would have been considered but cannot guarantee the formation of a unique insoluble material as suspected for polymeric matrixes.

The second objective deals with the possibility to tune the adsorption properties of the new hybrid catalysts. The hydrophilic/hydrophobic character of the catalyst was claimed to have a drastic impact on oxidation reactions in liquid phase. The matrix polarity would have to be tunable to screen the matrix polarity effect on the reaction. This can be achieved by changing the chemical composition of the monomers in order to influence the polymer polarity, and *in fine*, the whole hybrid catalyst polarity.

Finally, by the third objective, it is expected that the organization of the inorganic species inside the organic materials may confer to the hybrid catalyst shape-specificity properties. To induce and control the morphology of the catalyst, we can take advantage of a support already structured or self-assembled. The self-assembling properties of a polymer may allow to form three-dimensionally organized catalysts during the insertion of the active species. This may confer shape-specificity properties on the catalyst.

To probe the performance of these new catalysts, a simple oxidation reaction must be considered. Easy to handle and interesting from an industrial point of view, the epoxidation of alkenes to form valuable epoxide products is selected.

9. EXPERIMENTAL STRATEGY

Based on the assumptions exposed in the previous part, the following experimental strategy was undertaken.

(i) Choice of the polyoxometalate species.

The literature survey suggests that polyoxometalates formed with tungsten and phosphorous atoms are largely considered as one of the best active polyoxometalate catalysts in oxidation reaction.

Thus, in a first stage, the highly stable Keggin $[PW_{12}O_{40}]^{3-}$ species was selected as model clusters to study the hybrid formation. In a second stage, different polyoxometalate species were employed and inserted to form the novel hybrid catalysts tested in liquid phase reaction. These species are the Keggin $[PW_{12}O_{40}]^{3-}$, the lacunary $[PW_{11}O_{39}]^{7-}$ and the well-known peroxo species, called the Ishii-Venturello anion $[PW_4O_{24}]^{3-}$ [42, 45, 54a].

(ii) Choice of the matrix

In order to meet all of the conditions required by the organic matrix, a polycationic self-assembled polymer was selected. The chosen matrix was formed by the homopolymerization of substituted diallylamine monomers [86] (Fig. I-6a). At low solution pH, the protonation of the amine function induces a polycationic character to the matrix. The polycationic character of this homopolymer is indeed crucial to guarantee the electrostatic interactions between the polymer and the polyoxometalate anions. Moreover, the diallylamine monomer bears an alkyl side chain composed of 6, 12 and 18 carbon atoms. Two effects are attributed to the presence of these chains. On the one hand, they are responsible for a supramolecular organization of the matrix in a comb-like polymer structure (Fig. I-7). This organization is needed to confer to the hybrid catalyst shape-specificity properties. On the other hand, the length of these alkyl side chains would allow to control the hydrophilic/hydrophobic character of the matrix and thus, the polarity of the hybrid catalysts.

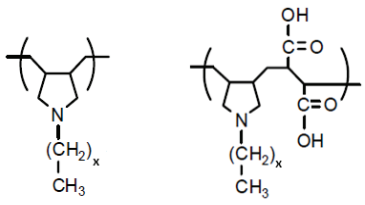

Figure I-6 – Ideal schematic representation of the two repeating units of the polymeric matrixes used as supports for hybrid catalysts. The alkyl side chains are composed of 6, 12 or 18 carbon atoms (x = 5, 11 or 17 respectively). (a) Homopolymers and (b) Copolymers.

In addition to these hydrophobic chains, the adsorption properties of the organic support were tuned by modifying the repeating unit of the polymer. The addition of a second monomer constituted of maleic acid in the repeating unit would increase the polarity of the polymer backbone (Fig. I-6b). The resulting copolymer still conserves a supramolecular structure. The repeating unit of the homopolymer and the copolymer are presented in Figure I-6.

