"Non-hydrolytic sol-gel routes to heterogeneous catalysts"

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Abstract

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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).

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...
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, 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) 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, or solvent exchange and derivatization of the hydroxylated surface by silylation before the evaporation step. 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. 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 microporous 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” (NHSG) was coined by Vioux and coworkers. The NHSG 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, organic–inorganic hybrids, oxide nanoparticles, thin films by atomic layer deposition and nanostructures.

In the present review we wish to address the application of a NHSG 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 NHSG 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, acetylatonates, 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. Here we will focus on the reactions which were involved in the preparation of catalytic materials.

2.1.1. Alkyl chloride elimination. The NHSG 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)):

$$\text{M–Cl} + \text{M–OR} \rightarrow \text{M–O–M} + \text{R–Cl}$$

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; otherwise, tert-butyl or benzyl groups are needed. 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, Pr₂O), which react in a second step with chloride groups according to eqn (1).

$$\text{M–Cl} + \text{ROR} \rightarrow \text{M–OR} + \text{R–Cl}$$

The alkoxide and ether routes have been used for the preparation of a wide variety of metal oxides. They have proven particularly useful for the synthesis of mixed oxides with an excellent control over their homogeneity and their texture. They also provided simple and effective...
syntheses of oxide nanoparticles, with or without capping agents.\textsuperscript{44–46}

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

\[
\text{M–Cl} + \text{ROH} \rightarrow \text{M–OR} + \text{H–Cl} \quad (3)
\]

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

\[
\text{M–Cl} + \text{ROH} \rightarrow \text{M–OH} + \text{R–Cl} \quad (4)
\]

\[
\text{M–Cl} + \text{MOH} \rightarrow \text{M–OM} + \text{H–Cl} \quad (5)
\]

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.\textsuperscript{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 dibenzy ether or complicated C–C bond formation reactions with elimination of 4-phenyl-2-butanol or 1,2-diphenylethanone for instance.\textsuperscript{34,49}

\subsection{2.1.2. Ester elimination.}

The condensation between metal carboxylates \(\text{M(OCOR)}_x\) and metal alkoxides \(\text{M' (OR')}_y\) (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.\textsuperscript{50,51}

\[
\text{M–OCOR}^2 + \text{M–OR}^1 \rightarrow \text{M–O–M} + \text{R}^2\text{COOR}^1 \quad (6)
\]

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

\[
\text{M(OR)}^1_{n–1} + \text{R}^2\text{COOH} \rightarrow \text{M(OR)}^1_{n–1}(\text{OCOR})^2 + \text{R}^1\text{OH} \quad (7)
\]

\[
\text{R}^1\text{OH} + \text{R}^2\text{COOH} \rightarrow \text{R}^2\text{COOR}^2 + \text{H}_2\text{O} \quad (8)
\]

Nevertheless, formic acid\textsuperscript{52} or acetic acid\textsuperscript{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\textsubscript{2} nanorods in multi-gram amounts.\textsuperscript{55} The reaction of alkoxide precursors with carboxylic acids is particularly interesting for sol–gel synthesis in unusual media, such as perfluoro solvents,\textsuperscript{52} ionic liquids,\textsuperscript{56–58} or supercritical CO\textsubscript{2} (scCO\textsubscript{2}).\textsuperscript{59,60}

Conversely, the reaction of metal or silicon alkoxides with an acid anhydride (eqn (9)) leads to the \textit{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.

\[
\text{M(OR)}^1_{n} + (\text{R}^2\text{CO})_2\text{O} \rightarrow \text{M(OR)}^1_{n–1}(\text{OCOR})^2 + \text{R}^2\text{COOR}^1 \quad (9)
\]

This “anhydride route” was successfully used to prepare titania (in the presence of TiCl\textsubscript{4} catalyst),\textsuperscript{61} silica–titania mixed oxides\textsuperscript{62} and titania photocatalysts.\textsuperscript{63}

\subsection{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 (triocetylphosphine oxide, oleic acid, oleylamine, etc.), providing size and also shape control of the nanoparticles.\textsuperscript{34,64,65,68}

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

\subsection{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.

\subsection{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).

\subsection{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. Even in the alcohol route, the hydroxyl content appears much lower than in conventional sol–gel. 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.

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 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 \( \text{SiO}_2 – \text{MO}_n \) \((\text{M} = \text{Ti}, \text{Zr}, \text{Al}, \text{etc.})\): 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. 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. Microwave-assisted synthesis is generally considered much faster, cleaner, and more economical than the conventional methods. Recently, Niederberger and co-workers have applied microwave heating to the NH synthesis of highly crystalline NP by the benzyl alcohol route. 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.

