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Synthesis of Thermally Stable MCM-41 at Ambient Temperature

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A new process to synthesize thermally stable mesoporous molecular sieves of MCM-41 structure based on delayed neutralization at ambient temperature was investigated. All samples synthesized by this new method have BET surface areas of about 1100 m^2/g and possess high thermal stability up to 900 °C. Higher crystallinity and less lattice constriction after calcination were observed for samples with a longer aging period. Those samples with aging time longer than 10 days exhibited four characteristic XRD peaks of MCM-41 both before and after calcination at 560 °C. The N_2 adsorption-desorption isotherms of the calcined samples showed larger average pore size and more homogenous pore size distribution. The method was also successfully applied to the synthesis of MCM-41 with different surfactants of hydrocarbon length with 10-18 carbons and proves to be a simple route for obtaining thermally stable MCM-41 at room temperature.

The discovery of a new family of mesoporous molecular sieves M41S was recently reported by researchers at Mobil.[1,2] One form of this series, MCM-41, which possesses a uniform arrangement of hexagonally shaped mesopores of diameter varying from 1.5 to 10.0 nm, has received great attention in material science and catalysis. Previous reports showed that MCM-41 molecular sieve of hydrothermal, thermal and mechanical stability could only be obtained from hydrothermal reaction.[3-5] Although Stucky et al.[6] and Edler et al.[7] tried to synthesize MCM-41 at ambient temperature, their results revealed that the products were either not thermally stable[6] or the structures did not show the character of MCM-41.[7] We report in this paper a simple method to prepare thermally stable MCM-41 at ambient temperature.

To prepare pure silica MCM-41 materials, 6.08 g of C_{16}TMAB (Cetyltrimethylammonium bromide, 99%, Merck) was dissolved in 45.0 g H_2O to form a clear solution. The solution was mixed with 8.80 g of sodium silicate (14 wt % NaOH, 27 wt % SiO_2, Aldrich) and stirred for 10 min. Then, an 1.0 M H_2SO_4 (Merck) solution was added and the pH value of the slurry was adjusted to about 10, followed by stirring for 30 min. The resulting gel was tightly sealed and kept sitting statically at ambient temperature for up to 30 days. The solid products recovered by filtration were washed with deionized water to a pH value lower than 8 and dried at ambient condition. The as-synthesized material was calcined in air at 560 °C for 6 hours (heated from room temperature at a rate of 1.5 °C/min) to remove the organic species occluded in the pores of MCM-41. The other MCM-41 samples obtained from surfactants with different carbon chain length of 8 to 18 were prepared by the above process and allowed to sit statically at room temperature for 10 days.

Fig. 1 shows the x-ray diffraction (XRD) patterns of products synthesized at ambient temperature with aging time that varied from 0 to 30 days before and after calcination. No amorphous silica powder was formed, since the baselines of Fig. 1 are flat up to $2\theta = 30$ degrees. Notice that right after the complete addition of the acid, a well-defined XRD pattern with a characteristic MCM-41 structure was obtained. These results suggest that the hexagonal phase was probably formed during the gel formation. Moreover, no lamellar phase was detected in the synthesized gel at any time, in contrast to results observed by Monnier et al.[8]

As the aging time increases, the XRD peaks of the as-synthesized material become sharper and more distinct. Four characteristic peaks of MCM-41 at $2\theta = 2.25$, 3.88, 4.43, and 5.84° were detected in the samples with aging time greater than 10 days. However, calcination caused some lattice constriction. It was found that less aged products became less crystalline and the d-spacings of their structure shrank more after calcination. For unaged samples, the strong diffraction peak at 3.9 nm shrank to 3.3 nm. Whereas, for the samples with aging time greater than 10 days the lattice constriction was about 0.3 nm, which is less than that observed by other methods.[7,9] These results reveal that the condensation of silica walls was almost complete and stable MCM-41 structure was formed after 10 days of aging. It was also found that the characteristic XRD patterns of the samples prepared with different aging times remain unchanged under prolonged heating at 900 °C for six hours. Comparing with the d-spacings of the samples calcined at 550 °C, there are only about 0.3 nm shrinkage of the low 2θ peaks after heating at 900 °C. These results indicate that these samples synthesized at ambient temperature have high thermal stability.

