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SYNTHESIS OF MICROPORE/MESOPORE COMPOSITE MATERIALS

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Abstract

The objective of this study was to synthesize micropore-mesopore composite materials by two-step crystallization. The colloidal MFI was first synthesized using a structure-directing agent tetrapropylammonium hydroxide as a template in the first step. This colloid was then self-assembled to form mesoporous structure by using cetyltrimethylammonium bromide as a surfactant. These materials were characterized by powder X-ray diffraction, nitrogen sorption, SEM and TEM. Due to the thick walls produced, it cannot sustain the local strain caused by the crystallization: the mesostructure is collapsed upon heating. The mixed phases of MFI and MCM-41 were obtained by optimizing the synthesis times and reaction temperatures.

Keywords: MCM-41, MFI zeolite, mesoporous, microporous

INTRODUCTION

The recently discovered uniform mesoporous materials like the MCM-41 reveal a large potential as catalyst component, support and adsorbent [1]. However, the available mesoporous materials have limitations with respect to

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their use due to the amorphous character of the pore walls. The hydrothermal stability of MCM-41 is very low [2]. In addition, the acidity of MCM-41 is reported to be comparable to that of amorphous silica-alumina [2]. Introduction of an ordered, well-structured pore wall should result in an increase of hydrothermal stability and acidity, and thus extend the potential application. Karlsoon *et al.* [3-4] used a two-template syntheses gel system to introduce “crystallinity” into the pore walls while maintaining the mesoporous structure. Huang *et al.* [5] used a dual-templating method through a process of two-step crystallization to prepare MCM-41/ZSM-5 composites. MCM-41 was first synthesized and subsequently the amorphous wall of MCM-41 was recrystallized. However, the mixed phases of MFI and MCM-41 were obtained. Chen *et al.* [6] used a two-step approach to introduce local D5R structure into mesoporous sili*ca.* The structure was collapsed upon high temperature calcination.

The thickness of pore wall of MCM-41 was reported to be around 1 nm in the literature [1]. If one can synthesize the nanosized ZSM-5 nuclei, say 1 nm, it is possible to assemble these nanocrystals to form mesoporous structure. In addition, MFI structure has a very good hydrothermal stability and a very high acidity, both are desired for practical application. It is known [7] that colloid MFI can be made as small as 5 nm by lowering the temperature and raising the TPAOH to template ratio. One could even limit the reaction temperature to such an extent that only the crystalline precursor, the so-called “nanoslab”, [8] which is about 1/3 of a unit cell and less than 1 nm in size, is produced.

The objective of this study was to synthesize nano-sized MFI nuclei first, then assemble the nano-sized nuclei into meso-structure by surfactant.

EXPERIMENTAL

In the synthesis of micropore-mesopore composite materials, the nano-sized MFI nuclei were hydrothermally synthesized first by using tetraethyl orthosilicate (TEOS) as a silicon source and tetrapropylammonium hydroxide (TPAOH) as a template, following the method reported by Tsai and Chiang [7]. Various amounts of tetramethylammonium hydroxide (TMAOH) were added to adjust the pH value of the solution. The synthesis was in a round-bottomed glass reactor with a reflux system at ambient pressure. By changing the synthesis time and temperature, one was able to obtain various sizes of colloidal MFI.

After the cetyltrimethylammonium bromide (CTABr) was completely dissolved in water, colloidal MFI was added. The mixture was stirred vigorously for *ca.* 30 min, the pH was then adjusted to *ca.* 10 by careful addition of 1 M H_2SO_4. Subsequently, the gels were transferred to PTFE-lined autoclaves and heated at various temperatures for various times. The products were quenched in cool water, washed 3 times with distilled water, filtered, dried overnight in ambient air, and then calcined in air at 550^{o}C. Table 1 lists the most successful combinations of two-step synthesis procedures used in this study. Various synthesis times and temperatures were tried as well, but the results provided no improvements and will not be discussed in this paper.

