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CRITICAL REVIEW

Non-hydrolytic sol–gel routes to heterogeneous catalysts

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Oxides and mixed oxides have a tremendous importance in the field of heterogeneous catalysis, serving either as catalysts or as supports for active species. The performance of a catalyst depends directly on its composition, texture, structure and surface properties, which have to be precisely controlled and adapted to each application. In this context, the sol–gel process is a unique tool for the preparation and understanding of catalytic materials, owing to its exceptional versatility. In the last 10 years, the non-hydrolytic sol–gel (NHSG) or non-aqueous sol–gel process based on nonhydrolytic condensations in nonaqueous media has established itself as a simple and powerful method for the design of a wide range of oxide, mixed oxide and hybrid materials with controlled composition, morphology, texture and structure. NHSG proved particularly interesting for the preparation of catalytic materials, notably mesoporous xerogels, single site catalysts and highly crystalline nanoparticles. This *critical review* addresses the application of NHSG to the preparation of heterogeneous catalysts, emphasizing the specificities of this process, and giving a comprehensive overview of the literature (251 references).

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1. Introduction

Oxides and mixed oxides have a tremendous importance in the field of heterogeneous catalysis, serving either as catalysts themselves or as supports for other catalytically active species (metallic nanoparticles, oxides, organometallic compounds, enzymes, etc.).^{1–3} Oxides are selected for their thermal and chemical stability, mechanical strength when used as supports and also for their intrinsic activity (acidic, basic, redox) when used as catalysts. As the catalytic act occurs at the surface of



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the catalyst, high surface area is generally sought for. Controlling the pore size is also important, since for a porous catalyst the diffusion rate of the reactants and products is a function of the pore size. In the case of mixed oxides, the catalytic properties do not vary linearly with the average composition but strongly depend on the level of homogeneity.

In this context, it is not surprising that the conventional sol–gel process, based on the formation of oxo bridges by hydrolysis and polycondensation of molecular precursors,^{4–6} has been so successful in the preparation and understanding of catalytic oxide materials.^{7–12}

Indeed, sol–gel chemistry can offer several decisive advantages, notably:

- (i) high purity of the materials and precise control of the composition,
- (ii) control of the structure and homogeneity at the molecular level,
- (iii) control of the texture.

The unique versatility of sol–gel chemistry is due to the large number of adjustable parameters, including nature and concentration of precursors, water amount, temperature, solvent, catalysis, aging and drying conditions. However, achieving simultaneous control of composition, homogeneity and texture in mixed oxide materials is not straightforward and often requires complicated, time-consuming or expensive procedures. The first problem encountered in conventional sol–gel is the disparity in the reaction rates of the different sol–gel precursors. Indeed, the homogeneity in multi-component systems is directly related to the hydrolysis and condensation rate of each precursor, and the reactivity of the different precursors has to be matched to obtain a homogeneous mixed oxide gel. This can be done by different methods, such as acidic prehydrolysis of the less reactive precursors (often the silicon alkoxide precursors)¹³ or chemical modification of the most reactive ones (usually the metal alkoxide precursors) with acetic acid or acetylacetone for instance.¹⁴ A second major problem is the collapse of the pore network when the gels are dried by evaporation. This collapse, which is due to capillary forces, can be avoided using for instance supercritical drying,¹⁵ or solvent exchange and derivatization of the hydroxylated surface by silylation before the evaporation step.¹⁶ Another approach relies on the use of templating agents to prepare ordered mesoporous materials.^{17,18} This strategy can be advantageously combined with aerosol processing to allow multi-scale texturation.^{19,20} The versatility and complexity of conventional sol–gel are well illustrated by the example of amorphous mesoporous titania–silica mixed oxides, which have attracted considerable attention as alternatives to micro-porous titanosilicalite epoxidation catalysts (see Section 3.1.1).

In the last two decades, several alternative sol–gel routes were proposed, in which the oxo bridges originate from oxygen-donors other than water (*e.g.* alkoxides, ethers, alcohols...), and the term “non-hydrolytic sol–gel” (NHS) was coined by Vioux and coworkers.^{21–23} The NHS chemistry involves completely different condensation reactions and non-aqueous media, which significantly affects the texture, homogeneity, and surface properties of the resulting materials. Recent reviews have been published on the application of non-hydrolytic sol–gel routes to the preparation of oxides,^{24,25}

organic–inorganic hybrids,^{26,27} oxide nanoparticles,^{28,29} thin films by atomic layer deposition^{30,31} and nanostructures.^{32,33}

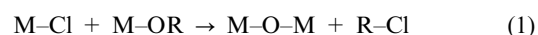
In the present review we wish to address the application of a NHS process to the preparation of heterogeneous catalysts and give a comprehensive overview of the literature emphasizing the specificities of this process and the reactions catalyzed. Our aim is to provide better understanding of the potentialities offered by NHS routes for addressing the major problems encountered in conventional sol–gel in the preparation of catalytic materials, while keeping particularly simple and cost-effective procedures.

2. Non-hydrolytic sol–gel chemistry

2.1. Basic reactions

Sol–gel syntheses are considered as non-hydrolytic when the oxygen donor is not water, and when water is not generated *in situ*. In the past 20 years, several non-hydrolytic syntheses of oxides and mixed oxides have been described, involving the reactions of precursors (chlorides, alkoxides, acetylacetonates, *etc.*) with oxygen-donors (alkoxides, ethers, alcohols, acetates, aldehydes, ketones, *etc.*). The reactions involved and their proposed mechanisms have been detailed previously in several reviews.^{24,25,34} Here we will focus on the reactions which were involved in the preparation of catalytic materials.

2.1.1. Alkyl chloride elimination. The NHS routes used to prepare catalytic materials were in most cases based on the reaction of chloride precursors with either alkoxide, ether or alcohol oxygen donors, accompanied by the elimination of alkyl chloride. The reaction between a metal chloride and a metal alkoxide (“*alkoxide route*”) directly leads to the formation of oxo bridges, with elimination of alkyl chloride (eqn (1)):



In the case of metals and transition metals, this non-hydrolytic condensation reaction takes place at mild temperature (80–150 °C) with simple primary or secondary R groups. The reaction rates are thus much lower than in conventional sol–gel. The reactivity is even lower in the case of silicon and catalysis by Lewis acids such as FeCl₃ or AlCl₃ is required;³⁵ otherwise, *tert*-butyl or benzyl groups are needed.³⁶ In all cases, one must keep in mind that the first reactions that take place when chloride and alkoxide precursors are mixed are ligand exchange (or redistribution) reactions leading to a mixture of chloroalkoxides, which are thus the true precursors in this non-hydrolytic condensation.

In the “*ether route*”, formation of oxo bridges involves in a first step the *in situ* formation of alkoxide groups (eqn (2)) by reaction of chloride groups with an organic ether (often diisopropyl ether, ¹Pr₂O), which react in a second step with chloride groups according to eqn (1).



The alkoxide and ether routes have been used for the preparation of a wide variety of metal oxides.^{22,35–38} They have proven particularly useful for the synthesis of mixed oxides with an excellent control over their homogeneity and their texture.^{21,39–43} They also provided simple and effective

syntheses of oxide nanoparticles, with or without capping agents.^{44–46}

In the “*alcohol route*”, the reactions involved depend on the nature of the alcohol. Primary and secondary alcohols lead to the *in situ* formation of alkoxide groups (eqn (3)), which react in a second step with chloride groups according to eqn (1):



Tertiary and benzylic alcohols can also lead to the *in situ* formation of hydroxyl groups (eqn (4)), which react in a second step with chloride groups according to eqn (5).⁴⁷ In addition, the HCl released (eqn (3) and (5)) may catalyze secondary reactions, leading to complex pathways.

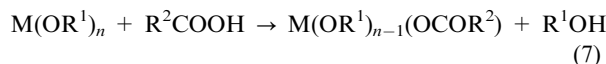


The alcohol route has been much less investigated for the preparation of oxides and mixed oxides than the alkoxide and the ether routes. However, the reaction of chloride precursors at 40–175 °C in benzyl alcohol used as a solvent, oxygen donor and capping agent (“*benzyl alcohol route*”) has proven highly successful for the synthesis of crystalline oxide nanoparticles.⁴⁸ This route has been later extended to other precursors, such as metal alkoxides or acetylacetonates. Higher temperatures (between 200 and 250 °C) are then required. The reactions involved depend on the nature of the precursor and can involve the elimination of dibenzylether or complicated C–C bond formation reactions with elimination of 4-phenyl-2-butanol or 1,2-diphenylethanol for instance.^{34,49}

2.1.2. Ester elimination. The condensation between metal carboxylates M(OCOR)_x and metal alkoxides M'(OR')_y (eqn (9)) in nonpolar, aprotic solvents directly leads to the formation of oxo bridges and has been proposed as a general sol–gel route to (mixed) metal oxides.^{50,51}



The reaction of alkoxide precursors with carboxylic acids is not strictly non-hydrolytic, as water is most likely generated *in situ* by reaction of the acid with alcohol formed in a first step by the exchange of carboxylate and alkoxy groups (eqn (7) and (8)).



Nevertheless, formic acid⁵² or acetic acid^{53,54} was successfully used for the synthesis of silica or hybrid materials. Hyeon and coworkers used the reaction between titanium tetraisopropoxide and oleic acid at 270 °C to produce TiO_2 nanorods in multi-gram amounts.⁵⁵ The reaction of alkoxide precursors with carboxylic acids is particularly interesting for sol–gel synthesis in unusual media, such as perfluoro solvents,⁵² ionic liquids,^{56–58} or supercritical CO_2 (scCO_2).^{59,60}

Conversely, the reaction of metal or silicon alkoxides with an acid anhydride (eqn (9)) leads to the *in situ* formation of carboxylate groups, which can then condense with

alkoxide groups (eqn (6)), providing a truly non-hydrolytic (and hydroxyl-free) sol–gel route.



This “*anhydride route*” was successfully used to prepare titania (in the presence of TiCl_4 catalyst),⁶¹ silica–titania mixed oxides⁶² and titania photocatalysts.⁶³

2.1.3. Thermal decomposition. In the former non-hydrolytic routes, the complexity of the reaction pathways increases with the reaction temperature, as expected if one keeps in mind that precursors, intermediate compounds and oxide products can act as catalysts in various reactions such as dehydrohalogenation, polymerization, oxidation, or thermal decomposition of the precursors.

For instance, alkoxide precursors usually decompose above 250–300 °C by alkene elimination and formation of hydroxyl groups, which then condense with other alkoxide groups to form oxo-bridges with elimination of alcohol. The hydroxyl groups may also condense with each other, leading to the formation of water; however, as long as M–OH self-condensation is prevented by kinetics, these thermal decomposition reactions can be considered as non-hydrolytic. Thus, several non-hydrolytic routes based on the rapid thermal decomposition at relatively high temperature of various precursors (alkoxides, acetates, acetylacetonates, chlorides, *etc.*) have been proposed, notably for the preparation of nanoparticles. These reactions are usually performed in hot surfactant solutions (trioctylphosphine oxide, oleic acid, oleylamine, *etc.*), providing size and also shape control of the nanoparticles.^{44,64,65–68}

Tri-*tert*-butoxysiloxy derivatives $\text{M(OR)}_n(\text{OSi(O}^t\text{Bu)}_3)_n$ decompose at relatively mild temperatures (100–180 °C) and have been used to prepare mixed metal oxides^{69–71} by thermolysis. They have also been used for grafting isolated catalytic species at the surface of silica supports.^{72,73} This route has been included in the present review, although both isobutylene and water may form in these reactions.⁶⁹

2.2. Characteristics of NHSG routes

Compared to conventional hydrolytic sol–gel routes, NHSG routes feature completely different reactions and reaction conditions, which significantly affect the surface chemistry, the homogeneity and the texture of the resulting oxide materials.

2.2.1. Reaction medium. The first characteristic of NHSG routes is that they take place in a non-aqueous medium, ideally anhydrous. NHSG syntheses can be performed either in an organic solvent or in the oxygen donor itself (*e.g.* benzyl alcohol), and in some cases in the absence of solvent (*e.g.* when the precursors are liquids as in the case of silicon and titanium alkoxides and chlorides).

2.2.2. Surface chemistry. In the case of the alkoxide, ether and anhydride routes, the reactions do not involve the formation of hydroxyl groups. Thus, in the absence of secondary reactions and before calcination or exposure to ambient air, the residual surface groups are not hydroxyl groups but chloride, alkoxide or acetoxy groups. For instance, silica-based and metal oxide

nanoparticles terminated by chloride and isopropoxide groups were obtained recently using the ether route; their surface chemistry makes these nanoparticles organosoluble in the absence of surfactants and reactive toward water, alcohols or hydroxylated surfaces.^{46,74,75} Even in the alcohol route, the hydroxyl content appears much lower than in conventional sol–gel.⁷⁶ In the benzyl alcohol route, the surface of the nanoparticles appears to be capped by adsorbed benzyl alcohol molecules which prevent the agglomeration of the particles and make them organosoluble.⁷⁷

2.2.3. Reaction kinetics. Generally speaking, NH reactions feature easily controllable kinetics. Thus, there is no need to use reactivity modifiers or elaborated procedures to avoid the formation of precipitates even in the case of metal oxides. The reaction rates around different metal precursors appear much less sensitive to the nature of the metal, which facilitates the preparation of homogeneous mixed metal oxide systems^{24,40,77,78} and metastable phases.^{41–43}

Although the reactions around silicon tend to be too slow, their rate can be easily increased using a Lewis acid catalyst. This is particularly important in the preparation of silicates $\text{SiO}_2\text{--MO}_n$ ($M = \text{Ti, Zr, Al, etc.}$): in this case the metal species efficiently catalyze the reactions around silicon, leading to a leveling of the reaction rates of silicon and metal precursors. As a consequence, NH condensation routes are especially interesting for the preparation of homogeneous silicates $\text{SiO}_2\text{--MO}_n$.

Microwave heating offers interesting perspectives for the control of NH reactions kinetics, particularly for the preparation of nanoparticles. Microwave chemistry is widely used in organic synthesis.⁷⁹ Although there are much less examples in materials synthesis, the use of microwaves in the synthesis of materials is gaining importance and a wide variety of materials and nanomaterials were prepared using microwave heating, including carbides, nitrides, oxides, chalcogenides, phosphates and metals.^{80–82} Microwave-assisted synthesis is generally considered much faster, cleaner, and more economical than the conventional methods.⁸³ Recently, Niederberger and co-workers have applied microwave heating to the NH synthesis of highly crystalline NP by the benzyl alcohol route.^{81,84,85} Microwave irradiation significantly accelerates nanoparticle production, by increasing the rate constants for the condensation rate and the crystal growth. There is no doubt that microwave heating will prove particularly useful for the production of catalysts by NH routes, as it is already the case for syntheses in aqueous media.⁸⁶

2.2.4. Control of structure and morphology. One important consequence of the moderate reaction rates in NH syntheses is the formation of well-crystallized metal oxides at temperatures lower than that used in aqueous or solvothermal methods. In addition, the versatility of NHSG offers several possibilities for controlling the crystal structure. For instance, in the preparation of titania at 110 °C from TiCl_4 and different oxygen donors, Arnal *et al.* showed that the crystalline form depended on the nature of the oxygen donor: whereas $\text{TiO}(\text{iPr})_4$, iPr_2O , or iPrOH led at 110 °C (and after calcination at 500 °C) exclusively to the formation of anatase, EtOH led to the formation of rutile, and iBuOH led to a mixture of brookite and rutile.⁶¹ The high, molecular scale, homogeneity

in NH mixed oxides allows the formation at low temperature of metastable phases on annealing, as shown in the case of $\beta\text{-Al}_2\text{TiO}_5$,⁹ trigonal ZrW_2O_8 ,⁴² and monoclinic $\text{Ga}_2\text{Mo}_3\text{O}_{12}$.⁴³ Portehault *et al.* recently reported the first NHSG example of lamellar titanates intercalated by tetramethylammonium (TMA) ions.⁸⁷ The synthesis is based on the reaction at 220 °C of TiCl_4 with triethyleneglycoldimethylether (triglyme) as an oxygen donor, in the presence of an $\text{Me}_3\text{N--BH}_3$ (or $\text{Me}_2\text{NH--BH}_3$) complex. BH_3 acts as an amine-sequester, avoiding the formation of a $\text{TiCl}_4\text{--amine}$ adduct. The formation of the titanium-oxo species, as well as the *in situ* formation of the TMA was rationalized on the basis of the analysis of the organic byproducts. The texture of the final material could be tuned by the addition of bulkier trialkylamines, which were not intercalated but apparently stabilized the basal (0 1 0) faces.

In the case of nanocrystals, both the structure and morphology of the particles strongly depend on the synthesis parameters. The adsorption of organic species to the surface plays a major part. These organic species can either be surfactants added in the synthesis^{44,65,68} or, in surfactant-free routes, the organic solvent and/or the oxygen donor (or species formed during the reaction).^{48,74} As a result, crystalline nanoparticles with an impressive variety of sizes and shapes (spheres, rods, platelets, multipods...) were prepared by NH routes, as detailed in former review articles.^{28,29,32,33} Several recent works illustrate the dynamism of this field. Thus, Buonsanti *et al.* reported the selective formation of TiO_2 brookite nanorods by high temperature reaction of TiCl_4 with oleic acid and oleylamine.⁸⁸ A structural transition was observed at a critical titania nanocrystal size threshold: the nanorods with dimensions lower than ~20 nm crystallized in the tetragonal anatase polymorph, whereas the nanorods above ~25–30 nm crystallized in the orthorhombic brookite polymorph. Koziej *et al.*⁸⁹ reported the synthesis of highly crystalline MoO_2 nanorods by reaction of MoO_2Cl_2 in benzyl alcohol–acetophenone mixtures. Depending on the benzyl alcohol-to-acetophenone ratio, various particle morphologies and crystal structures (hexagonal and monoclinic) were formed *via* complex mechanisms. The fast reduction of MoO_2Cl_2 to Mo(IV) initially led to the nucleation of 2 nm spherical MoO_2 particles with hexagonal structure, which aggregated into oriented assemblies. The increase in particle size induced the phase transition from hexagonal to monoclinic form, and finally the transformation into rods. Buonsanti *et al.* reported the formation of hyperbranched TiO_2 anatase nanocrystals by sequential thermal activation of the aminolysis and pyrolysis reactions of titanium carboxylate complexes in mixtures of oleic acid and oleyl amine at 240–320 °C, using a simple multi-injection reactant delivery technique.⁹⁰

The possibility to obtain by NH routes oxides with metastable structures and nanoparticles with such an exquisite control on morphology will continue to stimulate progress in heterogeneous catalysis and photocatalysis (*cf.* Section 3.1.6).

2.2.5. Texture control. As mentioned in the Introduction, a major problem in conventional sol–gel is the collapse of the pore network when the gels are dried by evaporation. NHSG (notably the ether and alkoxide routes) offer extremely simple ways to address this challenging issue, enabling us to prepare high-surface-area, high-pore-volume materials with disordered

pores in the absence of structure directing agents (templates) and without supercritical drying. Several groups have also attempted to prepare materials with ordered mesopores using templates.

Without templates. As in conventional sol-gel processing, the first template is the liquid phase (solvent plus byproducts) trapped in the gel, and pores result from the removal of this liquid phase. The porosity of NH xerogels depends on synthesis parameters, such as concentration, metal precursor, oxygen donor, and catalyst.³⁵ Moreover, non-hydrolytic gels prepared by the alkoxide or the ether route are able to withstand the capillary stresses generated by solvent evaporation and to retain a high pore volume during drying, without using supercritical conditions. This has been ascribed to the high degree of condensation that can be reached using these routes, which confers a high mechanical strength to NH gels compared to hydrolytic ones. In addition, the capillary forces are likely reduced owing to (i) the weak interactions between the surface (terminated by chloride and alkoxide groups) and the liquid phase (*e.g.* the dichloromethane solvent and the isopropyl chloride by-product) and (ii) the low surface tension of the liquid phase compared to water.

Thus, mesoporous xerogels and oxides with controlled textures can be obtained by NHSG methods. For instance, the porosity of amorphous silica-titania xerogels made by the ether or the alkoxide route was shown to be governed by the volume fraction of liquid phase and by the degree of condensation of the gel, enabling fine control of the texture simply by changing the volume of solvent, the reaction time, or the reaction temperature (Fig. 1).⁹¹

By playing on these parameters, mesoporous silica-titania xerogels with specific surface areas as high as $1200 \text{ m}^2 \text{ g}^{-1}$ and pore volumes up to $2.4 \text{ cm}^3 \text{ g}^{-1}$ after calcination can be obtained by the ether route, without any template or resorting to supercritical drying.⁹² Mesoporous crystalline titania-vanadia catalysts with narrow pore size distribution and specific surface areas ranging from 64 to $88 \text{ m}^2 \text{ g}^{-1}$ were prepared in one step by the ether route.^{93–95} In this case, scanning electron microscopy (SEM) images show the presence of spherical particles ($\sim 3 \mu\text{m}$ in diameter) made of an agglomeration of primary nanoparticles of about 20 nm (Fig. 2). The narrow mesopore distribution in these crystalline materials results from the interspace between

the well-calibrated nanoparticles. Mesoporous, amorphous silica-alumina-molybdena catalysts⁹⁶ with specific surface areas around $500 \text{ m}^2 \text{ g}^{-1}$ could be obtained by the same route (Fig. 2). Other examples will be reviewed in Section 3 of this review, in relation to their use in heterogeneous catalysis applications.

With templates. In conventional sol-gel, templating has been used to prepare mesoporous oxides with ordered porosity and narrow pore size distributions. This templating is based on the cooperative self-assembly of surfactants leading to ordered mesostructures that are maintained in the solids after template elimination by calcination or washing. Micelle or mesophase formation is based on hydrophobic/hydrophilic interactions, thus most procedures involve the use of water. The general method proposed by Stucky and co-workers^{97,98} to prepare ordered mesoporous metal oxides (TiO_2 , ZrO_2 , Nb_2O_5 , Ta_2O_5 , Al_2O_3 , SnO_2 , HfO_2 , WO_3 , *etc.*) is based on the reaction of metal chlorides with alcohols in the presence of amphiphilic block copolymers as structure-directing agents. Non-hydrolytic reactions are likely involved in this method even though water (arising from atmospheric moisture, from the solvent and in some cases from the precursors) is present in the process. Actually, it is not clear whether highly ordered mesoporous oxides can be produced by this method using purely non-hydrolytic routes. The materials prepared by this method will not be discussed in this review.

Tilley and coworkers⁷⁰ used the thermal decomposition of *tert*-butoxy(siloxy) derivatives in the presence of block copolymers to obtain mesoporous, multicomponent oxides ($\text{ZrO}_2 \cdot 4\text{SiO}_2$, $\text{Ta}_2\text{O}_5 \cdot 6\text{SiO}_2$, $\text{Fe}_2\text{O}_3 \cdot 6\text{SiO}_2$) with wormhole-like pore structure, and narrow pore size distributions. The templated materials exhibited surface areas and pore volumes ranging from 450 – $550 \text{ m}^2 \text{ g}^{-1}$ and 0.35 to $0.45 \text{ cm}^3 \text{ g}^{-1}$, respectively. However, the untemplated solids showed comparable specific surface areas (415 – $555 \text{ m}^2 \text{ g}^{-1}$) and larger pore volumes (0.7 – $1.0 \text{ cm}^3 \text{ g}^{-1}$).