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 TiCl4 and different oxygen donors, Arnal et al. showed that the crystalline form depended on the nature of the oxygen donor: whereas TiO(OPr)4, Pr2O5 or PrOH led at 110 °C (and after calcination at 500 °C) exclusively to the formation of anatase, EtOH led to the formation of rutile, and BuOH led to a mixture of brookite and rutile. 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 \( \beta – \text{Al}_2 \text{TiO}_5 \), trigonal \( \text{ZrW}_2 \text{O}_8 \), and monoclinic \( \text{Ga}_2 \text{Mo}_3 \text{O}_{12} \). Portehault et al. recently reported the first NHSG example of lamellar titanates intercalated by tetramethylammonium (TMA) ions. The synthesis is based on the reaction at 220 °C of TiCl4 with triethylenglycoldimethylether (triglyme) as an oxygen donor, in the presence of an Me,N–BH3 (or Me2NH–BH3) complex. BH3 acts as an amine-sequester, avoiding the formation of a TiCl4–amine adduct. The formation of the titanium-oxo complex is particularly fast, cleaner, and more economical than the conventional methods. Recently, Niederberger et al. reported the selective formation of TiO2 brookite nanorods by high temperature reaction of TiCl4 with oleic acid and oleylamine. 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. reported the synthesis of highly crystalline MoO2 nanorods by reaction of MoO2Cl2 in benzyl alcohol-acetophenone mixtures. Depending on the benzyl alcohol-acetophenone ratio, various particle morphologies and crystal structures (hexagonal and monoclinic) were formed via complex mechanisms. The fast reduction of MoO2Cl2 to Mo(IV) initially led to the nucleation of 2 nm spherical MoO2 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 TiO2 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. 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. 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). By playing on these parameters, mesoporous silica–titania xerogels with specific surface areas as high as 1200 m² g⁻¹ and pore volumes up to 2.4 cm³ g⁻¹ after calcination can be obtained by the ether route, without any template or resorting to supercritical drying. Mesoporous crystalline titanias–vanadia catalysts with narrow pore size distribution and specific surface areas ranging from 64 to 88 m² g⁻¹ were prepared in one step by the ether route. In this case, scanning electron microscopy (SEM) images show the presence of spherical particles (~3 μm 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 silic–alumina–molybdena catalysts with specific surface areas around 500 m² 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 to prepare ordered mesoporous metal oxides (TiO₂, ZrO₂, Nb₂O₅, Ta₂O₅, Al₂O₃, SnO₂, HfO₂, WO₃, 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 coworkers used the thermal decomposition of teri-butyloloxy(siloxy) derivatives in the presence of block copolymers to obtain mesoporous, multicomponent oxides (ZrO₂–4SiO₂, Ta₂O₅–6SiO₂, Fe₂O₃–6SiO₂) with wormhole-like pore structure, and narrow pore size distributions. The templated materials exhibited surface areas and pore volumes ranging from 450–550 m² g⁻¹ and 0.35 to 0.45 cm³ g⁻¹, respectively. However, the untemplated solids showed comparable specific surface areas (415–555 m² g⁻¹) and larger pore volumes (0.7–1.0 cm³ 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

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**Fig. 1** N₂ physisorption isotherms at –196 °C (left) and corresponding pore size distributions (right) of Si–Ti xerogels (Si/Ti = 10) prepared by the ether route at 110 °C with different reaction times (redrawn from ref. 91).
the self-assembly of nanocrystals and block copolymer micelles. Highly ordered mesoporous tin and cerium oxides were obtained after calcination.

More recently, Lee, Orilall and co-workers\(^{101}\) 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 (TiO\(_2\) and Nb\(_2\)O\(_5\)) with well-ordered mesopores. However, the specific surface area remained moderate (54 to 89 m\(^2\) 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 TiO\(_2\)-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 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 noble metals supported on oxides.

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 TiO\(_2\) 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 liquid\(^{147}\)).

The alcohol route (benzyl alcohol, tert-butanol) has been mostly used for the synthesis of TiO\(_2\)-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.\(^{149,150}\)

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**Fig. 2** SEM images of TiV mixed oxide used as VOC total oxidation catalyst\(^{93}\) (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.
Table 1 Oxide catalysts and photocatalysts prepared by non-hydrolytic routes

<table>
<thead>
<tr>
<th>Material</th>
<th>Route: precursors</th>
<th>Reaction catalyzed</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb–V–Si</td>
<td>Alkoxide route: (VO(OiPr)3, NbCl5, Si(OEt)4)</td>
<td>Oxidative dehydrogenation of propane</td>
<td>102–104</td>
</tr>
<tr>
<td>V–Ti</td>
<td>Ether route: VOCl3, TiCl4, Pr2O</td>
<td>Reduction of NO with NH3</td>
<td>94 and 105</td>
</tr>
<tr>
<td>V–Ti</td>
<td>Ether route: VOCl3, TiCl4, Pr2O</td>
<td>Selective oxidation of H2S</td>
<td>95</td>
</tr>
<tr>
<td>V–Ti(–W)(–Mo)</td>
<td>Ether route: VOCl3, TiCl4, WCl6, MoCl6, Pr2O</td>
<td>Total oxidation</td>
<td>93 and 106</td>
</tr>
<tr>
<td>Ti–Si</td>
<td>Alkoxide route: SiCl4, Ti(OiPr)4, Si(OiPr)4</td>
<td>Olefin epoxidation with organic hydroperoxides</td>
<td>107</td>
</tr>
<tr>
<td>Ti–Si</td>
<td>Ether route: SiCl4, TiCl4, Pr2O</td>
<td>Mild oxidation with hydrogen peroxide</td>
<td>92, 108–110</td>
</tr>
<tr>
<td>Ti–Si–MeSi</td>
<td>Ether route: SiCl4, TiCl4, MeSiCl3 or Me2SiCl or Pr2O</td>
<td>Olefin epoxidation with organic hydroperoxides</td>
<td>111</td>
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<tr>
<td>Ti–Si–MeSi</td>
<td>Ether route: SiCl4, TiCl4, Pr2O</td>
<td>Olefin epoxidation with organic hydroperoxides</td>
<td>112</td>
</tr>
<tr>
<td>Ti–Si</td>
<td>Thermolysis: Ti(OSi(OBu)2)3</td>
<td>Olefin epoxidation with hydrogen peroxide</td>
<td>113</td>
</tr>
<tr>
<td>Ta–Si</td>
<td>Thermolysis: [(PrO)2Ta(OSi(OBu))3] (and HOSi(OBu))</td>
<td>Olefin epoxidation with hydrogen peroxide</td>
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<td>Cr–Si</td>
<td>Thermolysis: [(BuO)2CrOSi(OBu)]</td>
<td>Oxidative dehydrogenation of propane</td>
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<tr>
<td>Co–Al</td>
<td>Ether route: AlCl3, CoCl3, Pr2O</td>
<td>Olefin epoxidation with isosilybenzene</td>
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<tr>
<td>Co–Si–Al</td>
<td>Ether route: SiCl4, AlCl3, CoCl3, Pr2O</td>
<td>Mild oxidation with isosilybenzene</td>
<td>115</td>
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<tr>
<td>Fe–Al</td>
<td>Ether route: AlCl3, FeCl3, Pr2O</td>
<td>Mild oxidation with hydrogen peroxide</td>
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<tr>
<td>Mo–Al–Si</td>
<td>Ether route: MoCl5, SiCl4, AlCl3, Pr2O</td>
<td>Alkene metathesis</td>
<td>96 and 117</td>
</tr>
<tr>
<td>Chlorinated SnO2</td>
<td>Benzyl alcohol route: SnCl4 in BzOH</td>
<td>Etherification, alkylation</td>
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<tr>
<td>W16O48 nanowires</td>
<td>Benzyl alcohol route: W(OPr)4 in BzOH</td>
<td>Oligomerization of benzylic alcohols</td>
<td>119</td>
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<tr>
<td>Ag–Al–(Nb)</td>
<td>Ether route: AlCl3, AgCl, Pr2O, NbCl5</td>
<td>Reduction of NO with decane</td>
<td>120</td>
</tr>
<tr>
<td>Pt–Al</td>
<td>Ether route: AlCl3, Pr2O, (C6H5CN)2PtCl2 or PtBr4</td>
<td>NA</td>
<td>121</td>
</tr>
</tbody>
</table>