The samples were analyzed by XRD (Siemens D5000 diffractometer with a Ge monochromator and Cu $K_{\alpha1}$ radiation, step time 7.0 s (2Θ region 1-8^{o}) and 1 s (2Θ region 3-40^{o}) step size 0.020^{o}, wave length: 0.15406 nm) and nitrogen sorption isotherm (Micromeritics 2000). Selected samples were investigated by dynamic light scattering (DLS) analysis (Malvern Instrument Co., ZetaSizer-3000, 10 mW He-Ne laser), SEM (Hitachi S-800) and TEM (JEOL, JEM-1200 EX II, operated at 160 kV, magnifications varied between X 5 k and X 300 k).

Table 1

Synthesis conditions

Sample	1st step Temp. (time)	2nd step TMAOH/TEOH	Temp. (time)
1	90^{o}C (1.5 h)	0.070	150^{o}C (48 h)
2	90^{o}C (1.5 h)	0.070	90^{o}C (2 h),150^{o}C (48 h)
3	90^{o}C (1.5 h)	0.140	150 ^{o}C (48 h)
4	90^{o}C (1.5 h)	0.140	90^{o}C (5h), 150^{o}C (48 h)
5	90^{o}C (1.5 h)	0.140	90^{o}C (5 h)
6	90^{o}C (0.5 h)	0.070	25^{o}C (2 h)
7	90^{o}C (0.5 h)	0.070	90^{o}C(7h),150^{o}C (48 h)

RESULTS AND DISCUSSION

Colloidal nano-sized MFI nuclei were synthesized from a clear alkaline precursor solution prepared from TEOS and TPAOH [7]. After the reaction at 90^{o}C for 10 h, the original clear solution turned slightly hazed. DLS analysis indicates that the particle population in the product was dominated by the 5 nm class.

The crystalline phases of all samples were checked by XRD, and the resulting diffractograms clearly showed MFI and MCM-like reflections. Figure 1 shows that there are broad peaks at low angles, indicating that it is a porous material. However, the spectrum is somewhat different from that of standard

MCM-41 spectrum. The characteristic peaks of MFI were observed at $2\theta > 7^o$. Both the SEM and TEM investigations reveal the formation of two phases of MFI and MCM-41. Samples 1 and 2 have different peak positions at low angle, indicating that they have different structures. The appearance of low-angle diffraction peaks indicates that mesoscopic order was preserved in the calcined materials. It should be noted that once the MFI crystalline phase was observed, it would be too large to form the pore walls of MCM-41.

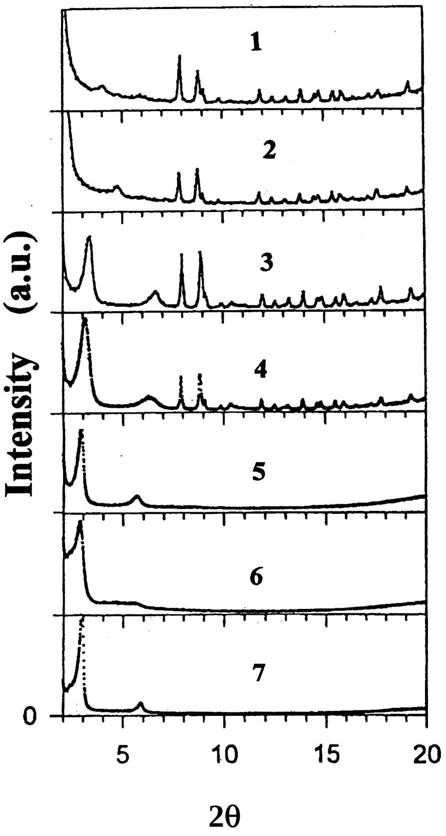
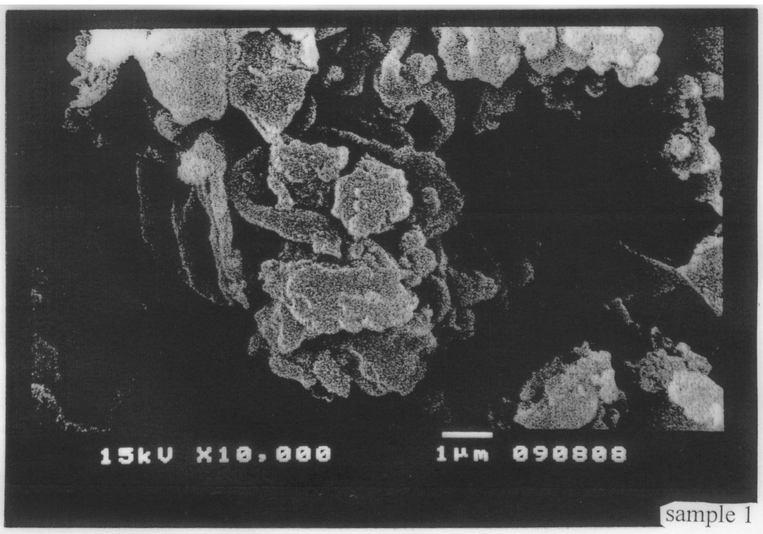


