Mesoporous Materials

Organometallic Chemistry Inside the Pore Walls of Mesostructured Silica Materials**

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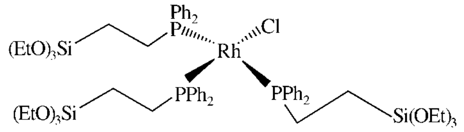
Recently a new class of porous organic–inorganic hybrid materials was prepared through the surfactant-templated polycondensation of bridged silsesquioxane organic molecules. These new materials, which are also referred to as periodic mesoporous organosilicas (PMOs), are unique as their channel walls contain both inorganic and organic fragments.[1] These fragments are uniformly distributed within the framework by covalent bonding of two or more terminal silyl groups, which leaves the void space unoccupied after template removal. This new approach extends the field of mesoporous materials into the chemistry of channel walls. Through choice or design of the organic functionality, one may create new materials that have truly unique properties and behaviors. These embedded fragments are readily accessible for chemical reaction, thus opening the possibility of using such materials as catalysts.[2]

Herein, we report the development of new methodologies for the preparation of inorganic–organometallic hybrid materials in which the organometallic complexes, which are structurally well defined at the molecular level, are integrated within the pore walls of highly ordered mesostructured silicas. This integration of the complex into the solid, rather than the grafting of a complex to the surface, should reduce some of the problems commonly associated with supported homogeneous systems, notably, catalyst leaching, pore blockage, and distribution inhomogeneity.

The first step in the accomplishment of this goal was the synthesis of an organometallic precursor that had multiple polycondensable organosiloxane functionalized donor ligands.[3] The rhodium organophosphine complex **1** was chosen to provide a wide range of potential catalytic applications (e.g., hydrogenation, hydroformylation).



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We wished to use this precursor directly in the synthesis of a hybrid MCM-type silica by cohydrolysis and polycondensation of **1** with tetraethylorthosilicate (TEOS) in the presence of cetyltrimethylammonium bromide (CTAB) as a structure-directing agent (SDA), but this precursor (and indeed, many catalytically interesting transition-metal complexes) was insoluble in water and unlikely to be stable under the classical aqueous basic conditions of this process.[4] Thus, we adapted the condensation reaction under the mild, acidic conditions reported by Stucky and co-workers (which led to the formation of SBA-3 mesostructured silicas)[5] to add an organic cosolvent, acetonitrile,[6] to better dissolve the transition-metal complex. Various combinations of **1**, TEOS, water, acetonitrile, CTAB, and HCl were attempted. The best results were obtained with 7.5 % wt acetonitrile, which led to materials that had a rhodium content of up to a 2 % wt in a highly ordered solid and contained the structure-directing agent CTAB in the channels.[7]

To render the organometallic sites of the as-made solid accessible, the surfactant template was removed by extraction.[8] It was found that if the extraction was performed directly on the as-made materials, all the structural order was lost. This instability, which is likely to be a consequence of the low temperature at which the condensation reaction was performed, disappeared when the as-made material was first silylated with $(CH_3)_3SiCl$ or $(CH_3)_2SiCl_2$ before the CTAB was extracted.[9]

The solids thus obtained were characterized by methods appropriate to molecular species (e.g., solid-state ^{13}C, ^{31}P, and ^{29}Si NMR spectroscopy, IR spectroscopy, and elemental analysis) as well as techniques more commonly associated with the characterization of mesoporous solids (nitrogen sorption isotherms, powder X-ray diffraction (XRD), thermogravimetric analysis (TGA), transmission electron microscopy (TEM), and energy dispersive X-ray (EDX) analysis). The characterization of one material (**2**, lot 1), which had been silylated with $(CH_3)_3SiCl$ and was shown by microanalysis to have 1.7 % wt Rh is presented below.