Oxide and mixed oxide photocatalysts

<table>
<thead>
<tr>
<th>Material</th>
<th>Route: precursors</th>
<th>Reaction catalyzed</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO2</td>
<td>Alkoxide route: TiCl4, Ti(OiPr)4 in hexane or hexane–TOPO solutions</td>
<td>Photooxidation</td>
<td>122–125</td>
</tr>
<tr>
<td>TiO2 (spherical or nanorods)</td>
<td>Benzyl alcohol route: TiCl4 in BzOH</td>
<td>Photooxidation</td>
<td>126 and 127</td>
</tr>
<tr>
<td>TiO2</td>
<td>Benzyl alcohol route: TiCl4 in BzOH</td>
<td>Photooxidation</td>
<td>127</td>
</tr>
<tr>
<td>TiO2</td>
<td>Anhydride route: Ti(OiPr)4, (CX3CO)O2, (X = H, F)</td>
<td>Photooxidation</td>
<td>63</td>
</tr>
<tr>
<td>TiO2 (nanorods)</td>
<td>Ester elimination route or carboxylic acid route</td>
<td>Photocatalytic disinfection</td>
<td>55</td>
</tr>
<tr>
<td>Layered titanate</td>
<td>Ether route: TiCl4, in diglyme in the presence of BH3 amine complex</td>
<td>Photocatalytic disinfection</td>
<td>128</td>
</tr>
<tr>
<td>TiO2–SiO2</td>
<td>Formic acid route in scCO2–Si(OEt)4, Ti(OiPr)4, formic acid</td>
<td>Photocatalysis</td>
<td>87</td>
</tr>
<tr>
<td>TOPO-capped TiO2</td>
<td>Alkoxide route: TiCl4, Ti(OiPr)4 in TOPO</td>
<td>Photocatalysis</td>
<td>129</td>
</tr>
<tr>
<td>Phosphated Zr-doped TiO2</td>
<td>Alkoxide route: TiCl4, Ti(OiPr)4, ZrCl4, Zr(OiPr)4, PrOH in TOPO</td>
<td>Photocatalysis</td>
<td>130</td>
</tr>
<tr>
<td>Fe-doped TiO2</td>
<td>Alcohol route: TiCl4, Fe(NO3)3, in 1BuOH</td>
<td>Photocatalysis</td>
<td>131</td>
</tr>
<tr>
<td>Fe,N-doped TiO2</td>
<td>Alcohol route: TiCl4, Fe(NO3)3, in 1BuOH</td>
<td>Photocatalysis</td>
<td>132</td>
</tr>
<tr>
<td>ZnO</td>
<td>High temperature decomposition of Zn(OAc)4</td>
<td>Photocatalysis</td>
<td>122–123</td>
</tr>
<tr>
<td>InNbO4</td>
<td>Benzyl alcohol route: In(acac), NbCl5, in BzOH</td>
<td>Photocatalysis</td>
<td>133</td>
</tr>
</tbody>
</table>

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

\textbf{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.\textsuperscript{140,153–155} 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, CO2 and various oxygenates are classical side products). Mixed Nb-V oxides have proved more interesting\textsuperscript{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.\textsuperscript{102} and then Moggi et al.\textsuperscript{103,104} prepared vanadia-based catalysts (Nb–V, and Nb–V–Si) using the NH alkoxide route. The catalysts were prepared under N2 by reaction of VO(OiPr), NbCl5, Si(OiPr)4, and/or SiCl4 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 NbVO5 prismatic crystallites of about 1 μm in size (Fig. 3), with very low specific surface area (3–6 m2 g–1). The ternary Nb–V–Si (1 : 1 : 5) samples remained predominantly amorphous after calcination and exhibited much higher specific surface areas (150 m2 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.\textsuperscript{104}
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 (tBuO)₃Cr–O–Si(OtBu)₃. After calcination at 500 °C, 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-b, 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. 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 TiIV 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.