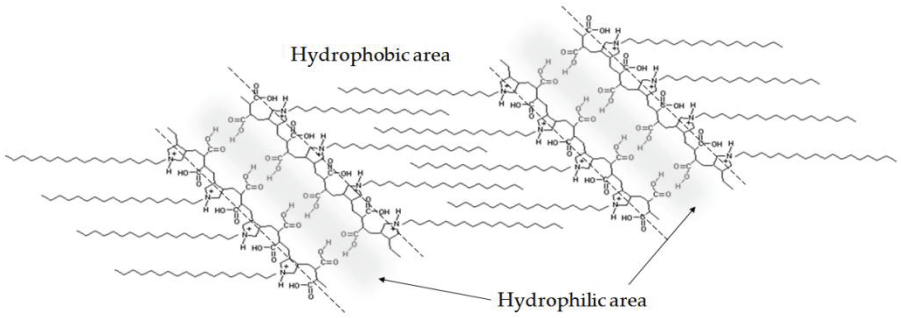

Figure I-7 – Schematic representation of the supramolecular self-organization of the polymer matrixes used in this project. Here the copolymer matrix bearing octadecyl alkyl side chains is represented (inspired from [86]).

To summarize, these matrixes possess (i) positive charges to fix the inorganic anions, (ii) a supramolecular organization to structure and arrange three-dimensionally in space these inorganic species and (iii) a tunable hydrophilic/hydrophobic balance to modulate their polarity.

(iii) Choice of the catalytic reaction

Concerning the catalytic application, cyclooctene epoxidation is often used in the literature to probe the activity of catalysts in the epoxidation reaction [87]. Consequently, the cyclooctene epoxidation was selected as the main probe reaction. In this study, the epoxidation was carried out in a monophasic medium composed of hydrogen peroxide as oxidizing agent and acetonitrile as solvent. Hydrogen peroxide is a cheap and easy to handle oxidant. Furthermore, water is the only coproduct [88]. Figure I-8 gathers the most likely reactions involving the cyclooctene molecule in the presence of H_2O_2 and a catalyst The oxidation of the alkene forms mainly the epoxide but allylic oxidation can occur and produce the corresponding allylic alcohol and allylic ketone [89]. Also, the alkene can be oxidized by breaking the

double bond and form aldehyde, and then carbonyl compounds [90]. Besides, polarity and ring strain of an epoxide make the oxirane ring highly reactive [32b]. In acidic conditions, the epoxide can rearrange to form a ketone or, suffer hydrolysis to give a diol [89]. Over-oxidation of the diol could produce hydroxyketone [89]. Finally, before the alkene oxidation, acidic conditions in water can favor the alcohol formation from the alkene and a further catalytic oxidation could induce the formation of a carbonyl compound [91].

Although all these reactions are imaginable, the particular stability of the cyclooctene allows to reach high selectivity in epoxide and prevents allylic oxidations [92]. Also, as the stability of an epoxide is governed by both steric and electronic effects, the cyclooctene epoxide stability is enhanced by the steric hindrance of the ring [34].

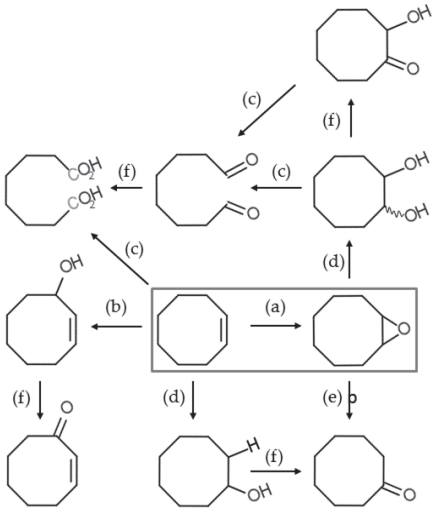

Figure I-8 – Schematic representation of the cyclooctene reactivity in the presence of H_2O_2 and a catalyst in acidic conditions. (a) epoxidation (main reaction), (b) allylic oxidation, (c) oxidative cleavage, (d) electrophilic addition of water, (e) acid catalyzed rearrangement, (f) over-oxidation reactions.

