ChemComm

Simultaneous modification of mesopores and extraction of template molecules from MCM-41 with trialkylchlorosilanes

Valentyn Antochshuk and Mietek Jaroniec*

Department of Chemistry, Kent State University, Kent, Ohio 44242, USA. E-mail: jaroniec@columbo.kent.edu

Received (in Bloomington, IN, USA) 29th June 1999, Accepted 13th October 1999

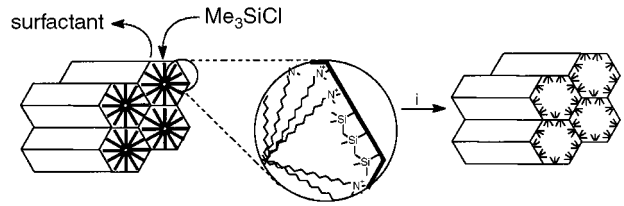
The simultaneous removal of a surfactant template and attachment of trialkylsilyl groups has been successfully achieved by treating uncalcined MCM-41 with trialkylchlorosilanes, resulting in the synthesis of mesoporous hydrophobic materials of highly uniform pore structure.

The preparation of MCM-41 materials[1] usually includes a high temperature calcination step that in fact opens mesopores as well as resulting in structure shrinkage.[2] Functionalization with silanes is often employed to achieve materials with the desired surface properties for advanced adsorption and catalytic applications[3] and to increase their stability with respect to atmospheric humidity.[4] The main drawback of the conventional modification procedure[5] lies in the necessity for template removal prior to attachment of the ligands to the MCM-41 pore walls by either calcination (which leads to structure shrinkage) or solvent/HCl extraction. Another shortcoming of this conventional modification is the low bonding density of the resulting materials, especially when larger groups are attached. So far, only a few attempts at the modification of uncalcined MCM-41 materials have been reported.[6–8] The first two reports describe the modification of somewhat different materials, *i.e.* alkyltrimethylammonium–kanemite complexes[6] and MCM-48,[7] without providing clear information about the degree of surfactant removal and the structure of the bonded layer. Another report[8] deals with a stepwise post-synthesis silylation procedure, the first step of which was intended to modify only the external surface of MCM-41, whereas two additional subsequent steps were proposed to remove the template from the mesopores *via* HCl/ETOH extraction and to attach functional groups to their walls.

The current work shows that a one-step silylation of uncalcined MCM-41 materials leads not only to external surface modification, but also to the removal of the surfactant template from the mesopores and chemical modification of their walls. The proposed one-step treatment of uncalcined MCM-41 materials with trialkylchlorosilanes allows one to achieve several goals: (i) preparation of functionalized mesoporous materials with hydrophobic surfaces; (ii) removal of surfactant molecules from the mesopores; (iii) avoiding high temperature calcination or solvent extraction procedures; and (iv) avoiding structure shrinkage during the calcination process. Templating and charge balancing surfactant molecules, which interact with the silica surface *via* van der Waals and electrostatic forces, were replaced by more strongly (chemically) interacting groups, *e.g.* trialkylsilyl groups. The method reported here could be useful in the low temperature synthesis of catalytic materials and adsorbents with a high surface coverage of attached ligands (especially when larger silanes are used) and with a high degree of pore uniformity. The one-step procedure makes extraction or calcination of as-synthesized samples a redundant and superfluous step in the preparation of modified MCM materials.

The MCM-41 sample studied was prepared by a method involving post-synthesis hydrothermal restructuring.[9] Two unmodified samples were used: MCM-41U (uncalcined 'as prepared' mesoporous material) and MCM-41C (the same sample but calcined). Both samples were subjected to modification. The uncalcined material with template molecules inside the mesopores was functionalized in a one-step process that includes simultaneous trialkylsilanization and extraction of the template. Two modified samples were prepared: MCM-41UM and MCM-41UO, with attached trimethyl- and octyldimethylchlorosilyl groups, respectively. Calcined mesoporous material was modified with the trimethyl- and octyldimethyl-chlorosilanes using a conventional modification procedure,[10] and the resulting samples were designated as MCM-41CM and MCM-41CO, respectively.

