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A new MFI-type zeolite containing uniform supermicropores: synthesis by structural transformation of CTA$^+$-MCM-41 and application in SCR of NO$_x$

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A new MFI-type zeolite containing uniform 17 Å supermicropores has been successfully synthesized through structural transformation of CTA$^+$-MCM-41 and shows better activity for SCR of NO$_x$ than conventional ZSM-5 under lean burn conditions.

The discovery of ordered mesoporous materials, due to their tailor-made pore sizes from 20 to 100 Å, has inaugurated potential pathways to selective catalysis and separation of large molecules.[1,2] Unfortunately, the hydrolysis of the amorphous silica framework and collapse of mesostructures under hydrothermal conditions or even at room atmosphere prevent practical applications of these surfactant-templated silicates.[3,4] Microporous zeolites are widely used as catalysts and sorbents due to their crystalline structure.[5] However, micropores restrict the diffusion rates of reactant and products,[6] hence limiting the activity of zeolite catalysts for certain reactions. Therefore, an attempt to synthesize or fabricate new porous crystalline materials having the advantages of both microporous and ordered macroporous structures is of interest recently for potential industrial applications.[7]

The difference between the synthesis of amorphous mesoporous and crystalline microporous materials lies primarily in the use of templates with different alkyl-chain quaternary ammoniumions. Long-chain quaternary ammoniumions ($\geqslant C_{12}$) form regular arrays of micelles to cast amorphous frameworks of mesostructures;[1] however, short-chain ones (C_1–C_4) template the formation of crystalline microporous zeolites.[8] Detailed investigation by different alkyltrimethylammonium surfactants $C_nH_{2n+1}NMe_3Br$ (n = 6, 8, 10, 12, 14, 16) showed that the shortest chain length (n = 6) gave predominantly MFI-type materials, while longer chains (n = 14, 16) produced mesoporous MCM-41 or amorphous materials.[9] Only mixed phases of MFI/MCM-41 were obtained using a mixed template consisting of C_6- and C_{14}-trimethylammonium ions.[10] Crystalline microporous structures can be formed in the presence of CTA$^+$ only.[11,12] Recently a two-step crystallization process was introduced into the amorphous framework of mesoporous materials to form MCM-41/ZSM5 composites, where mesoporous MCM-41 was first formed by CTA$^+$ and the amorphous framework of MCM-41 was then crystallized with TPA$^+$.[13] However, no literature has ever reported the formation of a crystalline composite containing both micropores and supermicropores (D_p = 15 and 20 Å) by using CTA$^+$ as the only template. This approach is of importance both for the investigation of the templating role of the surfactant and for the synthesis of a new shape-selective catalysts as supermicropores bridge the gap between micropores and mesopores. Here we report, for the first time, the transformation of the CTA$^+$–MCM-41 mesostructure into a hydrothermally stable MFI-type composite containing additional uniform supermicropores of 17 Å.

The new MFI-type material was synthesized according to the reported hydrothermal procedure.[12] However, in this work, the starting gel of sodium silicate was not acidified and a final molar composition of SiO_2: x Al_2O_3: y CTAB: z H_2O (x = 0–0.03, y = 0.05–0.5, z = 60–120) was used. After stirring for 60 min at room temperature, the white and viscous surfactant-silicate mixture was transferred to a Teflon-lined autoclave and then heated at 170 °C for different times. The resulting solids were recovered by filtration, thoroughly washed with distilled water and then dried at 100 °C overnight. The products were finally calcined at 550 °C in air for 10 h. For a comparison, conventional ZSM-5 material was synthesized using TPAOH according to the literature procedure.[14]

When SiO_2: y CTA$^+$: 120 H_2O was treated at 170 °C for 144 h, XRD and FTIR spectra showed that the products are of typical MFI structure. Fig. 1 shows different morphologies of products obtained under different crystallization times, which correspond to hexagonal MCM-41, lamellar phase and MFI structure in XRD patterns, respectively. Fig. 2 shows XRD patterns of the resulting products with varying crystallization times. For the sample formed under 6 h, the XRD pattern of the resulting CTA$^+$–silica composite clearly shows the hexagonal mesoporous structure of MCM-41. However, the calcined MCM-41 mesostructure completely collapsed when the calcined sample was kept in air at room temperature for two months or treated in boiling water for only 24 h, as shown in Fig. 3(a). For the sample formed under 12 h of crystallization, the hexagonal MCM-41 is transformed to a typical lamellar structure characterized by XRD and N_2 adsorption/desorption