Highly ordered oxide mesostructures can be obtained in two steps *via* the block-copolymer-assisted assembly of nanoparticle sols prepared by non-hydrolytic routes. Thus tin oxide and cerium oxide nanoparticles obtained using the benzyl alcohol route could be dispersed in THF without the use of any stabilizers. Addition of a polybutadiene-poly(ethylene oxide) block copolymer and evaporation of THF induced

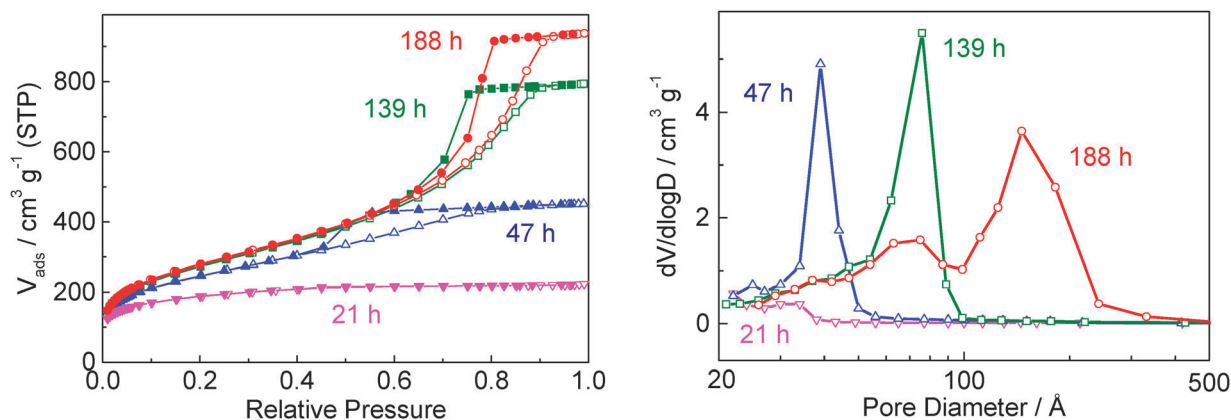


Fig. 1 N_2 physisorption isotherms at -196°C (left) and corresponding pore size distributions (right) of Si-Ti xerogels ($\text{Si/Ti} = 10$) prepared by the ether route at 110°C with different reaction times (redrawn from ref. 91).

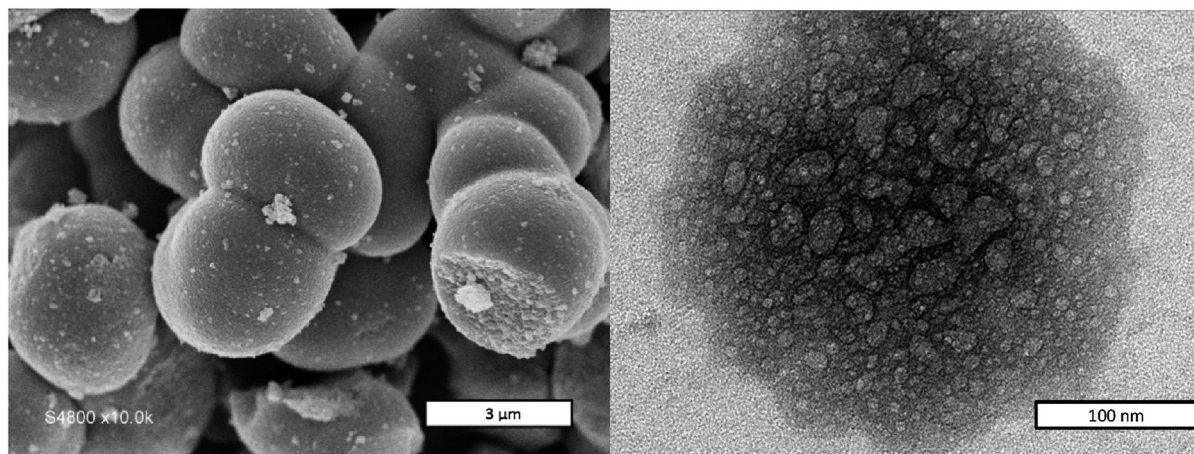


Fig. 2 SEM images of TiV mixed oxide used as VOC total oxidation catalyst⁹³ (left) and TEM image of SiAlMo mixed oxide used as an olefin metathesis catalyst (right).⁹⁶ Both samples were prepared by the ether route and calcined at 500 °C.

the self-assembly of nanocrystals and block copolymer micelles. Highly ordered mesoporous tin and cerium oxides were obtained after calcination.^{99,100}

More recently, Lee, Orilall and co-workers¹⁰¹ reported a direct non-hydrolytic synthesis of highly crystalline mesoporous metal oxides with uniform pores. Their method is based on block copolymers with an unsaturated polyisoprene block that could be converted into an amorphous carbon phase keeping the pores intact during crystallization under an inert atmosphere. Thus, a solution of poly(isoprene-*block*-ethylene oxide) and the metal chloride and alkoxide precursors in an organic solvent is used to cast films which are dried and then heated at 700 °C under argon, in order to induce the crystallization of the metal oxide phase. Finally, the amorphous carbon is removed by calcination in air at 450 °C, leading to crystalline metal oxides (TiO₂ and Nb₂O₅) with well-ordered mesopores. However, the specific surface area remained moderate (54 to 89 m² g⁻¹).

2.3. Application to the synthesis of catalytic materials. As shown in Tables 1 and 2, in the last 11 years a large variety of catalytic materials were prepared by the different NHSG routes mentioned above.

The alkoxide and ether routes appear to be the most successful routes. They have been used for the synthesis of numerous mesoporous mixed oxide catalysts or TiO₂-based photocatalysts as well as for the one-step synthesis of noble metals supported on oxides. These routes were also used to immobilize active organometallic compounds and, to a lesser extent, to prepare supports. Moreover, the ether route also allowed the one-step synthesis of mesoporous and hydrophobic SiO₂-TiO₂ epoxidation catalysts modified by methyl groups.

Tilley and co-workers have applied the thermal decomposition route to the synthesis of mixed oxide catalysts and to the grafting of isolated catalytic species on silica supports.

The carboxylic acid and anhydride routes were utilized for the synthesis of TiO₂ photocatalysts, for the encapsulation of various active species, and recently for the preparation of ionogel catalysts (gels in which the liquid phase is an ionic liquid¹⁴⁷).

The alcohol route (benzyl alcohol, *tert*-butanol) has been mostly used for the synthesis of TiO₂-based and mixed-oxide photocatalysts.

3. Catalysis with NHSG-made materials

3.1. Oxide and mixed oxide catalysts

Metal oxides and mixed oxides with acidic, basic and/or redox properties are applied as catalysts in a variety of chemical reactions. Some oxides can either be used as supports (*e.g.* for precious metals) or as active phases dispersed at the surface of a support. The support provides the textural properties of the final material and promotes the dispersion of the active phase; however, controlling the dispersion of the active phase and stabilizing its most active form remains challenging.

A major advantage of sol-gel processes is to allow the preparation of such catalysts in a single step. In this case, however, the sol-gel approaches suffer from a serious handicap compared to other approaches such as impregnation in which the active phase is dispersed at the surface of a pre-formed support. Indeed, in one-step sol-gel approaches a significant part of the active species can be “lost” in the bulk of the material (*e.g.* in pore walls), where they are not accessible to the reactants. Fortunately, the proportion of accessible surface species increases when the specific surface area increases. In addition, when the Tammann temperature of the active species is low enough (*e.g.* VO_x, MoO_x, AgO_x), appropriate thermal treatments can lead to the migration of active species toward the surface, effectively increasing the proportion of accessible sites. NHSG routes have led to promising results in both cases.^{93,96,120}

To the best of our knowledge, the first example of mixed oxide catalysts prepared by NHSG routes was reported in 2000 by Barbieri and coworkers,¹⁰² who prepared Nb-V and Nb-V-Si catalysts for the ODH of propane. Since then, catalysts prepared by non-hydrolytic sol-gel have been used in a wide range of chemical reactions, including mild and total oxidation, photodegradation, alkene metathesis, and selective catalytic reduction of NO_x.

3.1.1. Mild/selective oxidation. Oxides and mixed oxides are extensively used as catalysts to selectively oxidize various hydrocarbons and produce the oxygenates and alkenes demanded by the chemical industry.¹⁴⁸ An example is the selective oxidation of propane to provide either propene or acrylic acid.^{149,150}

Table 1 Oxide catalysts and photocatalysts prepared by non-hydrolytic routes

Material	Route: precursors	Reaction catalyzed	Ref.
Oxide and mixed oxide catalysts			
Nb–V(–Si)	Alkoxide route: $(VO(O^iPr)_3)_3$, $NbCl_5$, $Si(OEt)_4$	Oxidative dehydrogenation of propane	102–104
V–Ti	Ether route: $VOCl_3$, $TiCl_4$, iPr_2O	Reduction of NO_x with NH_3	94 and 105
V–Ti	Ether route: $VOCl_3$, $TiCl_4$, iPr_2O	Selective oxidation of H_2S	95
V–Ti(–W)(–Mo)	Ether route: $VOCl_3$, $TiCl_4$, WCl_5 , $MoCl_5$, iPr_2O	Total oxidation	93 and 106
Ti–Si	Alkoxide route: $SiCl_4$, $Ti(O^iPr)_4$, $Si(O^iPr)_4$	Olefin epoxidation with organic hydroperoxides	107
Ti–Si	Ether route: $SiCl_4$, $TiCl_4$, iPr_2O	Mild oxidation with hydrogen peroxide	92, 108–110
Ti–Si–MeSi and Ti–Si–Me ₃ Si	Ether route: $SiCl_4$, $TiCl_4$, $MeSiCl_3$ or Me_3SiCl , iPr_2O	Olefin epoxidation with organic hydroperoxides	111
Ti–Si	Thermolysis: $Ti[OSi(O^iBu)_3]_4$	Olefin epoxidation with organic hydroperoxides	112
Ta–Si	Thermolysis: $(^iPrO)_2Ta[OSi(O^iBu)_3]_3$ (and $HOSi(O^iBu)_3$)	Olefin epoxidation with hydrogen peroxide and organic hydroperoxides	113
Cr–Si	Thermolysis: $(^iBuO)_3CrOSi(O^iBu)_3$	Oxidative dehydrogenation of propane	71
Co–Al	Ether route: $AlCl_3$, $CoCl_2$, iPr_2O	Olefin epoxidation with iodosylbenzene	114
Co–Si–Al	Ether route: $SiCl_4$, $AlCl_3$, $CoCl_2$, iPr_2O	Mild oxidation with iodosylbenzene	115
Fe–Al	Ether route: $AlCl_3$, $FeCl_3$, iPr_2O	Mild oxidation with hydrogen peroxide	116
Mo–Al–Si	Ether route: $MoCl_5$, $SiCl_4$, $AlCl_3$, iPr_2O	Alkene metathesis	96 and 117
Chlorinated SnO_2	Benzyl alcohol route: $SnCl_4$ in $BzOH$	Etherification, alkylation	118
$W_{18}O_{49}$ nanowires	Benzyl alcohol route: $W(O^iPr)_6$ in $BzOH$	Oligomerization of benzylic alcohols	119
Ag–Al(–Nb)	Ether route: $AlCl_3$, $AgCl$, iPr_2O , $NbCl_5$	Reduction of NO_x with decane	120
Pt–Al	Ether route: $AlCl_3$, iPr_2O , $(C_6H_5CN)_2PtCl_2$ or $PtBr_4$	NA	121
Oxide and mixed oxide photocatalysts			
TiO_2	Alkoxide route: $TiCl_4$, $Ti(O^iPr)_4$ in hexane or hexane–TOPO solutions	Photooxidation	122–125
TiO_2 (spherical or nanorods)	Benzyl alcohol route: $TiCl_4$ in $BzOH$	Photooxidation	126 and 127
TiO_2	Benzyl alcohol route: $TiCl_4$ in $BzOH$	Photooxidation	127
TiO_2	Anhydride route: $Ti(O^iPr)_4$, $(CX_3CO)_2O$, ($X = H, F$)	Photooxidation	63
TiO_2 (nanorods)	Ester elimination route or carboxylic acid route $Ti(O^iPr)_4$, oleic acid	Photocatalytic disinfection	55
TiO_2	Benzyl alcohol route: $TiCl_4$ in $BzOH$	Photocatalytic disinfection	128
Layered titanate	Ether route: $TiCl_4$ in diglyme in the presence of BH_3 -amine complex	Photooxidation	87
TiO_2 – SiO_2	Formic acid route in $scCO_2$: $Si(OEt)_4$, $Ti(O^iPr)_4$, formic acid	Photooxidation	60
TOPO-capped TiO_2	Alkoxide route: $TiCl_4$, $Ti(O^iPr)_4$ in TOPO	Photooxidation	129
Phosphated Zr-doped TiO_2	Alkoxide route: $TiCl_4$, $Ti(O^iPr)_4$, $ZrCl_4$, $Zr(O^iPr)_4$, nPrOH in TOPO	Photooxidation	130
Fe-doped TiO_2	Alcohol route: $TiCl_4$, $Fe(NO_3)_3$ in iBuOH	Photooxidation	131
Fe,N-doped TiO_2	Alcohol route: $TiCl_4$, $Fe(NO_3)_3$, in iBuOH	Photooxidation	132
ZnO	High temperature decomposition of $Zn(OAc)_2$	Photooxidation	122–123
$InNbO_4$	Benzyl alcohol route: $In(acac)_3$, $NbCl_5$, in $BzOH$	Photooxidation	133

The epoxidation of alkenes is also a crucial reaction that can be catalyzed by oxides,¹⁵¹ as well as the oxidation of inorganic molecules like hydrogen sulfur.¹⁵²

Nb–V, *Nb–V–Si* or *Cr–Si* oxides catalysts for the oxidative dehydrogenation (ODH) of alkanes. ODH of light alkanes, which allows the production of highly demanded alkenes, is an important field of research in selective oxidation catalysis.^{149,153–155} Catalytic formulations based on vanadia or niobia are among the most investigated. Niobium oxide is rather poorly active but selective while vanadium oxide is active under oxidizing conditions but poorly selective (CO , CO_2 and various oxygenates are classical side products). Mixed Nb–V oxides have proved more interesting,¹⁵⁶ and the degree of homogeneity of the mixed oxide appears to be the key factor controlling the catalytic activity.

In that perspective, Barbieri *et al.*¹⁰² and then Moggi *et al.*^{103,104} prepared vanadia-based catalysts (Nb–V, and Nb–V–Si) using

the NH alkoxide route. The catalysts were prepared under N_2 by reaction of $VO(O^iPr)_3$, $NbCl_5$, $Si(OEt)_4$, and/or $SiCl_4$ in hexane at 100 °C. The resulting green-colored gels were dried and calcined in air at 550 °C.

All the xerogels (before calcination) were amorphous; the presence of residual Cl indicated that the condensation reactions were not complete. Calcination of the Nb–V samples led to the removal of residual chlorine and yielded $NbVO_5$ prismatic crystallites of about 1 μm in size (Fig. 3), with very low specific surface area (3–6 $m^2 g^{-1}$). The ternary Nb–V–Si (1 : 1 : 5) samples remained predominantly amorphous after calcination and exhibited much higher specific surface areas (150 $m^2 g^{-1}$). The catalytic performance of these catalysts in the ODH of propane at 450–550 °C was investigated and compared to that of catalysts prepared by hydrolytic sol–gel. The 1 : 1 : 5 Nb–V–Si samples prepared *via* the non-hydrolytic method gave the best results in terms of propane conversion and yield in propene.¹⁰⁴

Table 2 Immobilized catalysts and catalyst supports prepared by non-hydrolytic routes

Material	Route: precursors	Reaction catalyzed	Ref.
Entrapment of catalytic species			
Entrapment of zirconocene into NH SiO ₂ , SiO ₂ -TiO ₂ and SiO ₂ -WO ₃	Alkoxide route: SiCl ₄ , Si(OEt) ₄ or Si(O ⁱ Pr) ₄ , TiCl ₄ , WCl ₆ (FeCl ₃ catalyst), Cp ₂ ZrCl ₂	Olefin polymerization	134–136
Entrapment of a Jacobsen catalyst into NH Al ₂ O ₃	Ether route: AlCl ₃ , ⁱ Pr ₂ O, Mn or Fe Salen complex	Selective oxidation by various oxidants	137
Entrapment of metalloporphyrins in NH Al ₂ O ₃	Ether route: AlCl ₃ , ⁱ Pr ₂ O, metalloporphyrin	Epoxidation with iodosylbenzene	138 and 139
Entrapment of a Si–Ti complex in NH SiO ₂	Anhydride route: Si(OEt) ₄ , (CH ₃ CO) ₂ O, Si–Ti complex	Epoxidation with organic hydroperoxides	62
Entrapment of Pd nanoparticles in NH SiO ₂	Formic acid route in ionic liquid: Si(OEt) ₄ , formic acid, Pd nanoparticles	Hydrogenation and Heck C–C coupling reactions	57
Entrapment of a Rh complex in NH SiO ₂	Formic acid route in ionic liquid: Si(OEt) ₄ , formic acid, [RhCl(PPh ₃) ₃]	Hydrogenation of styrene	140
Entrapment of a Rh complex and an ionic liquid in NH SiO ₂	Formic acid route in ionic liquid: Si(OEt) ₄ , formic acid, [RhCl(PPh ₃) ₃] or [Rh ₂ (COD) ₂ (dppm)(μ ² -Cl)]BF ₄	Hydrogenation of styrene	141
Entrapment of a Pd complex in NH SiO ₂ ionogel	Formic acid route in ionic liquid: Si(OEt) ₄ , formic acid, Pd(OAc) ₂	Heck–Mizoroki C–C coupling reactions	142
Grafting of active sites			
Grafting of Ti sites onto SiO ₂ support	Thermolysis of (ⁱ PrO)Ti[OSi(O ⁱ Bu) ₃] ₃	Olefin epoxidation with organic hydroperoxides	72
Grafting of Fe sites onto SiO ₂ support	Thermolysis of Fe[OSi(O ⁱ Bu) ₃] ₃ ·THF	Mild oxidation with H ₂ O ₂	73
Grafting of Ta sites onto SiO ₂ support	Thermolysis of (ⁱ PrO) ₂ Ta[OSi(O ⁱ Bu) ₃] ₃	Olefin epoxidation with hydrogen peroxide and organic hydroperoxides	113
Supports			
SiO ₂ –Me ₂ SiO–Ind ₂ SiO supports grafted with zirconocene	Alkoxide route: Me ₂ SiCl ₂ or (ClMe ₂ Si) ₂ O, Ind ₂ SiCl ₂ , Si(OEt) ₄ (ZrCl ₄ catalyst)	Olefin polymerization	143
SiO ₂ –TiO ₂ supports for Au nanoparticles	Ether route: SiCl ₄ , TiCl ₄ , ⁱ Pr ₂ O	Epoxidation	144 and 145
TiO ₂ –Al ₂ O ₃ supports	Alkoxide and ether route: TiCl ₄ , Al(O ⁱ Bu) ₃ Ti(O ⁱ Pr) ₄ , AlCl ₃ ; TiCl ₄ , AlCl ₃ , ⁱ Pr ₂ O	NA	146
Al ₂ O ₃ supports for Pt nanoparticles	Ether route: AlCl ₃ , ⁱ Pr ₂ O	NA	121

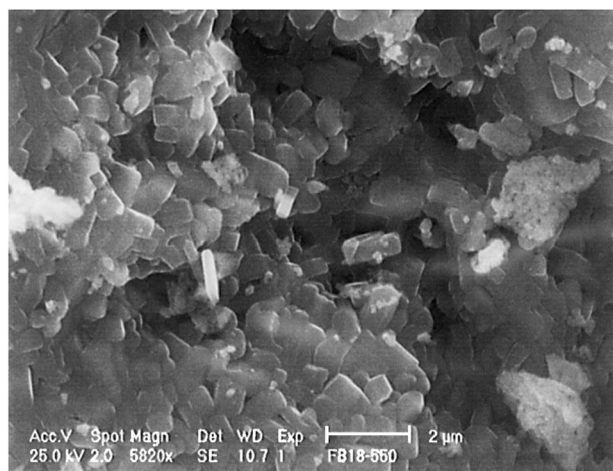


Fig. 3 SEM image of the Nb : V 1 : 1 catalyst prepared *via* NHSG by Barbieri *et al.*¹⁰² After thermal treatment at 550 °C, these catalysts exhibit uniform distribution of micrometre sized crystallites of NbVO₅. Reprinted with permission from ref. 102. Copyright 2000 Elsevier.

Fujdala and Tilley reported the preparation of Cr–Si catalysts for the ODH of propane by thermolysis in the solid state or in solution of the Cr(IV) alkoxysiloxy complex (ⁱBuO)₃Cr–O–Si(OⁱBu)₃.⁷¹ After calcination at 500 °C in O₂, the resulting Cr–Si mixed oxides (Cr : Si ratio ≈ 1 : 1) exhibited micro- and mesoporosity,

and specific surface areas of 205–275 m² g^{−1}. In the ODH of propane, the oxide obtained by thermolysis in solution was found more selective and up to 3 times more active for propene formation than the oxide obtained by thermolysis in the solid state, suggesting the presence of different catalytic centers in these catalysts, although they were derived by thermolysis of the same single-source molecular precursor.

Ti–Si and Ta–Si oxides for epoxidation and mild oxidation. Crystalline titanium-silicates (*e.g.* TS-1, TS-2, Ti-β, *etc.*) in the framework of which titanium(IV) is isomorphously substituted for silicon are widely used to catalyze selective oxidation reactions with hydrogen peroxide as oxidant under mild conditions.¹⁵⁷ However, these catalysts are microporous and are thus limited to small substrates and oxidants. As a result, much work has been carried out to prepare amorphous mesoporous titania–silica catalysts by sol–gel processes. The active sites in amorphous titania–silica catalysts are believed to be well-dispersed Ti^{IV} surface species bonded to the silica network by Si–O–Ti bridges, similar to the sites found in the crystalline catalysts. However, it was found difficult to control both the dispersion of the titanium and the texture of these catalysts when using conventional sol–gel methods based on the hydrolysis–condensation of titanium and silicon alkoxide precursors. Indeed, titanium and silicon alkoxides have very different reactivities, conducive to heterogeneous gels.

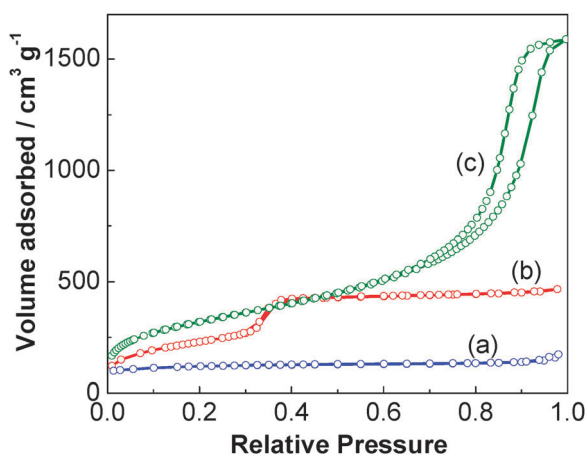


Fig. 4 Comparison of the N_2 physisorption isotherms of (a) TS-1, (b) Ti-MCM-41, (c) a SiO_2 - TiO_2 xerogel (4.6 wt% Ti, calcined 5 h at 500 °C) prepared by the NH ether route. Plot redrawn from ref. 92.

