Chinese Chemical Letters Vol. 15, No. 6, pp 737-740, 2004
http://www.imm.ac.cn/journal/ccl.html

Large Pore Mesoporous MCM-41 Templated from Cetyltriethylammonium Bromide

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Abstract: Following hydrothermal synthesis process, MCM-41 was synthesized by using cetyltriethylammonium bromide as templating agent. The experimental results showed that MCM-41 with pore diameter in the range of 4-7 nm can be obtained by adjusting $n_{Surf.}/n_{Si}$. It was proved that cetyltriethylammonium bromide is an effective templating agent for increasing pore diameter of molecular sieve MCM-41.

Keywords: Mesoporous molecular sieve MCM-41, synthesis, new template.

Since 1992, highly ordered mesoporous materials MCM (Mobil Crystalline Materials)[1~2], in particular hexagonal MCM-41，have opened a wide field of potential applications in catalysis and separation process. The synthetic ways of MCM-41 with larger pore diameter were as follows: use of nonionic surfactant[3] such as polyoxyethylene tridecylethers ($C_{13}EO_m$,m=6, 12 and 18) as templating agent to synthesize mesoporous materials with pore diameter in the range of 4-7 nm ; or use of surfactants of different chain lengths[1], or swelling of the surfactant micelles by organic additives, such as amines[4], 1,3,5-trimethylbenzene[1] or alkanes[5], but control of the amount of additives is difficult.

In the present work, we use cetyltriethylammonium bromide as templating agent for the synthesis of mesoporous MCM-41 with large pore diameter and tailored pore size without any auxiliary additive. The structures of products were characterized by XRD, FT-IR, N_2 adsorption-desorption analysis.

Experimental

n-Hexadecylbromide, triethylamine and acetone are analytical reagent for the pareparation of templating agent. Sodium hydroxide (NaOH) and silicasol (SiO_2, 6.05mol/L) were used as source of alkali and source of silicon respectively.

Cetyltriethylammonium bromide (CTEAB) was synthesized by reacting *n*-hexadecylbromide with triethylamine in acetone at 373K for 3 days, purified twice *via* dissolution in chloroform and subsequent recrystallization by addition of ethyl acetate.

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Then CTEAB had been used as templating agent for the synthesis of MCM-41 by hydrothermal synthesis at 373K. MCM-41 can be attained with the following gel compositions (by mol): 2 Na_2O ∶ 10 SiO_2 ∶ (0.4~6.0) CTEAB ∶ 400 H_2O.

The solid products were filtered, washed well and dried at 353K, calcined in air at 573 K for 3 h , 673 K for 3 h , 823 K for 6 h.

Nitrogen adsorption-desorption isotherms were obtained with a Micromeritics ASAP 2010 sorptometer at 77 K. The surface area was determined from nitrogen adsorption isotherm by the BET method and determination of the pore size distribution from adsorption branch by the BJH method.

Powder-XRD patterns were measured with Rigaku D/max 2500 X-ray powder diffractometer(Cu K α_1) with Bragge-Brentano geometry over a 2θ range from 1 to 8°.

The framework vibration of the calicned samples were obtained on a Digilab FT-IR (FTS-25P) spectrophotometer using KBr pellets at room temperature.

Results and Discussion

The effect of surfactant/silica molar ratio, heating time and the amount of alkalinity on the synthesized sample had been investigated. The pore structure properties of some selected samples were listed in **Table 1** , the MCM-41 with pore diameter in the range of 4~7 nm can be obtained by adjusting the $n_{Surf.}/n_{Si}$. The amount of alkalinity and crystalline time have important impacts on the MCM-41 pore structure properties.

Table 1 The pore structure properties of samples obtained from different synthesis parameters

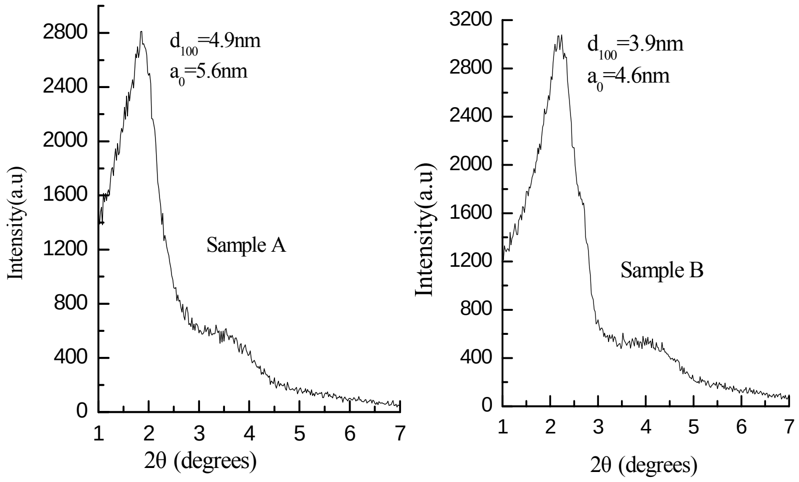
No.	$n_{Surf.}/n_{Si}$	n_{Na2O}/n_{SiO2}	time (days)	S_{BET} (m^2/g)	V_p (cm^3/g)	D_p(nm)^A
1	0.04	0.2	5	871	0.89	4.07
2	0.13	0.2	5	1018	1.12	4.40
3	0.25	0.2	5	902	1.25	5.55
4	0.4	0.2	5	714	1.18	6.64
5	0.13	0.1	5	680	0.78	4.60
6	0.13	0.2	1	733	0.94	5.15

A ∶ Average pore diameter (4V/A By BET)

In order to investigate the effects of the hydrophilic group size of quaternary ammonium surfactants on the pore size, under the same synthesis condition, another MCM-41 was synthesized by using cetyltrimethylammonium bromide (CTAB) as structure directing agent . the two samples were compared and analyzed by XRD, N_2 adsorption-desorption and IR.

