Immobilisation of heteropoly anions in Si-MCM-41 channels by means of chemical bonding to aminosilane groups

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Heteropoly acids (HPA) have been immobilised inside the channels of Si-MCM-41 mesoporous molecular sieve by means of chemical bonding with amine groups introduced into the system during a previous aminosilylation procedure, which resulted in the strong anchoring of heteropoly anions and prevented the HPA leaching when applied as a catalyst in polar solvent media.

The encapsulation of heteropoly compounds of Keggin structure into the pores of a molecular sieve may provide an active, stable catalyst. However, the anchoring of HPA into MCM-41 walls occurs by means of the interaction of the HPA acidic protons with the silanol groups and results in the formation of only very weak bonds between HPA and MCM-41. As a consequence, leaching of heteropoly acid was always observed when the HPA/MCM-41 system was applied in polar solvent media.[1–3] Our earlier reports[3] and those of others[4] have shown that the generation of insoluble non-stoichiometric caesium or ammonium salts of HPA inside the channels of the support prevents leaching of active phase.

In the following study we utilised modification of the silica gel surface with aminoalkoxysilanes, as reported by Vansant and coworkers,[5–7] in order to incorporate functional groups inside the channels of the mesoporous molecular sieve which would be able to react with heteropoly acid and form strong bonds. According to the mechanism proposed by Vansant and Van der Voort,[6,7] aminosilane molecules, initially connected to the silica surface *via* the amine groups, turn to display an amine-upward position as a result of the so-called flip mechanism.[6,7] It seems probable that the exposed basic amine groups might react with heteropoly acids to form the salt $\equiv Si(CH_2)_3NH_3 \cdot HPA$, which will be linked strongly to the modified surface.

Two samples of MCM-41 molecular sieves of different pore size were synthesised using $C_{14}H_{29}(CH_3)_3NBr$ [merystyltrimethylammonium bromide (MTMABr)] and $C_{16}H_{31}(CH_3)_3NBr$ [cetyltrimethylammonium bromide (CTMABr)] as surfactants according to ref. 8. These samples are denoted MCM-41-A and MCM-41-B, respectively.

After template removal the calcined materials were treated with the aqueous solution of ammonium nitrate to remove the sodium cations remaining after the synthesis. The samples were calcined again at 400 °C under nitrogen. The aminosilylation procedure was performed with γ-aminopropyltriethoxysilane (APTS) according to the procedure given in ref. 5 with some minor modification. MCM–41 dehydrated at 400 °C was contacted with a refluxing toluene solution containing 1% APTS for 5 h. The resulting materials were filtered off, washed with toluene and the remaining solvent removed under vacuum, firstly at RT and then at 140 °C for 20 h. MCM-41 modified by aminosilylation is denoted as ASIL/MCM-41 (A or B). The modified samples (1 g) were treated with 60 mL of a refluxing methanol solution containing 5% $H_6PMo_9V_3O_{40}$ for 3 h. After this time the samples were allowed to cool and the solids subsequently filtered off and washed four times with methanol. Finally, the filtered samples were heated *in vacuo* at 100 °C to remove the remaining methanol. The two resulting samples, HPMoV/ASIL/MCM-41-A and HPMoV/ASIL/MCM-41-B contained 10 and 30 wt% of HPMoV, respectively, the amount of heteropoly acid immobilised in the MCM-41 channels being estimated from analysis of the remaining methanol solution. The presence of heteropoly anions in the modified systems was also monitored by FTIR spectra.

We also introduced heteropoly acid (HPMoV) into MCM-41-B (unmodified with aminotriethoxysilane) using exactly the same procedure as for the modified sample. MCM-41-B after impregnation with HPMoV from methanol solution (denoted HPMoV/MCM-41-B) showed distinctive yellow colour indicating the introduction of heteropoly acid into the molecular sieve. Washing the sample with methanol (four times) resulted, however, in decoloration of the sample indicating removal of the HPMoV. By contrast, the aminosilane modified matrix releases very few Keggin units even after extraction with boiling methanol. Only 0.8 wt% of HPA anchored in APTS modified MCM-41 was removed after 2 h extraction with boiling methanol, while 95 wt% of HPA was removed from the unmodified support when treated with methanol at RT.

XRD patterns of MCM-41-A and MCM-41-B indicated that mesoporous materials were obtained (Fig. 1, curve 1). The APTS modified sample (ASIL/MCM-41-B) showed an XRD pattern which was almost unchanged relative to the parent MCM–41 matrix (Fig. 1, curve 2), while the XRD pattern of ASIL/MCM-41-B modified with 30 wt% heteropoly acid showed almost no reflectance in the low angle region (Fig. 1, curve 3). The disappearance of XRD patterns characteristic of the MCM structure has already been observed as a result of introduction of a relatively high number of HPA anions into MCM-48 channels.[9,10] The removal of heteropoly compound from unmodified MCM-41-B upon rinsing with methanol restored the XRD patterns characteristic of the MCM-41 structure (Fig. 1, curve 4). Considering that the heteropoly anions introduced into APTS modified samples are firmly connected to the MCM-41 by chemical bonds, destruction of the amine group by relatively high temperature treatment (320 °C) and subsequent removal of the HPA by washing with polar solvents (methanol and water) was performed. Removal of heteropoly anions from the MCM-41-B matrix restored the XRD pattern which were very similar to that of the parent MCM-41 sample (Fig. 1, curve 5).