Several methods have been used to reach a good dispersion of titanium sites, including: strongly acidic hydrolysis,¹⁵⁸ prehydrolysis of the silicon alkoxide and modification of the titanium alkoxides by a chelating ligand,^{159,160} controlling the rate of addition of water,¹⁶¹ or using a single-source precursor with preexisting Si-O-Ti linkages.¹⁶² In all cases, acidic conditions are required to obtain well-dispersed Ti sites, but unfortunately under these conditions the xerogels formed by evaporative drying are microporous,^{158,159} due to the collapse of the relatively loose acidic gel structure. Elaborate drying procedures are thus needed in order to obtain mesoporous materials. The direct removal of water and alcohol under supercritical conditions (high-temperature aerogels) leads to nearly inactive materials and it was found necessary to extract the gels with supercritical CO_2 (low-temperature aerogels).¹⁵⁹ After calcination at 400 °C, the mesoporous aerogels obtained by this method displayed surface areas and pore volumes up to 680 $m^2 g^{-1}$ and 1.9 $cm^3 g^{-1}$, respectively. Alternatively, the collapse of the pore structure of the xerogels could be minimized by aging the wet gels for 10 days then washing them with *n*-heptane, a low surface tension solvent¹⁶³ or by exchanging the solvent with *n*-hexane then silylation of the gels before drying.^{161,164}

Tilley and co-workers used the thermal decomposition of the tris(*tert*-butoxy)siloxy complex $Ti[OSi(O^tBu)_3]_4$ (**1**) to prepare SiO_2 - TiO_2 catalysts with a Si/Ti ratio of 4 (TiO_2 -4 SiO_2).¹¹² The solid-state transformation of **1** led after calcination to a low-surface-area material but solution-phase thermolysis of **1** led to xerogels with high surface area and pore volume (550 $m^2 g^{-1}$ and 1.8 $cm^3 g^{-1}$ after calcination at 500 °C). Supercritical drying in CO_2 led to an aerogel with even higher specific surface area and pore volume (680 $m^2 g^{-1}$ and 2.5 $cm^3 g^{-1}$ after calcination at 500 °C). The xerogels showed moderate performances in the epoxidation of cyclohexene using organic hydroperoxides as oxidants. The aerogel was more active, comparable to a “Shell catalyst” prepared by grafting $Ti(O^iPr)_4$ onto a silica support. However, it remained significantly less active than titania-silica aerogels reported by Baiker and coworkers.

Similarly, the thermal decomposition of the complex $(O^iPr)_2Ta[OSi(O^tBu)_3]_3$ (**2**) in toluene was used to prepare

Ta_2O_5 - SiO_2 materials with Si/Ta ratios of 6 and 18, exhibiting surface areas up to 440 $m^2 g^{-1}$ after calcination at 500 °C.¹¹³ Interestingly, in contrast with the TiO_2 -4 SiO_2 catalysts which were essentially inactive with H_2O_2 , the Ta_2O_5 - SiO_2 materials showed moderate activities and selectivities in the epoxidation of cyclohexene with H_2O_2 , indicating that these catalysts were more tolerant to the presence of water.

Lafond *et al.*¹⁰⁷ reported the straightforward preparation of a SiO_2 - TiO_2 catalyst (10.7 wt% Ti) by the alkoxide route. The precursors ($SiCl_4$, $Si(O^iPr)_4$, $Ti(O^iPr)_4$) were heated (without solvent) at 110 °C under autogenous pressure in a sealed Pyrex ampoule. After drying under vacuum, the xerogel was calcined for 2 h at 550 °C, leading to an amorphous, mesoporous (780 $m^2 g^{-1}$, 0.54 $cm^3 g^{-1}$) mixed oxide, which showed excellent performances in the epoxidation of cyclohexene using organic cumylhydroperoxide as oxidant. The epoxide yield and the initial rate were comparable to those reported by Baiker and coworkers for a calcined aerogel sample.¹⁶⁵

After these promising results, Lafond *et al.*⁹¹ reported that the texture of SiO_2 - TiO_2 mixed oxides prepared using the alkoxide or the ether route could be controlled by playing on different reaction parameters (*e.g.* volume of solvent, reaction time, reaction temperature). Xerogels with surface areas and pore volumes up to 1040 $m^2 g^{-1}$ and 1.53 $cm^3 g^{-1}$ could be obtained. Recently, Cojocariu *et al.*⁹² reported the synthesis by the ether route of a SiO_2 - TiO_2 xerogel (Si/Ti = 16) with an outstanding texture (Fig. 4). The gel was obtained by reacting $SiCl_4$, $TiCl_4$, and iPr_2O in CH_2Cl_2 in a Teflon-lined autoclave at 150 °C for 4 days. The specific surface area and pore volume (1215 $m^2 g^{-1}$, 2.4 $cm^3 g^{-1}$ after calcination for 5 h at 500 °C) were significantly higher than those reported for SiO_2 - TiO_2 calcined aerogels with similar compositions.¹⁶⁵

The amorphous SiO_2 - TiO_2 calcined xerogels prepared by this method were found to be excellent catalysts for the oxidation with aqueous H_2O_2 of a wide range of organic compounds (Table 3). Even very bulky substrates, such as anthracene or 4,6-dimethyldibenzothiophene (4,6-DMBT, a poorly reactive molecule which is present in the fuels processed by the hydrodesulfurization plants), could be effectively oxidized with H_2O_2 under mild conditions.^{108–110} High conversions (67–92%), high selectivities (>95%) and excellent H_2O_2 efficiencies (80–95%) were obtained for the oxidation under mild conditions (6 h at 60 °C) of anthracene to anthraquinone, of cyclooctene to cyclooctene oxide and of α -naphthol to naphthoquinone. Similarly, sulfur compounds such as DMSO, methyl-phenylsulfide (MPS), dibenzothiophene (DBT) and 4,6-DMBT were oxidized to the corresponding sulfone with excellent conversions (80–97%), selectivities (>99%) and H_2O_2 efficiencies (90–99%). The catalyst could be reused 4 times in the oxidation of DBT without any significant loss of activity. In the case of styrene, playing on the reaction parameters (temperature, mode of addition of H_2O_2 , H_2O_2 /styrene ratio, solvent) allowed us to tune the selectivity toward benzaldehyde (up to 90%) or toward styrene oxide (up to 49%).¹⁰⁹

The catalytic performances and the stability of this amorphous SiO_2 - TiO_2 xerogel were ascribed to its exceptional mesoporous texture and also to the very high degree of condensation typical of non-hydrolytic xerogels, which probably also accounts for

Table 3 Catalytic behaviour of NH TiO₂–SiO₂ xerogels for the oxidation of different molecules¹⁰⁹

Substrate (S)	H ₂ O ₂ /S (mol/mol)	C _i ^a /mol L ^{−1}	Solvent	Temp./°C	Time/min	Conversion (%)	H ₂ O ₂ efficiency ^b (%)
Anthracene	5/1	0.01	MeCN	60	360	92	91
Cyclooctene	5/1	0.08	MeCN	60	360	67	90
Styrene	5/1	0.1	MeCN	60	1000	77	80
α-Naphthol	5/1	0.01	MeCN	60	360	65	87
Phenylsulfide	2/1	0.06	MeCN	40	60	95	99
DBT	2/1	0.1	MeCN	60	120	97	98
4,6-DMDBT	2/1	0.01	MeOH	60	240	80	90

^a Initial concentration of substrate. ^b H₂O₂ efficiency (selectivity) = (mole of H₂O₂ consumed in the formation of products/mole H₂O₂ converted) × 100.

both the low hydrophilicity of the surface and the stability of the Ti sites after exposure to aqueous H₂O₂.¹⁰⁹

The activity and selectivity of SiO₂–TiO₂ epoxidation catalysts can be tuned by introducing hydrophobic organic groups (e.g. SiMe, SiPh or SiMe₃), either by post-modification or during the synthesis.^{161,166–169} However, the one-step synthesis of such hybrid catalysts by hydrolytic sol–gel procedures remains challenging, owing to the very different reaction rates of the titanium, silicon, and organosilicon precursors and to the collapse of pores during routine evaporative drying of the gels that usually leads to microporous xerogels.¹¹¹

Hybrid titania silica xerogels could also be prepared in one-step by non-hydrolytic sol–gel (ether route). Xerogels incorporating up to 60 mol% MeSiO_{1.5} (T) units with high specific surface area and pore volume (1060 m² g^{−1}, 1.3 cm³ g^{−1}) were obtained by reaction of the chloride precursors (SiCl₄, TiCl₄, MeSiCl₃) and ¹Pr₂O at 110 °C under autogenous pressure. In addition xerogels modified by up to 20 mol% Me₃SiO_{0.5} (M) units could also be prepared for the first time by this route starting from SiCl₄, TiCl₄ and Me₃SiCl; the incorporation of Me₃SiO_{0.5} groups led to a lowering of the specific surface area and pore volume (930 m² g^{−1} and 0.72 cm³ g^{−1} for the sample with 20 mol% M units) but the xerogels remained mesoporous. Both hybrid materials were evaluated in the epoxidation of cyclohexene (50 mmol) with cumylhydroperoxide (10 mmol) in toluene at 90 °C, using 100 mg of catalyst. The yield in cyclohexene oxide reached 98% after only 30 min. The initial epoxidation rates (~15 mmol g^{−1} min^{−1}) were significantly higher than those reported for the epoxidation of cyclohexene at 90 °C with Si–Ti aerogels post-modified by MeSiO_{1.5} or PhSiO_{1.5} units.¹⁷⁰

Co–Al and Co–Si–Al oxides for the selective oxidation of various hydrocarbons. Ciuffi and coworkers have utilized the ether route to prepare Co–Al and Co–Si–Al oxidation catalysts.^{114,115} The synthesis involved refluxing at 110 °C under an inert atmosphere AlCl₃, CoCl₂ and ¹Pr₂O in dichloromethane. Si(OEt)₄ was added after one hour of reaction in the case of the Co–Si–Al sample. The authors particularly studied the influence of the calcination temperature on the structure, texture and catalytic performance of the materials.

The Co–Al oxide obtained after calcination at 750 °C exhibited moderate specific surface area and pore volume (45 m² g^{−1} and 0.23 cm³ g^{−1}) and XRD evidenced the crystallization of a transition alumina. Higher calcination temperature (1000 and 1100 °C) led to a further decrease of the specific surface area and to the crystallization of CoO. Interestingly, no cobalt leaching was observed for the samples

prepared by NHSg, in contrast to the samples prepared by conventional hydrolytic sol–gel. The Co–Al oxide obtained after calcination at 750 °C showed the highest activity in the epoxidation of (Z)-cyclooctene with iodosylbenzene, PhIO.¹¹⁴

The Co–Si–Al sample was heat-treated at 25, 400, 750 and 1000 °C in air. The resulting blue or black powders were evaluated in the liquid phase oxidation of (Z)-cyclooctene, cyclohexane, cyclohexanol and *n*-heptane with iodosylbenzene. Increasing the heat-treatment temperature had a drastic impact on the texture and crystallinity of the solid, on the oxidation state of the Co species and on the catalytic activity.¹¹⁵ The best catalyst, obtained by calcination at 400 °C, exhibited higher specific surface area and pore volume (53 m² g^{−1} and 0.05 cm³ g^{−1}) than samples calcined at higher temperature and consisted of an amorphous silica–alumina matrix doped with Co²⁺ ions in tetrahedral coordination and Co³⁺ octahedral species. Interestingly, the activity of this catalyst compared well with the second-generation FeP iron(III) mesotetrakis(pentafluorophenylporphyrin) catalysts, which is recognized as one of the most efficient catalysts for biomimetic oxidation reactions but is both much more expensive and prone to rapid deactivation.¹⁷¹

Fe–Al oxides for the selective oxidation of cyclohexene and cyclohexane. Ricci *et al.* developed efficient iron-promoted alumina catalysts for hydrocarbon oxidation with hydrogen peroxide.¹¹⁶ The materials were prepared by the ether route, by refluxing AlCl₃, FeCl₃ and ¹Pr₂O in dichloromethane under an argon atmosphere at 110 °C for 4 h. After aging for 24 h at room temperature and drying, the xerogels were calcined at different temperatures for 8 h under nitrogen. The xerogel remained amorphous after calcination at 400 °C; γ-alumina was detected in the catalyst calcined at 750 °C, α-alumina was found in the catalyst calcined at 1100 °C. No crystalline iron oxide phase was detected. The presence of Fe^{III} in the matrix was evidenced by UV-Vis and EPR spectroscopies. UV-Vis spectroscopy and lixiviation tests suggested that Fe cations were not simply adsorbed on the alumina matrix but instead strongly bound to it. Unfortunately, the textural properties of the materials were not reported. The catalytic tests were carried out at 25–55 °C with 10 mg of catalyst (4.5 × 10^{−3} mmol of Fe^{III}) in 1 : 1 dichloromethane : acetonitrile solvent, using 0.45 mmol of cyclooctene or cyclohexane and 0.45, 0.9 or 2.25 mmol of H₂O₂. These conditions were milder than those reported in the literature.¹⁷² The catalysts performed promisingly in the epoxidation of cyclooctene. Surprisingly, the catalyst obtained by calcination at 1100 °C—well crystallized—exhibited the highest activity. This was tentatively

correlated to the absence of surface Brønsted acidity in the latter sample. The oxidation of cyclohexane is more challenging, due to the inertness of C–H bonds. Over the Fe–Al catalyst treated at 1100 °C the conversion of cyclohexane reached 22% (12% cyclohexanone and 10% cyclohexanol) after 48 h at 50–55 °C, using a 5-fold excess of H₂O₂.

V–Ti oxides for the selective oxidation of H₂S. The selective catalytic oxidation of hydrogen sulfide is an important application for both the reduction of SO_x emissions and the production of elemental sulfur.¹⁷³ Park *et al.*¹⁷⁴ developed a vapor phase catalytic process for the selective oxidation of hydrogen sulfide in the presence of excess water and ammonia leading to the formation of ammonium thiosulfate (ATS) and sulfur. V₂O₅/TiO₂ aerogels exhibited high performance in this process.¹⁷⁵

Thus Park *et al.* have applied to this reaction V–Ti catalysts prepared *via* the ether route, by reaction of VOCl₃ and TiCl₄ with ¹Pr₂O under autogenous pressure at 110 °C for 3 days.⁹⁵ After vacuum drying, the catalysts were calcined at 500 °C. The V₂O₅ loading ranged between 6.5 and 18.3 wt%. The specific surface area was relatively high (~80 m² g⁻¹) for the catalysts with the lowest loadings (6.5 to 10.6 wt%). XRD and Raman spectroscopy indicated that for loadings below ~12 wt% only well dispersed monomeric and polymeric vanadate species were present. At higher loadings, some crystallization of V₂O₅ was observed. As the main active species are dispersed VO_x species in close interaction with the support, the activity increased with increasing V₂O₅ loading up to *ca.* 10 wt% and then decreased. At the optimum V₂O₅ loading, the H₂S conversion reached 98.9% with selectivity for S and ATS of 21.5 and 78.5%, respectively; SO₂ was not detected (260 °C; GHSV = 300 000 h⁻¹; flow of H₂S/O₂/NH₃/H₂O/He = 5/2.5/5/20/67.5). The high activity of these NHSG-made catalysts compared to conventional (impregnated or HSG-made) catalysts was explained by their relatively high specific surface area and the excellent dispersion of vanadium species.

3.1.2. Total oxidation

V–Ti, V–Mo–Ti, V–W–Ti mixed oxides for total oxidation of organic pollutants. Vanadia–titania catalysts are widely studied and exploited industrially in the total oxidation of different

atmospheric pollutants.^{176,177} A current important application is the abatement, *via* total oxidation, of polychlorinated dibenzo-*p*-dioxins and furans (PCDDs and PCDFs) from the effluents of combustion plants.¹⁷⁸ As reviewed recently by Gaigneaux and co-workers,¹⁷⁶ V₂O₅/TiO₂ catalysts are classically prepared by impregnation of a preformed titania support with vanadium metavanadate. Less conventional preparation routes are proposed in the literature as well, like for example sol–gel,^{179,180} thermal decomposition¹⁸¹ or flame spray pyrolysis.¹⁸² Mo or W oxide promoters are often added to the formulation.^{183–185} These systems have high activities in total oxidation and are resistant to chlorine poisoning.

We have recently applied the NHSG method to the synthesis of V-based oxidation catalysts.^{93,106} V–Ti, V–Mo–Ti and V–W–Ti mixed oxides were prepared by the ether route, using VOCl₃, TiCl₄, WCl₃, and MoCl₅ precursors and a stoichiometric amount of ¹Pr₂O. The nominal V₂O₅ loadings explored were 3, 5 and 10 wt%, and the MoO₃ or WO₃ loading was 5 wt%. Dichloromethane was used as a solvent and the reaction was performed at 110 °C for 4 days under autogenous pressure. Dark brown gels were obtained, which after drying and calcination (500 °C in air) led to yellow powders. The resulting solids showed similar morphologies, with loosely aggregated spherical particles, a few μm in size, themselves formed by densely packed nanoparticles of about 30 nm (Fig. 5). The specific surface area varied from 53 to 109 m² g⁻¹ depending on the composition. The interstices formed by the packing of the nanoparticles resulted in a well-defined mesoporosity (*ca.* 11 nm pore diameter).

The xerogels (samples obtained after drying but before calcination) were also characterized: XRD indicated the presence at this stage of anatase domains, smaller than in the calcined catalysts; XPS analysis showed the presence of high carbon and chlorine concentrations, consistent with the synthesis used. Surface atomic V/Ti ratios calculated from the nominal bulk composition and from surface concentrations (XPS data) were in excellent agreement, showing that the xerogels were homogeneous V–Ti mixed oxides, with a statistical distribution of V atoms in the titania matrix. After calcination, however, the surface V/Ti atomic ratio increased significantly (typically by a factor 2 to 3), which implies the migration of

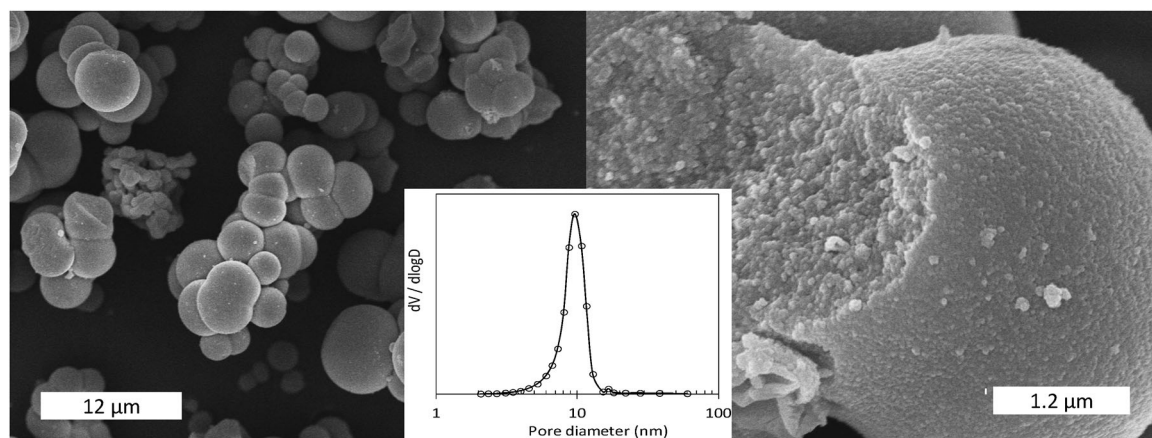


Fig. 5 Scanning electron microscopy images of a TiO₂–V₂O₅–WO₃ catalyst (92.2–3.3–4.5 wt%). Inset: pore size distribution of the same sample.¹⁰⁶

V species toward the surface during the calcination. This migration was explained by the low Tamman temperature of vanadia, allowing V atoms to be relatively mobile, and by the limited solubility of V_2O_5 in TiO_2 . In the promoted catalysts, the migration of Mo and W species toward the surface was also observed. A study of V surface species using time of flight secondary ion mass spectroscopy (ToF-SIMS) confirmed the presence of V–O–Ti bonds and showed the presence of monomeric and oligomeric vanadates.⁹³ Monomeric V species were favored at low V_2O_5 loadings. The V–Ti catalysts performed well in the abatement of benzene. Total oxidation was reached around 350 °C. By comparison of NHSG catalysts with different V_2O_5 loading and reference catalysts prepared *via* wet impregnation, it was concluded that oligomeric vanadates formed at high V_2O_5 loadings were more efficient than isolated species formed at low V_2O_5 loadings. The Mo- and W-promoted catalysts were tested in the total oxidation of benzene and chlorobenzene. Both doping oxides brought additional activity.¹⁰⁶

3.1.3. Reduction of nitrogen oxides. Owing to environmental concerns, ever more stringent regulations are being enacted to decrease nitrogen oxides (NO_x) air pollution. NO_x are produced by the combustion of fossil fuels in power plants and motor vehicles.^{186,187} Selective catalytic reduction (SCR) of NO_x is the main method for their removal from burnt gases and various catalytic systems can be used for that purpose.^{188,189}

V–Ti mixed oxides for SCR of NO_x by NH_3 . Ammonia is widely used as a reductant for the removal of NO_x emitted by stationary sources^{190,191} and vanadia-based catalysts supported on TiO_2 -anatase are very efficient for this application. Elaborated procedures have been proposed to increase the activity of V–Ti catalysts, such as multiple grafting, sol–gel synthesis using chemically modified precursors and 2-step procedures to improve the dispersion of vanadia species, or supercritical drying to increase the specific surface area of the catalyst.

