

Synthesis of Ordered Microporous Silicates with Organosulfur Surface Groups and Their Applications as Solid Acid Catalysts

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We report a direct surfactant-based synthesis of microporous hybrid silicates, uniformly coated with 3-mercaptopropyl groups (thiol-MCM-41) and further derivatization to create a solid acid ion exchanger or catalyst. By co-condensation of fast-hydrolyzing methoxy-based silanes, hexagonally ordered channels with a narrow pore size distribution were obtained, even at high concentrations of organic groups. The average pore diameter of 14 Å is smaller than in other MCM-41 structures and falls in the range between zeolites and MCM-41. These high surface area materials can therefore exhibit greater size selectivity than mesoporous structures, yet they can accommodate larger guests than zeolites. The thiol-MCM-41 is a good heavy metal absorber. Furthermore, it can act as a prestructured starting material for further chemical reactions. For example, after oxidation of thiol to sulfonic acid functionalities, a solid acid ion exchanger was created that possessed the advantages of the inorganic silicate support, including high surface area, controlled pore size, mechanical stability, as well as reduced swelling or contraction upon ion exchange, compared to polymeric sulfonic acids. The sulfonic acid functionalized material was found to be an efficient heterogeneous catalyst for the protection of alcohols by tetrahydropyranlation.

Mesoporous sieves of the type MCM-41 have generated much interest due to their high surface areas and ordered pores that are larger than those of zeolites, yet exhibit relatively narrow pore size distributions.¹ While these structural properties are interesting for many potential applications involving host–guest interactions, it is often necessary to modify the surface composition of these materials, for example, by attaching inorganic or organic components to the surface.² Organic surface modifications can be achieved either by grafting other molecules, such as siloxanes, to surface hydroxyl groups present on the inorganic supports^{3–5} or by incorporating

functionalities directly in a synthesis. Hybrid MCM-41 and clay materials containing organosulfur groups have recently been synthesized by postsynthesis grafting and were shown to exhibit a strong affinity for heavy metals in solution.^{4–6}

In postsynthesis grafting processes the surface concentration of organic groups is constrained by the number of reactive surface silanol groups present and by diffusion limitations. It is often necessary to employ a large excess of organic silane. These restrictions may be overcome by direct incorporation of organic groups during the synthesis of the mesoporous support, i.e., by co-condensing siloxane and organosiloxane precursors in a templating environment. This has been successfully demonstrated for alkyl and phenyl surface groups,^{7–9} and recently with more reactive functional groups, that can act as potential anchors for further surface modifications.^{10–12} While some of these materials were well ordered, their compositions were typically limited to a maximum organic siloxane:tetraethoxysilane (TEOS) ratio of 1:4; at higher ratios poorly ordered products were obtained.

We have improved the direct synthesis method to create well-ordered thiol-functionalized porous silicates with higher loadings of the organic group. These products were obtained from a mixture containing 1 (3-mercaptopropyl)triethoxysilane (MPTS):2.5 tetramethoxysilane (TMOS):0.42 cetyltrimethoxyammonium bromide (CTAB):0.96 NaOH:272 H₂O:66 MeOH. The product order depended on the hydrolysis and condensation kinetics of the inorganic precursors. Mixtures of MPTS and TMOS produced more ordered structures than corresponding mixtures of MPTS and TEOS, which hydrolyzes more slowly than TMOS.¹³ To minimize the chances of phase separation, MPTS and TMOS were mixed before addition to the surfactant solution. In addition, the hydrolysis rate was controlled by using a 70 wt % H₂O/30 wt % MeOH solvent mixture.¹⁴ The solution was stirred at room temperature for 12 h, followed by heating at 95 °C for 36 h. The surfactant was extracted without destroying the functional groups or the product structure, by refluxing with an HCl/MeOH/H₂O solution.¹⁰ The organic content of the extracted product was 14.31 wt % C, 3.17 wt % H, and

