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PERSONAL ACCOUNT

Innovative Sol-Gel Routes for the Bottom-up Preparation of Heterogeneous Catalysts

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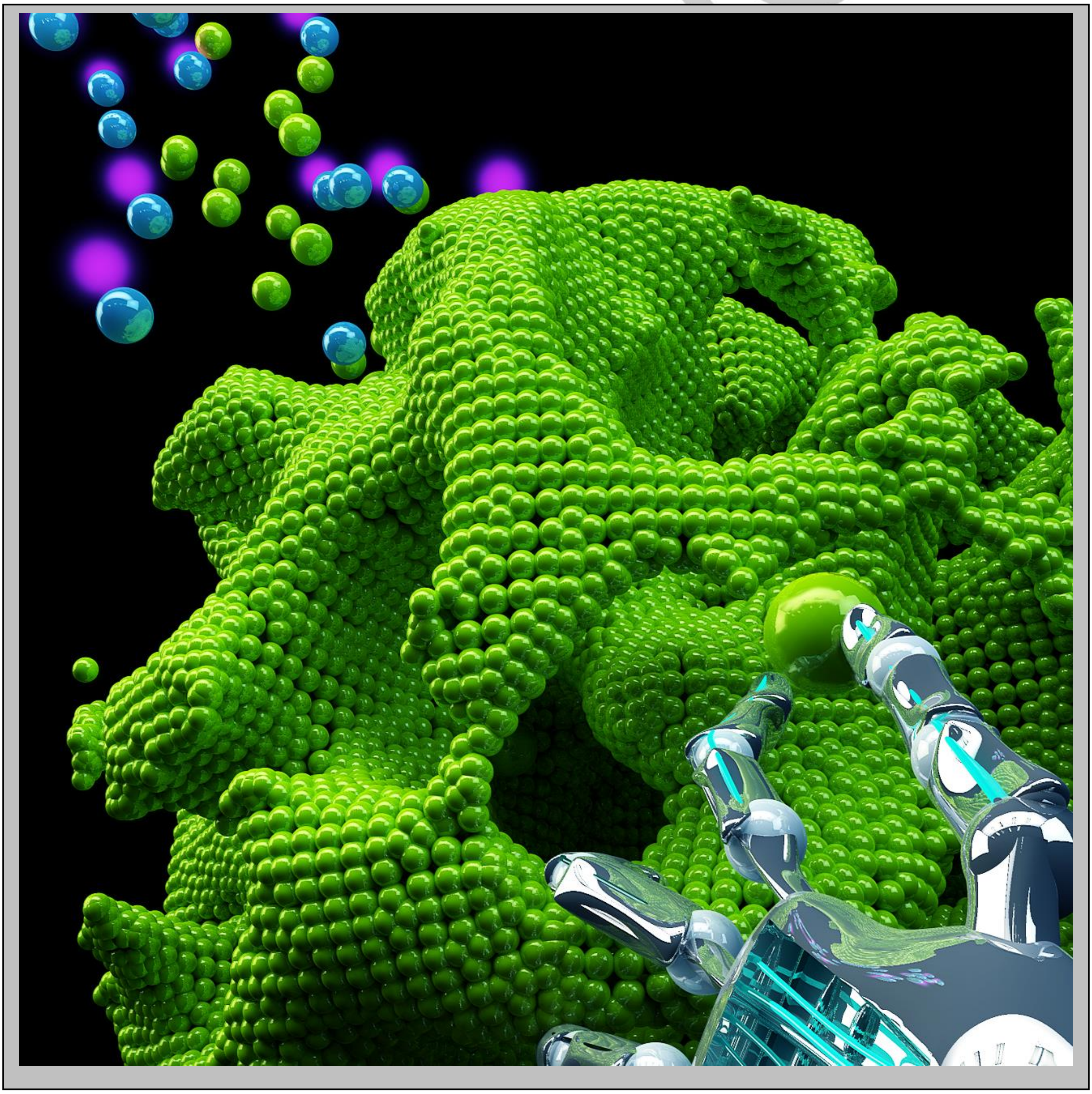


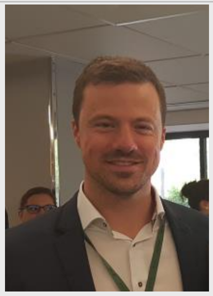
Abstract: Heterogeneous catalysts can be prepared by different methods offering various levels of control on the final properties of the solid. In this account, we exemplify bottom-up preparation routes that are based on the sol-gel chemistry and allow to tailor some decisive properties of solid catalysts. First, an emulsion templating strategy is shown to lead to macrocellular self-standing monoliths with a macroscopic 3D structure. The latter can be used as catalyst or catalyst supports in flow chemistry, without requiring any subsequent shaping step. Second, the aerosol-assisted sol-gel process allows for the one-step and continuous production of porous mixed oxides. Tailored textural properties can be obtained together with an excellent control on composition and homogeneity. Third, the application of non-hydrolytic sol-gel routes, in the absence of water, leads to mixed oxides with outstanding textural properties and with peculiar surface chemistry. In all cases, the resulting catalytic performance can be correlated with the specificities of the preparation routes presented. This is exemplified in catalytic reactions in the fields of biomass conversion, petro chemistry, enantioselective organic synthesis, and air pollution mitigation.

1. Introduction

Today, approximately 90% of all industrial chemicals are produced with the aid of catalysts.[1] Catalysts allow running chemical reactions at higher rates, with lower energy input and with high specificity and selectivity, thereby making it possible to run chemical processes at relatively low environmental costs.[2] Heterogeneous catalysts in particular address the objectives of green chemistry by providing the ease of separation of product and catalyst, thereby eliminating the need for separation through distillation or extraction.[3] They are also suitable for continuous processes which generally surpass discontinuous (batch) processes in terms of environmental performance.[4] In the perspective of a greener – mainly bio-based – chemical industry, innovative catalyst formulations are needed, with new requirements (e.g. stability in highly polar environment, ability to convert bulk molecules in the liquid phase, etc.). Another contemporary challenge is related to the vital obligation to mitigate our CO_2 emissions. This can be envisaged along two lines of complementary efforts where catalysis science has a central role: (i) designing more efficient chemical processes with higher atom efficiency and (ii) finding efficient ways to utilise CO_2.[5] Undoubtedly, catalysis science will remain a land of challenge, opportunities and innovation for the development of a more sustainable society.

In a perpetual quest for performance, catalysis scientists screen new catalysts formulations, improve catalyst preparation methods, optimise reaction conditions, etc. While research in heterogeneous catalysis has long been rather empirical,[6] the preparation of new heterogeneous catalysts is now increasingly being guided by rational design, based on the understanding of the key parameters which dictate their performance. Important effort is put into catalyst characterisation, to understand their working behaviour and to correlate their activity with their physico-chemical properties. In parallel, moving away from the simple but coarse catalyst preparation techniques like impregnation or co-precipitation, advanced preparation techniques are proposed frequently, allowing the practical catalysis researcher to tailor the properties of the solids – at the nanoscale – for the targeted applications.[7]

Indeed, materials chemists continuously explore new ways to produce solids with tailored properties and functionalities. In the last decades, sol-gel processes have emerged as powerful tools for the preparation of an enormous range of functional solid materials, including hierarchical porous oxides,[8] hybrid materials,[9] coating and films,[10] nanoparticles,[11] etc. Mainly using the "chimie douce" approach,[12] sol-gel routes have extraordinarily demonstrated their versatility and practicability for the preparation of materials that are actually used in our everyday life.[13] Sol-gel approaches can be described as bottom up preparation methods in which the solid is obtained via a succession of reactions between molecular precursors (Fig. 1). In the most typical sol-gel routes, alkoxide or chloride or carboxylate precursors are put in solution and allowed to hydrolyse and then poly-condense in a controlled manner. Upon peptidisation the solution first turns into a sol. Then, upon reticulation, it forms a wet gel which often undergoes a subsequent step of ageing. The gel is then typically dried and calcined to produce the final solid material.



Damien P. Debecker obtained his PhD in heterogeneous catalysis in 2010 at the University of Louvain in the group of Prof. E. Gaigneaux, under a fellowship from the Fonds National de la Recherche Scientifique (FNRS). He was then appointed FNRS post-doctoral researcher. In 2011 he was invited as a post-doctoral researcher in the group of Prof. C. Sanchez (Collège de France, Université Pierre et Marie Curie, France), to study original sol-gel methods for the preparation of porous catalysts. In 2012 he was invited as a post-doctoral researcher in the group of Prof. N.J. Turner at the Manchester Institute of Biotechnology (University of Manchester, UK), working on biocatalysis for organic synthesis. He was then appointed as an associate professor at the University of Louvain, teaching physical chemistry, process engineering and industrial waste treatment. His current research focuses on heterogeneous catalysis and biocatalysis applications, with a strong emphasis on sustainability. Targeted applications cover biomass upgrading, VOC total oxidation, CO_2 methanation, olefin metathesis, etc. He has authored 57 articles in international journals and 4 patents. Damien Debecker was the recipient of the "UMICORE scientific award" in 2010. Recently he was awarded with a "Green Chemistry for Life" grant from UNESCO, IUPAC and PhosAgro.

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One can cite three main challenges in sol-gel synthesis applied to the preparation of heterogeneous catalysts. The first is related to the control on the composition and on the homogeneity of the solid. Indeed, the success of the method is restricted to the cases where all precursors are soluble in the same medium and react with similar hydrolysis and condensation rates. The second challenge is related to the texture, which obviously needs to be controlled precisely for heterogeneous catalysts. When solvent is evaporated, surface tensions can cause pore collapse and result in materials with poor textural properties. A third challenge is related to the shaping of the powdery materials that are usually obtained by sol-gel techniques. In all cases, strategies are put in place to address such issues: modulating the reactivity of the precursors, switching to non-conventional reaction conditions, using supercritical drying, adding sacrificial templating agents, etc.