X-ray diffraction (XRD) patterns (**Figure 1**) of sample A and B are dominated by one sharp or relatively broad peak in the range 2θ=1~5˚ and reflect the hexagonal symmetry of mesoporous molecular sieves. The value of d_{100} and cell parameters a_0 ($a_0=2d_{100}/(3)^{1/2}$) are obviously larger for CTEAB (Sample A) than for CTAB (Sample B). The larger cell parameters maybe partially result from that CTEAB in aqueous solution form larger micell than CTAB, consequently, after calcination, the obtained MCM-41 has large cell parameter.

Figure 1 XRD patterns of samples (A, B) prepared with different templating agent (A, CTEAB ; B , CTAB)



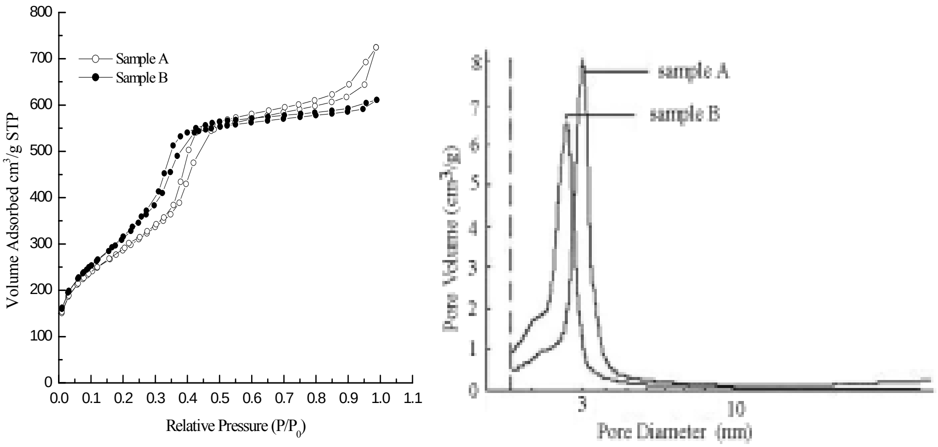
In addition, the infrared vibration bands of sample A (1435, 1084, 957, 802 and 465 cm^{-1}) are close to those of sample B (1400, 1086, 953, 802 and 465 cm^{-1}). The two samples exhibited bands at 957 and 953 cm^{-1} respectively, characteristic of mesoporous MCM-41, which could be assigned to the stretching vibration of Si-O^- groups[6]. The result shows that the internal local structures of both hexagonal silica frameworks are almost identical. Thus, the infrared spectra and XRD spectra can provide better characterization of MCM-41 mesoporous materials.

Figure 2 depicts the nitrogen adsorption-desorption isotherms and the pore size distribution of samples (A, B). Ⅳ type nitrogen isotherm, characteristic of mesoporous compounds, is observed in both two samples. The relative pressure, at which the capillary condensation occurs, increases from 0.32 to 0.39, where the P/P_0 position of inflection point is related to the pore diameter. This indicates that the MCM-41 obtained with CTEAB as template have larger pore diameter than those with CTAB. The suggestion is supported by the pore size distribution in **Figure 2**. The data listed in **Table 2** also indicated that the sample templating CTEAB have larger diameter and pore volume. The above results indicate that increased the hydrophilic group size of cationic alkylammonium surfactant can attain large pore mesoporous molecular sieves MCM-41.

Table 2 Effects of surfactant on the pore structure properties of the synthesized samples

Sample	surfactant	$n_{Surf.}/n_{Si}$	$S_{BET}(m^2/g)$	$V_p(cm^3/g)$	D_p(nm)		
					BET	BJH adsorption	BJH desorption
A	CTEAB	0.2	958.6	1.14	4.72	3.93	3.61
B	CTAB	0.2	1079.6	0.95	3.50	2.73	2.59

Figure 2 Nitrogen adsorption-desorption isotherms and pore size distribution of samples (A,B)



Conclusion

Under hydrothermal synthesis condition, mesoporous molecular sieves MCM-41 were successfully synthesized using cetyltriethylammonium bromide as templating agent. The product has large pore diameter (>4 nm) and narrow pore size distribution. The experimental results showed that MCM-41 with pore diameter in the range of 4-7 nm can be obtained by adjusting $n_{Surf.}/n_{Si}$. It was proved that cetyltriethylammonium bromide is an effective templating agent for increasing mesoporous molecular sieve MCM-41 pore diameter.

Acknowledgments

The authors greatly acknowledge the financial support of the National Natural Science Foundation of China (20233010) .

References

1. J. S. Beck, J. C. Vartuli, W. J. Roth, *et al.*, *J.Am.Chem.Soc.*, **1992,** *114*, 10834.
2. C. T Kresge, M. E. Leonowicz, W. J. Roth, *et al.*, *Nature*, **1992,** *359*,710.
3. J. L .Blin, A.Becue, B.Pauwels, *et al.*, *Microporous and Mesoporous Materials*, **2001,** *44*, 41.
4. A. H. Sayari, Y. Yang, *J.Phys.Chem.B*, **1999,** *103*, 3651.
5. J .L. Blin, B .L. Su, *Langmuir*, **2002**,*18* (13),5303.
6. M. A. Camblor, M.Constantini, A. Corma, *et al.*, *J.Chem.Soc.,Chem. Commun.*, **1996**,1339.

Received 20 May, 2003