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The design of selective catalysts from hybrid silica-based materials

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Contents

Abstract

The sol–gel processing of appropriated molecular precursors easily leads to a variety of mixed materials. Silica-based organic–inorganic hybrids constitute a very versatile class of solids. Their preparation in a controlled way can lead to materials with intrinsic properties. This paper will concentrate on the potential uses of hybrids for the preparation of catalytic materials by design. It offers unique possibilities (i) to obtain dispersed metal species or particles on oxide supports; (ii) to control the pore structure of the catalytic material; and (iii) to prepare new hybrid supports with selective properties. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

The sol–gel process constitutes one of the most important methods for the preparation of inorganic amorphous solids [1]. Owing to the very mild reaction conditions involved in this process, it has emerged as a very versatile and promising route by which to obtain hybrid organic–inorganic materials [2]. The latter are simply defined as solids containing both an organic and an inorganic component, and can exhibit the properties associated with the two constituents. Organic–inorganic hybrids have been divided into two classes according to the nature of the interaction between the two components [2]. Class I hybrids correspond to nanocomposites in which organic molecules or macromolecules are embedded in an inorganic matrix. Class II hybrids correspond to mixed networks where there is a strong bonding interaction between the organic and inorganic fragments. Chemistry plays an important role in the elaboration of these hybrid materials and in the understanding of their properties.

Silica-based hybrid materials have received considerable attention, because a wide variety of stable precursors can be synthesized which lead to hybrid silicas with specific properties (optical, electrical, electrochemical, etc.) [2–4]. Moreover, the sol–gel hydrolysis–condensation of organic molecules possessing trialkoxysilyl substituents attached by a non-hydrolysable Si–C bond has proved to be a very interesting route by which to obtain hybrid silsesquioxane networks [5–7]. Such hybrid solids are well defined at the molecular level and may allow a greater understanding and a more rational analysis of the structural relationship between precursors and materials. The controlled elaboration of condensed matter from molecular precursor, and that of materials with properties defined at the molecular level, are challenging areas for chemists. Organic–inorganic hybrids, in this field, seem a very promising class of solids.

Control and tuning of the properties of the solid are of great importance in the preparation of catalytic materials. The design and characterization of new heterogeneous catalysts are of major interest in chemistry and chemical engineering. They should allow the development of new chemical processes which are of economical as well as ecological interest to the chemical industry [8–10]. Our current interest in hybrid silica-based materials has led us to explore some preparations of heterogeneous catalysts by design. The elaboration of highly selective catalytic materials may result from controlling the formation of the pore structure of the material, or from controlling the formation of the three-dimensional solid network. Organic–inorganic hybrids are solids with tunable properties, which can allow us to tailor catalytic materials. The aim of this paper is to point out some approaches for the controlled synthesis of selective catalytic materials.

2. The sol–gel route to metal-containing catalytic materials

The sol–gel processing of molecular precursors (Eq. (1)) or stabilized sols of metal oxides is increasingly becoming an interesting way to prepare heterogeneous supported metal or metal-oxide catalysts [11,12].

$$(RO)_nM + (n/2)H_2O \rightarrow MO_{n/2} + nROH \qquad (1)$$

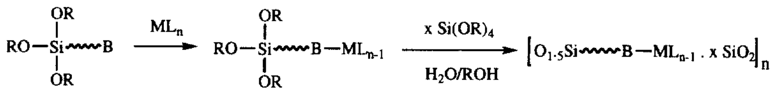
The sol–gel route has inherent advantages over the classical precipitation or impregnation methods. Through the choice of reagents, reaction and drying conditions, it allows one to control the pore structure, porosity, composition and surface polarity of metal oxides [13]. Microporous amorphous mixed-oxide catalysts with tunable surface polarity [14] or shape-selective activity [15] were obtained, for example.