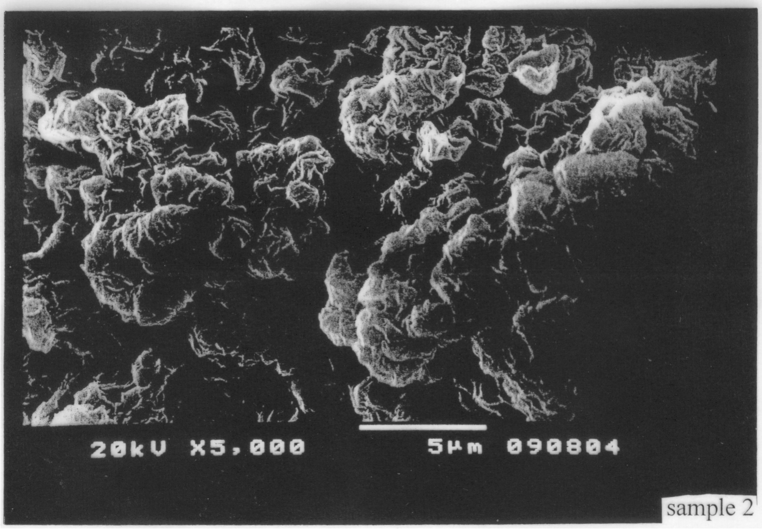
Fig. 1. XRD patterns of the samples

Samples 3 and 4 also demonstrate the MFI characteristic peaks as shown in Fig. 1. SEM and TEM investigations as shown in Fig. 2 also reveal the formation of mixed phases of MFI and MCM-41. The low angle peaks of samples 3 and 4 appear at different positions. Sample 5 did not give the MFI characteristic peak, possibly due to its small crystallite size.

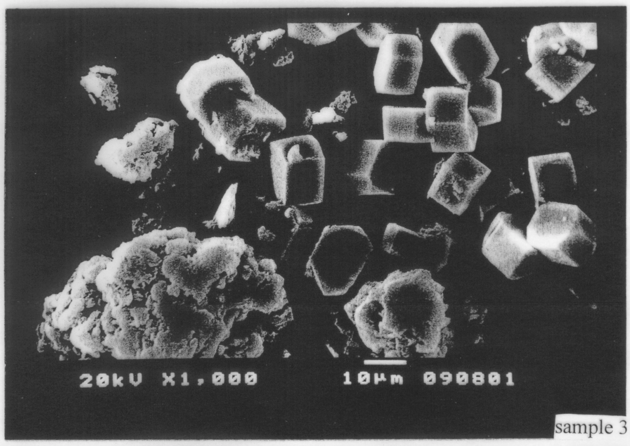
Both samples 6 and 7 showed low an angle peak at 3^o. However, an additional peak appeared at 6^o in sample 5. In addition, the intensities of XRD peaks of sample 7 were greater than those of sample 6. No characteristic peak of MFI appeared in samples 6 and 7. SEM results confirm this observation.