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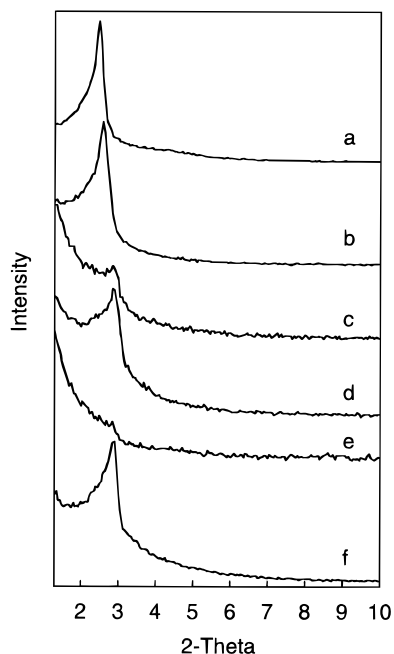


Figure 1. Powder XRD patterns of (a) thiol MCM-41 after surfactant extraction; (b) sulfonic acid-MCM-41; (c) sample b after Na^+ ion exchange; (d) sample c after washing with concentrated HCl solution; (e) sample a after treatment with aqueous HgCl_2 solution; (f) sample e after treatment with concentrated HCl solution.

10.88 wt % S (4.7 mmol of S/g of SiO_2 in product, 4.8 mmol of S/g of SiO_2 in reactant mixture).¹⁵ The relative S/ SiO_2 ratio is comparable to the highest amount reported for grafting.⁴

Figure 1a shows the powder X-ray diffraction (XRD) pattern of the extracted thiol-MCM-41 sample with a d_{100} reflection at 35 Å and a very weak d_{110} reflection at 21 Å. Contrast matching between the organic ligands and the silicate framework is responsible for the low intensity of higher order reflections (see also below).⁵ The well-ordered hexagonal symmetry of the product can be more clearly seen in the transmission electron microscopy (TEM) image and electron diffraction pattern shown in Figure 2. No large amorphous agglomerates were found in the sample. The elemental composition sampled under the TEM by energy-dispersive spectroscopy (EDS) in various regions of the sample indicates a relatively even distribution of sulfur throughout the sample (6–8 mmol of S/g of silica), comparable to the bulk analysis within the error of the technique. These materials are thermally stable up to ca. 240 °C before the 3-mercaptopropyl groups begin to decompose. Samples prepared at room temperature or with TEOS as co-reagent were considerably less ordered, especially at high organic loadings.

¹³C CP MAS solid-state NMR spectra show resonances that can be assigned to several types of organo-sulfur groups.^{4,5,16} The most prominent peaks arise from 3-mercaptopropyl groups with resonances at 27.9 ppm for the C^1 (adjacent to SH) and C^2 carbons and 11.8 ppm for the C^3 carbon. An additional minor resonance

at 23.0 ppm is assigned to C^1 and C^2 carbons of dipropyl disulfide, which may form as an oxidation product between adjacent thiol groups. The C^3 carbon of the disulfide produces an unresolved shoulder slightly downfield of the C^3 thiol carbon. Two additional weak resonances were observed at 50.7 ppm due to methanol used in the extraction and at 37 ppm. The latter peak is absent in samples prepared at room temperature. It is tentatively assigned to additional oxidation products, such as sulfinate groups. The ²⁹Si MAS NMR spectrum shows four resonances at -59, -66, -102 and -111 ppm, assigned to T^2 , T^3 , Q^3 , and Q^4 silicon atoms, respectively. On the basis of integration of the deconvoluted peaks, the product composition is $(\text{SiO}_2\text{HC}_3\text{H}_7\text{S})_{0.09}(\text{SiO}_{1.5}\text{C}_3\text{H}_7\text{S})_{0.21}(\text{SiO}_{2.5}\text{H})_{0.20}(\text{SiO}_2)_{0.49}$.

Nitrogen adsorption measurements of the thiol-MCM-41 yielded a type 1 isotherm with a narrow hysteresis loop, more typical for microporous solids, such as zeolites, than for mesoporous materials with an MCM-41 structure. A surface area of 792 m^2/g and a total pore volume of 0.47 cm^3/g were determined by the Brunauer–Emmett–Teller (BET) method. The pore size distribution peaked at ca. 14 Å. Thus, with the same surfactant used in the synthesis of mesoporous MCM-41, the pore diameter of thiol-MCM-41 falls in the range between MCM-41 and large-pore zeolites. One can therefore expect better size selectivity for guest molecules than is observed in mesoporous materials. On the basis of comparisons with calcined thiol-MCM-41 and with extracted MCM-41 prepared from TMOS only, the pore size difference can be attributed mainly to the presence of organic surface groups rather than a change in average wall thickness. As for MCM-41, further pore size control is possible by varying solvent and surfactant compositions.

