Synthesis and Characterization of a Reactive Vinyl-Functionalized MCM-41: Probing the Internal Pore Structure by a Bromination Reaction

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We report here a simple one-pot synthesis of MCM-41 functionalized with a reactive vinyl group (*v*-MCM-41). The reaction involves co-condensation of tetraethoxysilane (TEOS) and vinyltriethoxysilane (VTES) in a surfactant solution under basic conditions. A difficult question in many surface modifications of porous materials is whether functional groups are located on the internal pore surface, the external particle surface, or in the walls. Here a bromination reaction of *v*-MCM-41 provides evidence for attachment of most vinyl groups to the accessible surface *within* the mesopore channels. This model reaction also demonstrates that *v*-MCM-41 may be a versatile starting material for many other in situ reactions resulting in ordered, high surface area materials with specific functional groups.

The interest in inorganic−organic hybrid materials arises from the advantages that the inorganic and organic moieties bring to the systems.[1,2] The inorganic components can provide mechanical, thermal, or structural stability, while the organic features are often more readily modified for specific applications in catalysis, separation, or sensing.[3] One way of preparing these materials is based on sol-gel processing,[4] which involves hydrolysis and condensation of metal alkoxides, often permitting mild reaction temperatures and pressures. In preparations of inorganic−organic hybrid materials, typical precursors are organically functionalized metal alkoxides whose Si−C bonds should be hydrolytically stable under acid or base conditions. However, the materials obtained in a simple sol-gel process are usually amorphous or randomly ordered unless structure-directing materials are employed.

Mesoporous sieves of the type MCM-41 possess hexagonally packed arrays of channels with very high surface areas and narrow pore size distributions compared with amorphous silica. Since the first report of these structures in 1992,[5,6] numerous studies have been performed on modifications of the MCM-41 synthesis to increase the potential applicability of these materials. Postsynthesis grafting techniques have been used to attach organic functionalities to the silicate surface.[7,8] A recent study reports the first direct synthesis of inorganic−organic hybrid mesoporous materials with phenyl or alkyl functionalization.[9,10] However, further modification of these relatively inert groups to other organic groups is limited. Other organic groups introduced in a direct synthesis often result in materials with low-order or wide pore size distributions.[11,12] We are therefore exploring syntheses of ordered mesoscopic inorganic−organic hybrid materials containing easily modifiable organic functional groups for applications as catalysts, catalyst supports, and stationary phases in chromatography which take advantage of the high surface areas and specific size selectivities of the mesoporous silicate structures.

v-MCM-41 was prepared by vigorously stirring a mixture containing 1 TEOS:0.25 VTES:0.15 cetyltrimethylammonium bromide:0.38 NaOH:125 H_2O for 2 days, followed by heating at 87 °C for 1 day. While mesostructured products could be obtained by a room temperature reaction, the additional heat treatment greatly improved the structural order. A modified acid/solvent extraction was employed to remove the surfactant from the product without destroying the vinyl groups.[13] The extraction was complete, as confirmed by the absence of nitrogen in an elemental analysis,[14] by the disappearance of the characteristic IR absorptions of the surfactant (v_{as} CH_2, 2925 cm^{-1}; δ_s CH_2, 1488 cm^{-1}) and by the absence of alkyl resonances in the ^{13}C CP MAS NMR spectrum. In a subsequent bromination reaction, *v*-MCM-41 was dispersed in a solution of Br_2 in CH_2Cl_2 at a stoichiometric Br_2/vinyl ratio. The resulting mixture was stirred for up to 6 days. The product was filtered, washed with excess CH_2Cl_2, and dried at 85 °C for 1 day (Br content 22.7 wt %).

The powder X-ray diffraction (XRD) patterns of the organically functionalized samples are shown in Figure 1. After surfactant extraction, a long-range hexagonal arrangement of channels was observed, as indicated by the presence of d_{100}, d_{110}, and d_{200} reflections. The transmission electron microscopy (TEM) image and electron diffraction pattern (Figure 2) confirm the hexagonal symmetry of *v*-MCM-41. After bromination, the overall order was only slightly reduced. It should be noted that the d_{100} spacing contracted very little during the extraction or bromination processes (from 3.69 to 3.68 and 3.61 nm, respectively). In contrast, calcination at 550 °C resulted in a significant contraction to 3.21 nm. At this temperature, all of the vinyl groups were removed.