In the proposed one-step modification procedure of uncalcined samples no additional pretreatment was performed. A typical synthesis (Scheme 1) included dispersion of the mesoporous material (about 0.2 g) in 10 ml of trialkylsilane, and refluxing the mixture for 36 h. Upon addition of *ca.* 5 ml of anhydrous pyridine to the mixture, it was refluxed for a further 18 h. After cooling, the modified mesoporous material was filtered off and washed several times with small portions of EtOH, EtOH–n-heptane and finally n-heptane to remove excess modifier and pyridine as well as possible products of hydrolysis. Finally, the modified mesoporous material was dried overnight in an oven at 95–100 °C under vacuum.



Scheme 1 *Reagents and conditions*: i, $ClSiMe_2CH_2R$ [R = H or $(CH_2)_6Me$], reflux, 36 h, then pyridine, reflux, 18 h.

Modification of the silica surface with alkylsilanes, *via* chemical bonding of alkylsilyl ligands to the surface, was proved by means of ^{13}C CP-MAS (chemical shifts in the interval between 0 and 40 ppm) and ^{29}Si NMR spectroscopy (decrease in the amount of Q^3 silanols with simultaneous increase of Q^4 siloxane sites at −99 and −108 ppm, and an additional signal at 12–15 ppm which corresponds to silane molecules attached to the surface in a monomeric fashion).[10] Elemental analysis showed the presence of bonded alkylsilyl groups (appropriate ratio C : H) and the successful removal of all surfactant molecules and pyridine (complete absence of nitrogen). The concentration of immobilized ligands is shown in Table 1. A much higher amount of attached octyldimethylsilyl

Table 1. Structural features of the 'parent' MCM-41 and materials functionalized with trialkylchlorosilanes

Sample	BET surface area/$m^2\ g^{-1}$	Mesopore volume/$cm^3\ g^{-1}$	Pore diameter (BJH)/nm	Amount of attached groups/mmol g^{-1} SiO_2
MCM-41U	~3	—	—	—
MCM-41C	915	1.06	5.65	—
MCM-41UM	540	0.69	5.25	2.81
MCM-41CM	570	0.65	4.95	2.76
MCM-41UO	385	0.38	4.20	2.83
MCM-41CO	395	0.39	4.10	2.15

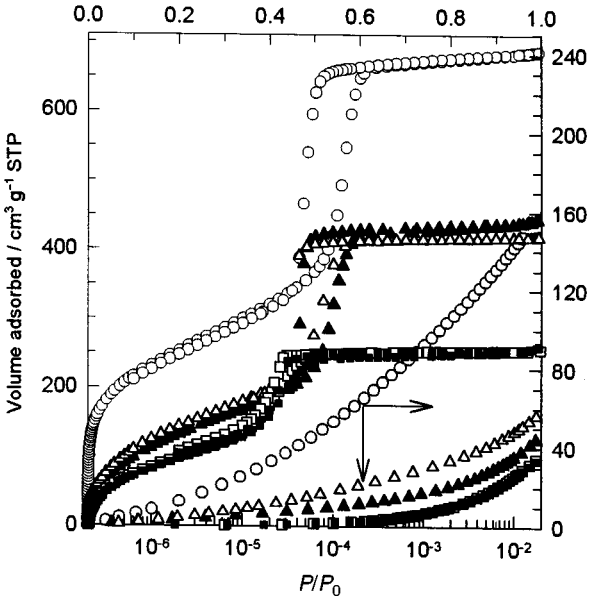


Fig. 1 Nitrogen adsorption isotherms and their low-pressure parts for (○) MCM-41C, (△) MCM-41CM, (▲) MCM-41UM, (□) MCM-41CO and (■) MCM-41UO.

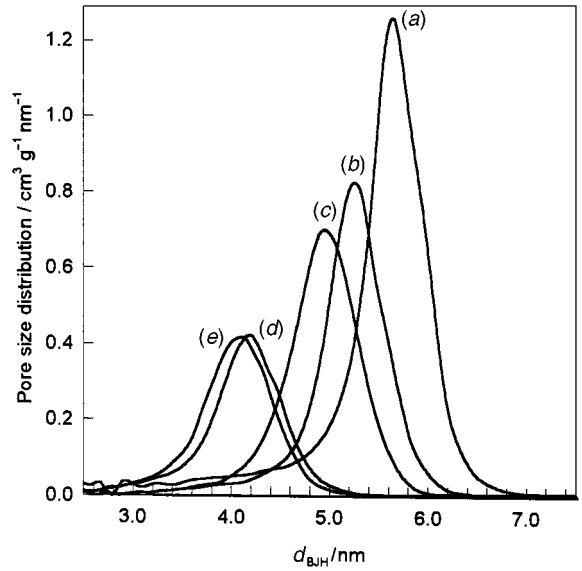


Fig. 2 Pore size distributions for (*a*) MCM-41C, (*b*) MCM-41UM, (*c*) MCM-41CM, (*d*) MCM-41UO and (*e*) MCM-41CO.

groups can be achieved in the one-step modification in comparison to the conventional procedure. The maximum number of attached groups in the one-step modification is probably limited by the size of the $SiMe_2CH_2R$ groups [where R = H or $(CH_2)_6Me$].