The non-hydrolytic sol–gel process offers a simple and efficient way to prepare highly active V–Ti catalysts.^{94,105} The reaction at 110 °C under autogenous pressure of $VOCl_3$ and $TiCl_4$ with a stoichiometric amount of iPr_2O led to dark brown gels, which after drying and calcinations (5 h at 500 °C in air) gave beige powders. Samples with V_2O_5 loadings ranging from 6 to 18 wt% were prepared. All the samples were mesoporous, and the specific surface area and pore volume decreased when the V_2O_5 loading increased, from 87 m² g^{−1} and 0.30 cm³ g^{−1} (6 wt% V_2O_5) to 26 m² g^{−1} and 0.22 cm³ g^{−1} (18 wt% V_2O_5). Scanning electron microscopy indicated the presence of bunch-like agglomerates of spherical porous particles (1–5 µm in diameter); these particles were themselves built of densely aggregated nanoparticles, around 20 nm in diameter. Most of the vanadium species (80–90%) were accessible to reduction by H_2 . The catalytic properties of these materials were evaluated in the SCR of NO by NH_3 . The estimated turnover frequency ‘TOF’ at 473 K (mole of NO converted per mole of V per hour) went through a maximum value (16.6 h^{−1}) at a V_2O_5 loading of 8 wt%. As previously

observed for catalysts prepared by impregnation, the N_2 selectivity decreased with the V_2O_5 loading. The sample containing 6 wt% V_2O_5 offered a good compromise between activity (estimated TOF 7.3 h^{−1}) and high N_2 selectivity (98% at 623 K). In terms of activity and selectivity, the catalysts prepared in one step by NH sol–gel with V_2O_5 loadings ranging from 6 to 10 wt% compared quite favorably with V_2O_5 – TiO_2 catalysts elaborated by multi-step processes, such as catalysts obtained by multi-step grafting of vanadyl triisopropoxide onto a titania aerogel.¹⁹²

Ag(–Nb)–Al mixed oxides for the SCR of NO_x by hydrocarbons. Hydrocarbons are attractive reductants for the abatement of NO_x produced by automotive vehicles, solving the problem of the storage of the reducing agent.^{193,194} Silver-based catalysts (e.g. Ag/ Al_2O_3) are among the most active and selective for this reaction. Recently, Petitto *et al.* reported the one-step NHSG synthesis of Ag–Al and Ag–Nb–Al catalysts for the SCR of NO by *n*-decane.¹²⁰ The materials were obtained by reaction of the metal chloride precursors ($AlCl_3$, $AgCl$, $NbCl_5$) with a stoichiometric amount of iPr_2O at 110 °C. After drying the xerogels were calcined at 550 °C for 5 hours then activated by hydrotreatment (in air + 10% H_2O) at 750 °C for 16 hours. The silver loading was ~2 wt%, and the niobium content (for the Ag–Nb–Al catalyst) was 1.5 wt%. After the calcination step the specific surface area of the samples reached 280 m² g^{−1} (Ag–Al) and 350 m² g^{−1} (Ag–Nb–Al). After the hydrotreatment step, the specific surface area of the catalysts decreased down to 160–170 m² g^{−1}, with average pore diameters of 7.4 nm (Ag–Al) and 11.0 nm (Ag–Nb–Al). XRD indicated the presence of γ - Al_2O_3 . Silver nanoparticles around 10 nm in diameter could be seen on TEM images of the catalysts.

Ag–Al and Ag–Nb–Al catalysts were evaluated in the SCR of NO by *n*-decane. The hydrotreatment remarkably improved the activity of these sol–gel catalysts, particularly the low temperature activity, although the specific surface area decreased by a factor of 2 or more (Fig. 6). This behavior was ascribed to the higher accessibility and dispersion of Ag (and Nb) species after this treatment, as suggested by the XPS analysis.

Most interestingly, Nb doping led to a significant increase of the low temperature activity of the catalysts after hydrotreatment: the NO conversion profile was shifted by at least 40 °C toward the low temperatures. Thus, on the Ag–Nb–Al catalyst the conversion of NO began as low as 210 °C, increasing rapidly to reach a 45–52% plateau above 330 °C. For comparison, a Ag/ Al_2O_3 catalyst (2 wt% Ag) was prepared by impregnation, calcination and hydrotreatment at 750 °C. This catalyst exhibited a significantly lower activity than Ag–Al and Ag–Nb–Al catalysts, confirming the interest of NHSG for the preparation of this type of catalysts, and the importance of Nb for increasing the activity at low temperature.

3.1.4. Alkene metathesis. Olefin metathesis is an important reaction for the chemical industry in several sectors (organic synthesis, polymerization chemistry, petro-chemistry).¹⁹⁵ The economic conversion of light olefins can be carried out at the refinery with MoO_3 -based catalysts. These catalysts are mainly prepared *via* wet or dry impregnation of a Mo salt onto silica, alumina, titania or silica–alumina supports.^{200–202}

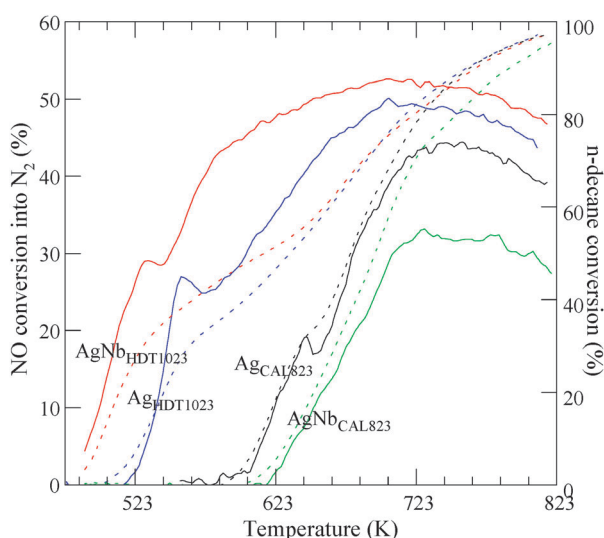


Fig. 6 Reaction temperature dependence of NO conversion (full lines) and *n*-decane conversion (dotted lines) over Ag-(Nb)-Al mixed oxides catalysts either calcined at 823 K (CAL823) or hydrotreated at 1023 K (HDT1023). Total flow rate = 6 L h⁻¹, catalyst amount = 40 mg [*n*-decane] = 0.02%, [NO] = 0.04%, [H₂O] = 2.50, [O₂] = 8.00% and balance with helium. Reprinted from Petitto *et al.*¹²⁰ Copyright 2011 Royal Society of Chemistry.

Composite supports (*e.g.* H-beta zeolite mixed with Al₂O₃)²⁰³ or ordered mesoporous supports (*e.g.* SBA-15, MCM-41, *etc.*)²⁰⁴ have also been frequently used. Experimental observations as well as theoretical works indicate that MoO_x species must be highly dispersed to be active.^{196,205} The acidity of the support is important too. For example, the superior acidity developed by silica-alumina supports compared to pure silica or pure alumina led to significant activity improvement.²⁰⁰ The interaction between the dispersed MoO_x surface species and the acidic Si-O(H)-Al sites of the support appears to play a crucial role.

Mo-Al-Si mixed oxides for propene metathesis. In this context, MoO₃-SiO₂-Al₂O₃ mixed oxides were prepared *via* non-hydrolytic sol-gel and evaluated in the metathesis of propene to ethene and butene.⁹⁶ The syntheses were performed under an argon atmosphere. SiCl₄, AlCl₃, MoCl₅ and a stoichiometric amount of ¹Pr₂O were dissolved in CH₂Cl₂ and then heated at 110 °C for 4 days under autogenous pressure. The xerogel obtained was crushed, dried at 120 °C under vacuum and finally calcined for 5 hours at 500 °C in air.

The texture of the obtained solids was strongly affected by the Si/Al ratio.¹¹⁷ The best texture (500 m² g⁻¹ with mesopores of about 13 nm and a pore volume of 1.6 cm³ g⁻¹) was obtained with the samples containing only 5 wt% of alumina. The addition of Al increased the acidity of the materials. MoO_x species appeared to be homogeneously dispersed in the Si-Al-Mo xerogel. XPS analysis demonstrated that the Mo surface concentration increased under the effect of the calcination. This migration of the species toward the surface was related to the low Tammann temperature of MoO₃. The NH Mo-Al-Si mixed oxides remained totally amorphous after calcination and exhibited metathesis activity significantly higher than other reference systems (Fig. 7). The specific

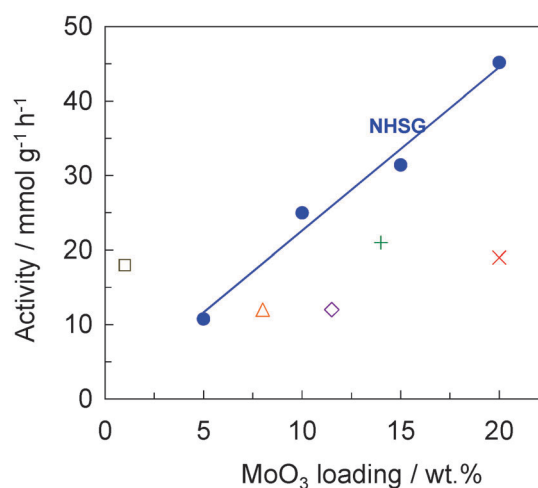


Fig. 7 Propene metathesis activity of different MoO₃-based catalysts studied by Debecker *et al.* Si-Al-Mo mixed oxides obtained by NHSG (●)¹¹⁷ are compared with the best MoO₃/SiO₂-Al₂O₃ metathesis catalysts obtained *via* other methods: flame spray pyrolysis (□),¹⁹⁶ wet impregnation of ammonium heptamolybdate (Δ),¹⁹⁷ thermal spreading of MoO₃ (◇),¹⁹⁸ wet impregnation of Mo hydrates (+)¹⁹⁹ and wet impregnation of ammonium heptamolybdate in the presence of oxalic acid (×).¹⁹⁹

activity increased with the MoO₃ loading, even up to 20 wt%. This was ascribed to the fact that the surface of the calcined solids exhibited mainly isolated MoO_x species, as demonstrated *via* ToF-SIMS. This contrasted with catalysts prepared *via* wet impregnation on preformed supports^{197,206} or *via* flame aerosol synthesis¹⁹⁶ in which the aggregation of Mo oxides and the formation of MoO₃ crystals limit the activity.

3.1.5. Alkylation. Recently, tin oxide nanoparticles, prepared by heating SnCl₄ in benzyl alcohol (100 °C, 24 h), have been used to catalyze alkylation reactions.¹¹⁸ Interestingly, it was found that the residual chloride groups found on the nanoparticles surface could promote the electrophilicity of benzyl alcohol *via* a chlorine borrowing mechanism. In the proposed mechanism, the chlorine atom present on the nanoparticle surface can be transferred to the benzyl alcohol to yield the corresponding benzyl chloride. The latter—being more electrophilic than the starting alcohol—can act as an efficient alkylating agent and return the chlorine atom to the nanoparticle surface. Thus, these SnO₂ nanoparticles catalyzed the formation of ethers of various alcohols. Importantly, no reaction occurred when chlorine-free SnO₂ nanoparticles (prepared from Sn(^{*i*}BuO)₄) were used; in addition, the particles could be re-used several times, although with decreasing activity and selectivity. The reactions were clearly shown to proceed in a catalytic way, even though the turnover numbers were modest. The chlorine-containing SnO₂ nanoparticles also catalyzed the Friedel-Crafts alkylation of aromatic compounds (benzene, toluene, anisole) with various benzylic alcohols. In this case too, chlorine-free SnO₂ nanoparticles were inactive, unless a small amount of benzyl chloride was added to the reaction mixture. Although the reaction conditions were quite harsh, this work opens new opportunities for the activation of alcohols.

3.1.6. Photocatalysis. The photocatalytic degradation of organic pollutants in waste water is a major field of investigation.^{207–209} TiO₂ is the choice material for this application

owing to its low cost, high chemical stability and non-toxicity. However, pure titania suffers from two major limitations: (i) its band gap is relatively wide (3.2 eV for anatase) implying that only a small fraction (*ca.* 5%) of solar light can be converted and (ii) the rate of recombination of the photo-generated electrons and holes is high.

It is thus needed to prepare modified TiO₂ materials with a reduced band gap to make them exploitable in the visible range and to enhance the charge separation of the photo-generated electrons–holes. Strategies include for instance the doping of TiO₂ with N, P, or transition metals, or the dispersion of TiO₂ species in a zeolite or a silica matrix.^{210–215} However, a dopant can act as a recombination center. Thus, many researchers are exploring undoped single-phase oxides working in the visible range.^{216,217}

TiO₂-based photocatalysts. The synthesis of TiO₂ nanocrystals by NHSG (alkoxide route) in the presence of trioctylphosphine oxide (TOPO) was first reported by Colvin and co-workers.⁴⁴ This method yields highly crystalline anatase nanoparticles with diameters ranging from 4 to 9 nm, with no surface hydroxyl groups, perfectly dispersible in hydrocarbon solvents. The high degree of crystallinity of the nanoparticles is a clear advantage of this method with respect to hydrolytic methods which often produce amorphous particles.

The group of Agostiano investigated TiO₂ photocatalysts prepared by a similar method. Curri *et al.* obtained highly crystalline anatase nanoparticles with an average size of 7 nm by reaction of TiCl₄ with Ti(OPr)₄ at 300 °C in heptadecane in the presence of TOPO.^{122,123} The surface chemistry of these particles made them organosoluble and they were thus suspended in CHCl₃ and subsequently deposited onto a transparent support. These coated photocatalysts were tested in the degradation of methyl red by UV light, showing excellent performances in comparison with coated Degussa P25 TiO₂ particles. This was ascribed to the small size of the anatase particles, leading to an increase of the active surface in the film and reducing the probability of electron–hole pairs recombination.

A couple of years later, the same group compared the photodegradation of methyl red and methyl orange over anatase nanoparticles deposited onto a quartz substrate. The particles were prepared either by NHSG in the presence of TOPO or by a hydrolytic route in oleic acid.¹²⁴ In both cases the nanoparticles showed similar size (*~*6 nm) and crystallinity. The nanoparticles prepared by NHSG were characterized by the absence of hydroxyl groups. These organosoluble nanoparticles could be easily suspended in a solvent and coated on various supports, for instance on the walls of a glass photo-reactor, designed for continuous flow processes, as demonstrated by Mascolo *et al.*¹²⁵ The TOPO-capped TiO₂ nanocrystals casted onto a quartz slide were active in the UV-induced photocatalytic degradation of methyl red and methyl orange.¹²⁴ However, they were less efficient than the TiO₂ nanocrystals capped with oleic acid. This was ascribed to the steric hindrance of the octyl chains in TOPO, together with the intrinsic low initial density of –OH groups on the particles prepared by NHSG. Nevertheless, when photodegradation was performed at pH 12, the TOPO-capped TiO₂ nanocrystals were found relatively stable, while the nanocrystals capped with oleic acid were prone to a UV-driven

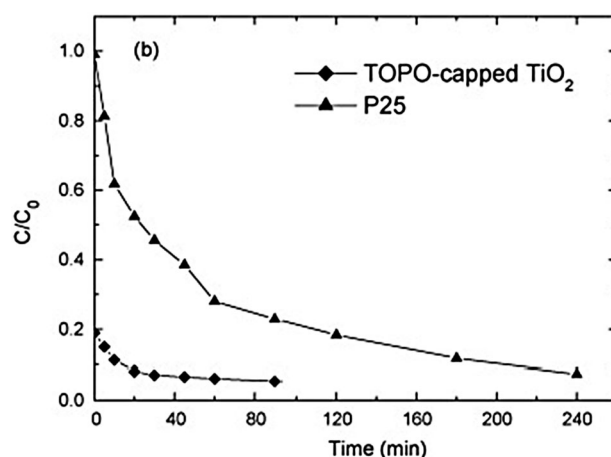


Fig. 8 Photocatalytic degradation of bisphenol A (10 mg L^{−1} initial concentration) with TOPO-capped TiO₂ nanoparticles prepared *via* NHSG (◆) and with P25 (▲). Test realized with 1 g_{cat} L^{−1} under an 8 W UV-lamps irradiation. Reprinted with permission from Chang *et al.*¹²⁹ Copyright 2009 Elsevier.

corrosion phenomenon. The higher stability of the TOPO-capped TiO₂ nanocrystals was ascribed to the hydrolytic stability of Ti–O–P bonds and to the negligible solubility of TOPO in water.

Chang *et al.* developed TiO₂ and Zr-doped TiO₂ nanophotocatalysts using a preparation method adapted from that described by Colvin *et al.*^{129,130,218} TOPO-capped TiO₂ photocatalysts were prepared from TiCl₄ and Ti(OⁱPr)₄, dissolved at 150 °C in molten TOPO under a nitrogen atmosphere, then heated at 400 °C for 3 h.¹²⁹ Then the solution was cooled down to 60 °C and acetone was added to trigger the precipitation of the nanoparticles. The latter were recovered by centrifugation and washed to remove excess TOPO. The particles had a typical size of *ca.* 5 nm and were highly crystalline. FTIR experiments demonstrated that TOPO was chemically bound to the surface of TiO₂ *via* the formation of Ti–O–P bonds. This hydrophobic modifier favored the adsorption of the pollutants (phenol and bisphenol A were tested as model compounds). The photocatalytic performance under UV irradiation of these TOPO-capped TiO₂ nanocrystals was significantly higher than that of Degussa P25 (Fig. 8).

TOPO-capped Zr-doped TiO₂ nanocrystals were prepared by the same method, using ZrCl₄ and Zr(OⁱPr)₄–ⁱPrOH as Zr precursors.²¹⁸ Zirconium was only partially incorporated into the nanocrystals. The Zr–Ti nanoparticles prepared at 320 °C exhibited irregular shapes and a wide size distribution, but increasing the reaction temperature to 400 °C led to more uniform sizes and shapes. Thus, faceted nanorods were obtained for ZrO₂ contents of 3 and 25 mol%. Such Zr doping was responsible for a significant increase of the photocatalytic activity in the degradation of rhodamine B by UV light (305 nm). The nanorods with ZrO₂ contents of 3 mol% exhibited the highest activity, 10 times higher than that of pure TiO₂. The surface TOPO species were partially decomposed during the photocatalytic reaction.

As P itself is an attractive dopant for TiO₂ photocatalysts, Chang *et al.* have also studied the performance of the TOPO-capped Zr–TiO₂ nanoparticles (Zr/Ti = 0.09) after calcination in air, for 3 h and at various temperatures.¹³⁰ The authors demonstrated that phosphate and pyrophosphate species were

incorporated into the surface lattice of Zr-doped TiO₂. The photocatalytic activity in the degradation of bisphenol A in UV light was highly dependent on the calcination temperature but systematically higher than that of TiO₂ P25. The most active phosphated Zr-doped TiO₂ sample was the one treated at 550 °C, exhibiting 6.6 times higher activity than P25. However, the specific surface area decreased dramatically with the calcination temperature, from 114 m² g⁻¹ (calcination at 550 °C) to 2.4 m² g⁻¹ (calcination at 950 °C). Thus, when the activity was normalized to the surface area of the particles, the 950 °C-treated sample was the most active, reaching areal activity 40 times higher than P25.

Portehault *et al.* investigated the photocatalytic activity of a NH layered titanate intercalated with tetramethyl ammonium ions (see Section 2.2.4) in the degradation of 4-chlorophenol in water under a Xe lamp ($\lambda \geq 300$ nm). The photocatalytic activity was significantly lower than that of P25, but it increased during the reaction. This behavior was ascribed to the degradation of the hybrid titanate under UV irradiation into anatase and rutile.⁸⁷

Zhu *et al.* used the benzyl alcohol route to prepare anatase TiO₂ photocatalysts.¹²⁷ TiCl₄ was slowly added to benzyl alcohol at 0 °C under an Ar atmosphere. After stirring for 30 min, the mixture was aged at 60 °C under ultrasound irradiation (8 h). Ultrasound irradiation was said to favor the alcoholysis/condensation reactions. The solid obtained was washed, dried and then calcined. Calcination temperature and calcination time were shown to be important parameters with strong effects on the surface chemistry, crystallinity, texture and photocatalytic activity of the materials. Thus, the calcination step had to be carefully balanced to find the best compromise: it helped removing the organic residues from the surface and improved the anatase crystallization, but if too harsh it favored excessive sintering and loss of specific surface area as well as anatase-to-rutile phase transition. The TiO₂ nanocrystals calcined under different conditions were tested in the photocatalytic degradation of phenol by UV light. Before calcination, the photocatalyst (specific surface area 280 m² g⁻¹) was as active as Degussa P25. The photocatalyst obtained after optimizing the calcination step (calcination at 400 °C for 3 h; specific surface area 72 m² g⁻¹) was significantly more active than Degussa P25.

Using the same benzyl alcohol route, Jia *et al.* obtained at 80 °C rod-like anatase crystals (4–8 nm by 10–60 nm) with a high specific surface area of 170 m² g⁻¹.¹²⁶ These TiO₂ nanorods exhibited good photocatalytic activity (significantly higher than that of P25) in the degradation of rhodamine B under artificial solar light.

TiO₂ photocatalysts were also prepared *via* the NHSG method in supercritical CO₂ (scCO₂).^{63,164} The conventional hydrolytic pathway to TiO₂ is problematic in scCO₂ because CO₂ is highly hydrophobic and water (needed for the hydrolysis reaction) is only slightly soluble in scCO₂. Conversely, organic anhydrides and titanium alkoxides are soluble in scCO₂ and the NH anhydride route is thus suitable for the synthesis of TiO₂ powders. Guo *et al.*⁶³ have reacted Ti(O^{*i*}Pr)₄ with acetic anhydride in scCO₂ at 110 °C and 17 MPa for 20 h, in the presence of a catalytic amount of TiCl₄.^{61,164} Since fluorinated moieties are known to be CO₂-philic, the use of trifluoroacetic anhydride allowed an even better solubility of the precursors. The as-prepared

powders were amorphous but crystallized to anatase by calcination at 500 °C for 5 h. Whatever the anhydride used, powders with a specific surface area of about 80 m² g⁻¹ (after calcination) were obtained. The powder prepared from trifluoroacetic anhydride showed good activity in the photocatalysis of 1-octanol under UV irradiation, higher than that of the powder prepared from acetic anhydride, or that of commercial T805 TiO₂.

The use of Fe for doping TiO₂ might narrow the energy band gap and diminish the recombination of photoinduced electrons and holes. Mixed Ti–Fe oxides have thus been widely studied.^{219–221} Zhu *et al.* have recently reported the preparation of Fe-doped TiO₂ photocatalysts using the NH alcohol route.¹³¹ They reacted TiCl₄ with Fe(NO₃)₃ in *tert*-butyl alcohol at 60 °C until a translucent gel formed. After drying in air at 80 °C, the gel was calcined for 5 h at different temperatures between 300 and 500 °C. Various Fe contents (0.05–0.2 mol%) were investigated. For comparison, corresponding samples were prepared *via* hydrolytic sol–gel (HSG). Their texture is compared in Fig. 9. The specific surface area of the powders calcined at 300 °C ranged from 130 to 200 m² g⁻¹ for the NH powders (depending on the Fe content), much higher than that of the HSG powder (27 m² g⁻¹). The degree of crystallization of the anatase powders was better in the NHSG process. All samples were tested in the degradation of methylene blue at 30 °C under visible light irradiation (>420 nm). The incorporation of Fe enhanced light absorbance in the UV and visible range, resulting in much higher photocatalytic activity. An optimum calcination temperature (300 °C) was found, leading to high degree of crystallization and high specific surface area. NHSG-prepared samples (both pure TiO₂ and Fe-doped TiO₂) showed higher photocatalytic activity than the corresponding samples prepared by hydrolytic sol–gel (Fig. 10). This was ascribed to the improved texture and crystallinity of NH catalysts. The highest activity (nearly 7 times higher than that of Degussa P25) was obtained for the sample prepared by NHSG and doped with 0.1% Fe (after calcination at 300 °C).