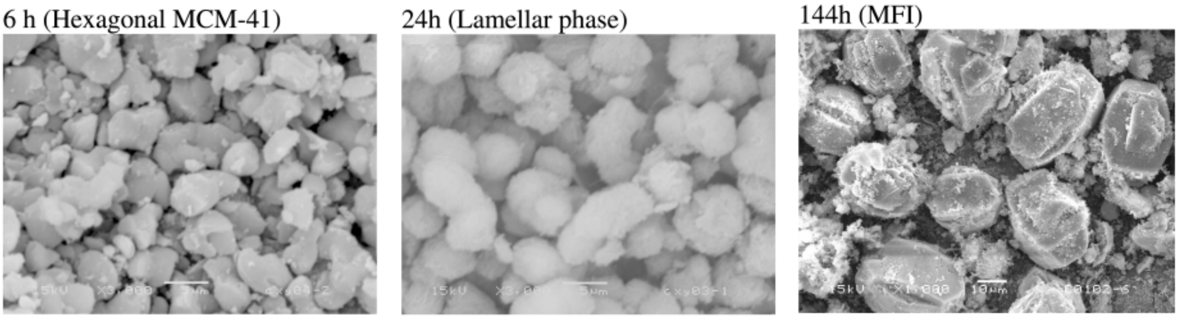
6 h (Hexagonal MCM-41)
24h (Lamellar phase)
144h (MFI)

Fig. 1 SEM images of products obtained after crystallization times of 6, 24 and 144 h. SEM was performed on a JEOL JSM-5600LV scanning electron microscope operating at 15 kV.

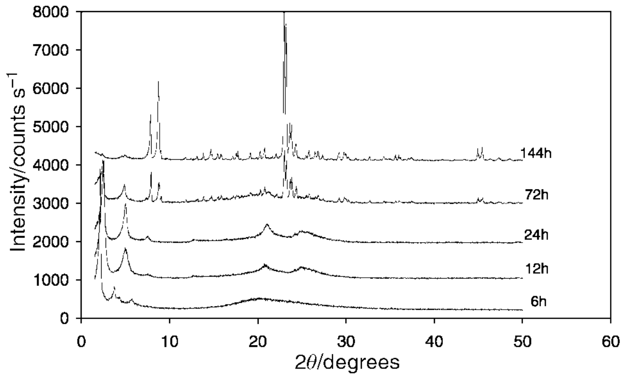

Fig. 2 XRD patterns of as-synthesized products obtained after different crystallization times.

isotherms.[12] Once this product was calcined at 550 °C, all the XRD peaks disappeared and its N_2 adsorption/desorption isotherms remain unchanged after being kept in air at room temperature for two months, as shown in Fig. 3(b). After increasing the crystallization time to 72 h, XRD patterns show that both lamellar phase and MFI structure are present in the resulting product. After further crystallization for 144 h, XRD patterns corresponding to the MFI structure only are observed.

The ratios CTA^+/Si, Si/H_2O and Si/Al are found to be crucial factors influencing the structural transformation of the resulting material. The optimal values of y for successful synthesis of the new MFI materials is 0.1–0.4. Too low a value for CTA^+/Si results in the formation of a mixture containing MFI materials and cristobalite. However, amorphous silica was easily formed at $CTA^+/Si \geqslant 0.5$. Using $y = 0.2$, the new MFI possesses BET surface area and pore volumes of micropores of 409 $m^2\ g^{-1}$ and 0.172 ml g^{-1}, respectively, higher than those for a sample formed from TPA^+ (358 $m^2\ g^{-1}$ and 0.160 ml g^{-1}). Furthermore, N_2 isotherms of the new MFI-type material display capillary condensation characteristics. A H1-type hysteresis loop is clearly observed at $P/P_0 < 0.2$ [Fig. 3(c)], which corresponds to a narrow pore size distribution with a diameter of 17 Å. This pore size is much lower than that of CTA^+-templated MCM-41.[1]