Acetonitrile was selected to facilitate the discussion. Indeed, although biphasic systems lead more favorably to higher selectivity, transfer limitation between the two phases could occur. Consequently, in biphasic conditions, the effect of the catalyst polarity would impact on both the reactant adsorption properties and the catalyst phase transfer. In the selected monophasic condition, only the desired adsorption properties of the catalyst were probed.

Finally, preliminary results showed that 50 °C and an excess of H_2O_2 were useful to favor the reaction rate. The adsorption and shape-selectivity properties of the catalysts were further probed by using different alkenes and solvents.

10.STRUCTURE OF THE THESIS

To reach the thesis objectives, a linear path during my research was followed. No iterative process between catalyst synthesis and catalyst performance was employed. Results and discussions learnt from this thesis are summarized in two parts. A first part debates about hybrid synthesis, hybrid characterization and understanding of hybrid formation and organization. The second part is focused on the catalytic application of hybrids in epoxidation reaction.

Before the study of the catalytic potential of the hybrids, their synthesis and their physicochemical properties must be understood. Thus, in the **first Chapter**, the organic constituent of the future hybrids is investigated in terms of its polyelectrolyte character, polarity and self-assembling properties. These properties were highlighted by characterization techniques as Infrared, X-Ray diffraction and water contact angle measurements. Then, in **Chapter 2**, based on these investigations, the hybrid synthesis is attempted with Keggin polyoxometalates as the inorganic constituents of the hybrids. Keggin species insertion was selected as hybrid synthesis model because these species are easily purchased and highly stable. Different physicochemical characterizations are carried out to understand the mechanism and the constraints linked to the hybrid formation. In oxidation reactions with polyoxometalate species, peroxo species are the best active clusters. In **Chapter 3**, according to the results obtained from the previous chapter, the best synthesis method is applied to insert the peroxo species into the organic matrixes and form the hybrid catalysts used in the second part of this thesis. Physicochemical characterization of these new materials is performed and discussed to identify the hybrid structure and the nature of inorganic species inserted.

A first screening of the hybridized active species in the epoxidation reaction is achieved in **Chapter 4**, as the first chapter of the catalytic part. Activity, recovery and recyclability properties of hybrid catalysts are studied in this chapter. **Chapter 5** discusses the influence of the support polarity on the cyclooctene epoxidation reaction performance.

A kinetic study is made to highlight the key parameters of the mechanism steps. Effect of the catalyst hydrophobicity is debated in this chapter. To conclude this second part, a further investigation of the matrix polarity is undertaken. A study of the influence of the solvent polarity and the alkene adsorption, shape and morphology was performed in **Chapter 6 and Chapter 7** respectively. This last chapter is dedicated to look over the shape-specificity properties of hybrid catalysts.

Finally, in a third part, a global conclusion gathers the main discoveries or remarks learnt from this research.

PART III

GENERAL CONCLUSION…

Polyoxometalates (POMs) are constituted by early transition metals in their highest oxidation state and form oxo anionic clusters. They have especially received much attention in the area of catalysis because their chemical properties such as redox potentials, acidities, and solubilities can be tuned by an appropriate choice of the constituting elements. Their efficient redox behavior makes of POMs highly efficient homogeneous catalysts in oxidation reactions. Yet, homogeneous systems share common drawbacks. As the catalyst is in the same phase as substrates and products, the catalyst/product separation and catalyst reuse are difficult. Moreover, in the case of POMs, these species do not possess specific adsorption and shape-specificity properties.

This project aimed at conferring to polyoxometalate catalyst, heterogeneous properties for easier and more valuable catalytic application. The selection of the appropriate support for the POM species heterogenization constituted the originality of this research. It was a polycationic organic matrix possessing a self-assembled supramolecular organization. In the present work, it was argued that electrostatic hybridization of anionic inorganic POMs with a polycationic organic support would be a suitable heterogenization strategy leading to the formation of efficient heterogeneous catalysts. But further improvements and more valuable effects were also targeted thanks to this method. First, the use of an organic environment as support was expected to allow the induction of specific adsorption properties of the reagents. Second, the geometrical constraints imposed by the organization of the organic part were assumed to control the reaction of the catalytic inorganic partner and confer new specificity and selectivity properties to the hybrid catalysts. The three main objectives of the work could thus be gathered as to (i) form efficient heterogeneous catalysts, (ii) incorporate specific adsorption properties and (iii) confer shape-specificity properties to the catalyst.