With the same aim to improve the visible light activity of TiO₂, Naik and Parida have prepared Fe_{*x*}Ti_{*x*-1}O_{2-*y*}N_{*y*} photocatalysts.¹³²

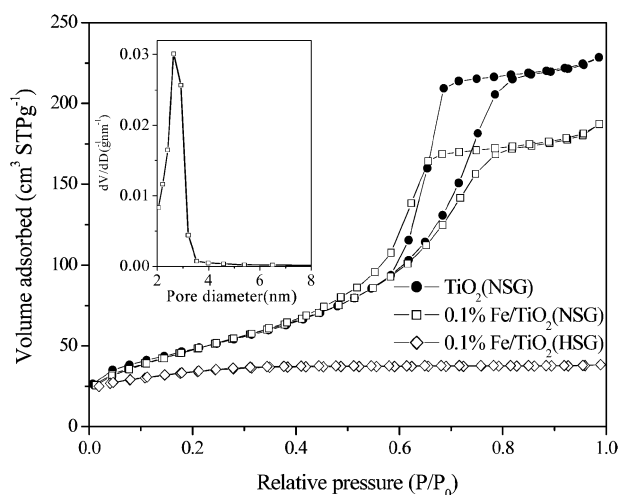


Fig. 9 N₂-sorption isotherms of different photocatalysts prepared under hydrolytic (HSG) or non-hydrolytic (NHG) conditions and with or without Fe-doping. Catalysts calcined at 573 K. Reprinted with permission from Zhu *et al.*¹³¹ Copyright 2007 American Chemical Society.

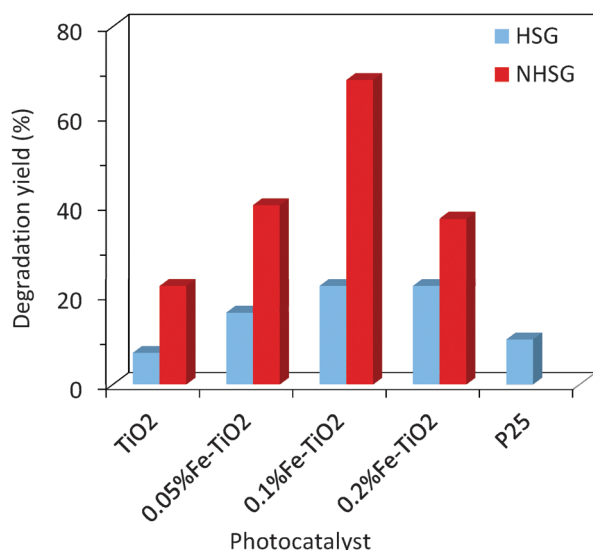


Fig. 10 Photocatalytic degradation of MB over HSG and NHSG-prepared (Fe)TiO₂ photocatalysts. Plot redrawn from Zhu *et al.*¹³¹ Reaction conditions: 50 mg of catalyst, 50 mL of 10 mg L⁻¹ MB solution, three 150 W xenon lamps (cutoff at 420 nm by a glass filter) 30 cm away from the reactor, reaction temperature 30 °C, stirring rate 1000 rpm, 3 h of reaction. Under these conditions, Degussa P25 yielded 10% degradation.

The preparation was done in two steps. Fe-doped TiO₂ was prepared by the NH alcohol route, *via* the reaction of *tert*-butyl alcohol, Fe(NO₃)₃·9H₂O and TiCl₄ at 40 °C to form a gel, which was dried at 80 °C and then crushed to yield a powder. N doping was then performed by heating the powders in an ammonia atmosphere at 500 or 550 °C. Reference samples were also prepared and studied: N-doped TiO₂, Fe-doped TiO₂ and a commercial TiO₂ (P25 Degussa). The Fe_xTi_{x-1}O_{2-y}N_y samples were polycrystalline, containing 85% anatase and 15% rutile, with small crystallites (Fig. 11) and high crystallinity. The N and Fe contents were around 0.45 and 0.9%, respectively. This method allowed the production (without surfactant)

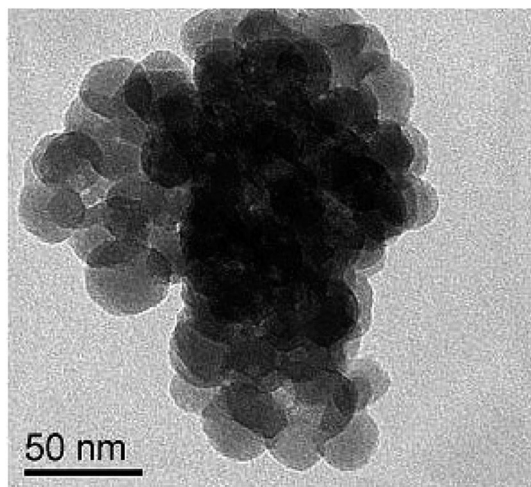


Fig. 11 TEM image of the Fe_xTi_{x-1}O_{2-y}N_y photocatalysts prepared by Naik and Parida *via* a two-step approach. Apparently, the mesoporosity developed by these samples accounts for the interspaces between elementary particles. Reprinted with permission from ref. 132. Copyright 2010 American Chemical Society.

of mesoporous N- and Fe-doped TiO₂ materials with relatively high surface area (70–90 m² g⁻¹) and pore volume (*ca.* 0.2 cm³ g⁻¹), exhibiting a narrow pore size distribution around 7–9 nm. These textural properties favored light harvesting and facilitated the diffusion of reactant molecules during the photodegradation. Under visible light irradiation, the photodegradation of phenol (model for phenolic pollutants which constitute a major environmental threat in various ecosystems)²²² was significantly faster with the new Fe_xTi_{x-1}O_{2-y}N_y catalysts than with TiO₂ Degussa P25. The catalyst also proved to be stable after three catalytic cycles. The observed photocatalytic activity was ascribed to the shift of the absorption band edge to the visible light region due to band gap narrowing by co-doping with N and Fe and to the effective inhibition of electron–hole recombination as confirmed from photoluminescence studies.

TiO₂–SiO₂ photocatalysts were recently prepared in scCO₂ by reacting Ti(OⁱPr)₄ and Si(OMe)₄ with formic acid, at 75 °C and under 8.5 MPa.⁶⁰ The resulting powders were calcined at 350 °C. Here also this NH route allowed overcoming the problems classically encountered under hydrolytic conditions, such as the differences in the hydrolysis and condensation kinetics of the Ti and Si alkoxide precursors and the poor solubility of water in scCO₂. Interestingly, Jammaer *et al.* also tried to use a templating agent (Pluronic surfactant), but the texture was more related to the composition of the composite. While pure TiO₂ had a specific surface area of 180 m² g⁻¹, the composite containing 40 wt% of titania exhibited a much higher specific surface area (above 500 m² g⁻¹) even without a template. The use of scCO₂ on the other hand had a marked effect: it allowed the formation of a homogeneous phase during synthesis, and its easy removal resulted in a more open porosity. These catalysts showed good activity in the UV-induced (350 nm) photocatalytic degradation of phenol in water and of acetaldehyde from air. The best performances were obtained with the sample containing 40% titania, which displayed a better TON than Degussa P25, demonstrating that the presence of silica and the use of scCO₂ as a solvent had a positive influence on the catalytic behavior. Moreover, the catalyst could be easily recovered and recycled without loss of activity.

ZnO and InNbO₄ photocatalysts. Agostiano *et al.* used a method based on the rapid thermal decomposition of molecular precursors in the presence of strong coordinating agents to produce highly crystalline ZnO nanoparticles with narrow size distribution.^{122,123} ZnAc₂ was thermally decomposed at 220–300 °C in the presence of long chain alkylamines and of *tert*-butylphosphonic acid (TBPA) as a capping agent. The resulting nanoparticles (7 nm in size) were resuspended in CHCl₃ and then deposited on a transparent support. The photocatalytic activity of the NH ZnO nanoparticles in the UV-induced degradation of methyl red was compared to that of commercial ZnO particles. When high irradiation intensity was used, the initial activity was higher in the case of the NH ZnO nanoparticles, but similar efficiencies were observed for longer degradation times. When the irradiation intensity was decreased, the activity of the NH ZnO nanoparticles was significantly higher than that of the commercial ZnO. This behavior was ascribed to a photocorrosion of the NH ZnO nanoparticles at high irradiation intensity. In a further study,²²³ these authors have compared

ZnO nanocrystals (6 nm in size) prepared *via* NHSG and HSG. The nanocrystals prepared by NHSG were stabilized by *tert*-butylphosphonic while those prepared by HSG were stabilized by acetate groups. The particles were cast on a quartz slide and tested in the photocatalytic degradation of methyl red and methyl orange. In this case also, the NHSG-made nanocrystals were less effective when the conditions were chosen close to the optimum (pH 6). However, HSG-made nano-photocatalysts were prone to dissolution at pH 2 and 12, and exhibited no activity under such harsh conditions. On the other hand, the TBPA-capped ZnO nanocrystals prepared *via* NHSG were resistant to acid or photochemical corrosion and still exhibited significant photocatalytic activity under extreme conditions. These studies show that the NHSG method coupled with the use of suitable capping agents is a valuable route toward more versatile photocatalysts.

As dopants can also act as recombination centers, many researchers are developing undoped, single-phase oxide visible-light photocatalysts.^{216,217} A good example is the preparation of $\text{In}_{1-x}\text{Ni}_x\text{TaO}_4$, which after NiO-loading could split water into H_2 and O_2 under visible-light irradiation.²²⁴ Such multinary metal oxide photocatalysts designed for visible-light applications are usually prepared by high-temperature ceramic methods (typically above 1000 °C), which implies high energy consumption and leads to oxides with very low specific surface areas (typically 0.5–2 m² g⁻¹). NHSG appears promising to circumvent these issues. Thus, Zhang *et al.* prepared InNbO_4 nanocrystals from indium acetylacetonate and niobium chloride in anhydrous benzyl alcohol at 200 °C (24 h).¹³³ Highly crystalline monoclinic InNbO_4 nanoparticles of 10–30 nm were obtained, with a specific surface area of 54 m² g⁻¹, which has to be compared to 0.7 m² g⁻¹ for a InNbO_4 sample prepared by high-temperature ceramic methods.²²⁵ In the photocatalytic degradation of rhodamine B under visible-light irradiation (>420 nm) the NHSG-prepared InNbO_4 nanoparticles were significantly more active (97% of conversion after 4 h irradiation) than bulk InNbO_4 (9%), Degussa P25 (15%) and even carbon-doped mesoporous TiO_2 (50%) previously reported as a very active photocatalyst.²²⁶

3.1.7. Photocatalytic disinfection. Photocatalysts can also be used as antimicrobial agents under UV-irradiation.^{227–229} TiO_2 is again the typical material used for photocatalytic antimicrobial applications, and its activity against bacteria, viruses and fungi has been largely studied. However, very few works report the application of photocatalysts prepared by NHSG to photocatalytic disinfection.

TiO_2 nanorods. Joo *et al.*⁵⁵ have reported the NH synthesis of TiO_2 nanorods with controlled morphologies and interesting antimicrobial activity, measured in the photocatalytic inactivation of *E. coli*. Under an argon atmosphere, $\text{Ti}(\text{O}^i\text{Pr})_4$ was added to oleic acid and the mixture was heated at 270 °C for 2 h in the presence of hexadecylamine co-surfactant. After addition of excess ethanol, a white precipitate formed that was recovered by centrifugation. Rods of 2.0–2.7 nm × 28–39 nm, grown along the [001] direction, were clearly observed by TEM (Fig. 12). Note that the rod diameter and length could be adjusted to some extent by adding hexadecylamine. This precipitate could be dispersed in nonpolar organic solvents. Oleic acid coordinated to the surface of the TiO_2 nanorods

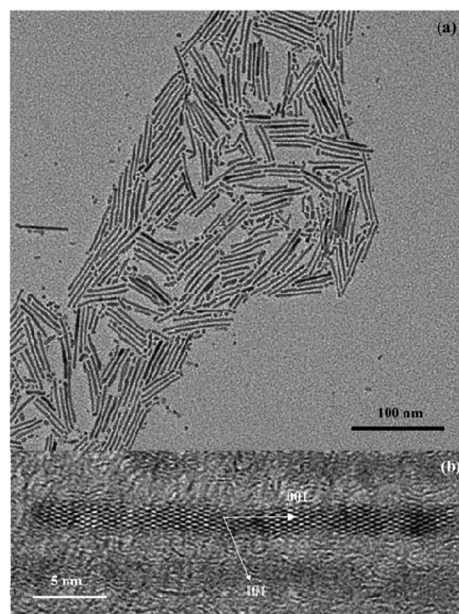


Fig. 12 (a) TEM image of as-synthesized TiO_2 nanocrystals. (b) HRTEM image of a TiO_2 nanorod. Reprinted with permission from Joo *et al.*⁵⁵ Copyright 2005 American Chemical Society.

could be easily removed by reduction of the carboxylic groups, leading to powders dispersible in water. These powders exhibited a specific surface area of 198 m² g⁻¹ and large number of hydroxyl groups. A slurry of *E. coli* and the photocatalyst in a Pyrex reactor (UV cutoff < 300 nm) was stirred magnetically under UV irradiation (black light blue lamp, 18 W) at 20 °C and the concentration of viable *E. coli* as a function of irradiation time was determined. The TiO_2 nanorods were significantly more efficient in the inactivation of the bacteria than commercial P25. This high efficiency was ascribed to the high surface area and large number of hydroxyl groups, leading to a large number of hydroxyl radicals under light irradiation.

TiO_2 nanoparticles. Stoyanova *et al.* have prepared 10–20 nm-sized anatase particles *via* the NH reaction of TiCl_4 with benzyl alcohol.¹²⁸ The reaction was carried out under vigorous stirring at 60 °C or 100 °C and then the vials were left for aging at room temperature. Anatase particles between 4 and 30 nm in size were obtained. Under UV irradiation, they catalyzed the photodegradation of malachite green and showed significant antibacterial effect against *Escherichia coli*, chosen as a representative water pathogen.

3.1.8. Oligomerization of benzylic alcohols. Olliges-Stadler *et al.*¹¹⁹ have exploited the catalytic activity of tungsten oxide nanoparticles to prepare a monolithic tungsten oxide–polybenzylene hybrid. The reaction of tungsten isopropoxide with benzyl alcohol did not lead to a suspension of oxide nanoparticles (as classically expected in the benzyl alcohol route), but yielded hard monoliths, consisting of $\text{W}_{18}\text{O}_{49}$ nanowires embedded in a short chain polybenzylene matrix ($n \approx 16$). To study the mechanism of formation of polybenzylene, the nanoparticles were extracted and used as catalysts in the polymerization of benzyl alcohol and of dibenzylether. It was concluded that the oligomerisation of benzyl alcohol

involved the intermediate formation of dibenzylether. Additionally, the extracted $W_{18}O_{49}$ nanowires exhibited good activity in the oligomerization of a variety of benzylic alcohols (substituted on the aromatic ring by methyl, *tert*-butyl or fluorine groups) and of 2-thiophene methanol.

3.2. Entrapment of active species in NH gels

There is a tremendous interest for the immobilization of homogeneous catalysts on a solid matrix. The aim is to benefit both from the high catalytic performances (activity, selectivity, stereoselectivity, *etc.*) of the active entity and from the classical advantages of heterogeneous catalysts (easy separation from the reaction media, improved recyclability and stability). Grafting methods may be used to immobilize active species (or their precursor) on a preformed support. Sol–gel routes allow for the direct entrapment of such active components in a porous matrix.^{11,230} In this context, non-hydrolytic conditions are particularly useful to overcome the difficulty of processing active species that are unstable or insoluble in aqueous media. Other advantages include easy access to homogeneous mixed oxides with high surface areas.

3.2.1. Metallocene olefin polymerization catalysts. Metallocenes are widely used catalysts for the polymerization of olefins due to their high activity and excellent stereochemical control and much work has been devoted to their heterogenization in the last 20 years.²³¹ Fisch *et al.* have studied the immobilization of metallocenes in NHSG-made silica,^{134,232} Si–Ti¹³⁵ and Si–W matrices.¹³⁶ Their first attempts consisted of entrapping various metallocenes (Cp_2ZrCl_2 , $(^nBuCp)_2ZrCl_2$, $(^iBuCp)_2ZrCl_2$, $(^iBuCp)_2ZrCl_2$, Cp_2TiCl_2 , Cp_2HfCl_2 , $Et(Ind)_2ZrCl_2$ and $Et(IndH_4)_2ZrCl_2$) in a silica matrix,^{134,232} prepared by an alkoxide route at moderate temperature to avoid thermal deactivation of the metallocene. Thus, a solution of the metallocene, $SiCl_4$ and $Si(OEt)_4$ in toluene was heated at 70 °C for *ca.* 3 h in the presence of $FeCl_3$, added to play the role of Lewis acid catalyst and trigger the condensation reactions.³⁵ Under these conditions, it is likely that the Zr–Cl groups also reacted, leading to a grafting of the complex rather than simple entrapment. The resulting oxide was washed with a triethylaluminium *n*-hexane solution to eliminate residual ethoxide groups. Then it was dried under vacuum at room temperature and milled under an inert atmosphere. The best catalysts for ethylene polymerization in the presence of methylaluminoxane (MAO) (classically used as a co-catalyst in such polymerization reactions) were those containing Cp_2ZrCl_2 , Cp_2HfCl_2 and $(^nBuCp)_2ZrCl_2$. No leaching of metal was observed. The catalytic activity was intermediate between that of the homogeneous metallocene and that of the metallocene grafted on silica.

More recently, Fisch *et al.* reported the immobilization of Cp_2ZrCl_2 in NHSG-made Ti–Si mixed oxides.¹³⁵ The method was based on the reaction of a solution of Cp_2ZrCl_2 , $SiCl_4$, $TiCl_4$ and $Si(OEt)_4$ or $Ti(O^iPr)_4$, in toluene at 70 °C and in the presence of a catalytic amount of $FeCl_3$. The resulting materials showed interesting specific surface area ranging from 140 to 370 m² g^{−1}, depending on the Ti loading. The catalytic activity of the immobilized complex in ethylene polymerization was related to the relative proportions of Ti and Si in the matrix.

Only the sample with about 70 wt% TiO_2 was more active than zirconocene-grafted silica, while the samples based on silica-rich matrices were only poorly active.

In addition, these authors used the same route to immobilize Cp_2ZrCl_2 in a Si–W mixed oxide matrix, in the hope that the increased acidity would yield catalysts of high activity and need a lower amount of MAO co-catalyst than the catalysts produced by immobilization of the metallocene within SiO_2 ¹³⁶ or Si–Ti matrices.¹³⁵ The complex was dissolved in toluene, then $FeCl_3$ (in catalytic amount), $SiCl_4$, WCl_6 and $Si(OEt)_4$ were added. Gelation took place after ~ 3 hours at 70 °C, leading to the complex entrapped in a WO_3 – SiO_2 matrix with about 10 wt% of WO_3 . The gel was then washed, dried and milled as described above. FTIR measurements suggested that W atoms were intimately incorporated into the silica network *via* isomorphous replacement of Si atoms, leading to coordinately unsaturated W atoms acting as Lewis acid sites. Entrapment of the metallocene did not affect significantly the texture of the WO_3 – SiO_2 mixed oxide. The activity of Cp_2ZrCl_2 encapsulated in WO_3 – SiO_2 in ethylene polymerization was significantly higher than that of catalysts prepared by grafting Cp_2ZrCl_2 on acidic supports such as sulfated alumina or zeolite, but it remained less active than the homogeneous complex. A small amount of MAO was still required to activate the catalyst, in contrast to Cp_2ZrCl_2 grafted on sulfated alumina, but the activity decreased when the amount of MAO increased. This behavior was ascribed to the intermediate acidity of the WO_3 – SiO_2 matrix, which decreased the electron density on the Zr center and assisted the MAO for the formation of highly active catalytic species. Conversely, an excess of MAO may compete with the monomer for coordinating to the active sites, thus reducing the activity.

3.2.2. Oxidation/epoxidation catalysts. Ciuffi's group used NHSG to encapsulate different oxidation catalysts such as metalloporphyrins and salen complexes in amorphous alumina matrices.^{137–139} The immobilized catalysts were obtained by refluxing a solution of $AlCl_3$ and iPr_2O in dichloromethane under an inert atmosphere, in the presence of the complex. The resulting gel was aged, dried under vacuum and washed thoroughly, then heat-treated at temperatures ranging from 60 to 270 °C.

Thus, de Lima *et al.* reported the synthesis of Fe(III) and Mn(III) 5,10,15,20-tetrakis(pentafluorophenyl) porphyrins entrapped in alumina.¹³⁹ The metalloporphyrin was homogeneously distributed into the material. Importantly, no leaching of the complex was observed during washing, contrasting with the complete leaching observed when the complex was adsorbed on an alumina support, or when it was entrapped *via* a conventional hydrolytic sol–gel method. The materials heat-treated at 60 °C after washing exhibited a smooth, compact morphology and low specific surface area (~ 5 m² g^{−1}), whereas the materials heat-treated at 270 °C showed a rough, particulate morphology and a much higher specific surface area (~ 600 m² g^{−1}). The new catalysts were tested in the epoxidation of (*Z*)-cyclooctene using iodosylbenzene as an oxidant. High epoxidation yields were obtained, similar to those obtained using the metalloporphyrin in solution or supported on a silica matrix. After 1 h of reaction, the catalysts that were heat-treated at 270 °C led to higher epoxide yields than those treated at 60 °C, as expected from their higher specific surface area. Surprisingly, the situation was

reversed after 24 h of reaction, indicating some deactivation of the catalysts heat-treated at 270 °C, which was ascribed by the authors to a lower mechanical stability of these catalysts.

Caiut *et al.* have used the same NHSG method to prepare an epoxidation catalyst by encapsulation of a Ni complex ([5,7,12,14-tetramethyldibenzo[*b,f*]-1,4,8,11-tetraaza[14]annuleno]nickel(II), abbreviated NiTMTAA) in an alumina matrix.¹³⁸ The reaction of AlCl₃ and ¹Pr₂O in the presence of NiTMTAA led to a yellow-brown powder. This color is characteristic of anhydrous Ni compounds, showing that the preparation was effectively carried out under anhydrous conditions. After drying, washing and treating at 130 °C, about 80% of the initial amount of the complex was encapsulated and UV-Vis spectroscopy showed that its structure was preserved in the alumina matrix. The specific surface area of the sample was relatively high (300 m² g⁻¹). (*Z*)-cyclooctene epoxidation with iodosylbenzene (PhIO) was used as a probe reaction to evaluate the oxidation potential of the catalysts. The heterogeneous hybrid was a moderately active catalyst in this reaction, whereas NiTMTAA used alone as a homogeneous catalyst was inactive. This suggested that the alumina matrix effectively prevented the chemical degradation of NiTMTAA under the reaction conditions. Interestingly, the same NiTMTAA complex was either entrapped in alumina *via* hydrolytic sol-gel or supported on a commercial alumina for comparison. In both cases, complete leaching of the complex from alumina was observed. Thus, NHSG was the only effective method for the immobilization of such an azo-compound in an alumina matrix.