Adsorption studies showed opening of pores upon modification from completely filled (uncalcined as-prepared sample) to fully accessible pores of different diameter (modified samples). The pore diameter of the modified samples as well as the surface area and mesopore volume depend on the size of the attached ligands (see Table 1). Unmodified calcined sample MCM-41C has a very pronounced step in capillary condensation at $P/P_0 \sim 0.57$ (Fig. 1), which shifts gradually to lower pressure for modified samples. The size of the hysteresis loop decreases with increasing size of grafted ligands.

Thermogravimetric studies showed great similarity for the samples modified *via* the conventional and one-step procedures. A notable difference in the shape of the DTG curves for the samples with similar ligands is attributed to the presence of different conformations of the attached alkyl groups.[10] The pore diameters and pore size distributions for all samples were calculated from nitrogen adsorption data using the BJH method with the corrected form of the Kelvin equation (see Fig. 2).[11] The decrease in the pore size upon modification of the surface with trimethylchlorosilane is typically about 0.50 nm.[10,12] For the MCM-41CM and MCM-41UM samples there is a significant difference in the size of the mesopores, emphasizing the well-known effect of structure shrinkage upon calcination.[2] A similar tendency is observed for the MCM-41CO and MCM-41UO samples, but in this case the difference is smaller because of two competing factors: higher surface coverage (about 30%) and no shrinkage when uncalcined sample is used.

In conclusion, the MCM-41 mesoporous silicate can be functionalized *via* a one-step procedure using an uncalcined sample. Such a procedure greatly simplifies modification of MCM-41 and pore opening, and makes high temperature calcination or solvent extraction unnecessary. This has advantages such as higher surface coverage of grafted ligands and avoidance of the structure shrinkage. The current study shows that further investigation is needed to determine the detailed synthetic procedure required for selective polyfunctionalization of uncalcined MCM-41 or its complete modification with one reagent only.

We thank Dr A.Sayari for providing the MCM-41 sample. The donors of the Petroleum Research Fund administrated by the American Chemical Society are gratefully acknowledged for partial support of this research.

Notes and references

1 C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, *Nature*, 1992, **359**, 710.
2 C.-Y. Chen, H.-X. Li and M.E. Davis, *Microporous Mat.*, 1993, **2**, 17.
3 X. Feng, G. E. Fryxell, L.-Q. Wang, A. Y. Kim, J. Liu and K. M. Kemner, *Science*, 1997, **276**, 923.
4 T. Tatsumi, K. A. Koyano, Y. Tanaka and S. Nakata, *Stud. Surf. Sci. Catal.*, 1998, **117**, 143.
5 K. Moller and T. Bein, *Stud. Surf. Sci. Catal.*, 1998, **117**, 53.
6 T. Yanagisawa, T. Shimizu, K. Kuroda and C. Kato, *Bull. Chem. Soc. Jpn.*, 1990, **63**, 1535.
7 J. C. Vartuli, K. D. Schmitt, C. T. Kresge, W. J. Roth, M. E. Leonowicz, S. B. McCullen, S. D. Hellring, J. S. Beck, J. L. Schlenker, D. H. Olson and E. W. Sheppard, *Chem. Mater.*, 1994, **6**, 2317.
8 M. Park and S. Komarneni, *Microporous Mesoporous Mater.*, 1998, **25**, 75.
9 A. Sayari, P. Liu, M. Kruk and M. Jaroniec, *Chem. Mater.*, 1997, **9**, 2499.
10 V. Antochshuk and M. Jaroniec, *J. Phys. Chem. B*, 1999, **103**, 6252.
11 M. Kruk, M. Jaroniec and A. Sayari, *Langmuir*, 1997, **13**, 6267.
12 C. P. Jaroniec, M. Kruk, M. Jaroniec and A. Sayari, *J. Phys. Chem. B*, 1998, **102**, 5503.

Communication 9/05242I