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

<table>
<thead>
<tr>
<th>Material</th>
<th>Route: precursors</th>
<th>Reaction catalyzed</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Entrapment of zirconocene into NH SiO₂, SiO₂–TiO₂ and SiO₂–WO₃</td>
<td>Alkoxide route: SiCl₄, Si(OEt)₄ or Si(OPr)₃-AlCl₃, WCl₆ (FeCl₃ catalyst), Cp₂ZrCl₂</td>
<td>Olefin polymerization, Selective oxidation by various oxidants</td>
<td>134–136, 137</td>
</tr>
<tr>
<td>Entrapment of a Jacobsen catalyst into NH Al₂O₃</td>
<td>Ether route: AlCl₃, Pr₂O₃, Mn or Fe Salen complex</td>
<td>Epoxidation with iodosylbenzene</td>
<td>138 and 139</td>
</tr>
<tr>
<td>Entrapment of metalloporphyrins in NH Al₂O₃</td>
<td>Ether route: AlCl₃, Pr₂O₃, metalloporphyrin</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Entrapment of a Si–Ti complex in NH SiO₂</td>
<td>Anhydride route: Si(OEt)₄, (CH₃CO)₂O, Si–Ti complex</td>
<td>Epoxidation with hydroperoxides</td>
<td>62</td>
</tr>
<tr>
<td>Entrapment of Pd nanoparticles in NH SiO₂</td>
<td>Formic acid route in ionic liquid: Si(OEt)₄, formic acid, Pd nanoparticles</td>
<td>Hydrogenation and Heck C–C coupling reactions</td>
<td>57</td>
</tr>
<tr>
<td>Entrapment of a Rh complex in NH SiO₂</td>
<td>Formic acid route in ionic liquid: Si(OEt)₄, formic acid, [RhCl(PPPh₃)₃] or [Rh₂(COD)₂(dpmm)(μ₂-Cl)]BF₄</td>
<td>Hydrogenation of styrene</td>
<td>140</td>
</tr>
<tr>
<td>Entrapment of a Pd complex in NH SiO₂</td>
<td>Formic acid route in ionic liquid: Si(OEt)₄, formic acid, Pd(OAc)₂</td>
<td>Heck–Mizoroki C–C coupling reactions</td>
<td>142</td>
</tr>
</tbody>
</table>

**Fig. 3** SEM image of the Nb : V 1 : 1 catalyst prepared via NHSG by Barbieri et al. 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.
Several methods have been used to reach a good dispersion of titanium sites, including: strongly acidic hydrolysis,\textsuperscript{158} prehydrolysis of the silicon alkoxide and modification of the titanium alkoxides by a chelating ligand,\textsuperscript{159,160} controlling the rate of addition of water,\textsuperscript{161} or using a single-source precursor with preexisting Si–O–Ti linkages.\textsuperscript{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,\textsuperscript{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\textsubscript{2} (low-temperature aerogels).\textsuperscript{159} After calcination at 400 °C, the mesoporous aerogels obtained by this method displayed surface areas and pore volumes up to 680 m\textsuperscript{2} g\textsuperscript{-1} and 1.9 cm\textsuperscript{3} g\textsuperscript{-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 solvent\textsuperscript{163} or by exchanging the solvent with n-hexane then silylation of the gels before drying.\textsuperscript{161,164}

Tilley and co-workers used the thermal decomposition of the tris(tert-butoxy)silox complex Ti(OSi(OtBu)\textsubscript{3})\textsubscript{3} (I) to prepare SiO\textsubscript{2}–TiO\textsubscript{2} catalysts with a Si/Ti ratio of 4 (TiO\textsubscript{2}–4SiO\textsubscript{2}).\textsuperscript{112} The solid-state transformation of I led after calcination to a low-surface-area material but solution-phase thermolysis of I led to xerogels with high surface area and pore volume (550 m\textsuperscript{2} g\textsuperscript{-1} and 1.8 cm\textsuperscript{3} g\textsuperscript{-1} after calcination at 500 °C). Supercritical drying in CO\textsubscript{2} led to an aerogel with even higher specific surface area and pore volume (1040 m\textsuperscript{2} g\textsuperscript{-1} and 1.53 cm\textsuperscript{3} g\textsuperscript{-1}). The texture of SiO\textsubscript{2}–TiO\textsubscript{2} mixed oxides prepared using the ether route of a SiO\textsubscript{2}–TiO\textsubscript{2} xerogel (Si/Ti = 16) with an outstanding texture (Fig. 4). The gel was obtained by reacting SiCl\textsubscript{4}, TiCl\textsubscript{4}, and iPr\textsubscript{2}O in n-C\textsubscript{8}H\textsubscript{18}Cl\textsubscript{2} in a Teflon-lined autoclave at 150 °C for 4 days. The specific surface area and pore volume (1215 m\textsuperscript{2} g\textsuperscript{-1}, 2.4 cm\textsuperscript{3} g\textsuperscript{-1}) after calcination at 500 °C were significantly higher than those reported for SiO\textsubscript{2}–TiO\textsubscript{2} calcined aerogels with similar compositions.\textsuperscript{165}

The amorphous SiO\textsubscript{2}–TiO\textsubscript{2} calcined xerogels prepared by this method were found to be excellent catalysts for the oxidation with aqueous H\textsubscript{2}O\textsubscript{2} of a wide range of organic compounds (Table 3). Even very bulky substrates, such as anthracene or 4,6-dimethyldibenzo[d]thiophene (4,6-DMDBT, a poorly reactive molecule which is present in the fuels processed by the hydrosulfuration plants), could be effectively oxidized with H\textsubscript{2}O\textsubscript{2} under mild conditions.\textsuperscript{108–110} High conversions (67–92%), high selectivities (>95%), and excellent H\textsubscript{2}O\textsubscript{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 benzaldehyde to benzaldehyde oxide. Similarly, sulfur compounds such as DMSO, methyl-phenylsulfide (MPS), dibenzo[d]thiophene (DBT) and 4,6-DMDBT were oxidized to the corresponding sulfone with excellent conversions (80–97%), selectivities (>99%), and H\textsubscript{2}O\textsubscript{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\textsubscript{2}O\textsubscript{2}, H\textsubscript{2}O\textsubscript{2}/styrene ratio, solvent) allowed us to tune the selectivity toward benzaldehyde (up to 90%) or toward styrene oxide (up to 49%).\textsuperscript{109}

The catalytic performances and the stability of this amorphous SiO\textsubscript{2}–TiO\textsubscript{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
both the low hydrophilicity of the surface and the stability of the Ti sites after exposure to aqueous $\text{H}_2\text{O}_2$.\textsuperscript{109}