2.1. Heterogenized metal complexes

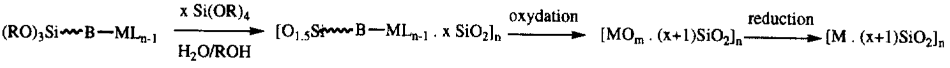
The introduction of organic or organometallic precursors during the sol–gel polycondensation led to hybrid catalysts consisting of heterogenized metal complexes [16–24]. The principle is shown in Scheme 1. It involves the use of a substituted alkoxysilane containing an attached Lewis base B capable of coordinating to metal atoms. The metal complex is then formed and used in a sol–gel hydrolysis–condensation in the presence of tetraalkoxysilane. This approach is quite different from the classical immobilization of transition metal complexes at the surface of silica [25]. The sol–gel approach allows one to adjust the catalyst loading, and the oxide matrix is built around the metal complex moieties. The drawback of the method is that part of the metal complex catalyst may not be accessible in the matrix. However, the catalytic active sites are homogeneously distributed throughout the whole material. This results in good catalyst stability and, owing to the porosity and high surface area, does not necessarily prevent the reactants from reaching the active site [26].

2.2. Metal and metal oxide particles on oxide supports

Sol–gel heterogenized metal complexes also proved to be interesting precursors for the preparation of highly dispersed metal, or metal oxide particles, deposited on high surface area porous supports [26,27]. As shown in Scheme 2, the preparation of dispersed metals proceeds in three steps. The hydrolysis of molecular metal complexes containing a trialkoxysilyl-substituted ligand leads to gels in which the



Scheme 1. Hybrid catalyst consisting of heterogenized metal complexes.



Scheme 2. Dispersed metals or metal-oxide particles in silica.

metal atom is anchored to the silicate matrix. This allows one to obtain a very homogeneous dispersion of the metallic species in the gel. In a second step, heating the metal-containing gel in air eliminates all organic components by oxidation and thermolysis. During this step, nanometric metal oxide particles develop. The small particle sizes are probably the result of the high dispersion of the metal species obtained in the first step. In the third step, the metal oxide particles are reduced by hydrogen to metal particles. The particle size appears to be mainly determined by the oxidation step. The metal particles obtained are highly dispersed and homogeneously distributed throughout the silica matrix. This procedure was shown to lead to a narrow particle size distribution, with a diameter ranging from 1 to 30 nm, and it has also been extended to the preparation of bimetallic particles Cu/Ru or Ni/Pd [26]. It represents an interesting way to tailor catalytic materials. The sol–gel route may permit one to control the metal particle size and the pore structure of the oxide support.

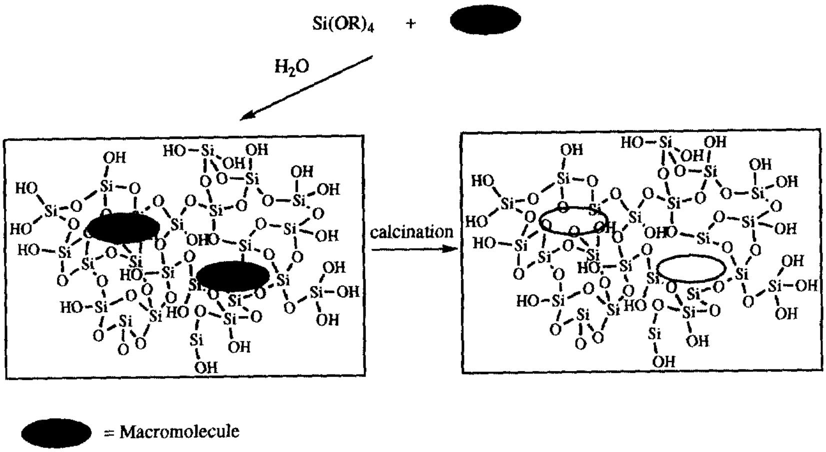
2.3. *The control of the pore structure*

The use of organic molecules or molecular aggregates as templating agents has allowed the controlled preparation of micro- or mesoporous aluminosilicates [28]. Whereas this approach is very well suited to the preparation of crystalline zeolites, the controlled synthesis of amorphous solids is sometimes more difficult. Efforts are being made, particularly using molecular imprinting techniques [29], to control the pore structure of the material during the preparation step of the catalytic material. Highly selective catalysts can result from this approach. Hybrid organic–inorganic solids constitute interesting precursors to inorganic materials with a defined pore structure. Two methods which involve the elimination of the organic component to create porosity seem promising.