Our research group has been consistently engaged in the development of innovative strategies for the three pillars of catalysis science: preparation, characterization, and performance evaluation. In the recent years, an important focus was put on the preparation part. Nurtured by effective collaboration with materials chemists, our strategy was to exploit the recent and innovative methods of bottom up sol-gel approaches for the design of highly efficient heterogeneous catalysts. Based on a good understanding of the parameters that dictate the performance of specific heterogeneous catalysts for specific chemical reactions, we selected the sol-gel routes that allow obtaining the most desirable features, leading to enhanced performance. This Personal Account describes representative examples of successful bottom-up sol-gel approaches which have led to advances in heterogeneous catalysis.

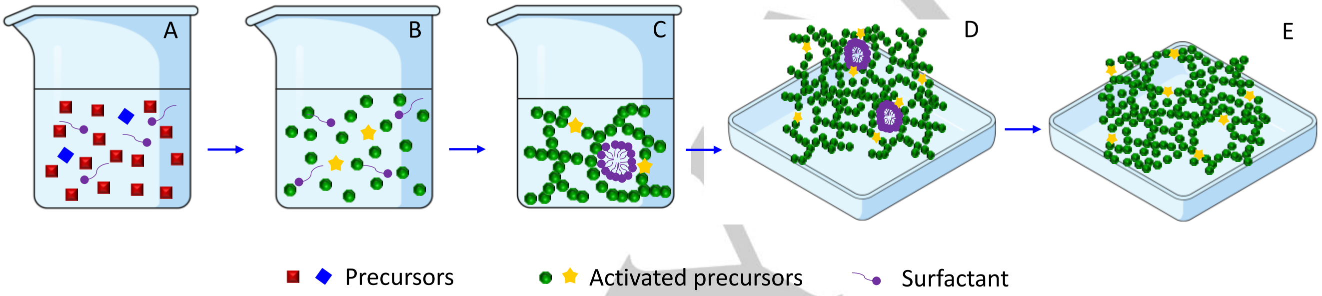


Figure 1. Schematic representation of the classical sol-gel procedure for the preparation of porous mixed oxides. (A) the starting solution contains molecular precursors (e.g. alkoxides, chlorides, etc.); (B) the precursors are activated by hydrolysis (or organolysis[14]) and are ready to polycondensate; (C) peptidisation and reticulation lead to the formation of a wet gel swollen by the solvent; (D) the gel may be aged for some time and is then dried; (E) the dry gel is thermally treated to strengthen the inorganic network and remove residual components from the precursors and solvent. Very often, a templating agent is added in the first step. For example, surfactant molecules self-assemble in the form of micelles which serve as a sacrificial template to generate pores. In this account we present variations of this classical procedure that allow us to obtain solids with improved properties in the perspective of their applications as heterogeneous catalysts. Originality arises either from the use of unusual templating strategies, or from unusual molecular precursors, solvent, or reaction conditions, or from a specific drying procedure.

2. Emulsion-templating for the preparation of macrocellular monolithic catalysts

Solid catalysts are usually developed in the form of divided powders. The fundamental studies associated with their development and optimization are systematically carried out on such powdery materials. However, in the perspective of an application in industrial flow processes, the catalysts have to be shaped in the form of extrudates, granules, pellets, or monoliths, so that high flows can be accommodated without excessive pressure drop.[15] The science of "catalyst shaping" remains essentially empirical and often part of the protected intellectual properties in companies. As far as monoliths are concerned, the classical strategy is to deposit the active catalyst on a preformed scaffold via methods such as wash coating.

Sol-gel techniques permit the bottom-up synthesis of macroscopic objects in the form of a self-standing gel. It appears interesting to take advantage of such multilevel porous architectures for the preparation of self-supported monolith.[8a] In particular, the processing of condensable emulsions leads to materials with attractive properties. Emulsions are thermodynamically metastable systems; their stability can be enhanced using tension-active molecules. "High internal phase emulsions" (HIPEs) are now widely applied as template to create very high porosity macroporous polymers ("polyHIPE"). One advantage of this process is that the template is liquid which allows moulding it to any desired shapes.[16] Working in collaboration with the Backov group – active in the field of polyHIPE materials[17] – we have recently demonstrated that these materials are excellent candidate for applications in the field of heterogeneous catalysis.

2.1. Acidic aluminosilicate monoliths for alcohol dehydration

Aluminosilicates are of utmost importance as acidic catalysts and catalyst supports.[18] Using various templating strategies hierarchical amorphous or crystalline, micro- or mesoporous catalytic materials can be prepared in the form of powders.[19] The latter have to be shaped or impregnated onto structured supports with active components, and this step is known to be difficult to control.[15c] One-step preparation of structured materials with desired mechanical, chemical and textural properties is highly desirable.

While polyHIPE of silica were already well described in the literature,[16a] the incorporation of alumina in such system is not straightforward since chemical synthesis conditions used for the preparation of such materials are based on colloidal or acidic silica chemistry. The latter routes are inefficient for the true incorporation of aluminum cationic species in the silica network. While Al in tetrahedral coordination is required to get strongly acid heterogeneous catalysts, classical routes usually generate aluminum oxide chunks in octahedral environment.[20]

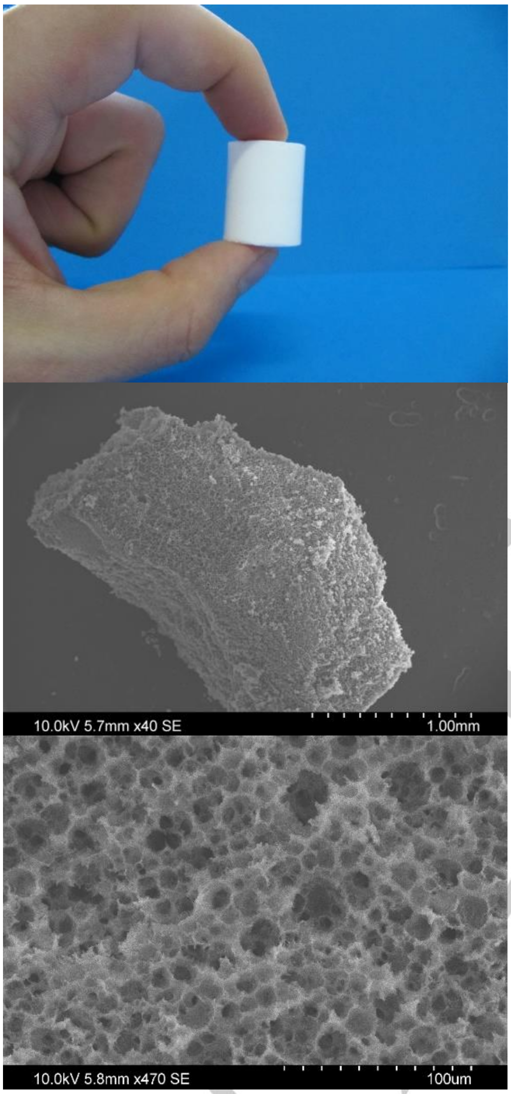
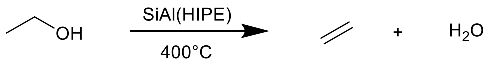


Figure 2. Picture (top) of a self-standing monolith of aluminosilicate prepared by the emulsion-templating sol-gel technique[21] and SEM micrographs (middle and bottom) of scratched pieces of this monolith.

Thus, a new type of acidic macrocellular and mesoporous silica-alumina foam was obtained by a modification of the classical Si(HIPE) synthesis protocol.[21] Tetraethylorthosilicate was incorporated into dodecane, along with a cationic surfactant, tetradecyltrimethylammonium bromide (TTAB). Aluminum isopropoxide was added in water, along with tetrapropylammonium hydroxide (TPAOH). Both solutions were mixed together and a stable emulsion was formed after vigorous stirring. The emulsion was aged for 1 week, washed and calcined.

Self-standing SiAl(HIPE) monoliths with a Si/Al ratio ~10 were prepared at the cm-scale (Fig. 2). Macroscopically, the materials appeared similar to Si(HIPE). SEM observations showed that SiAl(HIPE) exhibited open and interconnected macroporosity (macro-cells in the 5-45 µm range) (Fig. 2). Porosity and surface area reached 89% and 900 $m^2.g^{-1}$ respectively. The walls of the materials exhibited small mesorpores but no micropores. By NMR, it was possible to demonstrate that the alkaline conditions favoured the reaction between Si and Al precursors. The formation of a true mixed aluminosilicate with a majority of Al centres in tetrahedral coordination generates abundant and strong surface acid sites. The structured mixed oxide monolith exhibited high performance in the acid-catalysed dehydration of bioethanol to ethane (Scheme 1), outcompeting commercial mesoporous aluminosilicate of similar composition. Specific productivity reached 13.3 $g_{ethene}.g_{cat}^{-1}.h^{-1}$. While the selectivity to ethene was as high as ~95%, the distribution of by-products pointed to the superior acidic properties of the SiAl(HIPE) catalyst.