To reach these objectives, the adopted strategy first focused on the study of the selected homemade organic matrixes. Second, the synthesis of hybrid materials and their physicochemical characterization were investigated. Then, the final part assessed the hybrid materials as heterogeneous catalysts in epoxidation reactions.

The selected polycationic self-assembled polymer is formed by the homopolymerization of substituted diallylamine monomers. At low solution pH, the protonation of the amine function induces a polycationic character to the matrix. The polycationic character of this homopolymer is indeed crucial to guarantee the electrostatic interactions between the polymer and the polyoxometalate anions. Moreover, the diallylamine monomer bears an alkyl side chain composed of 6, 12 and 18 carbon atoms. Two effects are attributed to the presence of these chains. (i) On the one hand, they are responsible for a highly crystalline organization of the alkyl side chains, as observed by XRD and FTIR analyses. This crystallization is dependent on the carbon atom number constituting the alkyl chain. The more is the carbon number, the higher is the quality of the crystalline organization. However, in spite of the alkyl side chain packing, the polymer backbones of this homopolymer matrix are not arranged in a supramolecular organization. (ii) On the other hand, the different lengths of these alkyl side chains are responsible for the hydrophilic/hydrophobic character of the matrix. Water contact measurements confirm that the length of the chains is determinant on the polymer polarity: the longer is the chain, the higher is the polymer hydrophobicity (6 carbons < 12 carbons < 18 carbons).

Finally, in addition to these hydrophobic chains, the adsorption properties of the organic support were tuned by modifying the repeating unit of the polymer. The addition of a second monomer constituted of maleic acid in the repeating unit aimed at increasing the polarity of the polymer backbone. The effect of the polyampholytic character of the polymer backbone on the polymer charge state was determined by FTIR analysis. A pH lower than 2 is needed to ensure a polycationic character of the copolymer matrixes. Besides, XRD analysis reveals a supramolecular organization in a comb-like structure for the copolymer matrixes. This organization can be described as an alternation of hydrophilic backbone regions and hydrophobic alkyl chain regions.

After the matrixes study, two well-known homogeneous catalysts in oxidation reaction were successfully inserted inside the organic matrixes: the anionic polyoxometalate Keggin $[PW_{12}O_{40}]^{3-}$ (PW12) and the anionic peroxo Ishii-Venturello $[PW_4O_{24}]^{3-}$ (PW4) species.

At acidic pH, however, the stability of the PW4 is deteriorated and they undergo modification in solution. Consequently, a mixture of peroxo species was inserted during the synthesis of the PW4 hybrid materials.

Concerning the organization of the synthesized hybrid materials, the initial idea was to take advantage of the self-assembled structure of the organic matrixes to form organized hybrid materials. But both Keggin $[PW_{12}O_{40}]^{3-}$ or Ishii-Venturello $[PW_4O_{24}]^{3-}$ species induce a complete reorganization of the matrixes during the hybridization. The recovered solid hybrids can be classified as amorphous with a random distribution of the inorganic species throughout the organic matrixes. The encapsulation is governed by the electrostatic interactions of the polymer backbone charges around the inorganic clusters. The insertion and the organization of the hybrids are independent on the alkyl side chain length of the matrixes.

Once the hybrid synthesized, the heterogeneous catalytic properties of the hybrids were studied in the cyclooctene epoxidation reaction. The two classes of hybrid catalysts, namely the $[PW_{12}O_{40}]^{3-}$ and $[PW_4O_{24}]^{3-}$ hybrids, and their homogeneous counterparts, were compared. The peroxotungstophosphate cluster ($[PW_4O_{24}]^{3-}$) shows the highest activity in cyclooctene epoxidation reaction with hydrogen peroxide. Despite being slightly less active than homogeneous PW4 species, PW4 hybrids catalyze the epoxidation of cyclooctene with remarkable heterogeneous properties. Firstly, hybridization by electrostatic interactions is the key point which stabilizes heterogenized active species and prevents leaching under epoxidation conditions. Second, hybrid catalysts exhibit easy recovery and remarkable reusability. Third, protection against deactivation of PW4 species is brought by their immobilization inside the organic matrix.