Mac Leod *et al.* have used the same method to encapsulate a Jacobsen catalyst (Fig. 13) in an alumina matrix.¹³⁷ Such manganese salen complexes have been reported as versatile catalysts for the enantioselective epoxidation of unfunctionalized olefins.²³³ The authors demonstrated that the structure of the complex was preserved in the final solid. This hybrid material was totally amorphous, and the thermal stability of the complex was not affected by its incorporation into the aluminium matrix. It must be noted that previous attempts based on conventional hydrolytic sol-gel chemistry were unsuccessful, leading to the complete leaching of the complex out of the porous matrix.¹³⁸ The immobilized Mn(salen) catalyst was evaluated in the selective oxidation of styrene, (*Z*)-cyclopentene and cyclohexane with various oxidants. Although the specific surface area was rather low (31 m² g⁻¹), the immobilized complex was found more active than the corresponding homogeneous catalyst in the epoxidation of styrene and (*Z*)-cyclopentene and cyclohexane. Good results

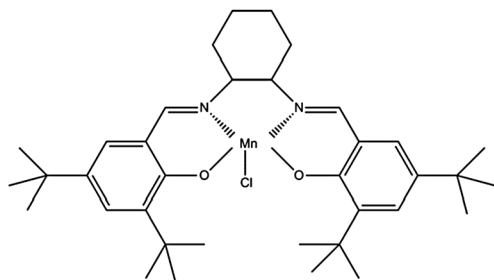


Fig. 13 Example of an organometallic complex (Jacobsen catalyst) that has been successfully entrapped in a NHSG alumina matrix by Mac Leod *et al.*¹³⁷ and successfully used in mild oxidation reactions.

were obtained using H₂O₂ 70%, whereas H₂O₂ 30% was not an effective oxidant. The leaching of active species was not observed, and the recyclability was shown to be excellent.

3.2.3. Hydrogenation catalysts. Anderson *et al.*⁵⁷ reported the entrapment of palladium nanoparticles in a silica matrix prepared by the formic acid route in ionic liquid medium previously reported by Dai *et al.*⁵⁶ In this one-pot synthesis, the Pd nanoparticles (diameter $\approx$ 1 nm) were obtained by reaction of palladium(II) acetate in 1-butyl-3-methylimidazolium bistrifluoromethylsulfonate ionic liquid ([bmim][NTf₂]) in the presence of 0.2 mol of triphenylphosphine at 80 °C. Then Si(OEt)₄ and formic acid were added to the suspension of the Pd nanoparticles stabilized within the ionic liquid, leading to the formation of an ionogel. After aging, the ionic liquid was extracted by refluxing in acetonitrile to yield a grey green monolith. The Pd loading in the resulting “aerogel” was 0.37 wt%, instead of the 1.85 wt% expected; unfortunately, the textural properties of this material were not reported. TEM images showed the formation of well-dispersed Pd nanoparticles (diameter $\approx$ 2 nm). This material was evaluated in the liquid-phase hydrogenation of cinnamaldehyde in toluene at 80 °C at 10 bar of H₂ pressure. After 1 h complete conversion to the desired product, hydrocinnamaldehyde, was found. However, recycling of the catalyst led to a significant decrease of the reaction rate (from 0.47 mM s⁻¹ to 0.28 mM s⁻¹). This catalyst was also evaluated in the Heck coupling reaction (see Section 3.2.4.).

Craythorne *et al.* utilized the same methodology for the entrapment of [RhCl(PPh₃)₃] and [Rh₂-(COD)₂(dppm)(μ₂-Cl)]BF₄ in a silica matrix.^{140,141} The complex was dissolved in a minimum of CH₂Cl₂ and added to a solution of ionic liquid ([bmim][NTf₂]) and Si(OEt)₄ under N₂. Once the catalyst was added no further precautions to exclude air were taken. After addition of formic acid, an ionogel formed rapidly. The ionogel was aged for 1 week, then it was continuously extracted with boiling CH₂Cl₂ to remove excess ionic liquid and catalyst. The specific surface areas of the catalysts was quite low (<20 m² g⁻¹). This was ascribed to the entrapment of ionic liquid within the pores of the material. Indeed, despite the extraction some ionic liquid remained in the gel, as shown by XPS analysis. In both cases, the Rh content in the materials was 0.06 wt%; the ionic liquid content was not reported. For comparison, [RhCl(PPh₃)₃] and [Rh₂-(COD)₂(dppm)(μ₂-Cl)]BF₄ were also entrapped in silica by a conventional sol-gel route (in the absence of ionic liquid). All these materials were tested as catalysts for styrene hydrogenation at 100 °C (27 bar) and their activity was compared with that of the parent homogeneous catalyst, and commercially available 5% Rh on carbon and 5% Rh on alumina. The catalysts based on entrapped [RhCl(PPh₃)₃] (by conventional sol-gel or by the formic acid route in ionic liquid) were the most active catalysts, exhibiting turnover frequencies of 0.20 and 0.32 min⁻¹, respectively, 4–6 times greater than the initial rate measured for the homogeneous catalyst. The leaching of Rh species from the entrapped catalysts was below the limit of detection, and all of these catalysts could be recycled well 4 times without any loss in activity. The formic acid route in ionic liquid reduces gelation times with respect to conventional methods and affords catalysts of reliable composition, varying very little from batch to batch and giving excellent selectivity and activity.

3.2.4. C–C coupling catalysts. Anderson *et al.* reported the Heck coupling of iodobenzene and butyl acrylate catalyzed by a silica “aerogel” containing entrapped palladium nanoparticles and prepared by the formic acid route (see Section 3.2.3.).⁵⁷ Complete conversion to *trans*-butyl cinnamate was obtained after 2 h in DMF at 80 °C (a trace of iodobenzene was also detected). The number of moles of substrate converted per mole of catalyst (TON) was 2092, while the number of moles of substrate converted per mole of catalyst per hour (TOF) was 1307 h^{−1}. ICP analysis showed that ~7% of the Pd was leached in the solution during the first reaction. However, the reaction rate decreased significantly on recycling, from 0.32 to 0.06 mM s^{−1}.

Volland *et al.* used the formic acid route in ionic liquid to encapsulate Pd(OAc)₂ in a silica ionogel or in a hybrid MeSiO_{1.5}–SiO₂ ionogel. Contrary to the former example, the authors did not remove the ionic liquid (1-butyl-3-methyl imidazolium bromide, [bmim][Br]) by extraction but used the resulting ionogel as a catalyst for the Heck–Mizoroki reaction.¹⁴² Three samples were prepared: Pd(OAc)₂–[bmim][Br] encapsulated in silica, Pd(OAc)₂–P(Ph)₃–[bmim][Br] encapsulated in silica, and Pd(OAc)₂–P(Ph)₃–[bmim][Br] encapsulated in MeSiO_{1.5}–SiO₂. The loading of palladium in the ionic liquid was ~1.1 wt% (phosphine free sample) or ~0.11% (phosphine containing samples). Pd(OAc)₂ and P(Ph)₃ (if any) dissolved in CH₂Cl₂ were mixed to [bmim][Br], formic acid and Si(OMe)₄ (and Me Si(OMe)₃ in the case of the hybrid ionogel). In all cases yellow, transparent monolithic ionogels were obtained, which could be cast as pellets or cones.

The silica-based ionogels were used as catalysts for the coupling reaction of ethyl acrylate with iodobenzene in toluene at 100 °C. The hybrid ionogel was used as a catalyst for the coupling reaction of 4-vinyl pyridine with 4-iodo-*N,N*-dibutylaniline. The monolithic ionogels were put into glass baskets immersed in the solution, thus avoiding grinding by the magnetic stir bar. In all cases, the ionogels were found to be slightly more active than the corresponding homogeneous systems (Pd(OAc)₂ and Pd(OAc)₂–P(Ph)₃). The reaction stopped when the ionogel was removed from the hot solution, indicating that no leaching of active Pd species occurred, although traces of Pd (~1 ppm) were found in the solution. At the end of the reaction the ionogels and the salt products formed an agglomerate that could be removed with the basket, thus facilitating the separation from the product. However, the ionogel was fragmented and could not be effectively recycled.

3.3. Grafting of active sites

An important aspect of heterogeneous catalysis research is the investigation of isolated and well-defined catalytic sites grafted at the surface of a support.²³⁴ Such model catalysts are invaluable for the fundamental understanding of the catalytic acts involved in the studied reactions, but also often lead to the development of new catalysts with potential applications.²³⁵ Non-hydrolytic routes have been used to build well-defined surface sites with molecular-level control.

3.3.1. Grafting of bimetallic V–Ti sites. Classical approaches to prepare V–Ti–Si catalysts (used in selective oxidation reactions or as SCR catalysts) are based on the impregnation of silica with a Ti precursor to form a titania layer, followed by the deposition

of a V precursor from solution, leading to surface vanadium oxide.²³⁶ Again, this route is limited by the tendency of impregnated species to agglomerate on the support surface during dehydration.¹⁵¹ Rice and Scott proposed to prepare model bimetallic V–Ti single sites catalysts using non-hydrolytic condensation reactions between chloride and alkoxide groups.²³⁷ The support used was the commercial silica Aerosil 200 from Degussa, which was partially dehydroxylated at 500 °C under vacuum. The gas–solid reaction of excess VOCl₃ with the surface hydroxyl groups of silica led to the formation of a surface site identified as ≡SiOVOC₃ (V loading of 2.2 wt%) and to the disappearance of hydroxyl groups. The reaction of this surface complex at room temperature with TiCl₄ vapor led to the formation of a ≡SiOTiCl₃ surface complex with elimination in the gas phase of VOCl₃, indicating the occurrence of an exchange reaction. Conversely, the reaction of SiOVOC₃ surface site at room temperature with Ti(O^{*i*}Pr)₄ vapor led to the formation of a 1 : 1 V–Ti surface complex, ≡SiOTi(O)₃V(O^{*i*}Pr)₂, and 2-propyl chloride, 2-propanol, and propene (but no HCl) in the gas phase. It is proposed that these systems could serve as reference catalysts for the active sites of V–Ti–Si catalysts; however, no catalytic test was reported. This sequential CVD technique could be useful for the “design” of well-defined isolated multifunctional active sites in heterometallic oxide catalysts.

3.3.2. Decomposition of tri-*tert*-butoxysiloxy derivatives.

Tilley and co-workers have extended their thermal decomposition route of tri-*tert*-butoxysiloxy derivatives to the construction of isolated MO_{*x*}–SiO₂ species on an oxide surface (Fig. 14).

Thus, isolated iron(III) sites were generated at the surface of a porous silica support (SBA-15) by grafting/thermal decomposition of the molecular precursor Fe[OSi(O^{*t*}Bu)₃]₃·THF (**3**).⁷³ The dried support (OH coverage of ~1 OH nm^{−2}) was reacted with **3** in dry hexane for 24 h at room temperature under an inert atmosphere, then filtered, dried under reduced pressure and washed with dry hexane. Fe loadings between 0.056 and 1.90 wt% could be obtained depending on the amount of complex **3** reacted with the support. The authors demonstrate that in this step the complex reacts with the hydroxyl groups of the support to yield mainly grafted ≡SiO–Fe[OSi(O^{*t*}Bu)₃]₂(THF) species, with elimination of HOSi(O^{*t*}Bu)₃. In the range of loading explored, the structure of the surface-bound iron species was not affected by the surface density. The solids were then calcined at 300 °C in O₂ to thermally decompose the grafted species. This treatment led to a dramatic decrease of the C and H content of the solid, indicating complete removal of the –O^{*t*}Bu and THF ligands. UV-vis characterization demonstrated that, whatever the Fe loading, the coordination environment of the iron was not significantly modified, showing that the iron species retained their isolated Fe³⁺ structure after calcination and did not yield iron oxide clusters. This was identified as a decisive advantage of this particular grafting process.

The resulting catalysts were tested in the selective oxidation of various hydrocarbons with H₂O₂. The oxidation of benzene to phenol was achieved with higher selectivity than on FeCl₃/SiO₂ and with a TOF of 2.5 × 10^{−3} s^{−1}, higher than other catalysts like FeCl₃/Al₂O₃, FeCl₃/silica–alumina, FeCl₃/TiO₂. One important result concerned the oxidation of toluene to benzaldehyde and cresols, performed with higher TOF than

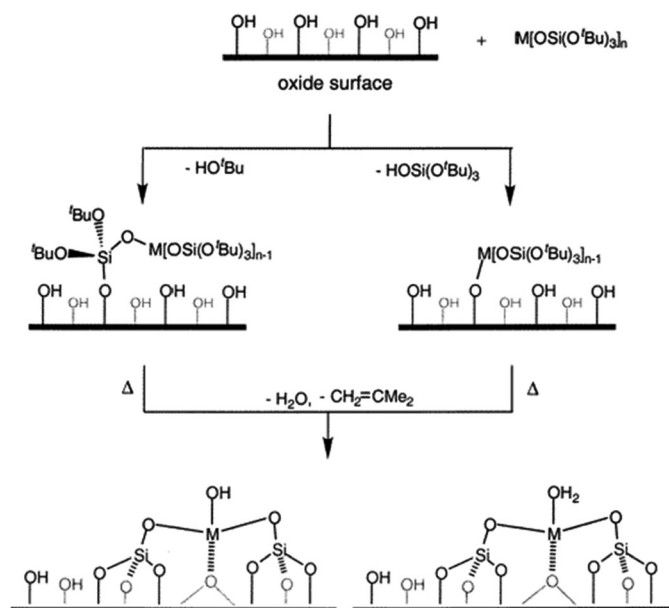


Fig. 14 Scheme of the thermal decomposition route developed by Tilley and co-workers. Tri-*tert*-butoxysiloxane derivatives are used to generate isolated MO_x-SiO_2 species on an oxide surface. Reprinted with permission from Nozaki *et al.*⁷³ Copyright 2002 American Chemical Society.

various homogeneous iron catalysts. The TOF did not change with the Fe loading, which is consistent with the presence of isolated iron sites in the calcined catalysts over the range of loading investigated. Conversely, calcination at 500 °C of the grafted samples yielded poorly active catalysts and the presence of iron oxide clusters was demonstrated. Thus, this molecular approach in a non-aqueous medium was successful because it allowed the covalent attachment of the molecular species and favored the grafting reaction while suppressing the unwanted intermolecular hydrolysis and condensation reactions between iron precursors. In addition, the remaining siloxide ligands of the grafted species contribute additional SiO_4 units to the surface upon calcination, which may help to stabilize the mononuclear inorganic iron center.

A similar strategy was used to prepare single-site titanium⁷² or tantalum¹¹³ catalysts for olefin epoxidation. Thus, under anhydrous conditions, the tri-*tert*-butoxysiloxane derivative $^iPrOTi[OSi(O^tBu)_3]_3$ (**4**) was reacted with the surface hydroxyls of various silica supports (Aerosil 200, MCM-41, SBA-15). The grafting proceeded *via* elimination of $HOSi(O^tBu)_3$ and yielded surface species largely characterized by an isolated, tetrahedral environment. The exclusion of water in the preparation prevents the formation of titania clusters. The grafted species appeared resistant to leaching. Before calcination, the catalytic activity in the epoxidation of cyclohexene in toluene, at 65 °C and with cumene hydroperoxide (CHP) or *tert*-butyl hydroperoxide (TBHP) was very high, with TOF values after 1 h up to 1500 h^{-1} , significantly higher than that found for catalysts prepared by grafting other Ti precursors. This was tentatively ascribed to the fact that the TiO_4 environment pre-exists in the precursors used. The higher activity of the catalysts derived from MCM41 and more particularly SBA15 was ascribed to the high surface areas of these supports compared to Aerosil 200. Calcination in O_2 at 300 °C provoked the decomposition of the grafted species into purely inorganic species. Slight changes in the Ti environment were observed during this treatment: while most

of the titanium was still present as isolated species, the presence of TiO_x oligomers and/or TiO_2 -like clusters was observed. These changes in the Ti environment were reflected by a decrease by a factor of ~ 2 of the TOF values.

The grafted catalysts were also much more active than the xerogels prepared by decomposition of tri-*tert*-butoxysiloxane titanium complexes,¹¹² presumably due to the better accessibility to the active sites.

A Ta/SiO₂ catalyst was obtained by a similar method, by reacting the complex $(O^iPr)_2Ta[OSi(O^tBu)_3]_3$ (**2**) with a mesoporous silica support (SBA15) in dry pentane at room temperature, followed by drying.¹¹³ This catalyst was found to be moderately active for the oxidation of cyclohexene at 65 °C in acetonitrile with aqueous H_2O_2 , CHP and TBHP. The leaching of catalytically active soluble tantalum species was negligible under these experimental conditions. Interestingly, aqueous H_2O_2 was the most active oxidant, in contrast to what was observed with the above-mentioned single site titanium catalysts, suggesting that Ta(v) sites are more tolerant to the presence of water for cyclohexene oxidation than the analogous Ti(IV) sites. The conversion reached 14% (relative to initial H_2O_2 concentration) after 2 h, with an initial rate of $6.7\text{ mol oxidation products mol}_{Ta}^{-1}\text{ min}^{-1}$; after calcination at 300 °C in O_2 the activity decreased by a factor of ~ 2 . In both cases the selectivity was low and a mixture of cyclohexene oxide, cyclohexenol and cyclohexanone was obtained.

3.4. Catalyst supports

Apart from carbon-based materials, most catalyst supports consist of oxides or mixed oxides chosen for their textural properties, mechanical strength or surface functionality. Silica, titania, alumina and zirconia are the most common catalyst supports. In mixed oxide supports the homogeneity (dispersion of one oxide in the other) is another crucial parameter. One can cite the important examples of Si–Al (amorphous or zeolitic),²³⁸

Mg–Al derived from hydrotalcites,²³⁹ Si–Ti,²⁴⁰ Ti–Zr,²⁴¹ Ti–Al,²⁴² etc.

Although NHSG offers very simple and cost effective routes to (mixed) oxides with outstanding textures, there are still very few examples in the literature of catalytic supports designed by these routes.

3.4.1. Silica, Si–Zr and Si–Ti supports. The group of dos Santos has reported on the synthesis of active heterogeneous metallocene catalysts by immobilization of metallocenes on a silica–zirconia²⁴³ support prepared by NHSG. This support was obtained by the alkoxide route, using Si(OEt)₄, SiCl₄ and ZrCl₄ precursors dissolved in toluene, resulting in a Si–Zr mixed oxide with a ~13 wt% Zr loading. After activation of the support at 450 °C under vacuum, (nBuCp)₂ZrCl₂ or Cp₂ZrCl₂ toluene solutions were contacted with the support at room temperature for 30 min. The solid recovered after filtration was simply washed with toluene and dried under vacuum. The zirconocene catalysts grafted on these various supports were active in ethylene polymerization. It was observed, however, that grafting resulted in a significant decrease in surface area (from 193 to 18 m² g⁻¹), presumably related to the blocking of the small pores by the grafted species. The high density of grafted species was presumably responsible for the stabilization of some bimolecular species, which—unlike monomolecular species—are inactive in ethylene polymerization. Further improvements are thus needed to stabilize highly dispersed and active zirconocene species on these supports.

Gold nanoparticles dispersed on Ti containing supports have attracted much attention as catalysts for the vapor phase epoxidation of propylene with O₂.^{244,245} The molecular dispersion of Ti in the silica matrix, as well as the presence of large pores are considered decisive parameters dictating the catalytic activity of the supported gold nanoparticles. Accordingly, Dai *et al.* have explored the potentiality of the NHSG method to prepare Ti–Si supports for Au nanoparticles.¹⁴⁴ Mixed oxides with variable Ti content (from 6 to 20 mol%) were prepared by the ether route: the chloride precursors and iPr₂O were heated in a sealed autoclave at 120 °C for 96 hours as previously reported.⁹¹ The xerogels were then calcined at 500 °C in air. Gold nanoparticles (4 wt%; 2–4 nm in size) were then generated at the surface of the supports by a deposition–precipitation method,^{246,247} using an aqueous solution of HAuCl₄. The samples containing less than 12 mol% Ti were amorphous, with specific surface areas ranging from 460 to 660 m² g⁻¹ and average pore diameters ranging from 3.0 to 3.8 nm. The gas-phase epoxidation of propylene in O₂ and H₂ was performed at 120 °C under atmospheric pressure at a GHSV of 4000 cm³ h⁻¹ g⁻¹_{cat}. The activity was found to vary with respect to the amount of Ti in the support, apparently linked to the stabilization of dispersed Ti sites in the silica matrix. The best catalyst (10 mol% of Ti in the support) exhibited a conversion as high as 6.8% and 95% selectivity to propylene oxide (PO), thus in the same order or significantly higher than previously reported catalytic productivities.^{145,248} Importantly, the study included Ti–Si supports prepared by hydrolytic sol–gel (HSG); the corresponding catalysts exhibited slightly lower specific surface areas (270–350 m² g⁻¹) than the NHSG-based catalysts and comparable pore diameters. These HSG-based catalysts showed

high selectivities (92.1 to 95.5%) to propylene oxide but were significantly less active (2.1–2.7%) than those based on supports prepared by the NHSG method.

3.4.2. Hybrid supports. Dever *et al.* have also used a NHSG route to prepare hybrid silicas functionalized by indenyl groups, which were then reacted with ZrCl₄ to form new immobilized zirconocene catalysts.¹⁴³ They first prepared a series of indenyl-modified silicas by reacting organochlorosilane derivatives (Me₂SiCl₂ or (ClMe₂Si)₂O), Ind₂SiCl₂ and Si(OEt)₄ in the presence of ZrCl₄ (which acts as the Lewis acid catalyst for the condensation reactions) at 110 °C. The gel was then dried under vacuum then crushed into powders. The use of (ClMe₂Si)₂O instead of Me₂SiCl₂ led to a higher content of residual Cl and OEt groups in the final material. The metallation of these hybrid supports with ZrCl₄ was done after intermediate treatments, including triethylaluminium to eliminate residual chloro and ethoxy functions and nBuLi to deprotonate the indenyl groups. This resulted in the formation of =Si(Ind)₂ZrCl₂ sites, active for the polymerization of ethylene. The effects of various parameters of the preparation were investigated. The molecular weight distribution of the polyethylenes (PE) was strongly dependent on the preparation conditions of the hybrid catalyst. The best catalysts exhibited promising activities in the range of 150–190 g_{PE} g_{cat}⁻¹ h⁻¹ bar⁻¹.

3.4.3. Alumina supports. The most common alumina supports are γ or η phases produced by hydrolysis of aluminium precursors. On the other hand, aluminas prepared by NHSG remain amorphous up to 750 °C, keeping large specific surface areas, up to 400 m² g⁻¹ after calcination for 5 h at 650 °C.³⁷

Dolev *et al.*¹²¹ have used the ether route to prepare a Pt-based catalyst supported on an amorphous alumina with large surface area. AlCl₃ was reacted with iPr₂O, using dichloromethane as a solvent, at 90 °C for 24 h. After vacuum drying, the alumina xerogels were calcined in dry air. The specific surface of this NH alumina decreased from 420 m² g⁻¹ (calcination for 5 h at 500 °C) to 274 m² g⁻¹ (calcination for 5 h at 750 °C). The non-hydrolytic alumina was then impregnated using either Pt(acac)₂ in toluene or H₂PtCl₆ in water. For comparison, the authors also used two commercial γ-Al₂O₃ supports (170 and 227 m² g⁻¹). The amount of Pt that could be accommodated by the alumina surface by impregnation with Pt(acac)₂ in toluene was shown to be directly related to the available surface area, which was not significantly modified after the impregnation step. The Pt uptake was thus higher with the NHSG-made alumina support, thereby allowing the preparation of catalysts with a higher Pt weight loading. On the other hand, impregnation with H₂PtCl₆ in water led to a significant decrease of the specific surface area, from 274 to 175 m² g⁻¹. In both cases, the Pt phase (up to 1 wt% of Pt) was stabilized in a highly dispersed form, not detectable by TEM or XRD. Dispersion measurements by H₂ chemisorption showed that the catalysts (especially those prepared by impregnation in toluene) had a high proportion of accessible Pt atoms (up to 49% Pt dispersion).