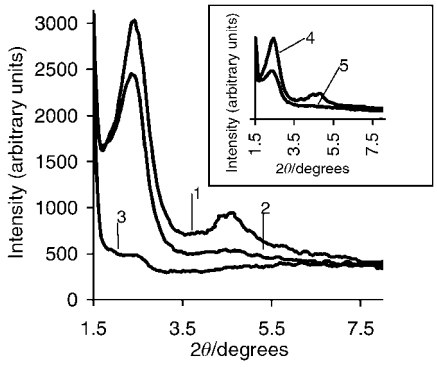

Fig. 1 XRD patterns of the MCM–41 samples before and after modification. 1, parent MCM–41; 2, ASIL/MCM-41 (aminosilylated MCM–41); 3, HPMoV/ASIL/MCM–41 (ASIL/MCM–41 modified with HPMoV); 4, HPMoV/MCM–41 (unmodified MCM–41 impregnated with HPMoV and subsequently rinsed with methanol); 5, HPMoV/ASIL/MVM–41 (after HPMoV removal).

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Table 1 Catalytic activity of MCM-41 modified with heteropoly acid for cyclohexane oxidation

Catalyst	Catalyst loading/mg	HPMoV content		Cyclohexane conversion (mol%)	TON
		mg	mmol of KU		
HPMoV(30)/ASIL/MCM-41-B (first run)	50	15	0.009	14.6	24.6
HPMoV(30)/ASIL/MCM-41-B (second run)	50	15	0.009	13.5	23
HPMoV(30)/ASIL/MCM-41-B (after previous treatment with oxidative mixture)	50	14.8	0.0087	13.5	24
HPMoV(10)/ASIL/MCM-41-A (first run)	50	5	0.003	13.0	68
Free HPMoV dissolved in the reaction mixture	5	5	0.003	15.0	78

BET surface areas and pore distributions were calculated using N_2 adsorption at 77 K (ASAP equipment, Micromeritics). Aminosilylation and introduction of heteropoly anions affect the surface area and pore distribution of the modified samples significantly [Fig. 2(a) and (b)]. The parent MCM-41 samples (A and B) show a maximum of pore diameter at 22 and 25 Å and surface areas of 1330 and 1000 $m^2\ g^{-1}$, respectively. Aminosilylation of the molecular sieves results in a shift of the pore maximum to lower diameters and a decrease of the pore volume and surface area (*ca.* 720 $m^2\ g^{-1}$). Introduction of heteropoly anions leads to a further decrease in surface area and in pore volume. Taking into consideration the pore diameter of the MCM-41 modified with APTS (Fig. 2), and the diameter of the Keggin unit (12 Å), monolayer coverage can be expected at an HPMoV loading of *ca.* of 30 wt% (only one Keggin unit may be located along the ASIL/MCM-41 channels). It is unlikely that an ideal distribution of the Keggin units inside the channels, will be obtained, so encapsulation of *ca.* 30 wt% of HPMoV into the ASIL/MCM-41 matrix may result in partial blocking of the pores and makes some of the Keggin units inaccessible to reagents which should also affect the catalytic activity of the modified samples. The catalytic activity of heteropoly anions (HPMoV) anchored in the ASIL/MCM-41 channels (10 and 30 wt%) as well as of free HPMoV heteropoly acid was examined for cyclohexane oxidation reaction in the liquid phase (Table 1). 12–Molybdophosphoric acid modified with vanadium has been reported to be an active catalyst for liquid-phase oxidation of different organic and inorganic substrates with H_2O_2 or organic peroxides as oxidants.[11] The oxidation reaction was carried out in the liquid phase (sealed vials, 90 °C, 20 h, no stirring, 50 mg of ASIL/MCM-41 modified with HPMoV or 5 mg of free HPMoV) using *tert*-butyl hydroperoxide (TBHP) and acetonitrile as oxidant and solvent, respectively. A negligible cyclohexane conversion was observed in the presence of unmodified ASIL/MCM-41. Comparing the activity of samples containing different amounts of HPMoV, the TON (mol of reacted cyclohexane per KU) was calculated (Table 1). The results presented in Table 1 indicate that the heteropoly anions occupying the pores in ASIL/MCM-41-A (50 mg of sample, 10 wt% of HPMoV) show almost the same activity (TON) as 5 mg of free heteropoly acid dissolved in the reaction medium. This suggests that the distribution of the Keggin units in the HPMoV(10)/ASIL/MCM-41 is very close to monomolecular coverage and almost every heteropoly anion is accessible to the reagents. When the concentration of the Keggin units in the mesoporous material was increased to 30 wt%, the activity for cyclohexane oxidation (expressed as TON), decreased, which shows that a proportion of the heteropoly anions introduced may not be accessible to the reagents because of the pores being blocked.