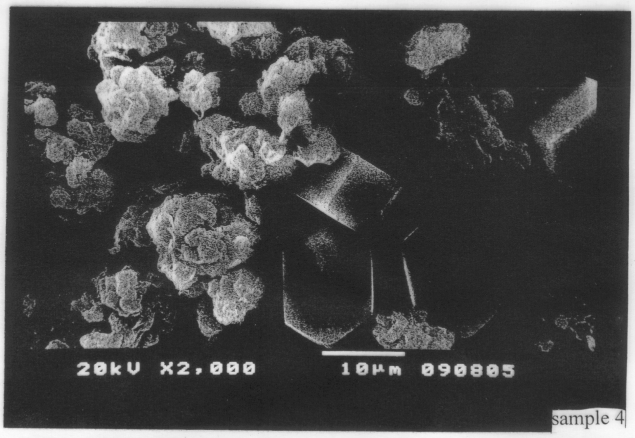
sample 1



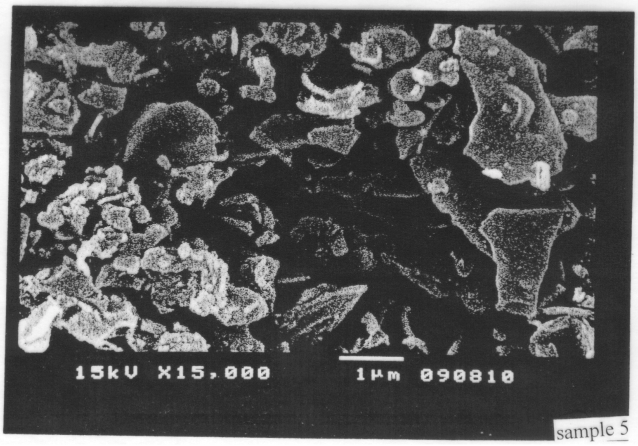
sample 2



sample 3



sample 4



sample 5

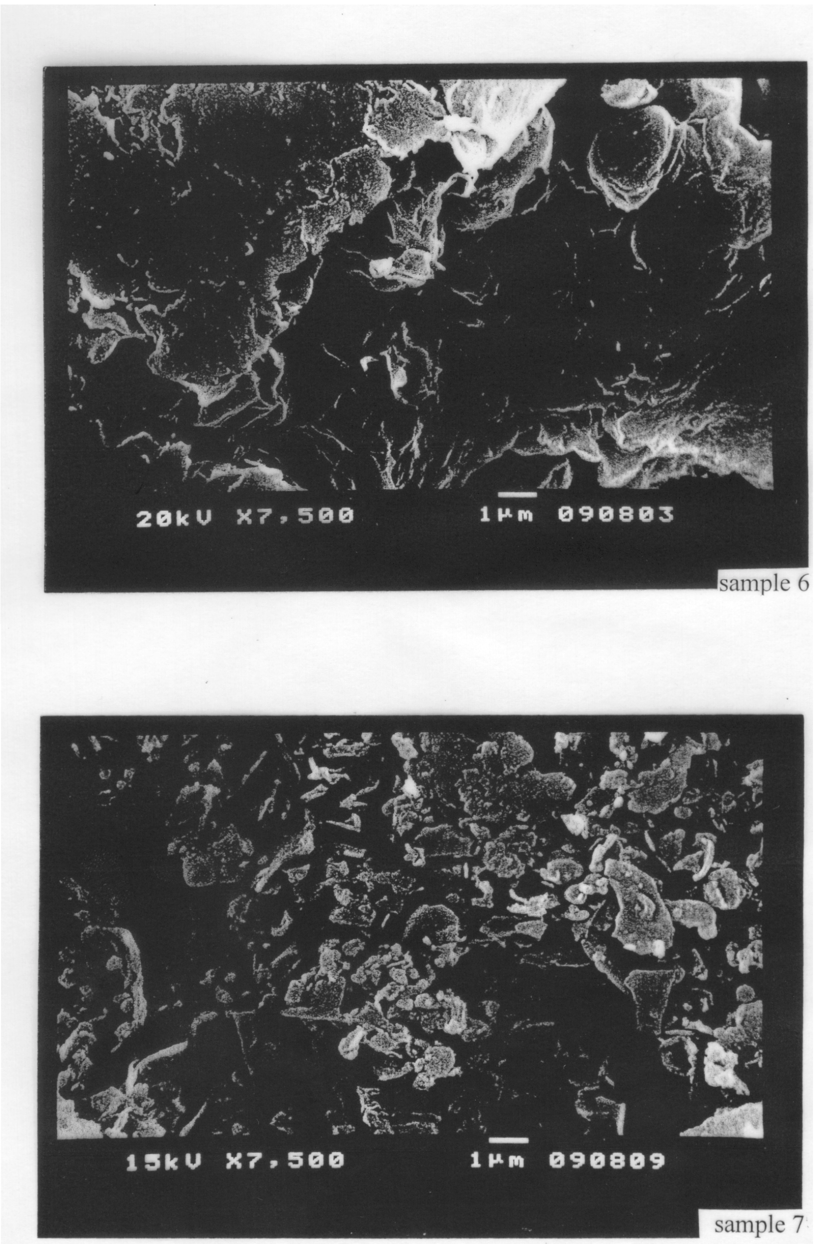


Fig. 2. SEM micrographs

After calcination at 550°C, the samples of 5-7 became amorphous, as detected by XRD. The results show that lamellar M41S was formed in such synthetic conditions. These samples were not stable upon calcination at high temperature. This indicates that the original lamellar structure collapsed after the removal of organic matter by calcination, resulting in the destruction of regular structure.

The nitrogen sorption isotherms of the calcined samples are given in Fig. 3. Samples 5-7 show a very low adsorption capacity due to the collapse of the lamellar structure upon calcination. Samples 3 and 4 exhibited certain meso-scale regularity. The high adsorption capacity at low P/Po indicated the formation of micropores.

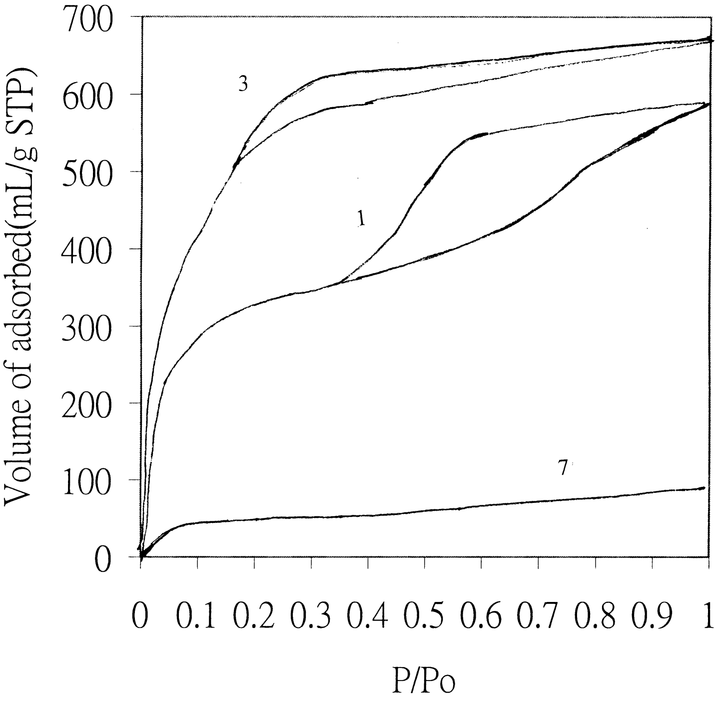


Fig. 3. Nitrogen sorption isotherms

Although we were not able to sustain MFI structure in the pore walls of MCM-41, a simultaneous synthesis of MFI/MCM-41 composite materials was observed. By variation of the synthesis conditions in the two stages, one was able to change the compositions of the MFI/MCM-41 composite materials.