Scheme 1. Bioethanol dehydration using a macrocellular aluminosilicate monolith, SiAl(HIPE).[21]

2.2. Macrocellular monoliths as supports for enzymes

Biocatalysis is probably the most exciting and blooming field of the research in catalysis. Enzymes are remarkable catalysts, capable of transforming a wide array of complex substrates with unparalleled chiral (enantio-) and positional (regio-) selectivities, which explains the current boom in industrial biocatalysis.[22] Almost endless possibilities are offered by the methods of genetic engineering, especially considering the success of strategies like “directed evolution”.[23] However, free enzymes remain homogeneous biocatalysts, which limits their practical applicability. Immobilization – to turn enzymes into heterogeneous biocatalysts – is the key to optimizing the operational performance of an enzyme in industrial processes.[24] Moreover, immobilization allows envisaging the design of continuous flow processes to replace discontinuous batch processes.

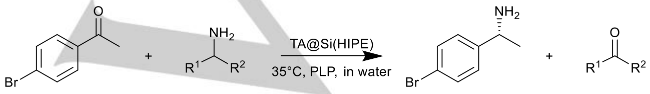
Si(HIPE) monoliths appear as a highly attractive material for the immobilization of enzymes because they feature high surface area and high void fractions, together with hydroxyl surface groups that can be easily functionalised. Backov et al. have grafted lipase enzymes into a Si(HIPE) matrix casted into a cylindrical reactor and demonstrated long-term performance in hydrolysis, esterification and transesterification reactions.[17b] Perhaps even more pertinent is synthesis of high-value chemicals – like chiral drug precursors – in a continuous process, with very high enantioselectivity and under mild reaction conditions.

We have recently reported the first example of a continuous biocatalytic process for enantioselective transamination reactions using immobilised transaminases.[25] Si(HIPE) monoliths were functionalised with (3-aminopropyl)triethoxysilane (APTES) to generate amino group at their surface. Transaminases were immobilised into this macrocellular support, using glutaradehyde as a linker between the amino group at the silica surface and the lysine residues at the enzyme surface (Scheme 2). A simple reactor was designed by casting the Si(HIPE) monolith into a heat shrinkable Teflon tube itself connected to a syringe pump (Fig. 3). The mechanical strength of the monolith was sufficient to ensure the robustness of the system and the silica porous structure ensured that the reactor worked in the plug flow regime without preferential flow paths.[25]

Scheme 2. Covalent grafting of an enzyme on the surface of a solid support. Here,[25] the surface of a macrocellular silica monolith is first functionalised with amino groups using aminopropyltriethoxysilane (APTES). Then gludaraldehyde is used as a coupling agent between the lysine residues at the surface of the enzyme and the amino groups at the surface of the support. Further reduction of the imines can be applied to further stabilise the anchorage.

Figure 3. Picture of the plug flow reactor applied for a continuous biocatalytic transamination reaction. The functionalised silica monolith is casted into a heat-shrinkable Teflon tube and both ends are respectively connected to (i) a syringe pump and (ii) a sample collector. The transaminase was immobilised by covalent grafting using glutaraldehyde as a coupling agent.[25]

Chiral amines are chiral precursors of many important drugs and can be obtained from a ketone intermediate and an amine donor, using enantioselective transaminase.[26] A model of chiral amine synthesis is shown in Scheme 3. In our work, the kinetic resolution of racemic bromo-α-methylbenzylamine into 4'-bromoacetophenone was studied as a model transamination reaction to evaluate the pertinence of the immobilisation strategy for a flow process. Upon immobilisation, the enzyme maintained its activity and enantioselectivity. Biocatalysts were shown to be stable both over time (vs. leaching) and upon cold storage. Full conversion could be obtained by tuning the residence time. This study showed that such heterogeneous biocatalyst exhibits all the required features for an enzymatic flow process. It paves the way to the development of industrially relevant processes in continuous flow mode, based on heterogeneous biocatalysis.



Scheme 3. Production of a chiral amine with a transaminase immobilised onto a macrocellular silica monolith (Si(HIPE)).[25] Bromoacetophenone is a model compound for other more sophisticated substrate of pharmaceutical interest (e.g. Sitagliptine).

3. Aerosol-assisted sol-gel process

Aerosol processes have long been used to synthesise divided materials.[27] The process relies on the atomization of a liquid sample (solution, suspension, etc.) in the form of a mist of small droplets, which are then processed to generate solid – usually spherical – particles. In the simple "spray drying" mode, the non-volatile species which are present in the liquid system are dried to the solid state. A successful example of catalyst preparation by spray drying is that of $NaAlO_2$ microspheres which consisted in the aggregation of relatively small crystallites, exhibiting enhanced surface basicity and outstanding activity in the base-catalysed synthesis of glycerol carbonate.[28] Spray drying can also be used to disperse active materials onto structured catalyst supports, as demonstrated recently in the case of soot combustion catalysts.[29] Interestingly, aerosol processing can be used to trigger chemical transformations during the drying of the droplets and generate new materials of high interest for heterogeneous catalysis. For instance, MOFs,[30] hydrotalcites,[31] or zeolites[32] have been prepared by aerosol processing.

A particularly interesting class of materials is that of mesoporous mixed oxides. Thus, sol-gel preparation methods have been modified so that the usual condensation of the inorganic oxide occurs during the drying of the aerosol droplets (Fig. 4). Remarkably, this can be combined with ingenious strategies of templating to generate the needed textural properties.[33] In particular, surfactant molecules can undergo the so-called evaporation-induced self-assembly (EISA)[34] during the drying. The process gradually concentrates the species present in each aerosol droplet until micelles form at the same time as the inorganic precursors react to form the solid oxide. Afterwards, the organic micelles can then be removed to generate calibrated pores. Similar results can be obtained using other templates like synthetic polymer beads[35] or natural biopolymers[36] to generate larger pores. Another decisive advantage of the aerosol-assisted sol-gel process is the excellent control on the composition of the solids. Provided that the starting precursor solution is stable and remains homogeneous over the duration of the atomization, each droplet has exactly the same composition as the starting solution, and therefore all solid particles also have the same final composition. Finally, the rapid drying of the droplets allows for the so-called kinetic quenching of the solution, allowing to obtain metastable states instead of the thermodynamically favoured products obtained during regular sol-gel syntheses.

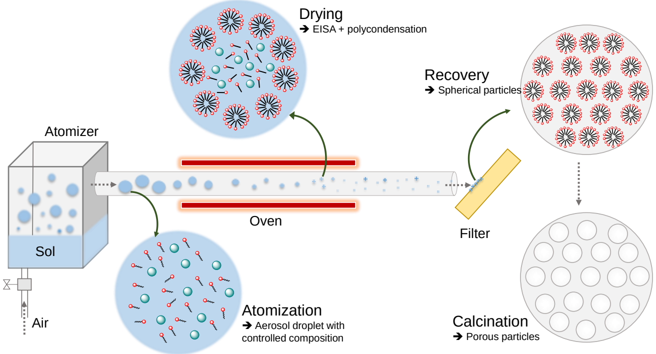
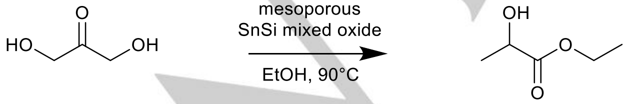


Figure 4. Working principle of the aerosol-assisted sol-gel process.[37] The starting precursor solution is relatively dilute and therefore stable so that gel formation does not start during atomization. The solution is atomised in the form of an aerosol. Each droplet has the same starting composition. Upon drying, solvent evaporation triggers the self-assembly of surfactant micelles (alternatively, pre-formed polymer beads can be used as a template). In parallel, the polycondensation of the inorganic network takes place, around the organic template. Dried particles are collected. They usually have a spherical shape. Porosity is released by removing the template by calcination (or solvent extraction).

It is important to note that the aerosol process has a high productivity and can be operated in a continuous mode. This is a decisive advantage over multistep catalyst preparation strategies, when it comes to industrialisation. The Sanchez and Boissière group in Paris (UPMC) is particularly active in the development of aerosol methods for the preparation of porous and hybrid materials.[33b, 38] Together, we have demonstrated that the aerosol-assisted sol-gel process offers unique opportunities for the preparation of advanced heterogeneous catalysts.

3.1. Mesoporous stanosilicates for the synthesis of ethyl lactate

The upgrading of glycerol is receiving a lot of attention since the dawn of the biodiesel industry, producing huge amounts of this low-cost bio-based chemical.[39] One of the envisaged routes is to oxidise glycerol into dihydroxyacetone (DHA), which can subsequently react with an alcohol to yield alkyl lactates.[40] For this last reaction, stanosilicates are known to be highly active and selective.[41] Catalytic activity is known to be brought about by a combination of Lewis and mild Brønsted acid sites.[42] Also, texture, particle size and Sn speciation are key factors for obtaining high activity. Thus, the best results have been obtained with small mesoporous particles featuring a high dispersion of Sn into the silica matrix – ideally as isolated sites.[41b]



Scheme 4. Synthesis of ethyl lactate from dihydroxyacetone and ethanol, using a mesoporous stanosilicate catalyst.[43]

We proposed the one step synthesis of mesoporous SnSi mixed oxides using the aerosol process.[43] Tetraethyl orthosilicate (TEOS) was hydrolysed in an acidic aqueous-ethanolic solution and then $SnCl_4{\cdot}5H_2O$ and Pluronic P123 were added right before atomization. Aerosol drying followed by calcination resulted in the formation of microspheres mainly in the range of 140-380 nm, with calibrated mesopores of 5-6 nm (Fig. 5). Surface area and pore volume reached 370 m².g^{-1} and 0.5 cm³.g^{-1} respectively. Mesoporosity is present down to the core of the particles. As it is generally the case with the aerosol-assisted sol-gel process, the actual composition was very close to the nominal one (i.e. Si/Sn ratio of 37 and 74). Importantly, solid state ^{119}Sn static NMR demonstrated that Sn was in tetrahedral coordination, truly incorporated into the silica matrix. The presence of such isolated sites at the surface is responsible for a relatively strong surface acidity (NH_3-chemisorption), which translated into record catalytic performance in the synthesis of ethyl lactate from DHA and ethanol.[43] The catalysts truly act in a heterogeneous mode – without Sn leaching – and could be used in multiple catalytic cycles thus proving its stability under the selected reaction conditions.