The activity and selectivity of $\text{SiO}_2$-$\text{TiO}_2$ epoxidation catalysts can be tuned by introducing hydrophilic organic groups (e.g. $\text{SiMe}$, $\text{SiPh}$ or $\text{SiMe}_3$), either by post-modification or during the synthesis.\textsuperscript{161–169} 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.\textsuperscript{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% $\text{MeSiO}_{1.5}$ (T) units with high specific surface area and pore volume ($1060 \text{ m}^2 \text{ g}^{-1}, 1.3 \text{ cm}^3 \text{ g}^{-1}$) were obtained by reaction of the chloride precursors ($\text{SiCl}_4$, $\text{TiCl}_4$, $\text{MeSiCl}_3$) and $\text{Pr}_2\text{O}$ at 110 °C under autogenous pressure. In addition xerogels modified by up to 20 mol% $\text{MeSiO}_{1.5}$ (M) units could also be prepared for the first time by this route starting from $\text{SiCl}_4$, $\text{TiCl}_4$ and $\text{Me}_3\text{SiCl}$; the incorporation of $\text{Me}_2\text{SiO}_{0.5}$ groups led to a lowering of the specific surface area and pore volume ($930 \text{ m}^2 \text{ g}^{-1}$ and 0.72 cm$^3$ 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 ($\sim 15$ 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 $\text{MeSiO}_{1.5}$ or $\text{PhSiO}_{1.5}$ units.\textsuperscript{170}

$\text{Co–Al}$ and $\text{Co–Si–Al}$ oxides for the selective oxidation of various hydrocarbons. Ciufli and coworkers have utilized the ether route to prepare $\text{Co–Al}$ and $\text{Co–Si–Al}$ oxidation catalysts.\textsuperscript{114,115} The synthesis involved refluxing at 110 °C under an inert atmosphere $\text{AlCl}_3$, $\text{CoCl}_2$ and $\text{Pr}_2\text{O}$ in dichloromethane. $\text{Si(OEt)}_3$ 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 $\text{Co–Al}$ oxide obtained after calcination at 750 °C exhibited moderate specific surface area and pore volume ($45 \text{ m}^2 \text{ g}^{-1}$ and 0.23 cm$^3$ 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 $\text{CoO}$. 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, $\text{PhIO}$.\textsuperscript{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, cyclohexene, 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.\textsuperscript{115} The best catalyst, obtained by calcination at 400 °C, exhibited higher specific surface area and pore volume (53 m$^2$ g$^{-1}$ and 0.05 cm$^3$ g$^{-1}$) than samples calcined at higher temperature and consisted of an amorphous silica–alumina matrix doped with $\text{Co}^{2+}$ ions in tetrahedral coordination and $\text{Co}^{3+}$ octahedral species. Interestingly, the activity of this catalyst compared well with the second-generation FeP iron(III) $\text{mesotetrakis(pentafluorophenyl)porphyrin}$ 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.\textsuperscript{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.\textsuperscript{116} The materials were prepared by the ether route, by refluxing $\text{AlCl}_3$, $\text{FeCl}_3$ and $\text{Pr}_2\text{O}$ 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; $\gamma$-alumina was detected in the catalyst calcined at 750 °C, $\alpha$-alumina was found in the catalyst calcined at 1100 °C. No crystalline iron oxide phase was detected. The presence of $\text{Fe}^{3+}$ 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 $\text{Fe}^{3+}$) in 1 : 1 dichloromethane : acetonitrile solvent, using 0.45 mmol of cyclooctene or cyclohexane and 0.45, 0.9 or 2.25 mmol of $\text{H}_2\text{O}_2$. These conditions were milder than those reported in the literature.\textsuperscript{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

### Table 3  Catalytic behaviour of NH $\text{TiO}_2$–$\text{SiO}_2$ xerogels for the oxidation of different molecules\textsuperscript{109}

<table>
<thead>
<tr>
<th>Substrate (S)</th>
<th>$\text{H}_2\text{O}_2$/S (mol/mol)</th>
<th>$C_1$/mol L$^{-1}$</th>
<th>Solvent</th>
<th>Temp./°C</th>
<th>Time/min</th>
<th>Conversion (%)</th>
<th>$\text{H}_2\text{O}_2$ efficiency$^b$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anthracene</td>
<td>5/1</td>
<td>0.01</td>
<td>MeCN</td>
<td>60</td>
<td>360</td>
<td>92</td>
<td>91</td>
</tr>
<tr>
<td>Cyclooctene</td>
<td>5/1</td>
<td>0.08</td>
<td>MeCN</td>
<td>60</td>
<td>360</td>
<td>67</td>
<td>90</td>
</tr>
<tr>
<td>Styrene</td>
<td>5/1</td>
<td>0.1</td>
<td>MeCN</td>
<td>60</td>
<td>1000</td>
<td>77</td>
<td>80</td>
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<tr>
<td>α-Naphthol</td>
<td>5/1</td>
<td>0.01</td>
<td>MeCN</td>
<td>60</td>
<td>360</td>
<td>65</td>
<td>87</td>
</tr>
<tr>
<td>Phenylsulide</td>
<td>2/1</td>
<td>0.06</td>
<td>MeCN</td>
<td>40</td>
<td>60</td>
<td>95</td>
<td>99</td>
</tr>
<tr>
<td>DBT</td>
<td>2/1</td>
<td>0.1</td>
<td>MeCN</td>
<td>60</td>
<td>120</td>
<td>97</td>
<td>98</td>
</tr>
<tr>
<td>4,6-DMDBT</td>
<td>2/1</td>
<td>0.01</td>
<td>MeOH</td>
<td>60</td>
<td>240</td>
<td>80</td>
<td>90</td>
</tr>
</tbody>
</table>

a Initial concentration of substrate. \textsuperscript{b} $\text{H}_2\text{O}_2$ efficiency (selectivity) = (mole of $\text{H}_2\text{O}_2$ consumed in the formation of products/mole $\text{H}_2\text{O}_2$ converted) × 100.
correlated to the absence of surface Bronsted 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 SOx emissions and the production of elemental sulfur.172 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 iPr2O 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 VOx 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 (C; GHSV = 300 000 h−1; flow of H2S/O2/NH3/H2O/He = 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).