Interestingly, the authors have also investigated the preparation of Pt/Al₂O₃ catalysts in one step *via* NHSG. The same reaction was performed, but the desired amount of (C₆H₅CN)₂PtCl₂ or PtBr₄ was added to the sol after 2 h of reaction. The resulting

Pt-doped xerogels (~ 1 wt% Pt) exhibited specific surface areas of $330 \text{ m}^2 \text{ g}^{-1}$ after calcination at 600°C . This one-step method shows the possibility to disperse Pt in the form of small and accessible nanoparticles. The Pt dispersion was quite high (32%) for the materials calcined at 500°C , but it decreased to 7–13% in the samples calcined at 600°C .

3.4.4. TiO_2 – Al_2O_3 supports. TiO_2 – Al_2O_3 mixed oxides are used as supports for various catalytic reactions.^{249–251} β - Al_2TiO_5 is known to be metastable below $\sim 1180^\circ\text{C}$, the stable phases being TiO_2 (rutile) and α - Al_2O_3 (corundum). Samples with an Al/Ti ratio of 2, prepared by the non-hydrolytic alkoxide and ether routes, have been found to crystallize as soon as 600°C to β - Al_2TiO_5 . This result was ascribed to the excellent molecular scale homogeneity of the nonhydrolytic gels that favors the direct crystallization of the metastable β - Al_2TiO_5 phase, rather than the phase separation to the stable rutile and corundum phases, which would require long-range ion diffusion.⁴¹

Linacero *et al.* have investigated the physical and structural properties of 0.6TiO_2 – $0.4\text{Al}_2\text{O}_3$ catalytic supports prepared by nonhydrolytic and hydrolytic routes.¹⁴⁶ Thus four samples were synthesized using the ether route (from chlorides and $^i\text{Pr}_2\text{O}$) or the alkoxide route (from TiCl_4 and $\text{Al}(\text{O}^i\text{Bu})_3$ or $\text{Al}(\text{O}^i\text{Pr})_3$, or from $\text{Ti}(\text{O}^i\text{Pr})_4$ and AlCl_3). Three samples were obtained by hydrolysis of aluminium alkoxides in alcohol solutions using various methods (simple hydrolysis, hydrolysis in the presence of ethylene glycol, or controlled hydrolysis using acetic acid). The authors found that the texture, the distribution of acid sites, and the crystallization behavior were influenced by the synthesis method. Thus, after calcination at 500°C , the NH samples prepared by the ether route or $\text{Al}(\text{O}^i\text{Bu})_3$ showed the highest specific surface areas (260 and $200 \text{ m}^2 \text{ g}^{-1}$).

4. Conclusions and outlook

The main advantage of sol–gel processes in the preparation of catalytic materials is the ability to control the structure and the composition at the molecular level. Another major advantage lies in the control over the texture of the catalyst. Carrying out these preparations in a single step is also a valuable asset.

However, in conventional sol–gel the simultaneous control of composition, structure and texture can be problematic, leading to sophisticated, multi-step and generally expensive procedures that hinder its industrial application. In a former review, Ward and Ko⁸ concluded that in anticipation of industrial catalytic applications of sol–gel materials, it would be necessary for economic reasons to consider using precursors other than metal alkoxides and to prepare high-surface-area, high-pore-volume materials without supercritical drying. For the same reasons it would be interesting to control the texture without using templating agents.

Many examples presented here show that the non-hydrolytic process can elegantly solve these problems, allowing the one step-synthesis of efficient mixed oxide catalysts with controlled compositional homogeneity and outstanding textural properties, starting from cheap chloride precursors and avoiding the use of any reactivity modifier, supercritical drying step or templating agent. This confirms that the interest of this process is far from being purely academic.

Actually, changing the oxo bridge-forming reactions and the reaction medium modifies the reaction kinetics, the degree of condensation and the nature of the residual groups in the gel. This in turn affects significantly the homogeneity, texture and surface properties of the materials.

NHSG has emerged as a simple but powerful method to prepare mesoporous multinary oxide materials, affording one-step syntheses of improved catalysts mimicking catalysts previously prepared by conventional sol–gel or impregnation methods. In addition, its versatility allows the easy incorporation of dopants or modifying organosilicon groups, providing unique opportunities for the discovery of new catalysts with superior catalytic performances. This method appears also highly promising for the synthesis of supports with improved textures and surface properties favoring the dispersion of active phases.

Non-hydrolytic condensations offer new possibilities for the design of model catalysts, and the development of multi-step procedures should lead to even better control of the distribution and structure and accessibility of active species. The non-aqueous conditions used in NHSG facilitate the immobilization of catalytic species sensitive to water or poorly soluble in aqueous media, as for instance organometallic complexes; they are also well suited to syntheses in hydrophobic ionic liquids or supercritical CO_2 .

NHSG is also recognized for the synthesis of highly crystalline nanoparticles with well-controlled shape and sizes. This is of particular interest for the development of photocatalysts and nanocatalysts, and here too the ability to obtain high specific surface areas and the ease of introducing dopants are decisive advantages. In addition, the organosoluble nanoparticles obtained can be easily deposited on appropriate supports.

In conclusion, the non-hydrolytic sol–gel process nicely complements the conventional sol–gel process; it offers several versatile routes which have already proven particularly useful for the preparation of a wide variety of heterogeneous catalysts. Much remains to be done to explore all the possibilities offered by this process, which we believe will find increasing application for the design of innovative catalytic materials.

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Notes and references

- 1 I. E. Wachs and C. A. Roberts, *Chem. Soc. Rev.*, 2010, **39**, 5002–5017.
- 2 J. R. H. Ross, *Heterogeneous catalysis - Fundamentals and applications*, Elsevier, Amsterdam, The Netherlands, 2012.
- 3 ed. S. D. Jackson and J. S. J. Hargreaves, *Metal oxide catalysis*, Wiley-VCH Verlag GmbH & Co KGaA, Weinheim, 2009.
- 4 J. Livage, M. Henry and C. Sanchez, *Prog. Solid State Chem.*, 1988, **18**, 259–341.
- 5 L. L. Hench and J. K. West, *Chem. Rev.*, 1990, **90**, 33–72.

- 6 C. J. Brinker and G. W. Scherer, *The Physics and Chemistry of Sol-Gel Processing*, Academic Press, New York, 1990.
- 7 C. Sanchez, P. Belleville, M. Popall and L. Nicole, *Chem. Soc. Rev.*, 2011, **40**, 696–753.
- 8 D. A. Ward and E. I. Ko, *Ind. Eng. Chem. Res.*, 1995, **34**, 421–433.
- 9 J. A. Schwarz, C. Contescu and A. Contescu, *Chem. Rev.*, 1995, **95**, 477–510.
- 10 R. Ciriminna and M. Pagliaro, *Org. Process Res. Dev.*, 2006, **10**, 320–326.
- 11 R. Ciriminna, M. Sciortino, G. Alonzo, A. de Schrijver and M. Pagliaro, *Chem. Rev.*, 2011, **111**, 765–789.
- 12 A. C. Marr and P. C. Marr, *Dalton Trans.*, 2011, **40**, 20–26.
- 13 B. E. Yoldas, *J. Mater. Sci.*, 1986, **21**, 1086.
- 14 C. Sanchez, J. Livage, M. Henry and F. Babonneau, *J. Non-Cryst. Solids*, 1988, **100**, 65–76.
- 15 G. M. Pajonk, *Appl. Catal.*, 1991, **72**, 217–266.
- 16 S. S. Prakash, C. J. Brinker, A. J. Hurd and S. M. Rao, *Nature*, 1995, **374**, 439–443.
- 17 A. Taguchi and F. Schüth, *Microporous Mesoporous Mater.*, 2005, **77**, 1–45.
- 18 A. Corma, *Chem. Rev.*, 1997, **97**, 2373–2419.
- 19 C. Boissiere, D. Grosso, A. Chaumonnot, L. Nicole and C. Sanchez, *Adv. Mater.*, 2011, **23**, 599–623.
- 20 D. P. Debecker, M. Stoyanova, F. Colbeau-Justin, U. Rodemerck, C. Boissière, E. M. Gaigneaux and C. Sanchez, *Angew. Chem., Int. Ed.*, 2012, DOI: 10.1002/anie.201106277.
- 21 R. Corriu, D. Leclercq, P. Lefevre, P. H. Mutin and A. Vioux, *Chem. Mater.*, 1992, **4**, 961–963.
- 22 R. J. P. Corriu, D. Leclercq, P. Lefevre, P. H. Mutin and A. Vioux, *J. Mater. Chem.*, 1992, **2**, 673–674.
- 23 R. J. P. Corriu, D. Leclercq, P. Lefevre, P. H. Mutin and A. Vioux, *J. Non-Cryst. Solids*, 1992, **146**, 301–303.
- 24 A. Vioux, *Chem. Mater.*, 1997, **9**, 2292–2299.
- 25 P. H. Mutin and A. Vioux, *Chem. Mater.*, 2009, **21**, 582–596.
- 26 J. N. Hay and H. M. Ravall, *Chem. Mater.*, 2001, **13**, 3396–3403.
- 27 N. Pinna, *J. Mater. Chem.*, 2007, **17**, 2769–2774.
- 28 Y.-w. Jun, J.-s. Choi and J. Cheon, *Angew. Chem., Int. Ed.*, 2006, **45**, 3414–3439.
- 29 M. Niederberger, *Acc. Chem. Res.*, 2007, **40**, 793–800.
- 30 M. Leskela and M. Ritala, *Angew. Chem., Int. Ed.*, 2003, **42**, 5548–5554.
- 31 G. Clavel, E. Rauwel, M. G. Willinger and N. Pinna, *J. Mater. Chem.*, 2009, **19**, 454–462.
- 32 N. Pinna and M. Niederberger, *Angew. Chem., Int. Ed.*, 2008, **47**, 5292–5304.
- 33 G. Garnweitner and M. Niederberger, *J. Mater. Chem.*, 2008, **18**, 1171–1182.
- 34 M. Niederberger and G. Garnweitner, *Chem.-Eur. J.*, 2006, **12**, 7282–7302.
- 35 L. Bourget, R. J. P. Corriu, D. Leclercq, P. H. Mutin and A. Vioux, *J. Non-Cryst. Solids*, 1998, **242**, 81–91.
- 36 R. J. P. Corriu, D. Leclercq, P. Lefevre, P. H. Mutin and A. Vioux, *J. Non-Cryst. Solids*, 1992, **146**, 301–303.
- 37 S. Acosta, R. J. P. Corriu, D. Leclercq, P. Lefevre, P. H. Mutin and A. Vioux, *J. Non-Cryst. Solids*, 1994, **170**, 234–242.
- 38 P. Arnal, R. J. P. Corriu, D. Leclercq, P. H. Mutin and A. Vioux, *Chem. Mater.*, 1997, **9**, 694–698.
- 39 M. Andrianainarivelo, R. Corriu, D. Leclercq, P. H. Mutin and A. Vioux, *J. Mater. Chem.*, 1996, **6**, 1665–1671.
- 40 M. Andrianainarivelo, R. J. P. Corriu, D. Leclercq, P. H. Mutin and A. Vioux, *J. Mater. Chem.*, 1997, **7**, 279–284.
- 41 M. Andrianainarivelo, R. J. P. Corriu, D. Leclercq, P. H. Mutin and A. Vioux, *Chem. Mater.*, 1997, **9**, 1098–1102.
- 42 A. P. Wilkinson, C. Lind and S. Pattanaik, *Chem. Mater.*, 1999, **11**, 101–108.
- 43 S. D. Gates, J. A. Colin and C. Lind, *J. Mater. Chem.*, 2006, **16**, 4214–4219.
- 44 T. J. Trentler, T. E. Denler, J. F. Bertone, A. Agrawal and V. L. Colvin, *J. Am. Chem. Soc.*, 1999, **121**, 1613–1614.
- 45 J. Joo, T. Yu, Y. W. Kim, H. M. Park, F. Wu, J. Z. Zhang and T. Hyeon, *J. Am. Chem. Soc.*, 2003, **125**, 6553–6557.
- 46 A. Aboulaich, O. Lorret, B. Boury and P. H. Mutin, *Chem. Mater.*, 2009, **21**, 2577–2579.
- 47 R. J. P. Corriu, D. Leclercq, P. Lefevre, P. H. Mutin and A. Vioux, *J. Non-Cryst. Solids*, 1992, **151**, 272.
- 48 M. Niederberger, M. H. Bartl and G. D. Stucky, *J. Am. Chem. Soc.*, 2002, **124**, 13642–13643.
- 49 M. Niederberger, G. Garnweitner, N. Pinna and M. Antonietti, *J. Am. Chem. Soc.*, 2004, **126**, 9120–9126.
- 50 J. Caruso and M. J. Hampden-Smith, *J. Sol-Gel Sci. Technol.*, 1997, **8**, 35–39.
- 51 M. Jansen and E. Guenther, *Chem. Mater.*, 1995, **7**, 2110–2114.
- 52 K. G. Sharp, *Adv. Mater.*, 1998, **10**, 1243–1248.
- 53 E. Stathatos, P. Lianos, U. Lavrencic-Stangar and B. Orel, *Adv. Mater.*, 2002, **14**, 354–357.
- 54 T. Brankova, V. Bekiari and P. Lianos, *Chem. Mater.*, 2003, **15**, 1855–1859.
- 55 J. Joo, S. G. Kwon, T. Yu, C. Min, J. Lee, J. Yoon and T. Hyeon, *J. Phys. Chem. B*, 2005, **109**, 15297–15302.
- 56 S. Dai, Y. H. Ju, H. J. Gao, J. S. Lin, S. J. Pennycook and C. E. Barnes, *Chem. Commun.*, 2000, 243–244.
- 57 K. Anderson, S. Cortinas Fernandez, C. Hardacre and P. C. Marr, *Inorg. Chem. Commun.*, 2004, 73–76.
- 58 M.-A. Neouze, J. Le Bideau, F. Leroux and A. Vioux, *Chem. Commun.*, 2005, 1082–1084.
- 59 R. Sui, A. S. Rizkalla and P. A. Charpentier, *J. Phys. Chem. B*, 2004, **108**, 11886–11892.
- 60 J. Jammaer, C. Aprile, S. W. Verbruggen, S. Lenaerts, P. P. Pescarmona and J. A. Martens, *ChemSusChem*, 2011, **4**, 1457–1463.
- 61 P. Arnal, R. J. P. Corriu, D. Leclercq, P. H. Mutin and A. Vioux, *J. Mater. Chem.*, 1996, **6**, 1925–1932.
- 62 M. Fujiwara, H. Wessel, H. S. Park and H. W. Roesky, *Chem. Mater.*, 2002, **14**, 4975–4981.
- 63 G. Guo, J. K. Whitesell and M. A. Fox, *J. Phys. Chem. B*, 2005, **109**, 18781–18785.
- 64 S. Sun and H. Zeng, *J. Am. Chem. Soc.*, 2002, **124**, 8204–8205.
- 65 B. Koo, J. Park, Y. Kim, S.-H. Choi, Y.-E. Sung and T. Hyeon, *J. Phys. Chem. B*, 2006, **110**, 24318–24323.
- 66 Y. W. Jun, M. F. Casula, J.-H. Sim, S. Y. Kim, J. Cheon and A. P. Alivisatos, *J. Am. Chem. Soc.*, 2003, **125**, 15981–15985.
- 67 J.-W. Seo, Y.-W. Jun, S. J. Ko and J. Cheon, *J. Phys. Chem. B*, 2005, **109**, 5389–5391.
- 68 J. Joo, S. G. Kwon, J. H. Yu and T. Hyeon, *Adv. Mater.*, 2005, **17**, 1873–1877.
- 69 K. W. Terry and T. D. Tilley, *Chem. Mater.*, 1991, **3**, 1001–1003.
- 70 J. W. Kriesel, M. S. Sander and T. D. Tilley, *Adv. Mater.*, 2001, **13**, 331–335.
- 71 K. L. Fajdala and T. D. Tilley, *Chem. Mater.*, 2001, **13**, 1817–1827.
- 72 J. Jarupatrakorn and T. D. Tilley, *J. Am. Chem. Soc.*, 2002, **124**, 8380–8388.
- 73 C. Nozaki, C. G. Lugmair, A. T. Bell and T. D. Tilley, *J. Am. Chem. Soc.*, 2002, **124**, 13194–13203.
- 74 A. Aboulaich, B. Boury and P. H. Mutin, *Chem. Mater.*, 2010, **22**, 4519–4521.
- 75 A. Aboulaich, B. Boury and P. H. Mutin, *Eur. J. Inorg. Chem.*, 2011, 3644–3649.
- 76 S.-K. Yuh, E. P. Bescher, F. Babonneau and J. D. Mackenzie, *Mater. Res. Soc. Symp. Proc.*, 1994, **346**, 803–808.
- 77 G. Garnweitner and M. Niederberger, *J. Am. Ceram. Soc.*, 2006, **89**, 1801–1808.
- 78 J. Tang, J. Fabbri, R. D. Robinson, Y. Zhu, I. P. Herman, M. L. Steigerwald and L. E. Brus, *Chem. Mater.*, 2004, **16**, 1336–1342.
- 79 A. de la Hoz, A. Diaz-Ortiz and A. Moreno, *Chem. Soc. Rev.*, 2005, **34**, 164–178.
- 80 K. J. Rao, B. Vaidhyanathan, M. Ganguli and P. A. Ramakrishnan, *Chem. Mater.*, 1999, **11**, 882–895.
- 81 I. Bilecka and M. Niederberger, *Nanoscale*, 2010, **2**, 1358–1374.
- 82 M. Baghbanzadeh, L. Carbone, P. D. Cozzoli and C. O. Kappe, *Angew. Chem., Int. Ed.*, 2011, **50**, 11312–11359.
- 83 J. D. Moseley and C. O. Kappe, *Green Chem.*, 2011, **13**, 794–806.
- 84 I. Bilecka, I. Djerdj and M. Niederberger, *Chem. Commun.*, 2008, 886–888.
- 85 I. Bilecka, P. Elser and M. Niederberger, *ACS Nano*, 2009, **3**, 467–477.
- 86 B. Baruwati, V. Polshettiwar and R. S. Varma, *RSC Green Chem. Ser.*, 2010, **7**, 176–216.
- 87 D. Portehault, C. Giordano, C. Sanchez and M. Antonietti, *Chem. Mater.*, 2010, **22**, 2125–2131.