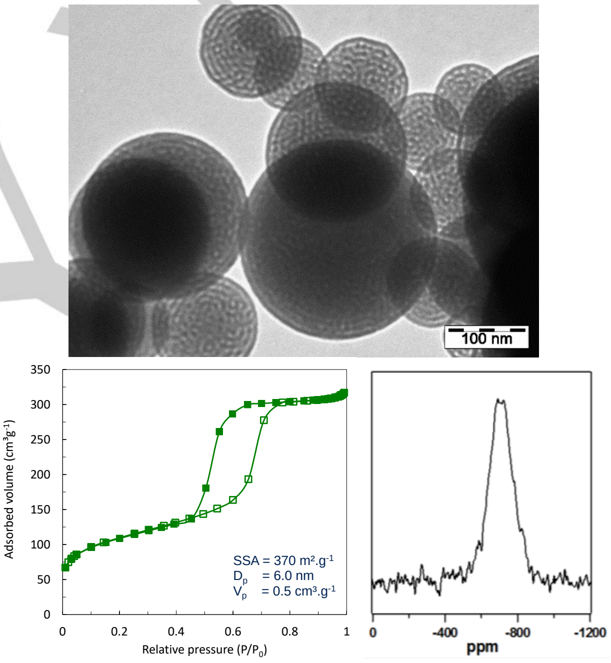
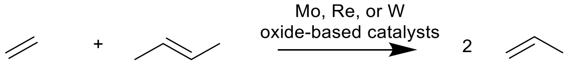


Figure 5. Description of the mesoporous SnSi mixed oxide prepared by the aerosol-assisted sol-gel process:[43] (top) TEM micrograph, (Bottom left) N_2-physisorption isotherms and textural properties, (Bottom right) ^{119}Sn static NMR showing the occurrence of Sn in tetrahedral coordination.

3.2. MoO_3- and WO_3-based mesoporous catalysts for olefin metathesis

Olefin metathesis, as a route to synthesizing small olefins, has gained renewed interest due to the recent world shortage of small olefin feedstocks.[44] Well-defined organometallic complexes can be immobilised onto appropriate supports and show excellent performance for the metathesis of small and large olefins,[45] but industrially, supported W, Mo, or Re oxides are applied.[46] Classically, transition metal oxide-based olefin metathesis catalysts are prepared by impregnation methods, starting from a porous support (silica, silica-alumina, alumina, titania, etc.) and from an aqueous solution of a salt of the active transition metal. A large part of the research has been focused on the optimization of such impregnation method, for example by testing different kinds of supports[47] or different kinds of precursors.[48] However, with impregnation techniques, it remains challenging to control precisely the dispersion and the speciation of the active oxide at the surface of the support.[49] Yet the catalyst activity is precisely governed by the speciation of Mo, W or Re oxide surface species.[44, 50] In particular, it is generally accepted that poorly dispersed or crystalline species are inactive, while highly dispersed (presumable isolated) species are the active sites in olefin metathesis.



Scheme 5. The production of propene from ethene and 2-butene is a typical application of light olefin metathesis, which can be catalysed by molybdenum, rhenium or tungsten oxide based formulations.

In this context it appears interesting to prepare catalysts with a high dispersion of the active elements. Thus, MoO_3-SiO_2-Al_2O_3,[37] WO_3-SiO_2[51] and WO_3-SiO_2-Al_2O_3[52] formulations have been prepared by the aerosol-assisted sol-gel process. Mo and W precursors could be either a heteropolyanion or the chloride. When Brij58 was used as a texturing agent, supermicroporous samples were obtained, with high specific surface area (480 $m^2.g^{-1}$) and calibrated pores of 1.8-2.0 nm (Fig. 6).[37, 51] Alternatively, larger amphiphilic molecules were also used (e.g. P123 or F127) to generate mesopores of ~5 nm).[52] In fact, the method is very flexible when it comes to choosing the pore size.

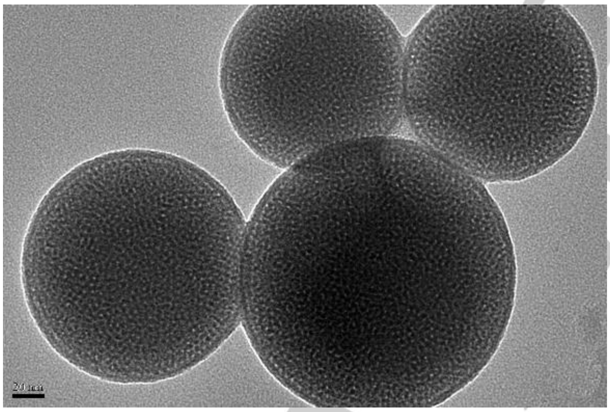


Figure 6. TEM micrograph of a MoO_3-SiO_2-Al_2O_3 catalyst obtained by the aerosol-assisted sol-gel process (MoO_3 (10.0 wt%):Al_2O_3 (5.7 wt%):SiO_2 (84.0 wt%):P_2O_5 (0.4 wt%).[37]

Importantly, we showed that the dispersion of MoO_x species or WO_x species was greatly improved in aerosol catalysts, as compared to the situation obtained with impregnation methods. No crystallites of MoO_3 or WO_3 were formed (unlike in impregnated catalysts with similar composition). Bulk composition and surface composition were similar, attesting that the samples are homogeneous in composition. It must be recalled that in sol-gel chemistry, part of the active element is lost in the walls of the materials, unable to participate in surface reactions. This is different in the case of impregnation techniques were the active element is deposited at the support surface. Yet, comparing the catalysts at similar Mo of W loading, the aerosol catalysts systematically exhibited higher performance, confirming the importance of active phase speciation and advantage of the aerosol method (Fig. 7). Together with these convincing performance, the fact that the aerosol assisted sol-gel method can be applied at large scale, in the continuous mode and with high production rates should foster future development in the field.

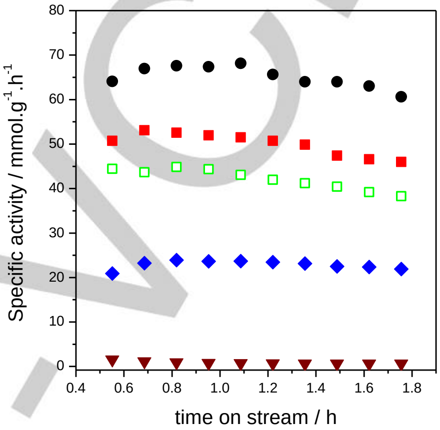


Figure 7. Specific metathesis activity (mmol of propene produced from ethene and 2-butene per g of catalyst and per hour) at 250°C with time on stream over (●) WO_3-SiO_2-Al_2O_3 made by aerosol, (■)WO_3-SiO_2-Al_2O_3 made by impregnation onto a $SiO_2Al_2O_3$ support made by aerosol, (□) WO_3/SiO_2-Al_2O_3 made by impregnation on a commercial mesoporous $SiO_2Al_2O_3$ support, (◆) WO_3/Al_2O_3 made by impregnation on a commercial Al_2O_3 support, (▼)WO_3/SiO_2 made by impregnation on a commercial SiO_2 support. Reproduced with authorisation from Debecker et al.[51]

4. Non-hydrolytic sol-gel

When it comes to preparing mixed oxides with a good control on composition, homogeneity and texture, classical hydrolytic sol-gel routes suffer from two main issues which can to a large extent be solved by non-hydrolytic sol-gel (NHSG).[53] Firstly, different metal precursors often have different reactivity in the classical hydrolysis-condensation reactions in water. Even worse is the case of silica, for which the alkoxides react very slowly.[54] As a result, inhomogeneous oxides are often obtained. In many cases – especially those where reactivity is brought about by the intimate mixing of different components of a mixed oxide – such inhomogeneity results in poor catalytic performance. Secondly, water – which is the main solvent of any hydrolytic sol-gel process – has a high surface tension. As a result, maintaining the porous architecture of the materials upon simple drying is often a challenge, as the collapsing of pores results in a poor control over the final textural properties.[55]

The power of the non-hydrolytic sol-gel method has been recently reviewed: via a large set of examples, Styskalik et al. show that non-hydrolytic routes allow to control the reactions at the atomic scale, resulting in homogeneous and well defined products.[56] The specific features of non-hydrolytic sol-gel routes make this chemistry highly valuable for the synthesis of a wide range of heterogeneous catalysts.[14] In particular, mesoporous mixed oxides with advantageous texture and excellent homogeneity can be prepared easily.[57] In fact, non-hydrolytic sol-gel routes feature two main advantages. Firstly, the kinetics of solvolysis-condensation tend to be much slower and to vary only to a limited extent among different precursors. As a result, a so-called “kinetic levelling” is commonly observed, resulting in homogeneous materials, even with complex formulations. Secondly, the synthesis occurs in organic solvent – in the total absence of water. As a result, the drying of the gel is much easier because the liquid that has to be removed from the pores has a low surface tension. This often leads to outstanding textural properties. Together with the group of P.H. Mutin (University of Montpellier, France), we have been able to demonstrate that the non-hydrolytic “ether route” is particularly successful for the preparation of mesoporous mixed oxide catalysts. We believe the examples below can be the motivation for future efforts on similar lines. Here, we would like to also suggest that the highly condensed gels formed in NHSG could be better exploited as macroscopic objects already suitably moulded for flow catalysis, eliminating a complicated step of shaping.