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 iPr2O. 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 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
V species toward the surface during the calcination. This migration was explained by the low Tammann temperature of vanadia, allowing V atoms to be relatively mobile, and by the limited solubility of V₂O₅ in TiO₂. 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. Monomeric V species were favored at low V₂O₅ 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 V₂O₅ loading and reference catalysts prepared via wet impregnation, it was concluded that oligomeric vanadates formed at high V₂O₅ loadings were more efficient than isolated species formed at low V₂O₅ 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, even more stringent regulations are being enacted to decrease nitrogen oxides (NOₓ) air pollution. NOₓ are produced by the combustion of fossil fuels in power plants and motor vehicles. Selective catalytic reduction (SCR) of NOₓ 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 NOₓ by NH₃.** Ammonia is widely used as a reductant for the removal of NOₓ emitted by stationary sources and vanadia-based catalysts supported on TiO₂-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. The reaction at 110 °C under autogenous pressure of VOCl₃ and TiCl₄ with a stoichiometric amount of iPr₂O led to dark brown gels, which after drying and calcinations (5 h at 500 °C in air) gave beige powders. Samples with V₂O₅ 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 V₂O₅ loading increased, from 87 m² g⁻¹ and 0.30 cm³ g⁻¹ (6 wt% V₂O₅) to 26 m² g⁻¹ and 0.22 cm³ g⁻¹ (18 wt% V₂O₅). 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 H₂. The catalytic properties of these materials were evaluated in the SCR of NO by NH₃. 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 V₂O₅ loading of 8 wt%. As previously observed for catalysts prepared by impregnation, the N₂ selectivity decreased with the V₂O₅ loading. The sample containing 6 wt% V₂O₅ offered a good compromise between activity (estimated TOF 7.3 h⁻¹) and high N₂ selectivity (98% at 623 K). In terms of activity and selectivity, the catalysts prepared in one step by NH sol-gel with V₂O₅ loadings ranging from 6 to 10 wt% compared quite favorably with V₂O₅–TiO₂ catalysts elaborated by multi-step processes, such as catalysts obtained by multi-step grafting of vanadyl trisopropoxide onto a titania aerogel.192

Ag(–Nb)–Al mixed oxides for the SCR of NOₓ by hydrocarbons. Hydrocarbons are attractive reductants for the abatement of NOₓ produced by automotive vehicles, solving the problem of the storage of the reducing agent. Silver-based catalysts (e.g. Ag/Al₂O₃) 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.129 The materials were obtained by reaction of the metal chloride precursors (AlCl₃, AgCl, NbCl₅) with a stoichiometric amount of iPr₂O at 110 °C. After drying the xerogels were calcined at 550 °C for 5 hours then activated by hydrotreatment (in air + 10% H₂O) 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-Al₂O₃. 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. For comparison, a Ag/Al₂O₃ 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). The economic conversion of light olefins can be carried out at the refinery with MoO₃-based catalysts. These catalysts are mainly prepared via wet or dry impregnation of a Mo salt onto silica, alumina, titania or silica-alumina supports.
Composite supports (e.g. H-beta zeolite mixed with Al₂O₃) or ordered mesoporous supports (e.g. SBA-15, MCM-41, etc.) have also been frequently used. Experimental observations as well as theoretical works indicate that MoO₃ species must be highly dispersed to be active. The acidity of the support is important too. For example, the superior acidity developed by silica–alumina supports compared to pure silica must be highly dispersed to be active. The acidity 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. The syntheses were performed under an argon atmosphere. SiCl₄, AlCl₃, MoCl₅ and a stoichiometric amount of PR₅ 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 calcined for 5 hours at 500 °C in air.

The texture of the obtained solids was strongly affected by the Si/Al ratio. 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. MoO₃ 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.

**Alkylation.** Recently, tin oxide nanoparticles, prepared by heating SnCl₄ in benzyl alcohol (100 °C, 24 h), have been used to catalyze alkylation reactions. 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(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.

**Photocatalysis.** The photocatalytic degradation of organic pollutants in waste water is a major field of investigation. 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.120–215 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(OPri)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 photoreactor, 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 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.128 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).

**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 gcat L−1 under an 8 W UV-lamps irradiation. Reprinted with permission from Chang et al.129 Copyright 2009 Elsevier.
incorporated into the surface lattice of Zr-doped TiO$_2$. 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 TiO$_2$ P25. The most active phosphated Zr-doped TiO$_2$ 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 m$^2$ g$^{-1}$ (calcination at 550 °C) to 2.4 m$^2$ 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 TiO$_2$ photocatalysts.$^{127}$ TiCl$_4$ 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 TiO$_2$ nanocrystals calcined under different conditions were tested in the photocatalytic degradation of phenol by UV light. Before calcination, the photocatalyst (specific surface area 280 m$^2$ 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 m$^2$ 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 m$^2$ g$^{-1}$. These TiO$_2$ nanorods exhibited good photocatalytic activity (significantly higher than that of P25) in the degradation of rhodamine B under artificial solar light.

TiO$_2$ photocatalysts were also prepared via the NHSG method in supercritical CO$_2$ (scCO$_2$).$^{63,164}$ The conventional hydrolytic pathway to TiO$_2$ is problematic in scCO$_2$ because CO$_2$ is highly hydrophobic and water (needed for the hydrolysis reaction) is only slightly soluble in scCO$_2$. Conversely, organic anhydrides and titanium alkoxides are soluble in scCO$_2$, and the NH anhydride route is thus suitable for the synthesis of TiO$_2$ powders. Guo et al.$^{61}$ have reacted Ti(OR)$_4$ with acetic anhydride in scCO$_2$ at 110 °C and 17 MPA for 20 h, in the presence of a catalytic amount of TiCl$_4$. Since fluorinated moieties are known to be CO$_2$-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 m$^2$ 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 TiO$_2$.