Mesoscopic order within **2** was shown to have been maintained after extraction of the SDA. The powder XRD pattern of **2** showed three clear peaks in the 2θ range of 1–10°, which is characteristic of 2D hexagonal ordered mesophases, with the d(10) spacing changing from 30 to 37 Å because of extraction of the template (Figure 1).[10] At this stage, the IR spectrum of **2** showed very little absorption in the 3000–2800 cm^{-1} range, thus indicating that the SDA had been removed.

Ordering was also clearly evident in the TEM image of **2** (Figure 2). Long-range ordering of the channels was observed with a spacing periodicity of approximately 3 nm. The TEM/EDX data were also important as they showed that metal complexes were localized in well-ordered phases of the solid

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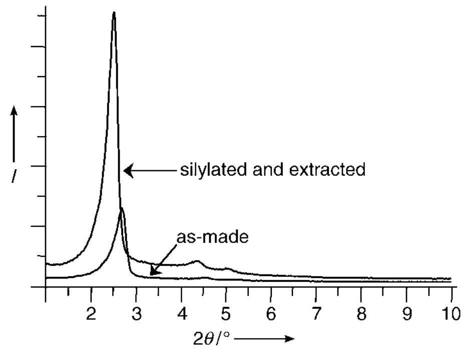

Figure 1. XRD pattern of rhodium-containing SBA-3 silica before and after extraction of the SDA.

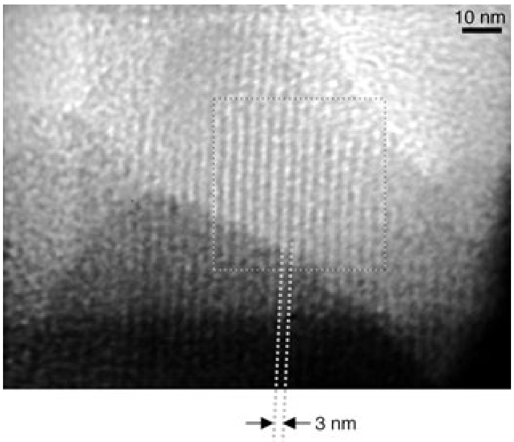

Figure 2. TEM micrographs of the extracted rhodium-modified hybrid material **2** (lot 1).

and the ligand-to-metal ratio (i.e., the P/Rh ratio) of the molecular precursor was maintained at 3 ± 0.3 (see the Supporting Information). This observation was confirmed over a large number of sample areas of the surface that was tested. Note that the elemental analysis of a sample of material on the milligram scale showed a P/Rh ratio of 2.96.[11]

The ^{31}P cross-polarization magic-angle spinning (CP-MAS) NMR spectroscopy showed a single signal at $\delta = 40.4$ ppm, which corresponds to a coordinated phosphine ligand. The ^{13}C CP-MAS NMR spectrum exhibited all of the aryl and alkyl resonances for the phosphine ligand as well as a strong signal at $\delta = -1.0$ ppm associated with the methyl of $(CH_3)_3Si-$ fragment, but no significant signal that could be associated with the CTAB template molecule was present. The ^{13}C CP-MAS NMR spectrum also showed evidence of a trace of the ethoxy fragment of the molecular precursor, which would indicate that some of the ethoxysilane was incompletely condensed. In the ^{29}Si CP-MAS NMR spectrum, the presence of T^2 and T^3 sites, as indicated by signals at $\delta = -60$ and 67.4 ppm, suggests that the precursor is not simply encapsulated but rather integrated into the silica network. Other signals were also observed in the $\delta = -90$ to -115 ppm spectral region (silica Q sites) and at $\delta = 15$ ppm ($(CH_3)_3Si-$ fragment).[12]

