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Thermal, hydrothermal and acid-base stability of highly siliceous MCM-41 mesoporous material

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Abstract. Influence of various thermal, hydrothermal and acid/base treatments on the structural stability of highly siliceous MCM-41 mesoporous material has been thoroughly investigated. It has good stability towards thermal treatment up to 650°C, hydrothermal treatment at low temperatures ($\leqslant$ 400°C), and concentrations of steam ($\leqslant$ 40 mol%), mechanical grinding and acid treatment (for 1 M HCl) but poor stability towards hydrothermal treatment with liquid water (even at 150°C) and base treatment, if it is dissolved in 0·1 M NaOH.

Keywords. Siliceous MCM-41; mesoporous zeolite; thermal and hydrothermal stability; acid–base stability.

1. Introduction

Recently, a new family of mesoporous crystalline materials, designated as M41S, has been discovered by Mobil, USA (Kresge *et al* 1992). MCM-41 is a member of this family and it possesses hexagonal arrays of uniform mesoporous channels varying in diameter from 15–100°A. It has large surface area ($> 800\,m^2\,g^{-1}$) and sorption capacity for hydrocarbons. It can be synthesised in both its high silica and high alumina forms (Schmidt *et al* 1994; Borade and Clearfield 1995). Structural Al in aluminosilicate MCM-41 is unstable even to mild thermochemical treatment (Luan *et al* 1995). The high silica form of MCM-41 has high potential for practical use as an adsorbent, a catalyst and/or a mesoporous support for depositing active catalyst components, particularly useful in the synthesis of fine chemicals involving bulky molecules (Maschmeyer *et al* 1995). From the point of view of its use, particularly for the regeneration of adsorbent or catalyst and the deposition of active catalyst component on the mesoporous MCM-41, a knowledge of the influence of various thermal, hydrothermal and acid-base treatments on its structural stability is of great practical interest.

The present investigation was therefore undertaken with the goal of studying in detail the effect of thermal, hydrothermal and acid-base treatments on structural stability of highly siliceous MCM-41 material.

2. Experimental

Highly siliceous MCM-41 was synthesised as per the procedure given by Beck *et al* (1992). The molar composition of the gel used in the hydrothermal synthesis was:

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1·0 SiO_2. 0·64 Na_2O. 0·49 $C_nH_{2n+1}(CH_3)_3N$. Br($n = 12$). 52 H_2O. The gel was heated at 100°C for 144 h in a teflon-lined autoclave under autogeneous pressure. The resulting solid material was filtered, washed thoroughly with deionized distilled water and dried in an air oven (at 110°C for 2 h). The dried material was calcined at 540°C for 6 h in static air. The MCM-41 structure (Kresge *et al* 1992; Maschmeyer *et al* 1995) of the material was confirmed by XRD. The surface area of the material (measured by the Surface Area Analyser, Quantachrome, USA) is 1326 $m^2 g^{-1}$.

For studying the influence of various thermal, hydrothermal, acid and base treatments on the structural stability of the siliceous MCM-41, it was subjected to the following treatment.

Thermal: It was calcined in static air at different temperatures (550°–950°C) for 6 h.
Hydrothermal: It was treated with steam at different concentrations (5–80 mol%) and temperatures (200°–650°C) for 4 h by passing a mixture of steam and N_2 (space velocity $\cong$ 5000 h^{-1}) over it in a quartz reactor. It was also treated with liquid water at 150°C under autogeneous pressure for 6 h in a stainless steel bomb and after the treatment it was filtered, dried and calcined at 540°C for 4 h.
Acid/base: MCM-41 (0·5 g) was treated with aqueous HCl and NaOH solutions (500 ml) of different concentrations (0·001 – 1·0 M) for 6 h. After the acid–base treatment, the samples were washed thoroughly with distilled water, dried and calcined at 540°C for 4 h.

For studying the effect of grinding on the structural stability, MCM-41 material was ground in a granite mortar for about 30 min.