It should be noted that the presence of additional structures in the samples, having for example very small regions of MFI or MCM-41 type structure is very difficult to identify. The wall thickness of MCM-41 is normally only around 10 Å, consequently, the presence of such structures might escape observation. However, the thinner walls cannot sustain the local strain caused by the crystallization and therefore the mesostructure would collapse.

Crystallization of nano-sized MFI species to form MCM-41 during the cooperative inorganic/organic assembly generally leads to a macroscopic phase separation of the inorganic and organic components. This is because crystallization energies often dominate the interaction energies that stabilize the inorganic-organic interface, thereby disrupting the establishment of curved surfaces with three-dimensional mesostructural order.

CONCLUSIONS

The objective of this study was to synthesize micropore-mesopore composite materials with two-step crystallization. The colloidal MFI was first synthesized using a structure-directing agent tetrapropylammonium hydroxide as a template in the first step. This colloid was then assembled to form a mesoporous structure by using cetyltrimethylammonium bromide as a surfactant. These materials were characterized by XRD, N_2 sorption, SEM and TEM. Due to the thick walls produced, it cannot sustain the local strain caused by the crystallization: the mesostructure was collapsed upon heating. The mixed phases of MFI and MCM-41 were obtained by optimizing the synthesis times and reaction temperatures.

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