The TGA profile showed four regions of weight loss. [13] At temperatures up to about 100 °C, weight loss was accompanied by an endothermic differential thermal analysis (DTA) peak, which was presumably because of desorption of water. A second region of weight loss followed at temperatures between 200 and 550 °C, which, may be considered n inspection of the first derivative of the profile as a peak centered at 360 °C and a shoulder at around 460 °C, both arising from the decomposition and desorption of volatile organic species. The embedded complex is thermally stable up to 200 °C. The weight loss taken between 200 and 460 °C, and attributed to the ligand, is in good agreement with the metal loading and the stoichiometry of the molecular precursor. Above 460 °C, the weight loss is mainly because of the decomposition of the trimethylsilyl groups and accounts for approximately two $(CH_3)_3Si-$ fragments per rhodium atom. Further weight loss occurred at temperatures above 650 °C, which is probably because of the condensation of silanols of the silica framework.

The results of the analysis of the adsorption–desorption isotherms and the pore-size-distribution curves of the extracted unmodified and rhodium-modified materials are shown in Figure 3. Both samples show a type IV isotherm, which is characteristic of mesoporous solids. Relatively narrow pore–diameter distributions were observed for both materials and the average pore diameter did not vary significantly between the two samples (2.0–2.2 nm), which would seem to indicate that the rhodium had indeed been incorporated into the walls of the silica rather than remaining in the pores or the channels. The Brunauer–Emmett–Teller (BET) specific surface area measured for the rhodium-modified material (930 $m^2 g^{-1}$) was also quite similar to that of the unmodified analogue (1090 $m^2 g^{-1}$).[14]

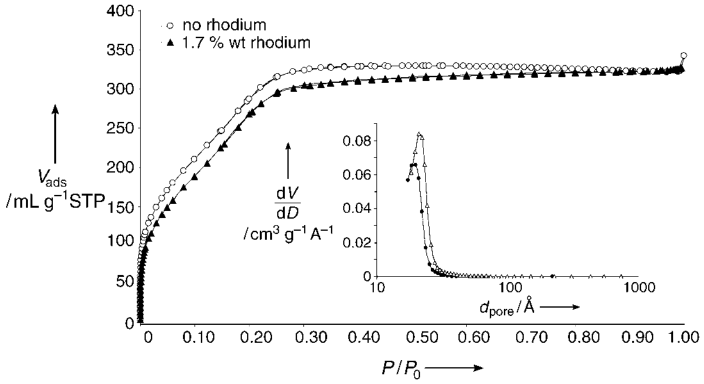

Figure 3. Nitrogen adsorption–desorption isotherms and pore-size distributions (from the Barret–Joiner–Halenda (BJH) calculations) of unmodified and rhodium-modified SBA-3 silicas.

Thus, we have a material in which intact triphosphanylrhodium chloride fragments have been covalently bound to the silica framework without the overall porosity or the degree of order of the material being affected. The complexes seem to be homogeneously distributed and embedded in the channel walls. The question remained whether the metal-containing sites of **2** were accessible for catalytic chemical reactions and whether the rhodium complex would exhibit typical behavior associated with its homogeneous analogue.

The catalytic activity of several hybrid materials for hydrogenation was evaluated by using substrates of varying steric encumbrance and compared to the activity of a homogeneous catalyst, $[RhCl(PPh_3)_3]$. Among the materials tested were two different lots of a model system prepared by postsynthetic grafting of precursor **1** onto calcined SBA-15 silica **3**. Results obtained for the catalytic tests are given in Table 1.

Table 1: Hydrogenation of alkenes by different rhodium-based catalysts.[a]

Substrate	Catalyst	% wt Rh[b]	Substrate/Rh	Conv [%]	TOF [h^{-1}]
styrene	**3**	0.8	7600	85	2150
	2	0.7	8500	93	2650
cyclohexene	**3**	0.8	7550	100	2590
	2	0.7	8560	100	2850
acrolein	**3**	0.8	7500	4	97
	2	0.7	8890	4	104
crotonaldehyde	**3**	1.1	5500	≈ 7[c]	20[c]
	2	1.7	3400	≈ 5[c]	9[c]
styrene	$[RhCl(PPh_3)_3]$	3.5×10^{-4} M solution	6600	75[d]	3300[d]

[a] Conditions: $P(H_2) = 20$ bar, 70 °C, 3 h in benzene. TOF = turnover frequency, conv = conversion. [b] From elemental analysis. [c] 19 h. [d] Homogeneous catalysis, 1.5 h.