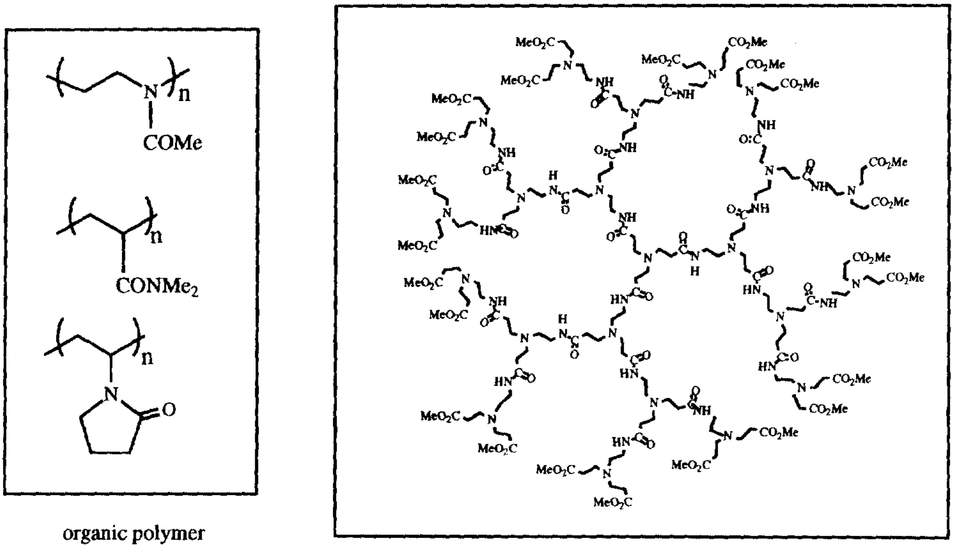
2.3.1. *Pyrolysis of organic–inorganic composites*

Control of the pore size in silica has been tentatively achieved via the temporary introduction of organic polymers into a silica matrix [30–32]. As shown in Scheme 3, silica gel was first formed in the presence of an organic polymer to lead to an organic–inorganic hybrid. The embedded polymer was then eliminated upon pyrolysis of the hybrid material in air. This gives porous carbon-free silica, where the pore structure varies according to the nature of the template macromolecule. The success of this strategy is strongly related to the high dispersion of the polymer within the silica matrix in the first step. The hybrid material must be homogeneous at the nanometer scale, and must not exhibit phase separation. This can be achieved by an appropriate functionalization of the polymer.

A dispersion of the organic component at the molecular level in the silica network was obtained as a result of the presence of a functional group capable of giving hydrogen bonding between the organic and inorganic components. Polymers containing an amide functional group were used successfully [30–32]. Interestingly, according to this strategy, control of the pore size in silica was obtained, based on the size of the organic component. Pyrolysis of a hybrid gel containing dendrimers (Fig. 1)



Scheme 3. Control of pore size in silicas by pyrolysis of organic-inorganic composites.



organic polymer

Dendrimer (generation 3.5)

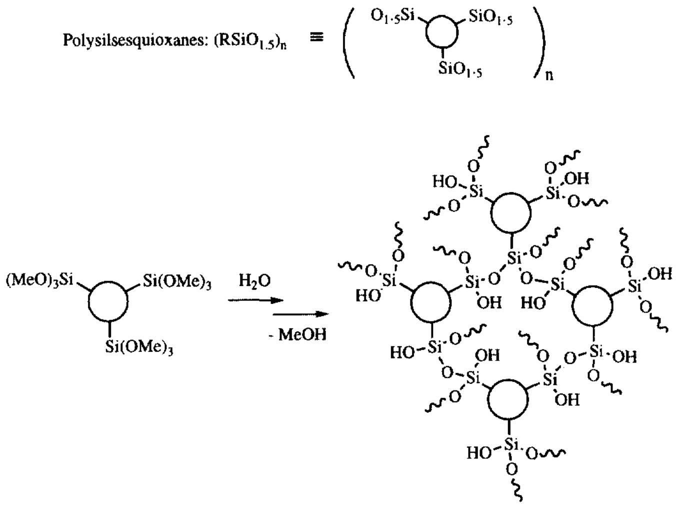
Fig. 1. Template macromolecules.

led, after calcination of the organic component, to silica with a defined porosity. The average pore diameter varied from 10 to 20 Å according to the generation of the dendrimer used [33]. This shows an interesting correlation between the size of the macromolecular template and the size of the pores which are generated after pyrolysis.