CTA^+-templated MCM-41 readily becomes amorphous when subjected to refluxing in water for short periods of time (24 h).[3,4] In order to eliminate the possibility that the new material contains a mixture of MFI and MCM-41 as those reported elsewhere,[10] hydrothermal treatment was performed on the calcined sample in boiling water for 1 to 30 days. Fig. 3(d) and 3(e) show the N_2 isotherms for these samples, respectively. The hysteresis loops for samples treated in boiling water are similar to that of the untreated one. The pore size distribution of the sample treated in boiling water for 30 days, as shown in Fig. 3 (inset), is still maintained at 17 Å. Furthermore, its BET surface area, morphology and framework structure (which were characterized by SEM, XRD and FTIR) also remain unchanged.

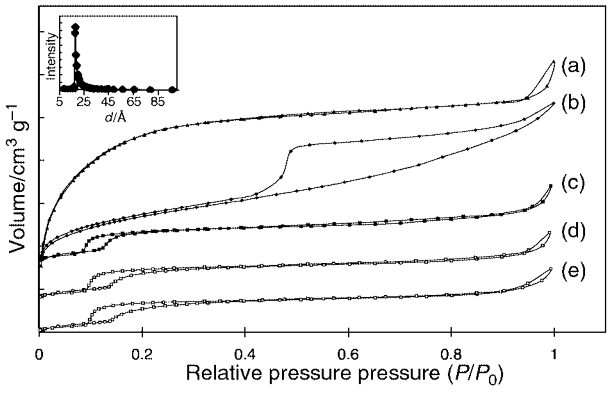

Fig. 3 N_2 adsorption/desorption isotherms of hexagonal MCM-41 (a), lamellar phase (b) and new MFI (c) after being kept in air at room temperature for 2 months prior to N_2 adsorption measurements. N_2 adsorption/desorption isotherms of the new MFI after being kept in boiling water for 10 days (d) and 30 days (e), and its BJH pore size distribution (Å) after 30 days in boiling water (inset).

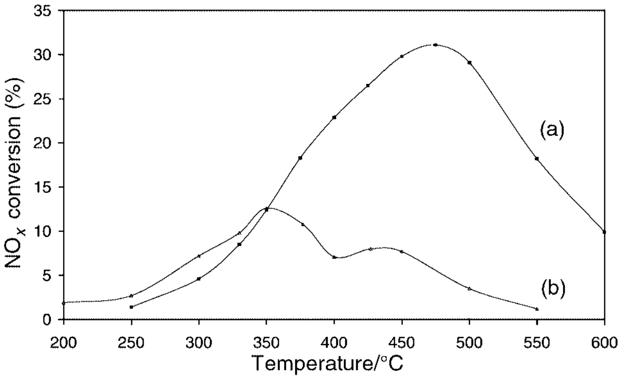

Fig. 4 Comparison of SCR of NO_x over new Co/MFI (a) and conventional Co/ZSM-5 (b). SCR of NO_x was carried out using a continuous flow reactor operating under 1 atm. *Reaction conditions*: 1000 ppm of NO, 1000 ppm of C_3H_8, 5% of O_2 (in He) and SV of 30 000 h^{-1}.

Small crystals of Co/ZSM-5 were reportedly more active than larger ones for selective catalytic reduction (SCR) of NO_x by propane, showing the influence of mass transfer diffusion on the activities of the catalyst.[15] In this work, we used a new aluminium-containing MFI (Si/Al = 40) with a pore size of 17 Å, which was successfully synthesized using the above method, to investigate the effect of pore size of a catalyst on the conversion of NO_x by propane under lean burn conditions. 1.2 wt% cobalt-supported catalysts were prepared from the new MFI and conventional ZSM-5 by solid-state ion exchange with cobalt nitrate solution. Fig. 4 compares the conversion curves of NO_x on these two catalysts. It is obvious that the NO_x conversion over the new Co/MFI catalyst is much higher than that over conventional Co/ZSM-5 catalyst. The presence of uniform supermicropores of 17 Å in the new MFI catalyst is believed to be helpful for the mass transfer of reactants and reaction products across the pores, hence increasing the activity of the catalyst as diffusion control in microporous channels generally predominates in shape-selective catalysts such as MFI zeolite.[6]

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