In all cases, the modified SBA-3 materials, including **2**, exhibited similar activity to that of model system **3**; thus, it is clear that the rhodium centers are available for catalysis. Indeed, for styrene hydrogenation, the activity is in the same range as that observed for the homogeneous complex. Furthermore, catalytic activity was observed even for the more hindered double bonds of cyclohexene and crotonaldehyde (see Table 1. The chemoselectivity (100 %) of the catalyst for the carbon–carbon double bond in α,β-unsaturated aldehydes is the same as that reported for the homogeneous catalyst.[15] Limited attempts at recycling the catalyst have shown that catalytic activity is undiminished over several cycles, but more rigorous testing is needed.

In summary, we have developed a new synthetic protocol that allows the incorporation of phosphine-ligated transition-metal complexes into SBA-3 type silicas without significant loss of the mesoscopic order of the silica framework or the coordination environment and catalytic activity of the transition-metal complex. Key novel aspects of the protocol are the use of acetonitrile as a cosolvent, the acidic conditions, the relatively low temperatures, and silylation of the material prior to extraction of the SDA. The method has been successfully extended to incorporate other siloxy organophosphanyl transition-metal complexes into hybrid materials, notably those of platinum and palladium. The evaluation of these materials, in terms of activity and stability, for a variety of catalytic applications is ongoing.

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[3] The transition-metal precursor, $[RhCl\{PPh_2(CH_2)_2Si(OCH_2CH_3)_3\}_3]$ (**1**), was prepared by treating $[\{RhCl(cod)\}_2]$ (cod = 1,5-cyclooctadiene) with $PPh_2(CH_2)_2Si(OCH_2CH_3)_3$ according to the procedure reported: O. Kröcher, R. A. Köppel, M. Fröba, A. Baiker, *J. Catal.* **1998**, *178*, 284.

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[6] In a typical procedure, CTAB was first dissolved in water, HCl, and half of the amount of acetonitrile used in the gel composition. TEOS was then prehydrolyzed over 15 min at room temperature prior to the addition of the organometallic precursor that had been dissolved in the remaining portion of acetonitrile. The resulting solution was stirred for 3 h at room temperature. The solid product was collected by filtration, washed with water, and dried under vacuum overnight at 25 °C.

[7] Optimized molar composition: TEOS 1; H_2O 120; CH_3CN 4.3; HCl 9.2; CTAB 0.12. When a siloxane-containing transition-metal complex is used, the calculation of the molar composition is based on the total number of condensable silicon centers, from TEOS and the complex.

[8] The template was removed from the as-made material by batch extraction with dry ethanol at 50 °C for 2 h. Three extraction cycles were necessary to complete the process.

[9] The postsilylation reaction was performed in dry toluene at 50 °C for 1 h using either $(CH_3)_3SiCl$ or $(CH_3)_2SiCl_2$ as the silylating agents.

[10] The expansion of the structure upon silylation and extraction, indicated by the increase of the d(10) spacing is likely to be related to the decreased degree of hydrogen-bonding interactions between the surface hydroxy groups, which leads to a partial release of the internal surface tension.

[11] Elemental analysis: 1.5 % wt P and 1.7 % wt Rh.

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[13] Thermogravimetric analyses were conducted from 25 to 1000 °C in air at a heating rate of 5 °C min^{-1}.

[14] We have demonstrated for an SBA-15 material that the postsynthetic grafting of the rhodium complex onto the surface of unmodified calcined silica dramatically reduces the specific area and the median pore-size diameter and that the effect varies inversely with rhodium loading (see the Supporting Information).

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