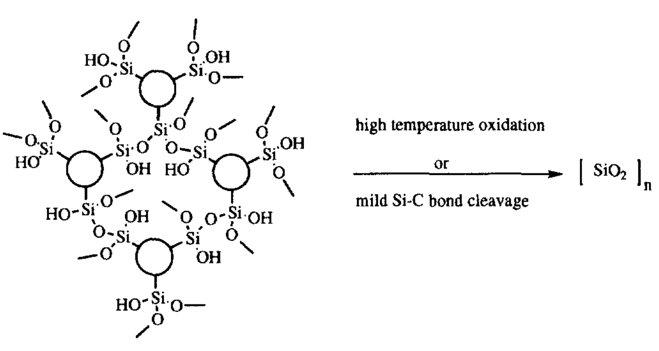
2.3.2. *Hybrid silsesquioxane gels as silica precursors*

Hybrid silsesquioxane gels are prepared by sol–gel hydrolysis–condensation of organic molecules containing two or more trialkoxysilyl substituents [34–36] (Scheme 4). These hybrids consist of a mixed three-dimensional network, where the organic fragment cross-linking siloxane chains is part of the framework. The solids are homogeneous single-phase materials and are well defined at the molecular level. The gels obtained after drying are most often microporous materials with high surface areas (500–1000 $m^2\,g^{-1}$).

Elimination of the organic components in these hybrid solids can, similarly to the previous case, lead to pure silicas. The question which arises is whether or not a control of the pore structure of the inorganic material can be obtained, on the basis of the nature or structure of the organic component eliminated from the hybrid (Scheme 5). The organic fragment is part of the mixed network, and its removal



Scheme 4. Synthesis of hybrid ploysilsesquioxanes from polysilylated organic molecules.



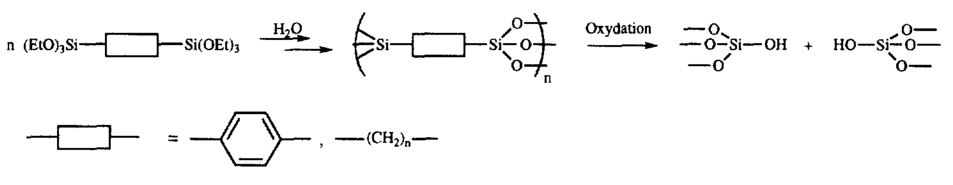
Scheme 5. Elimination of the organic moiety from hybrid polysilsesquioxanes.

will lead to Si–C bond cleavage. Therefore, during elimination, the hybrid network will rearrange to a purely inorganic network to form silica. The pore structure generated during this process should be dependent on the reaction conditions and on the rearrangement reaction involved.

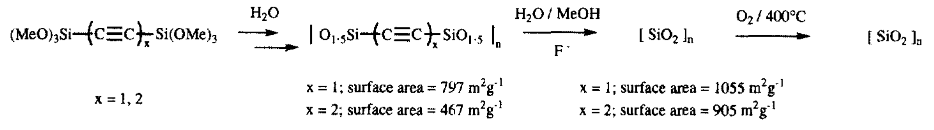
The oxidative elimination of the organic component in hybrid silsesquioxane was the first to be reported [37,38] (Scheme 6). Oxidation of the hydrocarbon template in polysilsesquioxanes led to silica with a reduced porosity. The silica gels showed a coarsening of the existing porosity, and the post-plasma material had a higher pore diameter and surface area (approximately 300 $m^2\ g^{-1}$). The majority of the porosity was in the mesopore range, with a small contribution from micropores [34,35].

The elimination of the organic fragment has to be carried out under mild reaction conditions in order to control the rearrangement of the network to form a purely inorganic material. Interestingly, we have shown that the organic fragment can be removed under very mild reaction conditions [39] (Scheme 7). Hybrid silsesquioxane gels containing a fragile Si–C bond were first obtained by mild hydrolysis of an acetylenic precursor. In a second step, the solid, as a suspension in methanol, was hydrolysed in the presence of a catalytic amount of ammonium fluoride. Room-temperature cleavage of the Si–C bond allows the elimination of the acetylenic unit, leaving silica behind. Compared with the hybrids, the resulting silicas were microporous materials with increased surface area and pore volume. It is noteworthy that the pore structure of the material, which is formed at a low temperature, was not affected by further heating at 400 °C.