Thermal stability of the organic functional groups within the mesoporous samples was determined by thermogravimetric analysis. After an initial loss of solvent, the removal of the vinyl or Br_2Et groups commenced at 280−290 °C and continued up to 440 or 520 °C, respectively. An additional weight loss occurred at higher temperatures due to futher condensation of the silicate walls, as observed in other mesoporous silicates.[15]

Nitrogen adsorption experiments yielded a Brunauer−Emmett−Teller (BET) surface area of 1424 m^2/g for *v*-MCM-41 and a total pore volume of 0.82 cm^3/g. The BET isotherm for *v*-MCM-41 showed a type 4 isotherm, typical for mesoporous materials with an MCM-41 structure (Figure 3). After bromination, both the surface area and the total pore volume dropped significantly (BET surface area 932 m^2/g; total pore volume 0.57 cm^3/g). The BET isotherm was similar to that of *v*-MCM-41 except for two small hysteresis loops. A narrow hysteresis loop on the steep low-pressure portion of the isotherm may be due to nitrogen filling slitlike micropores in the regions between adjacent organic groups and the silica wall.[16] A second narrow hysteresis loop on the horizontal portion is assigned to the ca 2

(1) Sanchez, C.; Ribot, F. *New J. Chem.* **1994,** *18,* 1007−1047.
(2) Schubert, U.; Husing, N.; Lorenz, A. *Chem. Mater.* **1995,** *7,* 2010−2027.
(3) Schubert, U. *New J. Chem.* **1994,** *18,* 1049−1058.
(4) Brinker, C. J.; Scherer, G. W. *Sol-Gel Science: the Physics and Chemistry of Sol-Gel Processing*; Academic Press: San Diego, CA, 1990.
(5) Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. *Nature* **1992,** *359,* 710−712.
(6) Beck, J. S.; Vartuli, J. C.; Roth, W. J.; Leonowicz, M. E.; Kresge, C. T.; Schmitt, K. D.; Chu, C. T.-W.; Olson, D. H.; Sheppard, E. W.; McCullen, S. B.; Higgins, J. B.; Schlenker, J. L. *J. Am. Chem. Soc.* **1992,** *114,* 10834−10843.
(7) Beck, J. S.; Calabro, D. C.; McCullen, S. B.; Pelrine, B. P.; Schmitt, K. D.; Vartuli, J. C. U.S. Pat. 5,145,816, 1992.
(8) Cauvel, A.; Renard, G.; Brunel, D. *J. Org. Chem.* **1997,** *62,* 749−751.
(9) Burkett, S. L.; Sims, S. D.; Mann, S. *Chem. Commun.* **1996,** 1367−1368.
(10) Sims, S. D.; Burkett, S. L.; Mann, S. *Mat. Res. Soc. Symp. Proc.* **1996,** *431,* 77−82.

(11) Macquarrie, D. J. *Chem. Commun.* **1996,** 1961−1962.
(12) Lim, M. H.; Stein, A. Unpublished results.
(13) Chen, C.-Y.; Li, H.-X.; Davis, M. E. *Microporous Mater.* **1993,** *2,* 17−26. In the present work, 2.0 g of *v*-MCM-41 were refluxed for 24 h in 177 g of 1.5 wt % HCl/2.5 wt % H_2O/MeOH.
(14) The C, H, N, Br analysis was carried out by Atlantic Microlab, Inc., Norcross, GA.
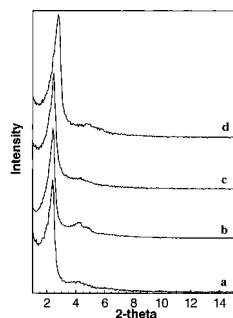(15) Steel, A.; Carr, S. W.; Anderson, M. W. *Chem. Mater.* **1995,** *7,* 1829−1832.

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Figure 1. Powder XRD patterns of (a) as-synthesized *v*-MCM-41 (1:4 VTES/TEOS); (b) *v*-MCM-41 after surfactant extraction; (c) sample b after bromination for 6 days; (d) sample a calcined in air at 550 °C for 10 h.
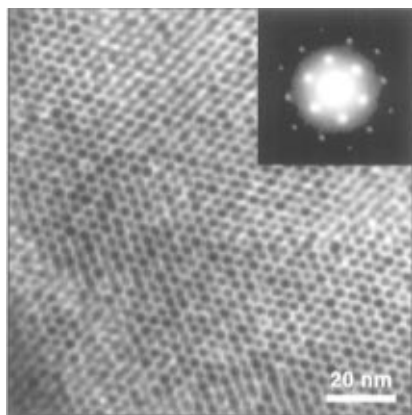

Figure 2. TEM image of a region of *v*-MCM-41 after surfactant extraction. The inset shows the selected area electron diffraction pattern from this region. The images were recorded on a JEOL JEM 1210 transmisison electron microscope operating at 120 kV.
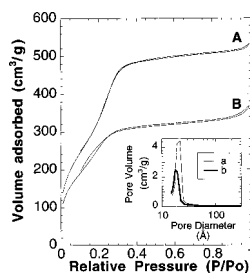

Figure 3. Nitrogen adsorption−desorption isotherms of (A) *v*-MCM-41 and (B) brominated *v*-MCM-41. The inset shows the pore size distribution of (a) *v*-MCM-41 (max at 2.2 nm) and (b) brominated *v*-MCM-41 (max at 1.8 nm).

