

Fabrication of Hierarchical Zeolitic Material from Zeolite Nanoprecursors and Macromolecular Template

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Hierarchical zeolitic material possessing three generations of micro-, meso-, and macroporosities was fabricated under controlled steaming at 145 °C through a dual-template approach using tetrapropylammonium hydroxide (TPAOH) and poly(methyl methacrylate) (PMMA) latex particles as micropore and macropore templates, respectively.

Materials with bimodal porosity can offer multiple benefits that arise from each of the pore-size regimes.¹⁻³ For example, micropores and mesopores can provide size and/or shape selectivity for guest molecules, whereas the presence of additional macropores can offer easier transport and access to the active sites.^{4,5} Such phenomena should improve reaction efficiencies and minimize channel blocking.

In the present work we demonstrate the fabrication of a hierarchical zeolite material having three generations, micro-, meso-, and macroporosities. The hierarchical zeolitic material was fabricated using a dual-template approach under controlled steaming at 145 °C. Tetrapropylammonium hydroxide (TPAOH) was used as a structure-directing agent for microporosity, and poly(methyl methacrylate) (PMMA) latex particles (Soken, particle size 400 nm) was used as a macropore template. At first, a clear solution containing zeolite nanoprecursors (NP) was prepared by following the procedure reported by Chiang and co-workers.^{6,7} Specifically, 11.6 g of tetraethyl orthosilicate (TEOS), 14.1 g of TPAOH (20% aqueous) and 68 g of H₂O were stirred at room temperature for 1 h in a polypropylene bottle to form a clear sol. The molar composition of this sol was 0.25 TPAOH /1TEOS /80H₂O. The sol was then hydrothermally treated at 80 °C for 14 h to form a clear solution containing zeolite NP. The size of the NP was estimated as ≈ 10 nm from dynamic light scattering (DLS) and transmission electron microscopy (TEM) studies. The NP/PMMA hybrid was formed by mixing 2.5 g of room-temperature-cooled NP sol with 0.5 g of solid PMMA powder. The NP/PMMA hybrid was dried at room temperature for 72 h to form a solid mass. Positively and negatively charged PMMA particles were used to prepare the hybrid; the zeta potentials of their aqueous suspensions were measured to be plus 28 mV and minus 30 mV, respectively. The dried composite (1 g) was later steamed in an autoclave (volume 100 cm³) at 145 °C for 24 h under two different humidity conditions. In the lower humidity case, referred to as ST-1, the steaming was carried out by placing 0.1 g of water into the autoclave. ST-2 refers to steaming at higher humidity, by placing 2 g of water into the autoclave. After steaming, the solid material was collected and directly calcined in air at 500 °C for 5 h. The zeolitic nature of the material was confirmed from the observed

MFI-type XRD pattern for the material. The material produced by steaming in the absence of any added water in the autoclave did not show any peaks in XRD.

The FE-SEM images of the calcined samples obtained under ST-1 condition are shown in Figure 1. We found that when the negatively charged PMMA particles were used as macropore template the material had only a limited long-range macropore order (Figure 1A). Much of this sample comprised segregated macroporous and nonmacroporous materials in the bulk. On the other hand, the use of positively charged PMMA produced high quality zeolitic hierarchical material. As seen from Figure 1B, this material shows almost uniformly sized macropores and absence of segregated material. The low magnification images shown in the Figures 1C and 1D for the same material proves that the macroporous order is extending over the entire bulk of sample, without any presence of segregated nonmacroporous material.

The zeta potential of the NP sol was measured⁸ to be minus 35 mV. When the zeolitic precursors are mixed with positively charged PMMA particles, strong attraction will be expected between NP and PMMA which will be resulting in the formation of

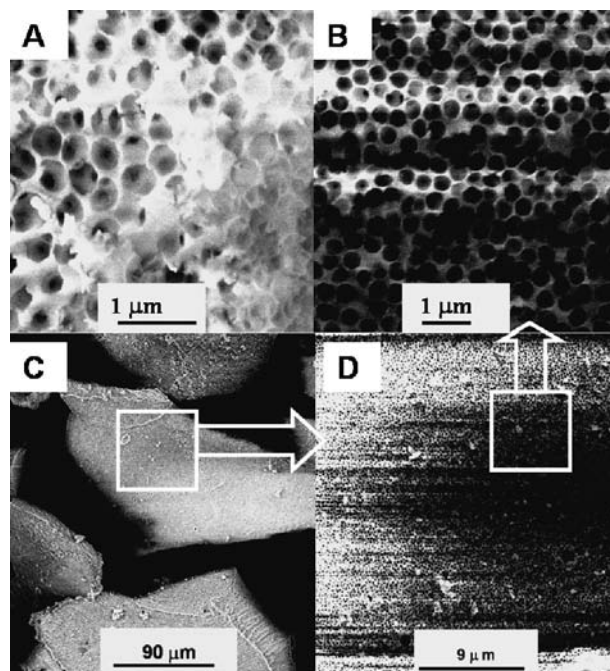


Figure 1. FE-SEM images of hierarchical zeolitic materials obtained under ST-1 (lower humidity) condition using negatively (A) and positively (B–D) charged PMMA.