4.1. MoO_3-, Re_2O_7- and WO_3-based mesoporous catalysts for olefin metathesis

In an effort to control the nature of active surface species in olefin metathesis catalysts, we have applied a NHSG process based on the etherolysis-condensation of chloride precursors to prepare various mesoporous mixed oxides based on Mo, W, or Re (Fig. 8).

Rhenium oxide-based catalysts are known as highly active olefin metathesis catalysts.[58] Using the ether route,[57] we prepared various Re-Si, Re-Al and Re-Si-Al mixed oxides with specific surface area between 150 and 800 $m^2.g^{-1}$ and pore volume between 0.3 and 1.5 $cm^3.g^{-1}$.[59] Both texture and activity were highly dependent on composition. The specific activity of the Re-Si-Al catalysts was much higher than that of Re-Al catalysts whereas the Re-Si sample was not active. The best Re-Si-Al catalysts displayed excellent specific activities in the propene self-metathesis at 40°C (up to 45 $mmol_{propene}.g^{-1}.h^{-1}$). However, calcination of the xerogels was shown to impact the final properties of the mixed oxides in two distinct ways. On the one hand, migration of rhenium toward the surface occurred, as evidenced by XPS and ToF-SIMS. After calcination, ToF-SIMS showed the presence of abundant and well-dispersed ReO_x surface species, presumably highly active in the metathesis reaction. On the other hand, calcination also resulted in the sublimation of rhenium heptoxide.[60] Rhenium losses were especially important in Si-rich samples. We showed that rhenium losses in Re-Si-Al mixed oxide catalysts can be totally suppressed providing that strictly anhydrous conditions are kept in all the preparation steps, including storage and calcination. Under such conditions Re-Si-Al materials with very high specific surface areas could be obtained whatever the Si/Al ratio or Re loading. This allowed us to obtain highly active mixed oxide metathesis catalysts, showing unprecedented specific activities (101 $mmol_{propene}.g^{-1}.h^{-1}$).[60]

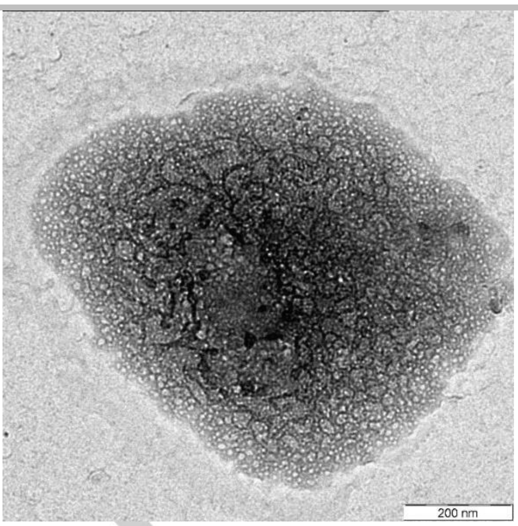


Figure 8. TEM micrograph of a MoO_3-Al_2O_3-SiO_2 catalysts (10:5:85 wt.%) prepared by non-hydrolytic sol-gel.[61]

Tungsten-based olefin catalysts – the industrially relevant system – were prepared for the first time using NHSG.[62] The WO_3-SiO_2 and WO_3-SiO_2-Al_2O_3 catalysts were evaluated in the cross-metathesis of ethene and trans-2-butene to propene at 450°C and compared with reference catalysts of similar composition prepared by impregnation on two commercial supports (silica and silica-alumina). These new catalysts reach high propene yields in the industrially relevant metathesis conditions, as they clearly outcompete the reference catalysts in terms of conversion, selectivity and stability. Characterization results show that the texture, tungsten dispersion, reducibility and surface acidity of the NHSG catalysts depended strongly on their composition. The method offered a good control on the final catalyst composition and provided mixed oxides with excellent textures (large mesopores, high surface area). NHSG catalysts featured high W dispersion, which correlated with lower reducibility, higher acidity and higher metathesis activity. Increasing the WO_3 loading in WO_3-SiO_2 led to higher activity. An optimum was found for the alumina content (10 wt.% Al_2O_3). While Al_2O_3 addition contributed to the better dispersion of tungsten oxide, it also appeared to favour side reactions towards1-butene, cis-2-butene and iso-butene, resulting in lower selectivity for propene.[62]

MoO_3-based metathesis catalysts are also active at moderate temperature (25-200°C) and their activity is known to be highly dependent on the nature of the MoO_x species stabilised at the surface and on the composition of the support or matrix.[63] NHSG allowed us to prepare a series of MoO_3-Al_2O_3-SiO_2 catalysts with wide range of composition.[61, 64] The Si/Al ratio was found to influence both the texture and the acidity of the materials, which had a marked impact on the performance in propene self-metathesis. Remarkably, it was possible to increase the MoO_3 loading as high as 20 wt.% without decreasing the TOF; i.e. specific activity increased proportionally with MoO_3 loading (Fig. 9). This contrasts with impregnated catalysts where a limit is rapidly reached, above which inactive MoO_3 crystalline species simply build up.[49a] In this case also, calcination was shown to trigger the migration of part of the Mo from the bulk of the homogeneous xerogel toward the surface of the mixed oxide, thereby enriching the latter in highly dispersed MoO_x species with high activity.[64] Thus, even if part of the Mo remains trapped in the walls of the materials, NHSG again appeared as a powerful means to disperse the catalytically active element in a carrier matrix, allowing to reach record levels of activity.

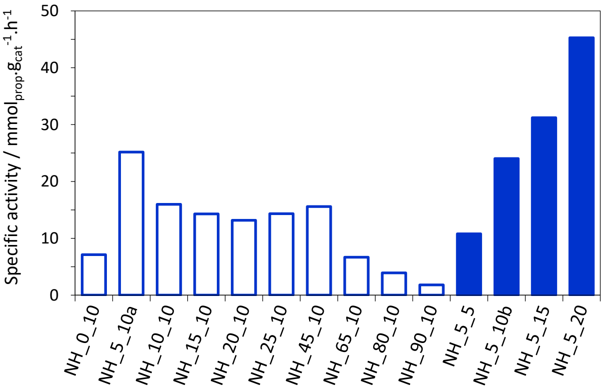
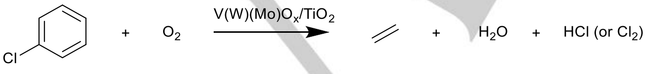


Figure 9. Specific activity of MoO_3-Al_2O_3-SiO_2 at 14 min time on stream in the self-metathesis of propene at 40°C.[61] Catalysts are denoted „NH_x_y“, where x represent the Al_2O_3 wt.% and where y represents the MoO_3 wt.% (the balance being SiO_2). Empty bars show that the alumina content has a marked influence: activity is low for binary formulations (MoO_3-SiO_2 and MoO_3-Al_2O_3) as compared to ternary formulations with moderate alumina content and an optimum is found at 5 wt.%. Keeping the Si/Al ratio constant, an increase in MoO_3 loading leads to higher activity.

4.2. Model V_2O_5-based catalysts for the total oxidation of atmospheric pollutants

Volatile organic compounds (VOC) like those contained in end-of-pipe effluents of incinerators can be destroyed using heterogeneous catalysts with a high total oxidation activity like V_2O_5/TiO_2 (Scheme 6).[65] These catalysts are classically prepared by impregnation of a titania support with a vanadium salt (e.g. ammonium metavanadate) followed by calcination. Promoters such as silver nanoparticles,[66] Ni nanoparticles,[67] Mo and W oxides,[68] Ce oxide,[69] or carbon nanotubes[70] are known to increase the performance of V-based total oxidation catalysts. Importantly, the catalysts must exhibit a relatively open texture because the space velocities in such applications are very high and diffusional limitations have to be avoided. Also, the speciation of VO_x at the catalyst surface has to be controlled.



Scheme 6. Total oxidation of chlorobenzene on vanadia-based catalysts. Chlorobenzene is often chosen as a model compound for polychlorinated dibenzo-p-dioxins (PCDD), dibenzofurans (PCDF) and polychlorinated biphenyls (PCB).

V_2O_5-TiO_2 mixed oxides were prepared by the ether route by reaction at 110 °C of $VOCl_3$ and $TiCl_4$ with a stoichiometric amount of $^iPr_2O$ in a closed autoclave under autogenous pressure, followed by calcination.[71] Similarly Mo- and W-promoted formulations were prepared by addition of $MoCl_3$ or WCl_3 to produce ternary mixed oxides.[72] Unlike for silica-based materials – which typically form sponge-like porous particles – titania-based materials consist of aggregates of nonporous nanoparticles partially fused together. SEM images showed 15-20 nm sized elementary particles aggregated together to form bigger spherical particles, a few µm in size (Fig. 10). The specific surface area was in the 60-100 $m^2.g^{-1}$ range with total pore volume of typically 0.2 – 0.3 $cm^3.g^{-1}$. The narrow pore size distribution around 10 nm corresponds to the interspaces between the calibrated elementary particles. Such large pores make these materials suitable for high flow catalytic applications. The size of the large aggregates however, may create internal diffusional limitations; it would be interesting to develop strategies aiming at keeping the size of these aggregates smaller.