nm wide mesopores generating the major channel structure. The reduction in total pore volume and shift in the pore size distribution peak from 2.2 to 1.8 nm imply a reduction in the free channel space as the vinyl groups were functionalized with bulkier bromine atoms.[17]

Infrared and solid state ^{13}C CP MAS NMR spectra confirmed the presence of vinyl groups. An IR absorption at 1410 cm^{-1} was assigned to the C−H bending mode of the vinyl group. By increasing the ratio of VTES/TEOS from 0.25 to 0.67 in the synthesis of *v*-MCM-41, additional C−H, C=C, and Si−C stretches could be observed at 3070, 1604, and 1270 cm^{-1}, respectively. Furthermore, the surfactant-extracted samples showed the same peaks, indicating that the covalently bound vinyl groups were not affected by the acid extraction. These IR peaks disappeared after bromination. The solid state ^{13}C

CP MAS NMR spectrum showed three resonances for surfactant-extracted *v*-MCM-41 corresponding to vinyl carbons at 129.0 and 134.8 ppm and methanol (solvent) at 49.9 ppm vs TMS. After bromination, a broad peak at 31.1 ppm confirmed the presence of C−Br bonds. Resonances due to vinyl carbon were still present after a 2-day bromination, but disappeared completely after a 6-day bromination.

The bromination reaction was monitored by UV−vis spectroscopy, following the decay of the UV absorption at $\lambda_{max} = 410$ nm. Immediately after the addition of an approximately stoichiometric amount of Br$_2$, the solution was dark red. As time progressed, the color changed very slowly to orange, to yellow, and then to pale yellow. A first-order reaction plot of ln(absorbance) vs. time resulted in a straight line (correlation coefficient $R = -0.9975$) with a rate constant of 2.95×10^{-3} min^{-1} and a half-life of 235 min. The unusually slow reaction compared to solution bromination of unsaturated organic compounds even with bulky protecting groups[18] implies that the vinyl groups are mostly located on internal surfaces of the bulk sample, i.e., *within* the mesopore channels. The rate is slower than expected for unhindered diffusion of Br$_2$ through 2 nm diameter mesopore channels.[19] We propose that vinyl groups line the walls throughout the channels, but groups near the channel openings are brominated first. They can cause some hindrance for additional Br$_2$ molecules through steric effects, induced dipole interactions, and weak charge transfer interactions. Solvent molecules present in the channels are likely to contribute to the hindered diffusion of Br$_2$. The rate deceleration may therefore be attributed not only to a decrease in the bromine concentration with time but also to slower diffusion rates as the number of dibromoethyl sites increases and the effective pore space decreases. It should be noted that eventually all vinyl groups are accessible for bromination, since no unreacted vinyl groups are observed in the solid state ^{13}C CP MAS NMR and IR spectra after bromination.

In conclusion, the synthesis of *v*-MCM-41 provides a convenient method of tailoring the surface properties of mesoporous silicates via organic functionalization. The one-pot synthesis presents an alternative to postsynthesis grafting methods, in cases where functional groups may concentrate near the openings of channels or where reactions with surface hydroxyl groups may be less suitable. Both *v*-MCM-41 and its brominated analog have relatively well-ordered structures and high surface areas, on the basis of XRD, TEM, and N$_2$ adsorption measurements. The average pore diameters lie on the border between micro- and mesoporous materials, thus permitting some size selectivity for large molecules. The reactivity of the surface vinyl groups that were proven to be within the channels renders *v*-MCM-41 an ideal starting material for many other surface modifications, resulting in mesoscopic inorganic−organic hybrid materials with specific functional groups. Experiments to modify the organic moieties for applications in catalysis or separation are currently underway.

Supporting Information Available: TGA and derivative TG curves of extracted *v*-MCM-41 and brominated *v*-MCM-41, UV-vis absorption spectra during Br$_2$ consumption and first-order reaction plot, and ^{13}C CP MAS NMR spectra (4 pages). See any current masthead page for ordering and Internet access instructions.

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(16) Sing, K. S. W.; Everett, D. H.; Haul, R. A. W.; Moscou, L.; Pierotti, R. A.; Rouquérol, J.; Siemieniewska, T. *Pure Appl. Chem.* **1985**, *57*, 603−619.

(17) The calcined *v*-MCM-41 exhibited a BET surface area of 1012 m^2/g and a pore volume of 0.59 cm^3/g.

(18) Brown, R. S.; Slebocka-Tilk, H.; Bennet, A. J.; Bellucci, G.; Bianchini, R.; Ambrosetti, R. *J. Am. Chem. Soc.* **1990**, *112*, 6310−6316.

(19) Gupta, V.; Nivarthi, S. S.; McCormick, A. V.; Davis, H. T. *Chem. Phys. Letters* **1995**, *247*, 596−600.