MATERIALS CHEMISTRY COMMUNICATION

Chiral organic–inorganic solids as enantioselective catalytic materials

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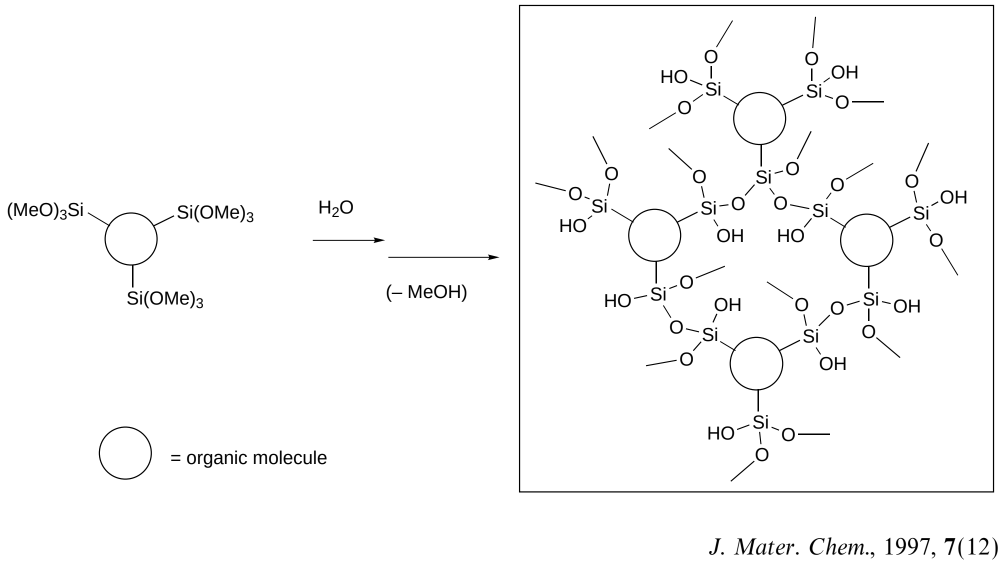
New enantioselective catalytic materials result from the sol–gel hydrolysis condensation of silyl-substituted chiral diamine–rhodium complexes.

In order to meet the increasing ecological and economic regulations for the development of chemical processes, more attention is being paid to the use of heterogeneous catalysts. Controlled synthesis of the catalytic material and appropriate tuning of the catalytic site is necessary to achieve the high selectivities required in organic transformations. Asymmetric heterogeneous catalysis and the design of enantioselective catalysts constitute challenging areas of research.[1]

Sol–gel chemistry has emerged as the most important and versatile method for the preparation of inorganic and mixed organic–inorganic materials.[2,3] Related materials also open the possibility of new approaches for selective heterogeneous catalysis.[4,5] The mild reaction conditions of the sol–gel approach allow the deliberate tailoring of the materials properties. Molecular imprinting, based on the temporary introduction of template organic molecules, which constitutes a very attractive approach to produce highly selective heterogeneous catalysts,[6–8] has been extended to the preparation of silica-based imprinted materials.[9,10]

New and very diverse selective catalytic materials may arise from the sol–gel route to hybrid organic–inorganic solids. Unique catalytic properties may be generated by combining the intrinsic properties of the organic component and the properties of the inorganic framework. Hybrid silsesquioxane materials[11,12] which are obtained by sol–gel hydrolysis of silylated organic molecules containing a non-hydrolysable Si—C bond [eqn. (1)] are of particular interest because they are well defined at the molecular level. They can allow control of the solid properties on the basis of the molecular parameters.[13]



(1)

The co-hydrolysis of substituted alkoxysilanes, containing a metal-coordinating ligand, and ethyl silicate has been shown to generate supported homogeneous catalysts and heterogeneous silica supported catalysts.[14,15] We have been considering the use of hybrid solids as catalyst supports and taking advantage of the large variability and tunability of the three-dimensional network for controlling the catalyst selectivity. We report here the preparation of hybrid materials containing chiral organic substructure and some uses of these materials for enantioselective reactions

We first prepared chiral trialkoxysilyl derivatives of (*R,R*)-*trans*-1,2-diaminocyclohexane **1**.[16] Heating **1** with γ-chloropropyl(triethoxy)silane **2** gave good yields of the γ-silylated secondary amines **3** and **4** [eqn. (2)].† The sol–gel hydrolysis condensation of **3** and **4** to produce the hybrid solid was then performed either using the pure precursors **3** and **4** or in the presence of added $Si(OEt)_4$. In all cases gelation occurred very rapidly (10 min to 1 h) upon addition of a stoichiometric amount of water [eqn. (3), (4)]. The hydrolysis