The structural stability of MCM-41 was determined in terms of its nitrogen sorption capacity, measured by N_2-sorption from a 30 mol% N_2/He mixture at liquid nitrogen temperature (−195°C) by a dynamic N_2-adsorption/desorption method, using the Quantachrome (USA) Surface Area Analyser.

3. Results and discussion

Figure 1 shows the influence of thermal and hydrothermal treatments on the structural stability of MCM-41 and the results showing the effects of the acid and base treatments on the stability are presented in table 1.

The results in figure 1a indicate that the gradual structural collapse of MCM-41 occurs only above the calcination temperature of 650°C. On thermal treatment up to 750°C, the structural collapse is quite small but is very pronounced above 750°C. The structure collapses almost completely above 950°C.

It is interesting to note from figure 1 (**a** and **b**) that although there is an increase in the structural collapse with increasing temperature both in hydrothermal treatment and concentration of steam, the structural collapse in both cases is quite small. It is appreciable only at severe hydrothermal treatment conditions (i.e. at high concentration of steam and temperature). These observations clearly show that siliceous MCM-41 has very good hydrothermal stability towards steam treatment, particularly when treated with steam at mild conditions (viz. at or below the steam concentration of 40 mol% and temperature of 400°C).

When MCM-41 was treated with liquid water at 150°C under autogeneous pressure, its N_2-sorption capacity decreased drastically from 17·9 mmol g^{-1} to 3·9 mmol g^{-1} and there was also a 10% wt. loss in the solid due to its dissolution. Thus, water

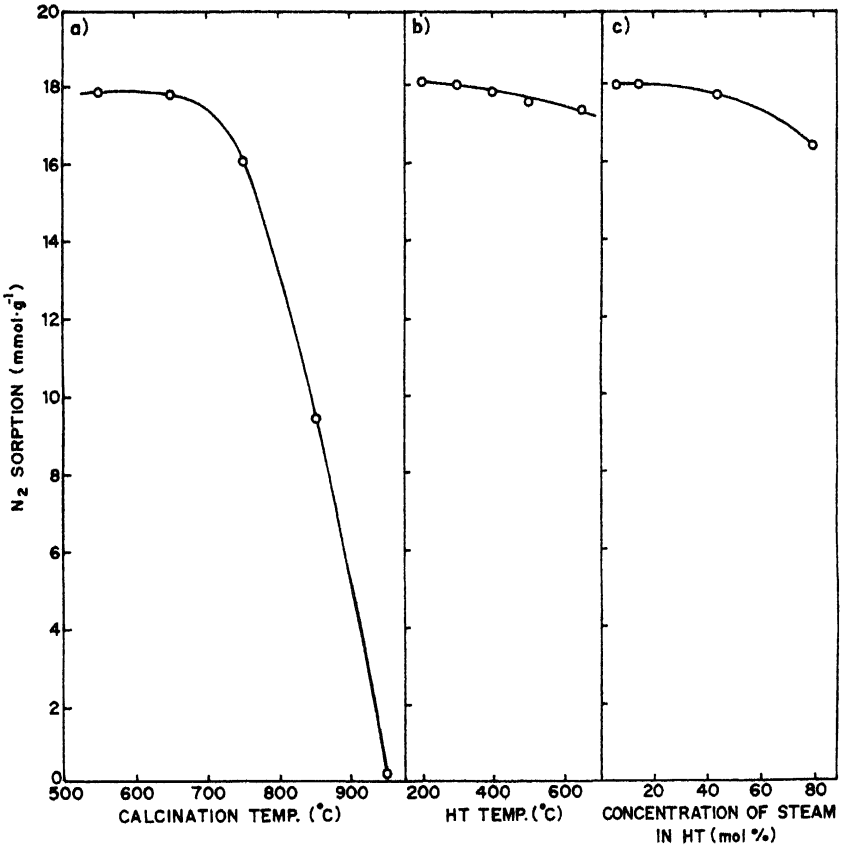

Figure 1. Influence of (**a**) calcination temperature, (**b**) hydrothermal treatment (HT) temperature (concentration of steam = 45 mol%), and (**c**) concentration of steam in hydrothermal treatment at 400°C on N_2-sorption capacity of MCM-41.