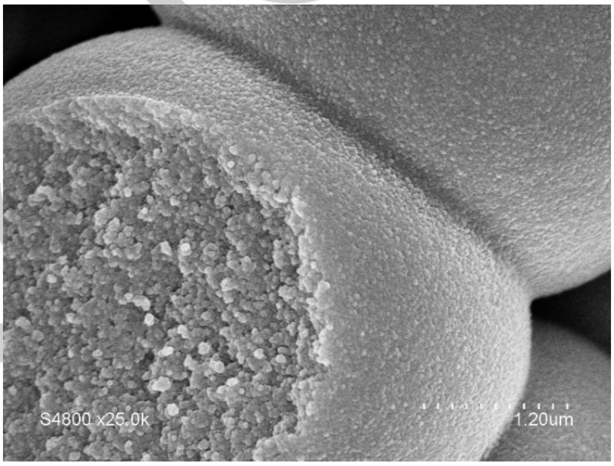


Figure 10. SEM micrograph of a V_2O_5-TiO_2 mixed oxide obtained by non-hydrolytic sol-gel.[73]

Under reaction conditions close to those encountered in VOC applications (high GHSV, low pollutant concentration), benzene and chlorobenzene were abated catalytically by total oxidation. However, the NHSG catalysts always remained less active than reference catalysts prepared by impregnation or flame spray pyrolysis.[74] This can be put in parallel with the modest performance reached with mesoporous V-Ti mixed oxide aerogels obtained by a hydrolytic sol-gel method followed by supercritical drying. Only moderate activity was achieved despite their excellent texture.[75]

In fact, NHSG catalysts allowed us to understand the parameters which dictate the catalytic performance level. Characterization showed that the xerogels obtained by NHSG (before calcination) were homogeneous in composition. That means that the active element (vanadium oxide) was dispersed in the titania matrix and that a significant part was not available at the surface to act as catalytic sites. Interestingly, calcination provoked the further crystallisation of anatase TiO_2 particles and the migration of V towards the surface. Since V was expelled from the bulk of the materials, its surface concentration rose. Nevertheless, it did not reach the surface concentration obtained in catalysts prepared by wet impregnation or flame spray pyrolysis, where strictly all the vanadium is deposited at the surface.

Another peculiarity of NHSG catalysts is that the VO_x species formed at the catalyst surface were much more dispersed as compared to those formed on reference catalysts. Small V_2O_5 crystallites were detected by XRD in reference catalysts, but never on NHSG. Interestingly, ToF-SIMS analysis allowed to demonstrate that the proportion of V-O-Ti bonds was significantly higher in NHSG catalysts as compared to reference catalysts where V-O-V bonds were predominant (Fig. 11). In other words, NHSG tends to favour the formation of highly dispersed vanadate inserted in the titania matrix while impregnation favours the formation of polyvanadates and small V_2O_5 crystallites. It was concluded that the more condensed vanadate species have a higher oxidation potential.

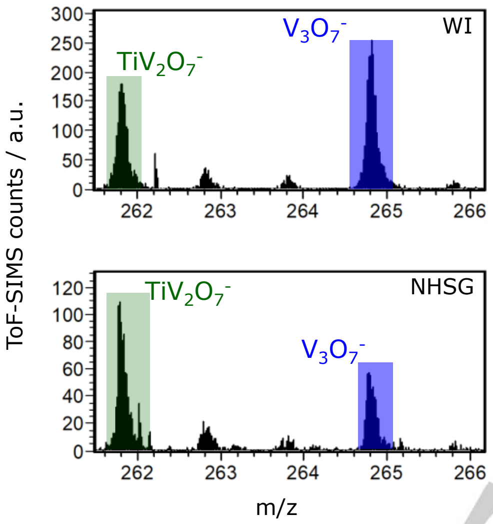


Figure 11. ToF-SIMS spectra in the region of the secondary $TiV_2O_7^-$ and $V_3O_7^-$ secondary ions, for two catalysts of similar bulk composition prepared by wet impregnation (WI, top) and non-hydrolytic sol-gel (NHSG, bottom). A larger proportion of mixed clusters – containing both Ti and V – are detected in the NHSG sample, indicating a more homogeneous distribution of VO_x into the titania matrix.

Thus, NHSG is not recommended for the preparation of highly active VOC total oxidation catalysts. It should be kept in mind that sol-gel approaches generally imply that part of the active element is lost for surface reactions. Nevertheless, NHSG should be seen as a powerful tool to prepare model catalysts with tailored properties. In particular, the stabilization of highly dispersed surface species is difficult to obtain by other methods. This allows to fundamentally understand the working behaviour of heterognenenous catalysts by highlighting the different intrinsic activity of different catalytic species.

5. Summary and outlook

In this account, I have shown by a series of specific examples, that the opportunities offered by sol-gel techniques for the preparation of tailored heterogeneous catalysts are tangible and broad. Three promising leads should be considered in the context of advanced heterogeneous catalysts preparation.

First, the gels that are obtained by sol-gel route may have sufficient mechanical resistance to be handled as self-standing 3D objects that can be further treated (washing, ageing, calcination, etc.) to yield a “shaped” catalyst. By doing so, one can skip a technologically demanding step of shaping powdery materials via tabletting, extrusion, or pelletizing. Emulsion-based templating is a straightforward example for which the shape, structure, and texture of the monolith seem particularly suited for flow catalysis. And we have shown that not only silica monolith supports, but also active catalysts like acidic aluminosilicates can be prepared in the form of monoliths using this technique.

Second, the coupling of sol-gel methods with specific processing techniques is up-and-coming. Apart from aerosol processing, other techniques must be considered as powerful ways to implement sol-gel chemistry: supercritical drying, reactive extrusion, film deposition, etc. Handling the starting precursors solution in the form of an aerosol allowed us to fasten the polycondensation step, which helps quenching the gel in a metastable system, and avoids the samples inhomogeneity that are otherwise often obtained when applying slow sol-gel procedures. The aerosol-assisted sol-gel process also proves highly versatile in accommodating various types of templating strategies resulting in tuneable textural properties.

Third, switching to less conventional media and precursors can help circumvent the issues of uneven reactivity in sol-gel chemistry. Non-hydrolytic sol-gel techniques proved to be resourceful when it comes to preparing mixed oxide catalysts with tailored composition, open texture, and specific surface properties. This results from a better control on the relative reactivity of the precursors in non-aqueous solvents and from the lower surface tension of organic solvents.

The three strategies detailed here are not exclusive and numerous other original solutions are proposed in the literature. One can imagine multiple combinations where the chemist will play with the nature of precursors, adapt the drying conditions, explore new templating strategies, shape the form of the gel, etc. The ingeniousness of materials chemists will continue to inspire catalysis scientists in their hunt for more efficient and more sustainable ways of running chemical transformations.

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[1] J. N. Armor, *Catal. Today* **2011**, *163*, 3-9.

[2] R. A. Sheldon, *Chem. Commun.* **2008**, 3352-3365.

[3] P. T. Anastas, M. M. Kirchhoff, T. C. Williamson, *Appl. Catal. A* **2001**, *221*, 3-13.

[4] C. Wiles, P. Watts, *Green Chem.* **2014**, *16*, 55-62.

[5] (a) M. Mikkelsen, M. Jorgensen, F. C. Krebs, *Energ. Env. Sci.* **2010**, *3*, 43-81; (b) M. A. A. Aziz, A. A. Jalil, S. Triwahyono, A. Ahmad, *Green Chem.* **2015**, *17*, 2647-2663; (c) J. Wei, Q. Ge, R. Yao, Z. Wen, C. Fang, L. Guo, H. Xu, J. Sun, *Nat. Commun.* **2017**, *8*, 15174; (d) W. Wang, S. Wang, X. Ma, J. Gong, *Chem. Soc. Rev.* **2011**, *40*, 3703-3727; (e) A. Kim, D. P. Debecker, F. Devred, V. Dubois, C. Sanchez, C. Sassoye, *Appl. Catal. B* **2018**, *220*, 615-625.

[6] R. Schlögl, *Angew. Chem. Int. Ed.* **2015**, *54*, 3465-3520.

[7] A. T. Bell, *Science* **2003**, *299*, 1688-1691.

[8] (a) A. Feinle, M. S. Elsaesser, N. Husing, *Chem. Soc. Rev.* **2016**, *45*, 3377-3399; (b) X.-Y. Yang, L.-H. Chen, Y. Li, J. C. Rooke, C. Sanchez, B.-L. Su, *Chem. Soc. Rev.* **2017**, *46*, 481-558.

[9] E. Ruiz-Hitzky, *Chem. Record* **2003**, *3*, 88-100.

[10] R. A. Caruso, M. Antonietti, *Chem. Mater.* **2001**, *13*, 3272-3282.

[11] (a) M. Niederberger, *Acc. Chem. Res.* **2007**, *40*, 793-800; (b) B. L. Cushing, V. L. Kolesnichenko, C. J. O'Connor, *Chem. Rev.* **2004**, *104*, 3893-3946; (c) C. Sassoye, G. Muller, D. P. Debecker, A. Karelovic, S. Cassaignon, C. Pizarro, P. Ruiz, C. Sanchez, *Green Chem.* **2011**, *13*, 3230-3237.

[12] C. Sanchez, L. Rozes, F. Ribot, C. Laberty-Robert, D. Grosso, C. Sassoye, C. Boissiere, L. Nicole, *C. R. Chimie* **2010**, *13*, 3-39.

[13] (a) L. Nicole, L. Rozes, C. Sanchez, *Adv. Mater.* **2010**, *22*, 3208-3214; (b) B. Arkles, *MRS Bull.* **2011**, *26*, 402-408.