The use of Fe for doping TiO$_2$ 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 TiO$_2$ photocatalysts using the NH alcohol route.$^{131}$ They reacted TiCl$_4$ with Fe(NO$_3$)$_3$ 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 m$^2$ g$^{-1}$ for the NH powders (depending on the Fe content), much higher than that of the HSG powder (27 m$^2$ 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 irradiance (>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 TiO$_2$ and Fe-doped TiO$_2$) 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 (near 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 TiO$_2$, Naik and Parida have prepared Fe$_x$Ti$_{1-x}$O$_2$–N$_y$ photocatalysts.$^{132}$

![Fig. 9 N$_2$-adsorption 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.$^{131}$](image)
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 FeₓTi₁₋ₓO₂₋ₓNₓ 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) 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) was significantly faster with the new FeₓTi₁₋ₓO₂₋ₓNₓ 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. 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. 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, 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 photo-chemical 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 In1−xNixTaO4, which after NiO-loading could split water into H2 and O2 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 InNbO4 nanocrystals from indium acetylacetonate and niobium chloride in anhydrous benzyl alcohol at 200 °C (24 h).133 Highly crystalline monoclinic InNbO4 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 InNbO4 sample prepared by high-temperature ceramic methods.225 In the photocatalytic degradation of rhodamine B under visible-light irradiation (>420 nm) the NHSG-prepared InNbO4 nanoparticles were significantly more active (97% of conversion after 4 h irradiation) than bulk InNbO4 (9%), Degussa P25 (15%) and even carbon-doped mesoporous TiO2 (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 TiO2 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.

TiO2 nanorods. Joo et al.55 have reported the NH synthesis of TiO2 nanorods with controlled morphologies and interesting antimicrobial activity, measured in the photocatalytic inactivation of E. coli. Under an argon atmosphere, Ti(OiPr)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 TiO2 nanorods 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 TiO2 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.

TiO2 nanoparticles. Stoyanova et al. have prepared 10–20 nm-sized anatase particles via the NH reaction of TiCl4 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-Stdler 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 W18O49 nanowires embedded in a short chain polybenzylene matrix (n ≈ 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\textsubscript{18}O\textsubscript{49} nanowires exhibited good activity in the oligomerization of a variety of benzylic alcohols (substituted on the aromatic ring by methyl, tert-butyl or fluorne 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.\(^\text{11,230}\) 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. Metalloocene olefin polymerization catalysts. Metalloccenes are widely used catalysts for the polymerization of olefins due to their high activity and excellent stereoregulatory control and much work has been devoted to their heterogenization in the last 20 years.\(^\text{231}\) Fisch et al. have studied the immobilization of metalloccenes in NHSG-made silica,\(^\text{134,232}\) Si–Ti\(^{\text{35}}\) and Si–W matrices.\(^\text{336}\) Their first attempts consisted of entrapping various metalloccenes (Cp\textsubscript{2}ZrCl\textsubscript{2}, (\textsuperscript{9}BuCp)\textsubscript{2}ZrCl\textsubscript{2}, (\textsuperscript{8}BuCp)\textsubscript{2}ZrCl\textsubscript{2}, (\textsuperscript{6}BuCp)\textsubscript{2}ZrCl\textsubscript{2}, Cp\textsubscript{2}TiCl\textsubscript{2}, Cp\textsubscript{2}HfCl\textsubscript{2}, EtInd\textsubscript{2}ZrCl\textsubscript{2} and Et(IndH\textsubscript{4})\textsubscript{2}ZrCl\textsubscript{2}) in a silica matrix,\(^\text{134,232}\) prepared by an alkoxide route at moderate temperature to avoid thermal deactivation of the metalloccene. Thus, a solution of the metalloccene, SiCl\textsubscript{4} and Si(OEt)\textsubscript{4} in toluene was heated at 70 °C for ca. 3 h in the presence of FeCl\textsubscript{3}, added to play the role of Lewis acid catalyst and trigger the condensation reactions.\(^\text{35}\) 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\textsubscript{2}ZrCl\textsubscript{2}, Cp\textsubscript{2}HfCl\textsubscript{2} and (\textsuperscript{6}BuCp)\textsubscript{2}ZrCl\textsubscript{2}. No leaching of metal was observed. The catalytic activity was intermediate between that of the homogeneous metalloccene and that of the metalloccene grafted on silica.

More recently, Fisch et al. reported the immobilization of Cp\textsubscript{2}ZrCl\textsubscript{2} in NHSG-made Ti–Si mixed oxides.\(^\text{135}\) The method was based on the reaction of a solution of Cp\textsubscript{2}ZrCl\textsubscript{2}, SiCl\textsubscript{4}, TiCl\textsubscript{4} and Si(OEt)\textsubscript{4} or Ti(OPr)\textsubscript{4} in toluene at 70 °C and in the presence of a catalytic amount of FeCl\textsubscript{3}. The resulting materials showed interesting specific surface area ranging from 140 to 370 m\textsuperscript{2} g\textsuperscript{−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\textsubscript{2} was more active than zirconocene-grafted silica, while the samples based on silica-richer matrices were only poorly active.