Mercury uptake has been previously demonstrated in thiol-functionalized MCM-41 prepared by postsynthesis grafting.^{4,5} The directly synthesized material exhibited a dry weight capacity of 2.1 mmol of Hg^{2+}/g of thiol-MCM-41. It is interesting to note that the XRD pattern of the mercury-treated material shows little intensity in the low angle region (Figure 1e). However, the d_{100} reflection was regenerated by extracting the mercury with concentrated HCl (Figure 1f). Some further condensation resulted in a decreased d_{100} parameter after this treatment. Similar observations apply to Na^+/H^+ exchange in a sulfonated sample (see below, Figure 1b–d). These results imply that the micropore structure is not destroyed by the uptake of mercury or sodium. Instead, the presence of these ions reduces the contrast between scattering by the walls and the channels. Random placement of cations and heavy metal absorption effects may be additional factors leading to reduced intensities.

To demonstrate surface-group modification, thiol-MCM-41 was oxidized to the corresponding sulfonic acid derivative by wetting the solid briefly with 20% HNO_3 , followed by careful addition of concentrated HNO_3 and stirring for 24 h at room temperature. After this reaction the sulfur content remained at 4.7 mmol of S/g of SiO_2 . The product was slightly less ordered, exhibiting lower intensity in the XRD pattern and lacking the d_{110} peak (Figure 1b). The BET surface area decreased to 574 m^2/g and the pore volume to 0.46 cm^3/g . The

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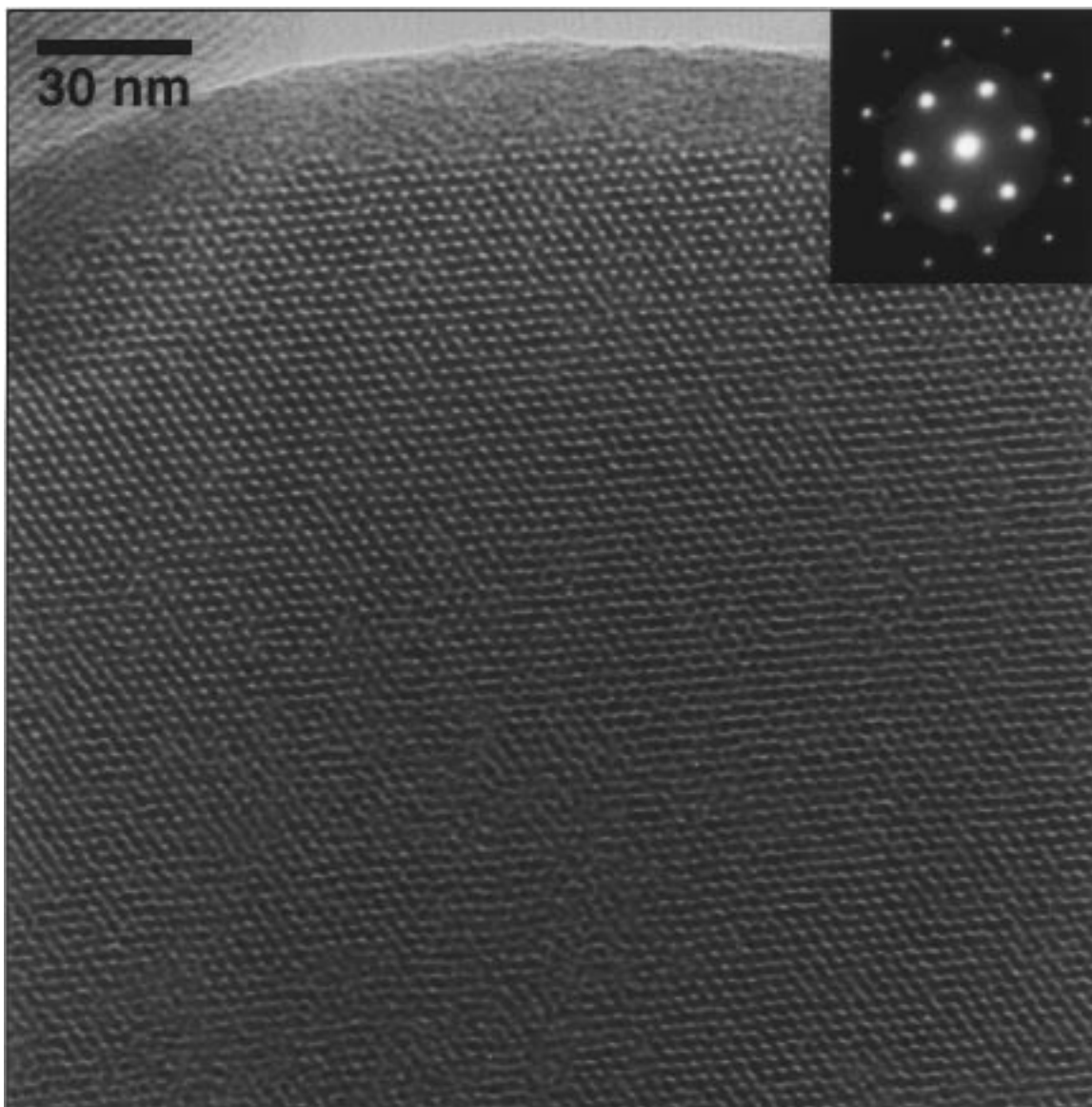