[14] D. P. Debecker, P. H. Mutin, *Chem. Soc. Rev.* **2012**, *41*, 3624-3650.

[15] (a) M. Campanati, G. Fornasari, A. Vaccari, *Catal. Today* **2003**, *77*, 299-314; (b) J. Freiding, F.-C. Patcas, B. Kraushaar-Czarnetzki, *Appl. Catal. A* **2007**, *328*, 210-218; (c) A. Cybulski, J. A. Moulijn, *Catal. Rev.* **1994**, *36*, 179-270.

[16] (a) N. Brun, S. Ungureanu, H. Deleuze, R. Backov, *Chem. Soc. Rev.* **2011**, *40*, 771-788; (b) N. R. Cameron, A. Barbetta, *J. Mater. Chem.* **2000**, *10*, 2466-2471; (c) M. S. Silverstein, *Prog. Polym. Sci.* **2014**, *39*, 199-234; (d) V. O. Ikem, A. Menner, T. S. Horozov, A. Bismarck, *Adv. Mater.* **2010**, *22*, 3588-3592.

[17] (a) R. Backov, *Soft Matter* **2006**, *2*, 452-464; (b) N. Brun, A. Babeau-Garcia, M.-F. Achard, C. Sanchez, F. Durand, G. Laurent, M. Birot, H. Deleuze, R. Backov, *Energ. Env. Sci.* **2011**, *4*, 2840-2844; (c) S. Ungureanu, M. Birot, G. Laurent, H. Deleuze, O. Babot, B. Julián-López, M.-F. Achard, M. I. Popa, C. Sanchez, R. Backov, *Chem. Mater.* **2007**, *19*, 5786-5796; (d) S. Ungureanu, H. Deleuze, C. Sanchez, M. I. Popa, R. Backov, *Chem. Mater.* **2008**, *20*, 6494-6500.

[18] (a) M. Caillot, A. Chaumonnot, M. Digne, C. Poleunis, D. P. Debecker, J. A. van Bokhoven, *Microporous Mesoporous Mater.* **2014**, *185*, 179-189; (b) G. Busca, *Chem. Rev.* **2007**, *107*, 5366-5410.

[19] K. Na, M. Choi, R. Ryoo, *Microporous Mesoporous Mater.* **2013**, *166*, 3-19.

[20] G. Busca, in *Heterogeneous Catalytic Materials*, Elsevier, Amsterdam, **2014**, pp. 103-195.

[21] D. P. Debecker, C. Boissiere, G. Laurent, S. Huet, P. Eliaers, C. Sanchez, R. Backov, *Chem. Commun.* **2015**, *51*, 14018-14021.

[22] (a) A. Schmid, J. S. Dordick, B. Hauer, A. Kiener, M. Wubbolts, B. Witholt, *Nature* **2001**, *409*, 258-268; (b) S. Jemli, D. Ayadi-Zouari, H. B. Hlima, S. Bejar, *Crit. Rev. Biotechnol.* **2016**, *36*, 246-258.

[23] (a) J. L. Porter, R. A. Rusli, D. L. Ollis, *ChemBioChem* **2016**, *17*, 197-203; (b) K. Faber, W.-D. Fessner, N. J. Turner, *Adv. Synth. Catal.* **2015**, *357*, 1565-1566.

[24] R. A. Sheldon, *Adv. Synth. Catal.* **2007**, *349*, 1289-1307.

[25] L. van den Biggelaar, P. Soumillion, D. P. Debecker, *Catalysts* **2017**, *7*, 54.

[26] T. Sehl, H. C. Hailes, J. M. Ward, R. Wardenga, E. von Lieres, H. Offermann, R. Westphal, M. Pohl, D. Rother, *Angew. Chem. Int. Ed.* **2013**, *52*, 6772-6775.

[27] E. Karl*, Vol. US2155119* (Ed.: A. L. CORPORATION), **1939**.

[28] S. Ramesh, D. P. Debecker, *Catal. Commun.* **2017**, *97*, 102-105.

[29] F. E. Tuler, E. M. Gaigneaux, E. E. Miró, V. G. Milt, D. P. Debecker, *Catal. Commun.* **2015**, *72*, 116-120.

[30] A. Carné-Sánchez, I. Imaz, M. Cano-Sarabia, D. Maspoch, *Nat Chem* **2013**, *5*, 203-211.

[31] (a) Y. Wang, F. Zhang, S. Xu, X. Wang, D. G. Evans, X. Duan, *Industrial & Engineering Chemistry Research* **2008**, *47*, 5746-5750; (b) V. Prevot, C. Szczepaniak, M. Jaber, *J. Colloid Interface Sci.* **2011**, *356*, 566-572.

[32] (a) Z. Guo, G. Xiong, L. liu, J. Yin, R. Zhao, S. Yu, *RSC Adv.* **2015**, *5*, 71433-71436; (b) G. Xiong, J. Yin, J. Liu, X. Liu, Z. Guo, L. Liu, *RSC Adv.* **2016**, *6*, 101365-101371.

[33] (a) H. Fan, Y. Lu, A. Stump, S. T. Reed, T. Baer, R. Schunk, V. Perez-Luna, G. P. Lopez, C. J. Brinker, *Nature* **2000**, *405*, 56-60; (b) C. Boissiere, D. Grosso, A. Chaumonnot, L. Nicole, C. Sanchez, *Adv. Mater.* **2011**, *23*, 599-623.

[34] C. J. Brinker, Y. Lu, A. Sellinger, H. Fan, *Adv. Mater.* **1999**, *11*, 579-585.

[35] Z. Jin, F. Wang, F. Wang, J. Wang, J. C. Yu, J. Wang, *Adv. Funct. Mater.* **2013**, *23*, 2137-2144.

[36] E. Belamie, M. Y. Boltoeva, K. Yang, T. Cacciaguerra, B. Alonso, *J. Mater. Chem.* **2011**, *21*, 16997-17006.

[37] D. P. Debecker, M. Stoyanova, F. Colbeau-Justin, U. Rodemerck, C. Boissière, E. M. Gaigneaux, C. Sanchez, *Angew. Chem. Int. Ed.* **2012**, *15*, 2129–2131.

[38] (a) S. Areva, C. Boissiere, D. Grosso, T. Asakawa, C. Sanchez, M. Linden, *Chem. Commun.* **2004**, 1630-1631; (b) C. Boissiere, D. Grosso, H. Amenitsch, A. Gibaud, A. Coupe, N. Baccile, C. Sanchez, *Chem. Commun.* **2003**, 2798-2799; (c) A. Chaumonnot, F. Tihay, A. Coupé, S. Pega, C. Boissière, D. Grosso, C. Sanchez, *Oil Gas Sci. Technol.* **2009**, *64*, 681-696; (d) F. Colbeau-Justin, C. Boissière, A. Chaumonnot, A. Bonduelle, C. Sanchez, *Adv. Funct. Mater.* **2014**, *24*, 233-239; (e) S. Pega, C. Boissiere, D. Grosso, T. Azais, A. Chaumonnot, C. Sanchez *Angew. Chem. Int. Ed.* **2009**, *48*, 2784-2787.

[39] (a) M. Ayoub, A. Z. Abdullah, *Renew. Sustainable Energy Rev.* **2012**, *16*, 2671-2686; (b) J. C. Serrano-Ruiz, R. Luque, A. Sepulveda-Escribano, *Chem. Soc. Rev.* **2011**, *40*, 5266-5281.

[40] M. Morales, P. Y. Dapsens, I. Giovinazzo, J. Witte, C. Mondelli, S. Papadokonstantakis, K. Hungerbuhler, J. Perez-Ramirez, *Energ. Env. Sci.* **2015**, *8*, 558-567.

[41] (a) Q. Guo, F. Fan, E. A. Pidko, W. N. P. van der Graaff, Z. Feng, C. Li, E. J. M. Hensen, *ChemSusChem* **2013**, *6*, 1352-1356; (b) L. Li, X. Collard, A. Bertrand, B. F. Sels, P. P. Pescarmona, C. Aprile, *J. Catal.* **2014**, *314*, 56-65; (c) L. Li, C. Stroobants, K. Lin, P. A. Jacobs, B. F. Sels, P. P. Pescarmona, *Green Chem.* **2011**, *13*, 1175-1181; (d) S. Tolborg, I. Sádaba, C. M. Osmundsen, P. Fristrup, M. S. Holm, E. Taarning, *ChemSusChem* **2015**, *8*, 613-617.

[42] F. de Clippel, M. Dusselier, R. Van Rompaey, P. Vanelderen, J. Dijkmans, E. Makshina, L. Giebeler, S. Oswald, G. V. Baron, J. F. M. Denayer, P. P. Pescarmona, P. A. Jacobs, B. F. Sels, *J. Am. Chem. Soc.* **2012**, *134*, 10089-10101.

[43] N. Godard, A. Vivian, L. Fusaro, L. Cannavicci, C. Aprile, D. P. Debecker, *ChemCatChem* **2017**, *9*, 2211-2218.

[44] (a) S. Lwin, I. E. Wachs, *ACS Catal.* **2014**, *4*, 2505-2520; (b) N. Gholampour, M. Yusubov, F. Verpoort, *Catal. Rev.* **2016**, *58*, 113-156.

[45] (a) N. Merle, F. Le Quéméner, Y. Bouhoute, K. C. Szeto, A. De Mallmann, S. Barman, M. K. Samantaray, L. Delevoye, R. M. Gauvin, M. Taoufik, J.-M. Basset, *J. Am. Chem. Soc.* **2017**, *139*, 2144-2147; (b) C. Copéret, J. M. Basset, *Adv. Synth. Catal.* **2007**, *349*, 78-92.