Typical N_2 adsorption-desorption isotherms of the calcined samples are shown in Fig. 2. The hysteresis loop at $p/p_0 > 0.5$ is probably due to packing defects in the sample. The steep increases in adsorption at p/p_0 of about 0.3 can be attributed to the filling of framework-confined mesopores.[10,11] It is also noticed that the isotherm for the sample that has been aged for 10 days is steeper in this region than that aged for one day. From the Kelvin equation, the former has a narrower pore size distribution (width at half maximum of about 0.24 nm) than the latter (width at half maximum of about 0.34 nm). Moreover, larger average pore size was obtained for the former (2.45 nm) than the latter (2.36 nm). These results can be explained by the fact that longer aging time leads to more silicate condensation and thicker wall.[12,13] The resultant samples have higher thermal stability, higher resistance to lattice constriction during calcination and more homogeneous distribution of pore size than previously reported samples. All samples synthesized by this method have BET surface areas around 1100 m^2/g.

The reported synthetic method has two advantages compared with those reported in the literature. One is that a lower pH value of the synthetic gel can be achieved by the addition of acid in the final step instead of acidification of silicate in advance. With a lower pH, more silicate condenses and crystallizes to form MCM-41 zeolite of a thicker wall and a higher thermal stability. Secondly, this method avoids the problem of mixing a highly-concentrated surfactant solution with a sticky acidified silicate, which may contain amorphous silica particles to give a broad x-ray diffraction pattern between 2θ = 20 to 30 degrees.

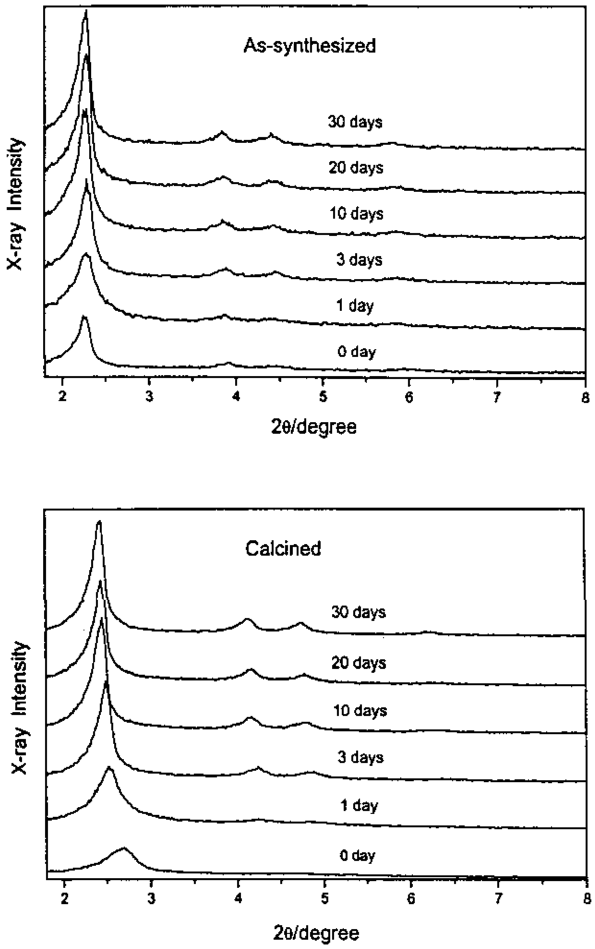

Fig. 1. XRD patterns of the solids synthesized at ambient temperature for various aging time before and after calcination at 560 °C for 6 h.