Figure 2. TEM image of a representative region of thiol-MCM-41 after surfactant extraction. The inset shows the selected area electron diffraction pattern from this region. The images were recorded on a Philips CM30 transmission electron microscope operating at 300 kV.

nitrogen adsorption isotherm indicated that in this material 10% of the surface area was due to mesopores (ca. 35–80 Å), caused by a small amount of pore degradation. However, 85% of the surface area arose from micropores (peak in pore size distribution: 14 Å). Low-pressure hysteresis and long desorption times suggest an activated passage of nitrogen molecules through constrictions in the molecular sieve. The ^{13}C CP MAS NMR spectrum of sulfonic acid-MCM-41 shows distinctive C^1 , C^2 , and C^3 carbon peaks at 54.0, 18.2, and 11.6 ppm, respectively, while the original thiol resonances have disappeared. Additional weaker resonances may arise from incomplete oxidation of organo-sulfur species. When the washed sulfonated product was placed in an aqueous NaCl solution, the solution pH dropped virtually instantaneously to pH 2, as ion exchange occurred between protons and sodium ions (proton exchange capacity: 1.76 mequiv/g of sulfonic acid-MCM-41).

This solid acid is an inorganic analogue of sulfonated polymers, which are used as catalysts for alcohol

dehydration and protection.^{17–19} We tested this application by adding 30 mg of sulfonic acid-MCM-41 to a mixture of 3,4-dihydro-2*H*-pyran (8.7 mmol) and ethanol (8.7 mmol) in 3.0 mL of hexane.²⁰ After stirring at 0 °C for 10 min and then at room temperature for only 40 min, conversion to 2-ethoxytetrahydropyran was 96% (by GC and ^1H NMR). Simple filtration and solvent evaporation permitted separation of the product and recovery of the catalyst. In control experiments with regular MCM-41, treated with nitric acid and washed identically to the sulfonic acid-MCM-41, the conversion was negligible. We are currently exploring further

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(20) Before this reaction, sulfonic acid-MCM-41 was washed with distilled water until the washings were neutral, followed by additional washing. The sample was then dried overnight under vacuum at 120 °C. No remaining nitrogen (e.g., due to nitric acid) was detected by chemical analysis.

applications of these versatile molecular sieves based on host–guest interactions with organosulfur surface groups.

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Supporting Information Available: TGA and derivative TG curves, nitrogen adsorption–desorption isotherms, ^{29}Si and ^{13}C CP MAS NMR spectra of extracted thiol-MCM-41, as well as ^{13}C CP MAS NMR spectra of sulfonic acid-MCM-41 and the mercury-treated sample (7 pages). See any current masthead page for ordering and Internet instructions.

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