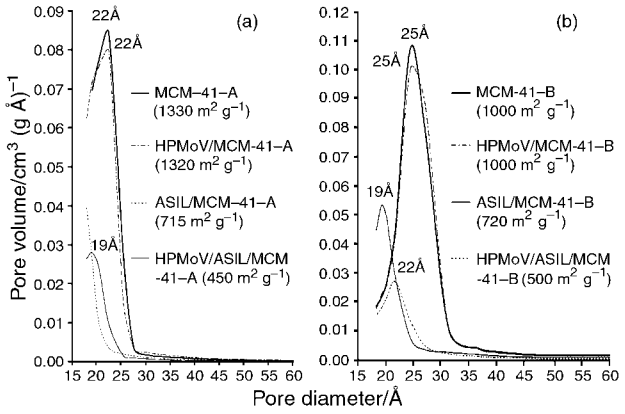

Fig. 2 Pore size distribution of the MCM–41 samples synthesised with MTMABr (a) and CTMABr (b) as surfactants before and after modification.

To investigate the stability of HPMoV/ASIL/MCM-41 system towards a powerful oxidant such as TBHP, two additional experiments have been carried out. The spent catalyst containing 30 wt% HPMoV (after cyclohexane oxidation process) was carefully separated from the products and reused for cyclohexane oxidation (second run, Table 1). The decrease in oxidative activity was insignificant. To check the effect of possible removal of HPMoV from the catalytic system as a result of potential oxidative degradation of aminopropyl groups, a fresh HPMoV(30)/ASIL/MCM-41 sample was treated with a mixture of TBHP and acetonitrile under exactly the same conditions as the oxidation process (90 °C, 20 h). The liquid phase was carefully separated and analysed for the presence of molybdenum. The remaining solid was treated again with the mixture of acetonitrile and TBHP under the same conditions with subsequent analysis for molybdenum. It was assumed that if partial decomposition of aminopropyl groups took place as a result of possible oxidation with TBHP it should result in some release of HPMoV. The first treatment resulted in the removal of 1.5 wt% HPMoV (anchored to ASIL/MCM-41) while the second treatment released an additional 0.8 wt% (ICP–AEC). These results indicate that 98 wt% of anchored HPMoV still remains in the HPA/ASIL/MCM-41 system and the leaching of HPA from this system is negligible even under drastic conditions. The HPA(30)/ASIL/MCM-41 sample was also used after the first treatment with a mixture of acetonitrile and TBHP as catalyst for cyclohexane oxidation. The decrease of oxidative activity was negligible.

Notes and references

1 M. J. Verhoef, P. J. Kooyman, J. A. Peters and H. van Bekkum, *Microporous Mesoporous Mater.*, 1999, **27**, 365.
2 B. L. C. Passoni, F. J. Luna, M. Wallau, R. Buffon and U. Schuchardt, *J. Mol. Catal.*, 1998, **134**, 229.
3 K. Nowińska and W. Kaleta, *Appl. Catal. A: Gen.*, 2000, **203**, 91.
4 Á. Molnár, T. Beregszászi, Á. Fudala, B. Török, M. Rózsa-Tarjáni and I. Kiricsi, *Proceedings of The Royal Society of Chemistry, Third International Symposium on Supported Reagents and Catalysts in Chemistry*, Limerick, RSC, Cambridge, 1998, p. 25.
5 K. C. Vrancken, P. Van Der Voort, K. Possemier and E. F. Vansant, *J. Colloid Interface Sci.*, 1995, **174**, 86.
6 P. Van Der Voort and E. F. Vansant, *J. Liq. Chromatogr. Rel. Technol.*, 1996, **19**, 2723.
7 P. Van Der Voort and E. F. Vansant, *Pol. J. Chem.*, 1997, **71**, 550.
8 W. A. Carvalho, P. B. Varaldo, M. Wallan and U. Schurchardt, *Zeolites*, 1997, **18**, 408.
9 I. V. Kozhevnikov, A. Sinnema, R. J. J. Jansen, K. Pamin and H. van Bekkum, *Catal. Lett.*, 1995, **30**, 241.
10 A. Ghanbari-Siahkali, A. Philippou, J. Dwyer and M. W. Andreas, *Appl. Catal.*, 2000, **192**, 57.
11 R. Neumann and M. Cohen, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1738.