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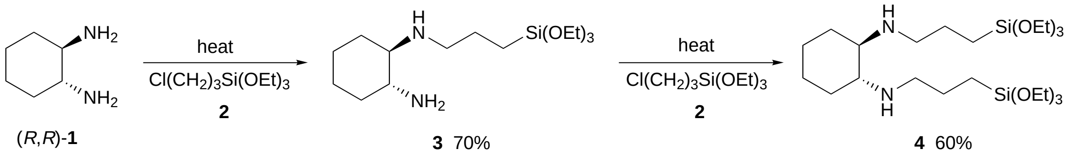
† The alkylation reactions are accompanied by the formation of (*R,R*)-*trans*-1,2-diaminocyclohexane hydrochloride. The chiral free amine was easily recovered upon base treatment of the collected salt. *Selected characterisation data*: **3**, ^{13}C NMR δ 8.0 (CH_2Si), 18.2 (CH_3CH_2O), 23.8 (CH_2CH_2Si), 25.3 ($NCHCH_2CH_2$), 31.5 (NH_2CHCH_2), 36.1 ($NHCHCH_2$), 50.0 ($CHNHCH_2$), 55.0 (NH_2CH), 58.0 (CH_2O), 63.9 (NHCH); ^{29}Si NMR δ −44.8. Mass spectrum (FAB): 318 (M^+). Analysis: Calc. for $C_{15}H_{34}N_2O_3Si$: C, 56.56; H, 10.76; N, 8.79%. Found: C, 55.98; H, 10.68; N, 8.56%. **4**, ^{13}C NMR δ 7.8 (CH_2Si), 18.0 (CH_3CH_2O), 23.5 (CH_2CH_2Si), 24.9 ($NCHCH_2CH_2$), 31.4 ($NHCHCH_2$), 49.6 ($CHNHCH_2$), 58.0 (CH_2O), 61.3 (NHCH); ^{29}Si NMR δ −44.9. Mass spectrum (FAB): 522 (M^+). Analysis: Calc. for $C_{24}H_{54}N_2O_6Si_2$: C, 55.14; H, 10.41; N, 5.35%; Found: C, 54.56; H, 10.30; N, 5.30%.



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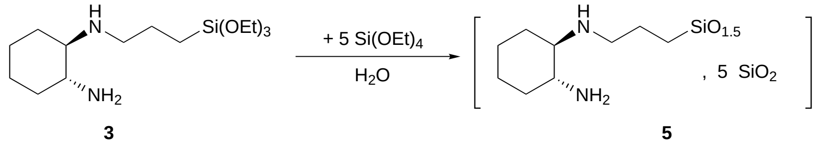

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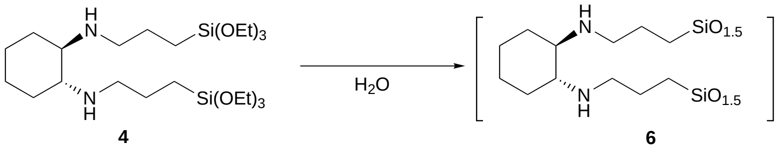

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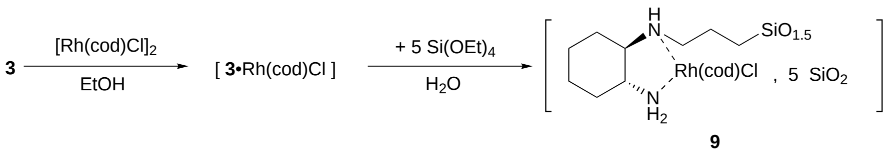

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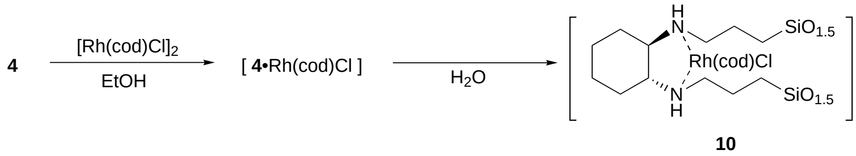

(6)

condensation of the amine-containing fragment was found to occur very rapidly without any added catalyst. The amino group probably provides intramolecular nucleophilic activation[17] of the hydrolysis and condensation reactions occurring at the silicon atoms. The gels which formed were allowed to stand at 25 °C for 7 days, and were then powdered and dried. The collected solids which formed quantitatively were analysed by ^{13}C and ^{29}Si CP MAS NMR spectroscopy.‡ It was established that no Si—C bond cleavage had occurred during the solid formation leading to quantitative incorporation of the organic moieties. ^{29}Si NMR spectra are consistent with the major formation of T^2 : CSi(OR)(OSi)$_2$ and T^3 : CSi(OSi)$_3$ substructures in the network, in agreement with observations in the case of related hybrid materials.[12] The hybrid solids **5**,**6** were porous materials, with N_2 BET surface areas up to 280 m^2 g^{-1}.[18]