In addition, these authors used the same route to immobilize Cp\textsubscript{2}ZrCl\textsubscript{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\textsubscript{2}\(^\text{136}\) or Si–Ti matrices.\(^\text{135}\) The complex was dissolved in toluene, then FeCl\textsubscript{3} (in catalytic amount), SiCl\textsubscript{4}, WCl\textsubscript{6} and Si(OEt)\textsubscript{4} were added. Gelation took place after ~ 3 hours at 70 °C, leading to the complex entrapped in a WO\textsubscript{3}–SiO\textsubscript{2} matrix with about 10 wt\% of WO\textsubscript{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\textsubscript{3}–SiO\textsubscript{2} mixed oxide. The activity of Cp\textsubscript{2}ZrCl\textsubscript{2} encapsulated in WO\textsubscript{3}–SiO\textsubscript{2} in ethylene polymerization was significantly higher than that of catalysts prepared by grafting Cp\textsubscript{2}ZrCl\textsubscript{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\textsubscript{2}ZrCl\textsubscript{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\textsubscript{3}–SiO\textsubscript{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.\(^\text{137,139}\) The immobilized catalysts were obtained by refluxing a solution of AlCl\textsubscript{3} and Pr\textsubscript{3}O 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(\textsuperscript{III}) and Mn(\textsuperscript{II}) 5,10,15,20-tetrakis(pentafluorophenyl) porphyrins entrapped in alumina.\(^\text{139}\) 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 m\textsuperscript{2} g\textsuperscript{−1}), whereas the materials heat-treated at 270 °C showed a rough, particulate morphology and a much higher specific surface area (~ 600 m\textsuperscript{2} g\textsuperscript{−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,d]-1,4,8,11-tetraaza[14]annuleno]nickel(II), abbreviated NiTMTAA) in an alumina matrix. The reaction of AlCl₃ and Pr₂O 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. Such manganese salen complexes have been reported as versatile catalysts for the enantioselective epoxidation of unfunctionalized olefins. 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 aluminum 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. 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 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. 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. In this one-pot synthesis, the Pd nanoparticles (diameter ≈ 1 nm) were obtained using H₂O₂ 30% was not an effective oxidant. The leaching of active species was not observed, and the recyclability was shown to be excellent.
3.2.4. 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). 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 MeSiO₁.₅–SiO₂ ionogel. Contrary to the former example, the authors did not remove the ionic liquid (1-butyl,3-methylimidazolium bromide, [bmim][Br]) by extraction but used the resulting ionogel as a catalyst for the Heck–Mizoroki reaction. 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 MeSiO₁.₅–SiO₂. The loading of palladium in the ionic liquid was ~1.1 wt% (phosphate free sample) or ~0.11% (phosphate containing samples). Pd(OAc)₂ and P(Ph)₃ (if any) dissolved in CH₂Cl₂ were mixed to [bmim][Br], formic acid and Si(OMe)₃ (and MeSi(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-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. Decomposition of tri-tert-butoxyxiloy derivatives. Tilley and co-workers have extended their thermal decomposition route of tri-tert-butoxyxiloy derivatives to the construction of isolated MOₓ–SiO₂ species on an oxide surface (Fig. 14).

Thus, isolated iron(ni)ites were generated at the surface of a porous silica support (SBA-15) by grafting/thermal decomposition of the molecular precursor Fe[OSi(OtBu)₃]₃,THF (3). 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 ≡Si–Fe[OSi(OtBu)₃]₃(THF) species, with elimination of HO[Si(OtBu)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[Si(OtBu)₃] 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 of a V precursor from solution, leading to surface vanadium oxide. Again, this route is limited by the tendency of impregnated species to agglomerate on the support surface during dehydration. Rice and Scott proposed to prepare bimetallic V–Ti single site catalysts using non-hydrolytic condensation reactions between chloride and alkoxide groups. 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 ≡SiOVOCl₂ (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 ≡SiOTiCl₂ surface complex with elimination in the gas phase of VOCl₃, indicating the occurrence of an exchange reaction. Conversely, the reaction of SiOVOCl₂ surface site at room temperature with Ti(O′Pr)₄ vapor led to the formation of a 1 : 1 V–Ti surface complex, ≡SiOTi(O′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.

3.3.1. 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.
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 titanium or tantalum catalysts for olefin epoxidation. Thus, under anhydrous conditions, the tri-tert-butoxysiloxy derivative (O$iPr$)$_2$Ta[OSi(O$tBu$)$_3$]$_3$ (2) 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-butoxysiloxy titanium complexes, presumably due to the better accessibility to the active sites.

A Ta/SiO$_2$ catalyst was obtained by a similar method, by reacting the complex (O$iPr$)$_2$Ta[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$_2$O$_2$, CHP and TBHP. The leaching of catalytically active soluble tantalium species was negligible under these experimental conditions. Interestingly, aqueous H$_2$O$_2$ 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$_2$O$_2$ concentration) after 2 h, with an initial rate of 6.7 mol oxidation products molTa$^{-1}$ 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),
Mg–Al derived from hydrotalcites, Si–Ti, Ti–Zr, Ti–Al, 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 metalloocene catalysts by immobilization of metalloccenes on a silica–zirconia 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, (t-BuCl)2ZrCl2 or Cp2ZrCl2 were dissolved in toluene and the support was 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. 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. Mixed oxides with variable Ti content (from 6 to 20 mol%) were prepared by the ethere route: the chloride precursors and PtO2 were heated in a sealed autoclave at 120 °C for 96 hours as previously reported. 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, 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. 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. They first prepared a series of indenyl-modified silicas by reacting organochlorosiloxane derivatives (Me3SiCl2 or (CMe3Si)2O), Ind3SiCl2 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 (CMe3Si)2O instead of Me3SiCl2 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 polyethylene (PE) was strongly dependent on the preparation conditions of the hybrid catalyst. The best catalysts exhibited promising activities in the range of 150–190 gPE g⁻¹ 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. Dolev et al. have used the ether route to prepare a Pt-based catalyst supported on an amorphous alumina with large surface area. AlCl3 was reacted with PrOCl, 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 m² 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. TiO₂–Al₂O₃ supports

TiO₂–Al₂O₃ mixed oxides are used as supports for various catalytic reactions.²⁴⁰⁻²⁴⁵ β-Al₂TiO₅ is known to be metastable below ~1180 °C, the stable phases being TiO₂ (rutile) and α-Al₂O₃ (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-Al₂TiO₅. This result was ascribed to the excellent molecular scale homogeneity of the nonhydrolytic gels that favors the direct crystallization of the metastable β-Al₂TiO₅ 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 0.6TiO₂–0.4Al₂O₃ catalytic supports prepared by nonhydrolytic and hydrolytic routes.¹⁴⁶ Thus four samples were synthesized using the ether route (from chlorides and iPr₂O) or the alkoxide route (from TiCl₄ and Al(O'Bu)₃ or Al(O'Pr)₃ or from Ti(O'Pr)₃ and AlCl₃). 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 Al(O'Bu)₃ showed the highest specific surface areas (260 and 200 m² 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 for the simple 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 CO₂.

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