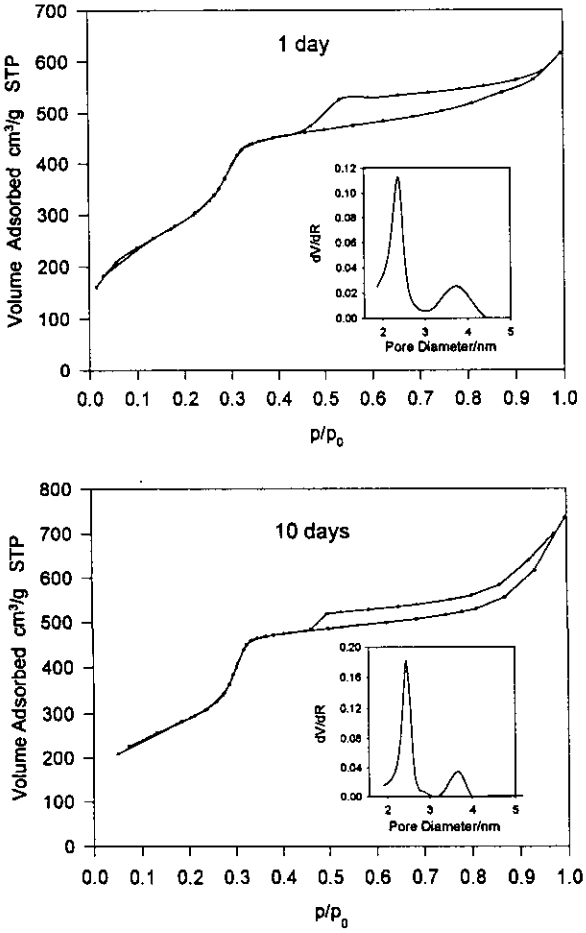

Fig. 2. N_2 adsorption-desorption isotherms for the solids prepared at ambient temperature for 1 and 10 aging-day. Before measurement, each sample was heated at 300 °C and 10^{-3} torr for 4 h.

Table 1. The Physical Properties of the MCM-41 Materials Prepared from Surfactants with Different Carbon Chain Length at Ambient Temperature and 10 Day Aging

Surfactant	d_{100}/nm as-syn.	d_{100}/nm calcined	BET surface area /m^2g^{-1}	pore diameter /nm
C_{18}TMACl	4.01	3.65	1180	2.63
C_{16}TMACl	3.71	3.38	1064	2.36
C_{14}TMAB	3.50	3.10	1126	2.08
C_{12}TMAB	3.20	2.85	1120	1.86
C_{10}TMAB	2.95	2.62	1132	1.65
C_8TMAB	2.63	2.30	1042	1.32

In addition to the synthesis of pure-silica MCM-41 with C_{16}TMAB at ambient temperature, we have also applied the method successfully in synthesis of pure silica MCM-41 with different surfactants of hydrocarbon lengths of 10 to 18 carbons (Table 1) as well as synthesis of aluminosilicate MCM-41 with C_{16}TMAB. Table 1 shows that for the MCM-41 material thus prepared, their d_{100} value and their pore diameter increase with the length of the surfactant carbon chain, as is generally observed on samples prepared by hydrothermal method. But we note that room temperature synthesis generally gives products with smaller d-spacing (about 0.5 to 0.6 nm differences) and pore diameter as compared to those of hydrothermal synthesis.[14] All these samples have a BET surface area greater than 1000 m^2g^{-1} and have well-defined XRD patterns of characteristic MCM-41 before and after calcination. Moreover, the lattice shrinkage is only about 0.35 nm, which is similar to that of the C_{16}TMAB-silicate system. These samples are also stable up to a calcination temperature of 900 °C.

The crucial factor leading to the successful synthesis of MCM-41 at room temperature is the delayed neutralization step. We started the synthesis at very high pH value using sodium silicate as the silica source. Only after the hexagonal structure of MCM-41 was formed by assembly did we add acid to initiate the condensation of silicate. That is, the strategy is to separate the self-assembly of surfactant/silicate and the wall- thickening as two consecutive steps. In the beginning, silicate exists as monomer or oligomers in the solution which is effective in forming liquid crystal assemblies. Condensation is allowed only after self-assembly is complete. This avoids the formation of amorphous silica and permits formation of more stable MCM-41 structures. In fact, this method can be further refined and used to synthesize more delicate hierarchical structures as we have reported recently.[15]

In conclusion, the results presented here demonstrate that by lowering the pH value of the synthesizing condition, a larger wall thickness of the MCM-41 product could be produced. The method offers an easy way to prepare thermally stable MCM-41 zeolites at ambient temperature.

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Key Words

MCM-41; Delayed neutralization; Mesoporous materials.

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