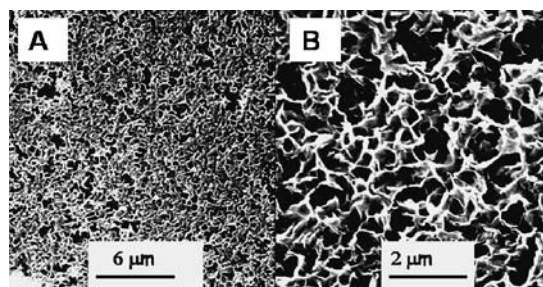


Figure 2. FE-SEM images of hierarchical zeolitic materials obtained from positively charged PMMA, under ST-2 (higher humidity) steaming condition, showing partially damaged macroporous structure.

high quality macroporous material with long-range order. Such is not the case with negatively charged PMMA wherein segregation of the NP and PMMA could take place because of almost identical surface charges on NP and PMMA. It was also realized that the appropriate steaming conditions are to be maintained for obtaining macroporous order in the final material. When steaming of the positively charged PMMA/NP hybrid was carried out under ST-2 conditions, the macroporous order of the obtained hierarchical zeolite material was partially damaged as seen from the FE-SEM images shown in Figures 2A and 2B.

The XRD patterns of the hierarchical zeolitic material obtained from positively charged PMMA under ST-1 and ST-2 conditions are shown in Figure 3. The as-mixed PMMA/NP hybrid (before steaming) did not show any XRD peaks.⁷ However, upon steaming of the hybrid the XRD peaks appeared owing to further zeolite growth from the NP. The XRD patterns shown in Figure 3 are of the steamed and calcined materials. From the results of FE-SEM and XRD shown in Figures 2 and 3, respectively, it is clear that the steaming at higher humidity leads to the growth of the macroporous zeolitic walls into larger particles partially damaging the macroporous order in the material.

The further growth of the macroporous zeolitic walls could have been caused by the partial dissolution of the macroporous walls and subsequent promotion of zeolitic growth under higher humidity at ST-2. From this experiment it is clear that the macroporous structure and the texture properties of the zeolitic hierarchical material can be influenced by the steaming temperature and maintained humidity.⁷ The N₂ adsorption/desorption studies were conducted on the zeolitic hierarchical material that was obtained using positively charged PMMA under two different steaming conditions, ST-1 and ST-2. A type I N₂ adsorption/desorption isotherm (not shown here) was obtained that indicated microporosity in the material. An upward rise in curve of the isotherm indicated filling of interparticle spaces among the nanocrystals comprising the macropore walls indicated mesoporous nature of the material. The total BET surface area of the materials obtained under ST-1 and ST-2 conditions were 747 m²/g and 369 m²/g, respectively; the external surface areas determined from t-plot were 500 m²/g and 200 m²/g, respectively. The BJH pore volumes were 0.80 cc/g and 0.31 cc/g, respectively. As seen from these data, steaming under higher humidity, in presence of excess water, brings about increase in the size of zeolite particles due to further zeolitization under higher

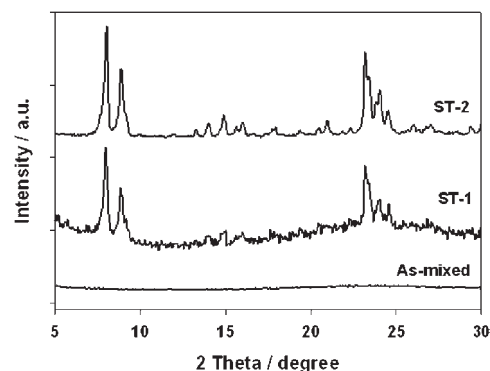


Figure 3. XRD patterns of the hierarchical zeolitic materials obtained from positively charged PMMA under two different steaming conditions ST-1 and ST-2 showing increase in the zeolitic crystallinity at ST-2 or higher humidity condition.

humidity.

This study has demonstrated that macroporous zeolites with desired crystallinity of the macropore walls and three generations of micro-, meso-, and macroporosities can be synthesized by combining zeolite NP and latex spheres under steaming at controlled humidity. We have found that the combination of positively charged PMMA and negatively charged zeolite NP yields zeolitic hierarchical material having long-range macropore order. Furthermore, because our process is carried out under controlled humidity, enhanced growth of the zeolite particles obeying dissolution–recrystallization mechanism is reduced considerably and long-range macroporous order is maintained in the synthesized material.

We believe that the present approach may be extended to the fabrication of films of hierarchical zeolite materials on various substrates. This should further open up applications of such hierarchical materials in micropatterning, separation and advanced electronic devices.

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References

- 1 S. A. Davis, S. L. Burkett, N. H. Mendelson, and S. Mann, *Nature*, **385**, 420 (1997).
- 2 H. Yang, N. Coombs, and G. A. Ozin, *Adv. Mater.*, **9**, 811 (1997).
- 3 P. Yang, T. Deng, D. Zhao, P. Feng, D. Pine, B. Chmelka, G. M. Whitesides, and G. D. Stucky, *Science*, **282**, 2244 (1998).
- 4 B. T. Holland, L. Abrams, and A. Stein, *J. Am. Chem. Soc.*, **121**, 4308 (1999).
- 5 B. T. Holland, C. F. Blanford, and A. Stein, *Science*, **281**, 538 (1998).
- 6 S. P. Naik, J. C. Chen, and A. S. T. Chiang, *Microporous Mesoporous Mater.*, **54**, 293 (2002).
- 7 S. P. Naik, R. W. Thompson, and A. S. T. Chiang, *J. Phys. Chem. B*, **107**, 7006 (2003).
- 8 T. Maurer, S. P. Muller, and B. Kraushaar-Czarnetzki, *Ind. Eng. Chem. Res.*, **40**, 2573 (2001).