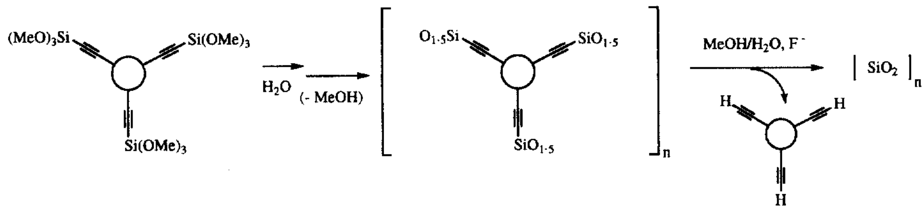
On the basis of these results, controlled generation of the pore structure in silicas has been obtained using a non-sacrificial route [40,41]. As shown in Scheme 8, this involved the preparation of a silsesquioxane gel, from an appropriate molecular precursor, where the organic fragment is attached to the silicate network by a labile Si–C bond. The mild recovery of the organic molecule led to silicas. Various molecules with different structural features were used as templates to generate porosity



Scheme 6. Oxidative elimination of organic templates in poly(silsesquioxanes) [37].



Scheme 7. Mild elimination of the acetylenic moieties [36,39].



Scheme 8. Non-sacrificial route for the controlled generation of the pore structure in silicas.

under mild cleavage, and these were compared with the pore structure resulting from the high-temperature sacrificial oxidation of organic templates.

The mild removal of the organic cross-linking fragments led to mesoporous silicas. Although the mean pore diameter was much larger than the size of the molecule eliminated, a tuning of the average pore size was obtained on the basis of molecular parameters. Only mild elimination of the template allowed control of the pore structure in the mesopore domain. High-temperature pyrolysis of the hybrid in air led to microporous silicas with similar properties, whatever the structure of the organic template. Interestingly, the use of a rigid paraphenylene unit led to silica with a very narrow pore-size distribution, whereas the use of a flexible hydrocarbon template gave a broad pore-size distribution.

It appears that the formation of the pore structure at low temperature results from the cleavage and rearrangement of the hybrid network to form a purely inorganic network. These reactions, which occur in the solid state with restricted mobility of the polymeric siloxane chains, play a determining role. The porosity generated is highly dependent on the properties of the three-dimensional polymeric hybrid network, which rearranges to silica while eliminating the organic molecule. These properties vary according to the nature of the organic cross-linking unit: as a result, pore formation is controlled by the nature and structure of the organic moieties.

3. The preparation of selective heterogeneous catalysts

Hybrid materials certainly offer some interesting approaches for the preparation of heterogeneous catalysts by design. The environment of the catalytic site in the solid material can be adjusted to induce selectivity. This can be obtained by achieving molecular imprints in the amorphous support, or by synthesizing new hybrid supports.

3.1. *Molecular imprinting*

With the aid of a molecular template, molecular imprints have been obtained in cross-linked polymers [29]. A large mumber of potential applications are being developed for this class of materials. Materials for catalysis, molecular recognition and enantiomeric resolution can be derived from imprinting techniques. The imprinting of polymers was recognized as a method for producing catalysts, particularly those which function similarly to enzymes [29].

In the case of silica gels, the first attempts to generate imprints appeared some time ago [42–49]. Silica gel was prepared in the presence of a molecular template. After extraction and drying, the resulting gels showed preferential adsorption of the imprinted molecule, indicating the existence of specific cavities capable of molecular recognition. Some specific adsorption of dyes or enantiomer enrichments by selective adsorption on silica gels have been reported [42–49].

A related approach described as "footprint catalysis" has been used to prepare selective catalysts [47–49]. The imprint was achieved by using a molecular template whose structure was close to that of the transition state of a chemical reaction, and by adding aluminium ions to generate catalytic activity. After drying and aging, surface cavities with Lewis acids in a definite arrangement are formed. After removal of the templates, the suitability of the material as a catalyst was investigated. Catalysts which exhibit substrate selectivity or cause enantiomers to react at different rates have been reported [50–58].