[46] W. Keim, *Angew. Chem. Int. Ed.* **2013**, *52*, 12492-12496.

[47] (a) H. Balcar, J. Čejka, *Coord. Chem. Rev.* **2013**, *257*, 3107-3124; (b) D. P. Debecker, D. Hauwaert, M. Stoyanova, A. Barkschat, U. Rodemerck, E. M. Gaigneaux, *Appl. Catal. A* **2011**, *391*, 78-85; (c) J. Handzlik, J. Ogonowski, J. Stoch, M. Mikołajczyk, P. Michorczyk, *Appl. Catal. A* **2006**, *312*, 213-219.

[48] (a) J. Handzlik, J. Ogonowski, J. Stoch, M. Mikołajczyk, *Appl. Catal. A* **2004**, *273*, 99-104; (b) D. P. Debecker, M. Stoyanova, U. Rodemerck, E. M. Gaigneaux, *J. Mol. Catal. A: Chem.* **2011**, *340*, 65-76.

[49] (a) D. P. Debecker, M. Stoyanova, U. Rodemerck, A. Leonard, B.-L. Su, E. M. Gaigneaux, *Catal. Today* **2011**, *169*, 60-68; (b) D. P. Debecker, M. Stoyanova, U. Rodemerck, P. Eloy, A. Leonard, B. L. Su, E. M. Gaigneaux, *J. Phys. Chem. C* **2010**, *114*, 18664-18673.

[50] T. Hahn, E. V. Kondratenko, D. Linke, *Chem. Commun.* **2014**, *50*, 9060-9063.

[51] S. Maksasithorn, P. Praserthdam, K. Suriye, D. P. Debecker, *Microporous Mesoporous Mater.* **2015**, *213*, 125-133.

[52] D. P. Debecker, M. Stoyanova, U. Rodemerck, F. Colbeau-Justin, C. Boissère, A. Chaumonnot, A. Bonduelle, C. Sanchez, *Appl. Catal. A* **2014**, *470*, 458-466.

[53] (a) A. M. Cojocariu, P. H. Mutin, E. Dumitriu, F. Fajula, A. Vioux, V. Hulea, *Chem. Commun.* **2008**, 5357-5359; (b) P. H. Mutin, A. Vioux, *Journal of Materials Chemistry A* **2013**, *1*, 11504-11512; (c) N. Pinna, M. Niederberger, *Angew. Chem. Int. Ed.* **2008**, *47*, 5292-5304.

[54] (a) J. B. Miller, E. I. Ko, *Catal. Today* **1997**, *35*, 269-292; (b) J. Livage, M. Henry, C. Sanchez, *Prog. Solid State Chem.* **1988**, *18*, 259-341.

[55] (a) A. I. Cooper, *Adv. Mater.* **2003**, *15*, 1049-1059; (b) J. E. Amonette, J. Matyáš, *Microporous Mesoporous Mater.* **2017**, *250*, 100-119.

[56] A. Styskalik, D. Skoda, C. Barnes, J. Pinkas, *Catalysts* **2017**, *7*, 168.

[57] D. P. Debecker, V. Hulea, P. H. Mutin, *Appl. Catal. A* **2013**, *451*, 192-206.

[58] (a) S. Vorakitkanvasin, S. K. N. Ayudhya, K. Suriye, P. Praserthdam, J. Panpranot, *Appl. Catal. A* **2016**, *517*, 39-46; (b) J. C. Mol, *Catal. Today* **1999**, *51*, 289-299.

[59] K. Bouchmella, P. Hubert Mutin, M. Stoyanova, C. Poleunis, P. Eloy, U. Rodemerck, E. M. Gaigneaux, D. P. Debecker, *J. Catal.* **2013**, *301*, 233-241.

[60] K. Bouchmella, M. Stoyanova, U. Rodemerck, D. P. Debecker, P. Hubert Mutin, *Catal. Commun.* **2015**, *58*, 183-186.

[61] D. P. Debecker, K. Bouchmella, M. Stoyanova, U. Rodemerck, E. M. Gaigneaux, P. H. Mutin, *Catal. Sci. Technol.* **2012**, *2*, 1157–1164.

[62] S. Maksasithorn, P. Praserthdam, K. Suriye, M. Devillers, D. P. Debecker, *Appl. Catal. A* **2014**, *488*, 200-207.

[63] K. Ding, A. Gulec, A. M. Johnson, T. L. Drake, W. Wu, Y. Lin, E. Weitz, L. D. Marks, P. C. Stair, *ACS Catal.* **2016**, *6*, 5740-5746.

[64] D. P. Debecker, K. Bouchmella, C. Poleunis, P. Eloy, P. Bertrand, E. M. Gaigneaux, P. H. Mutin, *Chem. Mat.* **2009**, *21*, 2817-2824.

[65] (a) A. Aranzabal, B. Pereda-Ayo, M. González-Marcos, J. González-Marcos, R. López-Fonseca, J. González-Velasco, *Chem. Pap.* **2014**, *68*, 1169; (b) C. Du, S. Lu, Q. Wang, A. G. Buekens, M. Ni, D. P. Debecker, *Chem. Eng. J*; (c) D. P. Debecker, R. Delaigle, P. C. Hung, A. Buekens, E. M. Gaigneaux, M. B. Chang, *Chemosphere* **2011**, *82*, 1337-1342; (d) H. Huang, Y. Xu, Q. Feng, D. Y. C. Leung, *Catal. Sci. Technol.* **2015**, *5*, 2649-2669; (e) M. S. Kamal, S. A. Razzak, M. M. Hossain, *Atmos. Environ.* **2016**, *140*, 117-134; (f) M. Tomatis, H. H. Xu, J. He, X. D. Zhang, *J. Chem.* **2016**, *2016*.

[66] (a) D. P. Debecker, C. Faure, M. E. Meyre, A. Derre, E. M. Gaigneaux, *Small* **2008**, *4*, 1806-1812; (b) R. Delaigle, M. M. F. Joseph, D. P. Debecker, P. Eloy, E. M. Gaigneaux, *Top. Catal.* **2013**, *56*, 1867-1874.

[67] X. Zhang, Z. Pei, X. Ning, H. Lu, H. Huang, *RSC Adv.* **2015**, *5*, 79192-79199.

[68] (a) M. A. Larrubia, G. Busca, *Appl. Catal. B* **2002**, *39*, 343-352; (b) R. Delaigle, D. P. Debecker, F. Bertinchamps, E. M. Gaigneaux, *Top. Catal.* **2009**, *52*, 501-516.

[69] M. F. Yu, X. Q. Lin, M. Yan, X. D. Li, T. Chen, J. H. Yan, *Environ. Sci. Pollut. Res.* **2016**, *23*, 17563-17570.

[70] C. Du, Q. Wang, Y. Peng, S. Lu, L. Ji, M. Ni, *Environ. Sci. Pollut. Res.* **2017**, *24*, 4894-4901.

[71] D. P. Debecker, K. Bouchmella, R. Delaigle, P. Eloy, C. Poleunis, P. Bertrand, E. M. Gaigneaux, P. H. Mutin, *Appl. Catal. B* **2010**, *94*, 38-45.

[72] D. P. Debecker, R. Delaigle, K. Bouchmella, P. Eloy, E. M. Gaigneaux, P. H. Mutin, *Catal. Today* **2010**, *157*, 125-130.

[73] D. P. Debecker, K. Bouchmella, R. Delaigle, P. Eloy, C. Poleunis, P. Bertrand, E. M. Gaigneaux, P. H. Mutin, *Appl. Catal. B* **2010**, *94*, 38-45.

[74] (a) B. Schimmoeller, R. Delaigle, D. P. Debecker, E. M. Gaigneaux, *Catal. Today* **2010**, *157*, 198-203; (b) D. P. Debecker, F. Bertinchamps, N. Blangenois, P. Eloy, E. M. Gaigneaux, *Appl. Catal. B* **2007**, *74*, 223-232.

[75] (a) C. Gannoun, R. Delaigle, P. Eloy, D. P. Debecker, A. Ghorbel, E. M. Gaigneaux, *Catal. Commun.* **2011**, *15*, 1-5; (b) C. Gannoun, R. Delaigle, D. P. Debecker, P. Eloy, A. Ghorbel, E. M. Gaigneaux, *Appl. Catal. A* **2012**, *447-448*, 1-6.

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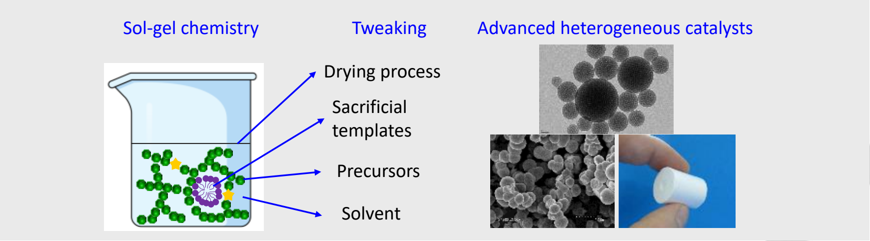

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Innovative Sol-Gel Routes for the Bottom-up Preparation of Heterogeneous Catalysts

Sol-gel chemistry is a resourceful toolbox for the preparation of advanced materials and this applies particularly to the design of advanced and tailored heterogeneous catalysts. By tweaking the classical sol-gel chemistry process it is possible to expand the scope of sol-gel routes and to yield new kinds of catalytic materials with remarkable properties and performance. This Personal Account exemplifies such strategies where one plays with the nature of the templating agent, the processing and drying conditions, the nature of the precursors or the nature of the solvent.