Table 1. Influence of acid and base treatments on the stability of high silica MCM-41.

Conc. of acid/base	Treatment temp. (°C)	*p*H		Dissolution (wt%)	N_2-sorption (mmol g^{-1})
		Initial	Final		
Acid treatment					
1·0 M HCl	27	0·52	0·54	9·5	17·24
0·1 M HCl	27	1·12	1·18	9·2	18·02
0·01 M HCl	27	2·24	2·34	8·9	22·43
0·1 M HCl	80	1·12	1·15	14·8	16·35
Base treatment					
0·001 M NaOH	27	8·53	7·79	12·2	14·15
0·01 M NaOH	27	11·44	8·93	19·9	2·02
0·1 M NaOH	27	13·53	13·50	100*	—
(without treatment)		—	—	—	17·95

*Dissolved completely

treatment causes the structural collapse of MCM-41 to a very large extent, with partial dissolution of the solid material. This is expected to be mostly due to the hydrolysis of the thin wall formed by silica layers between two cylinderical mesoporous channels of MCM-41 (Coustel *et al* 1994).

The grinding of MCM-41 (in a granite mortar for about 30 min), has shown no significant effect on its N_2-sorption capacity, indicating no effect of the grinding or crushing on its structural stability.

Because of the acid treatment (table 1) there is appreciable weight loss, indicating partial dissolution of MCM-41, the dissolution is higher at the higher temperature (80°C). However, the change in N_2-sorption capacity of MCM-41 due to acid treatment, particularly at room temperature (27°C), is very small. For the 0·1 M HCl treatment, there is a small decrease in the N_2-sorption capacity. The 0·1 M HCl treatment (at room temperature) has no significant effect on the N_2-sorption capacity. Interestingly, treatment with 0·01 M HCl results in MCM-41 with higher N_2-sorption capacity, most probably due to the dissolution of amorphous material from the MCM-41. These observations indicate that acid treatment, particularly at low concentrations ($< 0{\cdot}1$ M) and at room temperature, has little or no effect on the structure of MCM-41, except on its partial dissolution to some extent.

When MCM-41 is treated with aqueous NaOH (0·001 to 0·1 M) at room temperature (table 1), its dissolution increases markedly and its N_2-sorption capacity decreases sharply with increase in base concentration. When treated with 0·1 M NaOH, MCM-41 completely dissolves. The results clearly show that the stability of the MCM-41 towards base treatment, even at low concentrations of base, as low as 0·001 M NaOH, is very poor. The structural breakdown and dissolution of the MCM-41 is caused by the rapid hydrolysis of its thin walls because of the presence of hydroxyl ions at high concentrations.

From this investigation, the following important conclusions on the thermal, hydrothermal, acid and base stability of highly siliceous MCM-41 can be drawn.

4. Conclusions

(i) MCM-41 is thermally stable up to 650°C. Above this temperature its structure collapses gradually but only to a small extent up to 750°C, above which there is drastic structural collapse.

(ii) It has very good stability towards steam treatment at low concentration ($\leqslant 40$ mol%) and temperature ($\leqslant 400$°C) but very poor stability to liquid water treatment at 150°C under autogeneous pressure.

(iii) It is very stable to mechanical grinding/crushing.

(iv) Although it dissolves in aqueous HCl to an appreciable extent, it is structurally stable to acid treatment (at room temperature) even at acid concentrations as high as 1 M HCl.

(v) It has, however, very poor structural stability towards base treatment. Even at room temperature it completely dissolves in aqueous 0·1 M NaOH and collapses structurally with partial dissolution at low base concentrations.

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