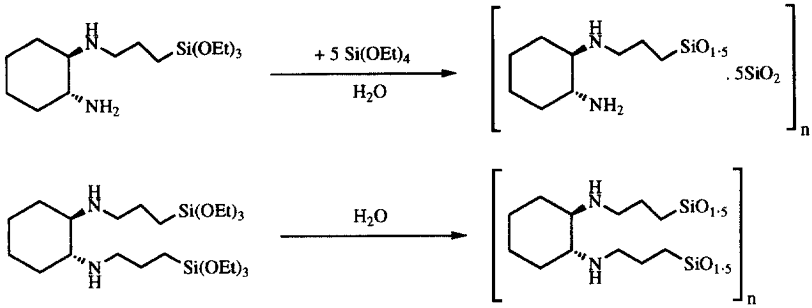
Recently, a related approach to prepare silica-containing substrate-selective cavities was reported [59,60]. A *trans*-esterification catalyst was produced by imprinting a phosphonate ester in silica gel. Although substrate selectivity was observed, the adsorption properties of the inorganic material were somewhat complex and difficult to rationalize [61,62]. Recent attempts to produce imprinted silicas seemed encouraging for the preparation of a specific amorphous solid [63]. However, the synthesis of silica catalytic materials suitable for enantiomer recognition is a challenging area.

3.2. *Hybrid supports*

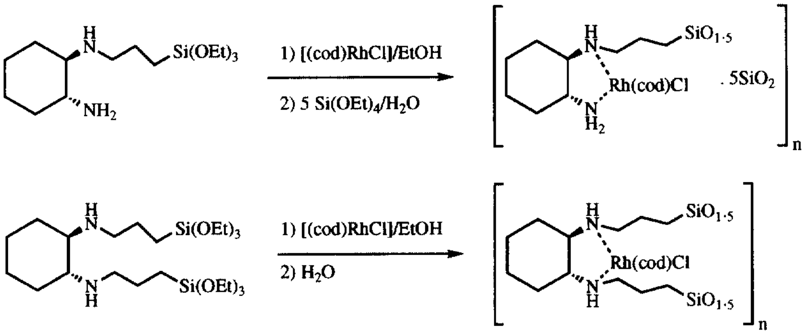
We have considered the use of hybrid solids as catalyst supports, taking advantage of the large variability and tunability of the three-dimensional network to control catalyst selectivity. For example, a chiral catalyst was prepared upon hydrolysis and condensation of a mixture of $Si(OEt)_4$ and $MeSi(OMe)_3$ in the presence of a soluble cyclopeptide. The gel was dried with CO_2 at its critical point. It retained the cyclopeptide molecule in the silica matrix. The composite material showed enantioselective catalytic activity in the hydrocyanation of benzaldehyde, leading to *R*-mandelonitrile in 94% e.e. [64].

We prepared a chiral silsesquioxane network upon hydrolysis–condensation of functionalized, optically active molecules. The sol–gel hydrolysis of silylated derivatives of (*R,R*)-*trans*-1,2- diaminocyclohexane readily gives rise to solid materials (Scheme 9) [65].

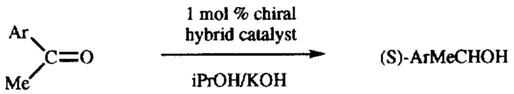
Such porous hybrid solids, containing chiral organic fragments attached to the inorganic silicate network by one or two C–Si bonds, are of interest as supports for heterogeneous catalysts. Rhodium complexes were prepared via reaction of the diamine precursors with $[(cod)RhCl]_2$. Hydrolysis of the organometallic complexes containing hydrolysable $Si(OEt)_3$ groups allows one to form hybrid gels containing rhodium complexes [65] (Scheme 10).



Scheme 9. Sol–gel hydrolysis of silated (*R*,*R*)-*trans*-1,2-diaminocyclohexane derivatives.



Scheme 10. Preparation of supported heterogeneous catalysts.



Scheme 11. Hydride transfer reduction of aromatic ketones.

The supported rhodium complexes were evaluated as catalysts in the asymmetric hydride transfer reduction of aromatic ketones, (Scheme 11). The use of hybrid catalysts led to (*S*)-2-phenylethanol with higher e.e. values as compared to the use of related soluble catalytic species. A hybrid solid in which the chiral moieties are part of the hybrid network gives rise to catalysts showing a high activity and selectivity. The chiral structure of the three-dimensional solid network has a great influence on the properties of the resulting catalyst.

This approach is quite general, and a variety of chiral precursors can be prepared from readily available natural chiral molecules. The preparation and use of new enantioselective catalytic materials from organic–inorganic hybrids is currently under investigation. Design of the three-dimensional network can lead to control of the properties of the catalyst. Hybrid networks constitute an interesting new class of tunable supports for heterogeneous catalysis.

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