Such porous hybrid solids containing chiral organic fragments attached to the inorganic silicate network by one or two silicon–carbon bonds are of interest as supports for heterogeneous catalysts. We examined the preparation and use of supported rhodium complexes. The rhodium complexes were first prepared in solution by reaction of 1 mmol of silylated amine **3** or **4** with 0.5 mmol of [Rh(cod)Cl]$_2$ in ethanol. Addition of Si(OEt)$_4$ and water then caused the hydrolysis condensation of the siloxy groups to generate a hybrid gel containing rhodium [eqn. (5), (6)]. The analysis of the collected dried gel is consistent with quantitative formation of the solid and a 1 : 1 amine–rhodium stoichiometry in the complex.§ These supported rhodium complexes were tested as catalysts in asymmetric hydride transfer reduction[19] of acetophenone and *o*-methoxyacetophenone. The results obtained by using the hybrid catalysts **9** and **10** are given in Table 1 (entries 2, 4, 6). Similar reactions were performed using soluble chiral diamine–rhodium complexes (entries 1, 3). The use of heterogeneous catalysts **9** and **10** led to (*S*)-2-phenylethanols with higher e.e. values compared to the use of soluble catalytic species. The best results were obtained using the catalyst **10** prepared from the disilylated diamine precursor (entries 4, 6). A related catalytic material[20] prepared by immobilisation of a diamine–rhodium complex at the surface of silica gel showed a much lower activity (entry 5). The use of a hybrid solid in which the chiral moieties are part of the hybrid network gives rise to catalysts showing high activity and selectivity. The chiral structure of the three-dimensional solid network has a large influence on the properties of the resulting catalyst.

In conclusion, we have shown that hybrid silsesquioxane materials containing chiral units are readily made upon sol–gel hydrolysis condensation of silylated chiral molecules. The resulting chiral solids are of interest for the preparation of

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‡ *Selected solid-state NMR data* for hybrid gels: **5**, ^{13}C CP MAS NMR δ 8.0 (CH$_2$Si), 18.0 (residual CH$_3$CH$_2$O), 20–40 (br, NCHCH$_2$ and CH$_2$CH$_2$Si), 50–65 (br, CN and residual CH$_2$O); ^{29}Si CP MAS NMR δ −65 (br, T group), −102, −109 (Q group). Found: C, 23.77; H, 4.90, N, 4.51; O, 37.32; Si, 29.50%. **6**, ^{13}C CP MAS NMR δ 8.1 (CH$_2$Si), 17.2 (residual CH$_3$CH$_2$O), 20–40 (br, NCHCH$_2$ and CH$_2$CH$_2$Si), 50–65 (br, CN and residual CH$_2$O); ^{29}Si CP MAS NMR δ −65 (br, T group).

§ The UV–VIS spectra of the chiral amine–rhodium complexes in solution are quite similar to that of the solid material. Absorption maxima centered at 383 nm for gel **9** and 381 nm for gel **10** were observed. The obtained material showed NMR characteristics which are similar to those of hybrid gels **5**,**6**. Additional lines in the ^{13}C CP MAS NMR spectra δ 70–90 indicated the presence of the cycloocta-1,4-diene ligand (cod). *Solid-state NMR data* for hybrid gels: **9**, ^{13}C CP MAS NMR δ 8.0 (CH$_2$Si), 18.0 (residual CH$_3$CH$_2$O), 20–40 (br, CH$_{2\text{-cod}}$, NCHCH$_2$ and CH$_2$CH$_2$Si), 50–65 (br, CN and residual CH$_2$O), 70–90 (br, CH$_{\text{vyn-cod}}$); ^{29}Si CP MAS NMR δ −65 (br, T group), −102, −109 (Q group). Found: C, 24.24; H, 4.40, N, 3.02; Cl, 3.6; Si, 21.80; Rh, 10.80%. **10** ^{13}C CP MAS NMR δ 8.1 (CH$_2$Si), 17.2 (residual CH$_3$CH$_2$O), 20–40 (br, CH$_{2\text{-cod}}$, NCHCH$_2$ and CH$_2$CH$_2$Si), 50–65 (br, CN and residual CH$_2$O), 70–90 (br, CH$_{\text{vyn-cod}}$); ^{29}Si CP MAS NMR δ −65 (br, T group). Found: C, 41.19, H, 6.89; N, 4.47; Cl, 6.66; Si, 9.75; Rh, 16.05%

Table 1 Asymmetric hydrogen transfer reduction of acetophenone (entries 1–5) and *o*-methoxyacetophenone (entry 6)[a]

entry	catalyst	reaction time/days	conversion (%)	e.e.[b] (%)	configuration[c]
1	[**3**·Rh(cod)Cl]	5	95	14	*S*
2	**9**	5	80	25	*S*
3	[**4**·Rh(cod)Cl]	5	95	26	*S*
4	**10**	5	75	58	*S*
5	[SiO_2·Rh(cod)Cl]	14	10	22	*S*
6	**10**	7	30	80	*S*

[a] The reactions were performed using 8.3 mmol of acetophenone or *o*-methoxyacetophenone in 20 ml of propan-2-ol in the presence of 2.5 mmol of KOH and a sample of catalyst containing 1 mol% of rhodium at room temperature. [b] Determined using HPLC on a chiracel column. [c] (*S*)-Phenylethanols are obtained with (*R*,*R*)-diamine.

selective heterogeneous catalysts. We are currently investigating the preparation and use of new enantioselective catalytic materials prepared from hybrid organic–inorganics. The design of the three-dimensional network can lead to control of the catalyst properties. Hybrid networks constitute an interesting class of tunable supports for heterogeneous catalysis.

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