Yet, as a mixture of peroxo species are hybridized, all these immobilized species are not or faintly active and their activation with hydrogen peroxide prior the epoxidation reaction is required. The reaction rate constants of this chemical catalyst transformation and the epoxidation reaction were determined by a kinetic modeling approach. The determination of these reaction rate constants highlights the influence of the hydrophilic/hydrophobic character of the matrixes on the hybrid catalyst

activity. In fact, while a hydrophilic matrix is needed to favor the activation of the polyoxometalate species with H_2O_2, high hydrophobicity promotes the epoxidation reaction rate and the epoxide selectivity. Thanks to cyclooctene adsorption experiments with the QCM technique, it is demonstrated that the best cyclooctene affinity is obtained with hydrophobic matrixes. Thus, the adsorption of cyclooctene on the hydrophobic catalyst surface is determinant for high catalytic performance. This adsorption specificity is underlined via the use of different cycloalkene molecules. Indeed, high adsorption appears for more apolar molecules, i.e. the longest cycloalkenes. Finally, the importance of the alkene adsorption on the epoxidation reaction is confirmed via the use of solvents with different polarities. Polar solvents are required to favor the alkene adsorption onto hydrophobic catalysts and to enhance the activity of the hybrid materials. The importance of the alkene adsorption allows to claim the existence of a Langmuir-Hinshelwood mechanism in the epoxidation reaction with hybrid catalysts.

In addition to facilitate the alkene adsorption, hybrid catalysts allow a further improvement in comparison with homogeneous active species. Actually, the organic matrix also controls the epoxide desorption. That avoids epoxide ring-opening, over-oxidation processes or over adsorption, giving rise to high selectivities to the desired epoxide without catalyst deactivation. This effect appears to be mainly obtained with the most hydrophobic matrix. The solvent also affects the selectivity. Lower epoxide selectivity is obtained for the homogeneous catalyst when a polar solvent is used. Inversely, polar solvents favor higher epoxide selectivity for the hybrid catalysts. It is claimed that the hydrophobic surface of the hybrids promotes the epoxide desorption into a polar medium, avoiding side reactions.

Finally, in addition to specific adsorption properties, the hybridization of these species induces the presence of steric limitation toward alkenes, allowing to envisage the presence of shape-specificity properties. The steric effect of the polymer chains indeed affects the diffusion of bulky molecules and decreases their reactivity. This effect is accentuated for hybrids possessing shorter alkyl side chains.

At the end of this research, polyoxometalate hybrid materials prove to be relevant materials for an application as heterogeneous catalysts. Results highlight the interest and the importance of hydrophobic catalysts in the cyclooctene epoxidation reaction. More than that, our observations validate the Sabatier principle and the crucial importance of an optimal reactant adsorption on the catalytic performance. The use of an organic matrix as support appears beneficial to modulate the catalyst polarity, and thus, the adsorption affinity. It can be postulated that this strategy can be implemented to other catalytic systems. Nevertheless, the lack of control of the hybrid catalyst organization and morphology is certainly the drawback of this electrostatic immobilization technique. Indeed, the strength of the electrostatic interactions, essential for the POM anchoring, actually appears too strong and dictates a reorganization of the organic matrix. This induces an encapsulation of the species, and inaccessibility for a part of them. In order to keep the intrinsic activity of POMs and allow a better control of the catalyst shape-specificity properties, encapsulation into well-defined inorganic support, as for instance zeolite, would be required. Organic functionalization of the support would lead to a control of the catalyst adsorption properties. This would combine, into a unique catalytic material, adsorption and shape-specificity properties.

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1. ARTICLES

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4. MASTER THESIS

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