- 88 R. Buonsanti, V. Grillo, E. Carlino, C. Giannini, T. Kipp, R. Cingolani and P. D. Cozzoli, *J. Am. Chem. Soc.*, 2008, **130**, 11223–11233.
- 89 D. Koziej, M. D. Rossell, B. Ludi, A. Hintennach, P. Novák, J.-D. Grunwaldt and M. Niederberger, *Small*, 2011, **7**, 377–387.
- 90 R. Buonsanti, E. Carlino, C. Giannini, D. Altamura, L. De Marco, R. Giannuzzi, M. Manca, G. Gigli and P. D. Cozzoli, *J. Am. Chem. Soc.*, 2011, **133**, 19216–19239.
- 91 V. Lafond, P. H. Mutin and A. Vioux, *Chem. Mater.*, 2004, **16**, 5380–5386.
- 92 A. M. Cojocariu, P. H. Mutin, E. Dumitriu, F. Fajula, A. Vioux and V. Hulea, *Chem. Commun.*, 2008, 5357–5359.
- 93 D. P. Debecker, K. Bouchmella, R. Delaigle, P. Eloy, C. Poleunis, P. Bertrand, E. M. Gaigneaux and P. H. Mutin, *Appl. Catal., B*, 2010, **94**, 38–45.
- 94 A. F. Popa, P. H. Mutin, A. Vioux, G. Delahay and B. Coq, *Chem. Commun.*, 2004, 2214–2215.
- 95 D. R. Cho, S. Y. Kim, D. W. Park and P. H. Mutin, *Korean J. Chem. Eng.*, 2009, **26**, 377–381.
- 96 D. P. Debecker, K. Bouchmella, C. Poleunis, P. Eloy, P. Bertrand, E. M. Gaigneaux and P. H. Mutin, *Chem. Mater.*, 2009, **21**, 2817–2824.
- 97 P. D. Yang, D. Y. Zhao, D. I. Margolese, B. F. Chmelka and G. D. Stucky, *Nature*, 1998, **396**, 152–155.
- 98 P. D. Yang, D. Y. Zhao, D. I. Margolese, B. F. Chmelka and G. D. Stucky, *Chem. Mater.*, 1999, **11**, 2813–2826.
- 99 J. Ba, A. Feldhoff, D. F. Rohlfing, M. Wark, M. Antonietti and M. Niederberger, *Small*, 2007, **3**, 310–317.
- 100 A. S. Deshpande, N. Pinna, B. Smarsly, M. Antonietti and M. Niederberger, *Small*, 2005, **1**, 313–316.
- 101 J. Lee, M. C. Orillall, S. C. Warren, M. Kamperman, F. J. DiSalvo and U. Wiesner, *Nat. Mater.*, 2008, **7**, 222–228.
- 102 F. Barbieri, D. Cauzzi, F. De Smet, M. Devillers, P. Moggi, G. Predieri and P. Ruiz, *Catal. Today*, 2000, **61**, 353–360.
- 103 P. Moggi, G. Predieri, D. Cauzzi, M. Devillers, P. Ruiz, S. Morselli and O. Ligabue, *Stud. Surf. Sci. Catal.*, 2002, **143**, 149–157.
- 104 P. Moggi, M. Devillers, P. Ruiz, G. Predieri, D. Cauzzi, S. Morselli and O. Ligabue, *Catal. Today*, 2003, **81**, 77–85.
- 105 P. H. Mutin, A. F. Popa, A. Vioux, G. Delahay and B. Coq, *Appl. Catal., B*, 2006, **69**, 49–57.
- 106 D. P. Debecker, R. Delaigle, K. Bouchmella, P. Eloy, E. M. Gaigneaux and P. H. Mutin, *Catal. Today*, 2010, **157**, 125–130.
- 107 V. Lafond, P. H. Mutin and A. Vioux, *J. Mol. Catal. A: Chem.*, 2002, **182**, 81–88.
- 108 A. M. Cojocariu, P. H. Mutin, E. Dumitriu, A. Aboulaich, A. Vioux, F. Fajula and V. Hulea, *Catal. Today*, 2010, **157**, 270–274.
- 109 A. M. Cojocariu, P. H. Mutin, E. Dumitriu, F. Fajula, A. Vioux and V. Hulea, *Appl. Catal., B*, 2010, **97**, 407–413.
- 110 A. M. Cojocariu, P. H. Mutin, E. Dumitriu, A. Vioux, F. Fajula and V. Hulea, *Chemosphere*, 2009, **77**, 1065–1068.
- 111 O. Lorret, V. Lafond, P. H. Mutin and A. Vioux, *Chem. Mater.*, 2006, **18**, 4707–4709.
- 112 M. P. Coles, C. G. Lugmair, K. W. Terry and T. D. Tilley, *Chem. Mater.*, 2000, **12**, 122–131.
- 113 R. L. Brutchey, C. G. Lugmair, L. O. Schebaum and T. D. Tilley, *J. Catal.*, 2005, **229**, 72–81.
- 114 O. J. de Lima, A. T. Papacidero, L. A. Rocha, H. C. Sacco, E. J. Nassar, K. J. Ciuffi, L. A. Bueno, Y. Messaddeq and S. J. L. Ribeiro, *Mater. Charact.*, 2003, **50**, 101–108.
- 115 B. L. Caetano, L. A. Rocha, E. Molina, Z. N. Rocha, G. Ricci, P. S. Calefi, O. J. de Lima, C. Mello, E. J. Nassar and K. J. Ciuffi, *Appl. Catal., A*, 2006, **311**, 122–134.
- 116 G. P. Ricci, Z. N. Rocha, S. Nakagaki, K. A. D. F. Castro, A. E. M. Crotti, P. S. Calefi, E. J. Nassar and K. J. Ciuffi, *Appl. Catal., A*, 2010, **389**, 147–154.
- 117 D. P. Debecker, K. Bouchmella, M. Stoyanova, U. Rodemerck, E. M. Gaigneaux and P. H. Mutin, *Catal. Sci. Technol.*, 2012, DOI: 10.1039/C1032CY00475E.
- 118 P. Makowski, R. Rothe, A. Thomas, M. Niederberger and F. Goettmann, *Green Chem.*, 2009, **11**, 34–37.
- 119 I. Olliges-Stadler, M. D. Rossell and M. Niederberger, *Small*, 2010, **6**, 960–966.
- 120 C. Petitto, H. P. Mutin and G. Delahay, *Chem. Commun.*, 2011, **47**, 10728–10730.
- 121 A. Dolev, G. E. Shter and G. S. Grader, *J. Catal.*, 2003, **214**, 146–152.
- 122 M. L. Curri, R. Comparelli, P. D. Cozzoli, G. Mascolo and A. Agostiano, *Mater. Sci. Eng., C*, 2003, **23**, 285–289.
- 123 R. Comparelli, P. D. Cozzoli, M. L. Curri, A. Agostiano, G. Mascolo and G. Lovecchio, *Water Sci. Technol.*, 2004, **49**, 183–188.
- 124 R. Comparelli, E. Fanizza, M. L. Curri, P. D. Cozzoli, G. Mascolo, R. Passino and A. Agostiano, *Appl. Catal., B*, 2005, **55**, 81–91.
- 125 G. Mascolo, R. Comparelli, M. L. Curri, G. Lovecchio, A. Lopez and A. Agostiano, *J. Hazard. Mater.*, 2007, **142**, 130–137.
- 126 H. Jia, Z. Zheng, H. Zhao, L. Zhang and Z. Zou, *Mater. Res. Bull.*, 2009, **44**, 1312–1316.
- 127 J. Zhu, J. Yang, Z. F. Bian, H. Ren, Y. M. Liu, Y. Cao, H. X. Li, H. Y. He and K. N. Fan, *Appl. Catal., B*, 2007, **76**, 82–91.
- 128 A. Stoyanova, M. Sredkova, A. Bachvarova-Nedelcheva, R. Iordanova, Y. Dimitriev, H. Hitkova and T. Iliev, *Optoelectron. Adv. Mater., Rapid Commun.*, 2010, **4**, 2059–2063.
- 129 S.-m. Chang, P.-h. Lo and C.-t. Chang, *Appl. Catal., B*, 2009, **91**, 619–627.
- 130 S. M. Chang, C. Y. Hou, P. H. Lo and C. T. Chang, *Appl. Catal., B*, 2009, **90**, 233–241.
- 131 J. Zhu, J. Ren, Y. Huo, Z. Bian and H. Li, *J. Phys. Chem. C*, 2007, **111**, 18965–18969.
- 132 B. Naik and K. M. Parida, *Ind. Eng. Chem. Res.*, 2010, **49**, 8339–8346.
- 133 L. Z. Zhang, I. Djerdj, M. Cao, M. Antonietti and M. Niederberger, *Adv. Mater.*, 2007, **19**, 2083–2086.
- 134 A. Fisch, C. F. Petry, D. Pozebon, F. C. Stedile, N. S. M. Cardozo, A. R. Secchi and J. H. Z. dos Santos, *Macromol. Symp.*, 2006, **245–246**, 77–86.
- 135 A. G. Fisch, N. S. M. Cardozo, A. R. Secchi, F. C. Stedile, P. R. Livotto, D. S. de Sa, Z. N. da Rocha and J. H. Z. dos Santos, *Appl. Catal., A*, 2009, **354**, 88–101.
- 136 A. G. Fisch, N. S. M. Cardozo, A. R. Secchi, F. C. Stedile, C. Radtke, D. S. De Sá, Z. N. da Rocha and J. H. Z. dos Santos, *Appl. Catal., A*, 2009, **370**, 114–122.
- 137 T. C. O. MacLeod, D. F. C. Guedes, M. R. Lelo, R. A. Rocha, B. L. Caetano, K. J. Ciuffi and M. D. Assis, *J. Mol. Catal. A: Chem.*, 2006, **259**, 319–327.
- 138 J. M. A. Caiut, S. Nakagaki, O. J. De Lima, C. Mello, C. A. P. Leite, E. J. Nassar, K. J. Ciuffi and H. C. Sacco, *J. Sol-Gel Sci. Technol.*, 2003, **28**, 57–64.
- 139 O. J. de Lima, D. P. de Aguirre, D. C. de Oliveira, M. A. da Silva, C. Mello, C. A. P. Leite, H. C. Sacco and K. J. Ciuffi, *J. Mater. Chem.*, 2001, **11**, 2476–2481.
- 140 S. J. Craythorne, A. R. Crozier, F. Lorenzini, A. C. Marr and P. C. Marr, *J. Organomet. Chem.*, 2005, **690**, 3518–3521.
- 141 S. J. Craythorne, K. Anderson, F. Lorenzini, C. McCausland, E. F. Smith, P. Licence, A. C. Marr and P. C. Marr, *Chem.-Eur. J.*, 2009, **15**, 7094–7100.
- 142 S. Volland, M. Gruit, T. Regnier, L. Viau, O. Lavastre and A. Vioux, *New J. Chem.*, 2009, **33**, 2015–2021.
- 143 C. Dever, A. Deffieux, H. Cramail and S. Mastroianni, *Macromol. Rapid Commun.*, 2003, **24**, 883–888.
- 144 M. H. Dai, D. L. Tang, Z. J. Lin, H. W. Yang and Y. Z. Yuan, *Chem. Lett.*, 2006, 878–879.
- 145 M. H. Dai, D. L. Tang and Y. Z. Yuan, *Chin. J. Catal.*, 2006, **27**, 1063–1068.
- 146 R. Linacero, M. L. Rojas-Cervantes and J. D. D. Lopez-Gonzalez, *J. Mater. Sci.*, 2000, **35**, 3269–3278.
- 147 J. Le Bideau, L. Viau and A. Vioux, *Chem. Soc. Rev.*, 2011, **40**, 907–925.
- 148 B. Grzybowska-Swierkosz, *Top. Catal.*, 2000, **11/12**, 23–42.
- 149 F. Cavani, N. Ballarini and A. Cericola, *Catal. Today*, 2007, **127**, 113–131.
- 150 H.-G. Lintz and S. P. Mueller, *Appl. Catal., A*, 2009, **357**, 178–183.
- 151 P. Ratnasamy, D. Srinivas and H. Knözinger, *Adv. Catal.*, 2004, **48**, 1–169.
- 152 J. Beckers and G. Rothenberg, *Green Chem.*, 2010, **12**, 939–948.
- 153 T. Blasco and J. M. L. Nieto, *Appl. Catal., A*, 1997, **157**, 117–142.

- 154 B. Savova, D. Filkova, D. Crisan, M. Crisan, M. Raileanu, N. Dragan, L. Petrov and J. C. Vedrine, *Appl. Catal., A*, 2009, **359**, 55–61.
- 155 B. Mitra, I. E. Wachs and G. Deo, *J. Catal.*, 2006, **240**, 151–159.
- 156 T. C. Watling, G. Deo, K. Seshan, I. E. Wachs and J. A. Lercher, *Catal. Today*, 1996, **28**, 139–145.
- 157 R. A. Sheldon, M. Wallau, I. W. C. E. Arends and U. Schuchardt, *Acc. Chem. Res.*, 1998, **31**, 485–493.
- 158 S. Klein, S. Thorimbert and W. F. Maier, *J. Catal.*, 1996, **163**, 476–488.
- 159 D. C. M. Dutoit, M. Schneider and A. Baiker, *J. Catal.*, 1995, **153**, 165–176.
- 160 R. J. Davis and Z. F. Liu, *Chem. Mater.*, 1997, **9**, 2311–2324.
- 161 R. Mariscal, M. Lopez-Granados, J. L. G. Fierro, J. L. Sotelo, C. Martos and R. Van Grieken, *Langmuir*, 2000, **16**, 9460–9467.
- 162 J. B. Miller, L. J. M. Athers and E. I. Ko, *J. Catal.*, 1994, **5**, 1759.
- 163 M. A. Holland, D. M. Pickup, G. Mountjoy, E. S. C. Tsang, G. W. Wallidge, R. J. Newport and M. E. Smith, *J. Mater. Chem.*, 2000, **10**, 2495–2501.
- 164 J. L. Sotelo, R. Van Grieken and C. Martos, *Chem. Commun.*, 1999, 549–550.
- 165 R. Hutter, T. Mallat and A. Baiker, *J. Catal.*, 1995, **153**, 177–189.
- 166 T. Tatsumi, K. A. Koyano and N. Igarashi, *Chem. Commun.*, 1998, 325–326.
- 167 H. Kochkar and F. Figueras, *J. Catal.*, 1997, **171**, 420–430.
- 168 C. A. Müller, M. Maciejewski, T. Mallat and A. Baiker, *J. Catal.*, 1999, **184**, 280–293.
- 169 Y. Deng and W. F. Maier, *J. Catal.*, 2001, **199**, 115–122.
- 170 C. A. Müller, R. Deck, T. Mallat and A. Baiker, *Top. Catal.*, 2000, **11/12**, 369–378.
- 171 Y. Iamamoto, M. D. Assis, K. J. Ciuffi, H. C. Sacco, L. Iwamoto, A. J. B. Melo, O. R. Nascimento and C. M. C. Prado, *J. Mol. Catal. A: Chem.*, 1996, **109**, 189–200.
- 172 J. M. Thomas and R. Raja, *Catal. Today*, 2006, **117**, 22–31.
- 173 J. S. Chung, S. C. Paik, H. S. Kim, D. S. Lee and I. S. Nam, *Catal. Today*, 1997, **35**, 37–43.
- 174 D.-W. Park, S.-W. Chun, J.-Y. Jang, H.-S. Kim, H.-C. Woo and J.-S. Chung, *Catal. Today*, 1998, **44**, 73–79.
- 175 M. I. Kim, D. W. Park, S. W. Park, X. Yang, J. S. Choi and D. J. Suh, *Catal. Today*, 2006, **111**, 212–216.
- 176 R. Delaigle, D. P. Debecker, F. Bertinchamps and E. M. Gaigneaux, *Top. Catal.*, 2009, **52**, 501–516.
- 177 W. B. Li, J. X. Wang and H. Gong, *Catal. Today*, 2009, **148**, 81–87.
- 178 D. P. Debecker, R. Delaigle, P. C. Hung, A. Buekens, E. M. Gaigneaux and M. B. Chang, *Chemosphere*, 2011, **82**, 1337–1342.
- 179 R.-a. Doong, P.-Y. Chang and C.-H. Huang, *J. Non-Cryst. Solids*, 2009, **355**, 2302–2308.
- 180 C. Gannoun, R. Delaigle, P. Eloy, D. P. Debecker, A. Ghorbel and E. M. Gaigneaux, *Catal. Commun.*, 2011, **15**, 1–5.
- 181 S. Chin, J. Jurng, J. H. Lee and S. J. Moon, *Chemosphere*, 2009, **75**, 1206–1209.
- 182 B. Schimmoeller, R. Delaigle, D. P. Debecker and E. M. Gaigneaux, *Catal. Today*, 2010, **157**, 198–203.
- 183 G. Busca, M. Baldi, C. Pistarino, J. M. G. Amores, V. S. Escribano, E. Finocchio, G. Romezzano, F. Bregani and G. P. Toledo, *Catal. Today*, 1999, **53**, 525–533.
- 184 D. P. Debecker, R. Delaigle, P. Eloy and E. M. Gaigneaux, *J. Mol. Catal. A: Chem.*, 2008, **289**, 38–43.
- 185 M. Nacken, S. Heidenreich, M. Hackel and G. Schaub, *Appl. Catal., B*, 2007, **70**, 370–376.
- 186 M. Shelef, *Chem. Rev.*, 1995, **95**, 209–225.
- 187 S. Roy and A. Baiker, *Chem. Rev.*, 2009, **109**, 4054–4091.
- 188 M. C. Kung and H. H. Kung, *Top. Catal.*, 2004, **28**, 105–110.
- 189 J. Zhu and A. Thomas, *Appl. Catal., B*, 2009, **92**, 225–233.
- 190 H. He and Y. Yu, *Catal. Today*, 2005, **100**, 37–47.
- 191 R. Burch, J. P. Breen and F. C. Meunier, *Appl. Catal., B*, 2002, **39**, 283–303.
- 192 M. A. Reiche, E. Ortelli and A. Baiker, *Appl. Catal., B*, 1999, **23**, 187–203.
- 193 P. Forzatti and L. Lietti, *Heterog. Chem. Rev.*, 1996, **3**, 33.
- 194 H. Bosch and F. Janssen, *Catal. Today*, 1988, **2**, 369.
- 195 J. C. Mol, *J. Mol. Catal. A: Chem.*, 2004, **213**, 39–45.
- 196 D. P. Debecker, B. Schimmoeller, M. Stoyanova, C. Poleunis, P. Bertrand, U. Rodemerck and E. M. Gaigneaux, *J. Catal.*, 2011, **277**, 154–163.
- 197 D. P. Debecker, M. Stoyanova, U. Rodemerck, A. Leonard, B.-L. Su and E. M. Gaigneaux, *Catal. Today*, 2011, **169**, 60–68.
- 198 D. P. Debecker, M. Stoyanova, U. Rodemerck, P. Eloy, A. Leonard, B. L. Su and E. M. Gaigneaux, *J. Phys. Chem. C*, 2010, **114**, 18664–18673.
- 199 D. P. Debecker, M. Stoyanova, U. Rodemerck and E. M. Gaigneaux, *J. Mol. Catal. A: Chem.*, 2011, **340**, 65–76.
- 200 D. P. Debecker, D. Hauwaert, M. Stoyanova, A. Barkschat, U. Rodemerck and E. M. Gaigneaux, *Appl. Catal., A*, 2011, **391**, 78–85.
- 201 J. Handzlik, J. Ogonowski, J. Stoch and M. Mikolajczyk, *Appl. Catal., A*, 2004, **273**, 99–104.
- 202 K. Tanaka, *J. Mol. Catal.*, 1988, **46**, 87–96.
- 203 X. Li, W. Zhang, S. Liu, L. Xu, X. Han and X. Bao, *J. Catal.*, 2007, **250**, 55–66.
- 204 H. Balcar, D. Mishra, E. Marceau, X. Carrier, N. Zilková and Z. Bastl, *Appl. Catal., A*, 2009, **359**, 129–135.
- 205 J. Handzlik and P. Sautet, *J. Catal.*, 2008, **256**, 1–14.
- 206 G. J. D. Soler-illia, C. Sanchez, B. Lebeau and J. Patarin, *Chem. Rev.*, 2002, **102**, 4093–4138.
- 207 S. Ahmed, M. G. Rasul, W. N. Martens, R. Brown and M. A. Hashib, *Desalination*, 2010, **261**, 3–18.
- 208 K. Kabra, R. Chaudhary and R. L. Sawhney, *Ind. Eng. Chem. Res.*, 2004, **43**, 7683–7696.
- 209 H. Lachheb, E. Puzenat, A. Houas, M. Ksibi, E. Elaloui, C. Guillard and J. M. Herrmann, *Appl. Catal., B*, 2002, **39**, 75–90.
- 210 R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki and Y. Taga, *Science*, 2001, **293**, 269–271.
- 211 M. Anpo and M. Takeuchi, *J. Catal.*, 2003, **216**, 505–516.
- 212 C. Burda, Y. B. Lou, X. B. Chen, A. C. S. Samia, J. Stout and J. L. Gole, *Nano Lett.*, 2003, **3**, 1049–1051.
- 213 X. Chen and S. S. Mao, *Chem. Rev.*, 2007, **107**, 2891–2959.
- 214 M. I. Litter, *Appl. Catal., B*, 1999, **23**, 89–114.
- 215 A. M. Tripathi, R. G. Nair and S. K. Samdarshi, *Sol. Energy Mater. Sol. Cells*, 2010, **94**, 2379–2385.
- 216 H. G. Kim, D. W. Hwang and J. S. Lee, *J. Am. Chem. Soc.*, 2004, **126**, 8912–8913.
- 217 J. Ren, W. Z. Wang, L. Zhang, J. Chang and S. Hu, *Catal. Commun.*, 2009, **10**, 1940–1943.
- 218 S.-m. Chang and R.-a. Doong, *J. Phys. Chem. B*, 2006, **110**, 20808–20814.
- 219 H. Yamashita, M. Harada, J. Misaka, M. Takeuchi, B. Neppolashan and M. Anpo, *Catal. Today*, 2003, **84**, 191–196.
- 220 M. H. Zhou, J. G. Yu, B. Cheng and H. G. Yu, *Mater. Chem. Phys.*, 2005, **93**, 159–163.
- 221 B. Wang, Q. Li, W. Wang, Y. Li and J. P. Zhai, *Appl. Surf. Sci.*, 2011, **257**, 3473–3479.
- 222 G. Busca, S. Berardinelli, C. Resini and L. Arrighi, *J. Hazard. Mater.*, 2008, **160**, 265–288.
- 223 R. Comparelli, E. Fanizza, M. L. Curri, P. D. Cozzoli, G. Mascolo and A. Agostino, *Appl. Catal., B*, 2005, **60**, 1–11.
- 224 Z. G. Zou, J. H. Ye, K. Sayama and H. Arakawa, *Nature*, 2001, **414**, 625–627.
- 225 Z. G. Zou, J. H. Ye and H. Arakawa, *Mater. Res. Bull.*, 2001, **36**, 1185–1193.
- 226 W. J. Ren, Z. H. Ai, F. L. Jia, L. Z. Zhang, X. X. Fan and Z. G. Zou, *Appl. Catal., B*, 2007, **69**, 138–144.
- 227 C. J. Chung, H. I. Lin, C. M. Chou, P. Y. Hsieh, C. H. Hsiao, Z. Y. Shi and J. L. He, *Surf. Coat. Technol.*, 2009, **203**, 1081–1085.
- 228 H. Kong, J. Song and J. Jang, *Environ. Sci. Technol.*, 2010, **44**, 5672–5676.
- 229 R. R. Shah, S. Kaewgun, B. I. Lee and T. R. J. Tzeng, *J. Biomed. Nanotechnol.*, 2008, **4**, 339–348.
- 230 M. Pagliaro, R. Ciriminna and G. Palmisano, *Chem. Soc. Rev.*, 2007, **36**, 932–940.
- 231 J. R. Severn, J. C. Chadwick, R. Duchateau and N. Friederichs, *Chem. Rev.*, 2005, **105**, 4073–4147.
- 232 A. G. Fisch, N. S. M. Cardozo, A. R. Secchi, F. C. Stedile, N. P. da Silveira and J. H. Z. dos Santos, *J. Non-Cryst. Solids*, 2008, **354**, 3973–3979.
- 233 W. Zhang, J. L. Loebach, S. R. Wilson and E. N. Jacobsen, *J. Am. Chem. Soc.*, 1990, **112**, 2801–2803.
- 234 C. Coperet, *Chem. Rev.*, 2010, **110**, 656–680.
- 235 J. A. Rodriguez and D. Stacchiola, *Phys. Chem. Chem. Phys.*, 2010, **12**, 9557–9565.

-
- 236 Y. Segura, L. Chmielarz, P. Kustrowski, P. Cool, R. Dziembaj and E. F. Vansant, *Appl. Catal., B*, 2005, **61**, 69–78.
- 237 G. L. Rice and S. L. Scott, *Chem. Mater.*, 1998, **10**, 620–625.
- 238 G. Busca, *Chem. Rev.*, 2007, **107**, 5366–5410.
- 239 D. P. Debecker, E. M. Gaigneaux and G. Busca, *Chem.–Eur. J.*, 2009, **15**, 3920–3935.
- 240 C. U. I. Odenbrand, J. G. M. Brandin and G. Busca, *J. Catal.*, 1992, **135**, 505–517.
- 241 B. Reddy and A. Khan, *Catal. Rev. Sci. Eng.*, 2005, **47**, 257–296.
- 242 G. M. Dhar, B. N. Srinivas, M. S. Rana, M. Kumar and S. K. Maity, *Catal. Today*, 2003, **86**, 45–60.
- 243 F. Silveira, M. D. M. Alves, F. C. Stedile, S. B. Pergher and J. H. Z. dos Santos, *J. Mol. Catal. A: Chem.*, 2010, **315**, 213–220.
- 244 A. K. Sinha, S. Seelan, M. Okumura, T. Akita, S. Tsubota and M. Haruta, *J. Phys. Chem. B*, 2005, **109**, 3956–3965.
- 245 A. K. Sinha, S. Seelan, S. Tsubota and M. Haruta, *Angew. Chem., Int. Ed.*, 2004, **43**, 1546–1548.
- 246 H. Sakurai, S. Tsubota and M. Haruta, *Appl. Catal., A*, 1993, **102**, 125–136.
- 247 G. C. Bond and D. T. Thompson, *Catal. Rev. Sci. Eng.*, 1999, **41**, 319–388.
- 248 E. Sacaliuc-Parvulescu, H. Friedrich, R. Palkovits, B. M. Weckhuysen and T. A. Nijhuis, *J. Catal.*, 2008, **259**, 43–53.
- 249 A. Guevara-Lara, R. Bicaud and M. Vrinat, *Appl. Catal., A*, 2007, **328**, 99–108.
- 250 G. Qi, R. T. Yang and F. C. Rinaldi, *J. Catal.*, 2006, **237**, 381–392.
- 251 Y. Saih, M. Nagata, T. Funamoto, Y. Masuyama and K. Segawa, *Appl. Catal., A*, 2005, **295**, 11–22.