Zeolites

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MFI Zeolite with Small and Uniform Intracrystal Mesopores**

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The catalytic activity of zeolites[1] often is limited by the diffusion of reagents and reaction products through the framework pore network. Recently, several efforts have been made to reduce the diffusion path length in zeolites by confining crystal growth to a nanometer length scale[2–8] or by providing intracrystal mesopores during synthesis.[9–13] The latter strategy is intrinsically appealing, in part, because it precludes the need for colloidal crystal formation and avoids the drawbacks associated with nanoparticle processing. Moreover, the presence of mesopores in zeolite crystals offers the possibility of improving product selectivity in the catalytic cracking of polymeric molecules.[14]

The embedding of carbon nanoparticles and certain polymers into zeolites crystals during synthesis has been shown to be an effective means of generating intracrystal mesopores.[9–13] These templating methods provide much better control of pore size than conventional steaming and chemical leaching approaches to mesopore formation in zeolites.[15] However, particle templates typically afford average pore sizes that are too large (≥ 10 nm) and pore size distributions that are too broad (> 10 nm widths at half maximum) for catalytic cracking reactions with high product selectivity.

Herein we report a method to prepare templated zeolites with small intracrystal mesopores (average pore size 2.0–3.0 nm) and narrow pore size distributions (ca. 1.0–1.5 nm width at half maximum). We selected the MFI zeolite ZSM-5 to illustrate our approach, in part, because it is widely recognized for its unique properties as a catalyst for NO_x reduction, Fisher–Tropsch chemistry, and toluene disproportionation, and as an additive for petroleum cracking. Scheme 1 illustrates our synthetic strategy for templating uniform mesopores within a zeolite matrix. In this scheme, a silane-functionalized polymer is used as a porogen for the formation of intracrystal mesopores. The presence of -SiO_3 units on the polymer allows it to be integrated into a silica–alumina sol–gel reaction mixture. Nucleation of the zeolite phase in the presence of the silylated polymer is accompanied by the grafting of the polymer to the zeolites surface through covalent Si-O-Si linkages. As the zeolite crystal grows, the

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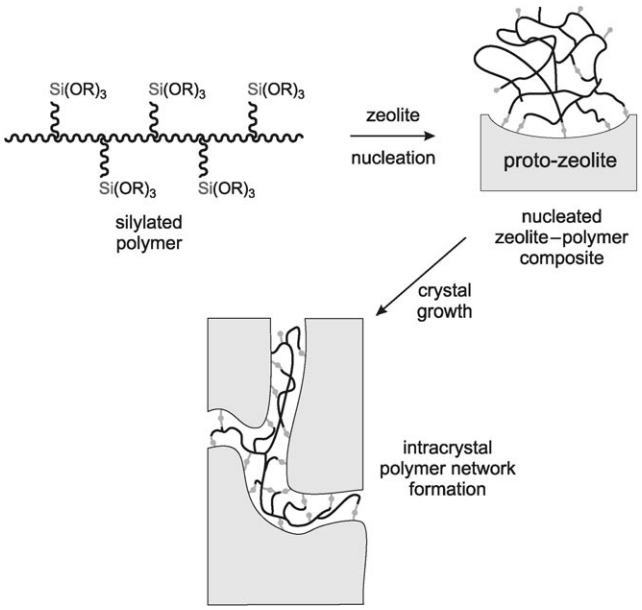

Scheme 1. Conceptional approach to the synthesis of a zeolite with intracrystal mesopores using a silylated polymer as the mesoporogen.

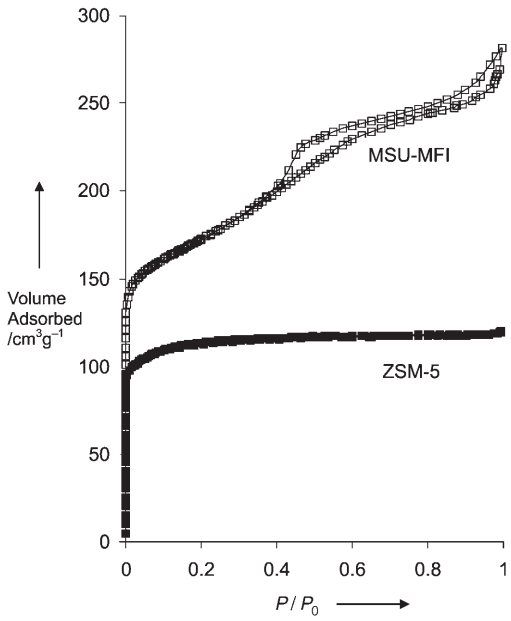

Figure 1. Nitrogen adsorption/desorption isotherms for MSU-MFI zeolites prepared in the presence of a silylated polyethylenimine oxide as an intracrystal porogen. The initial molecular weight of the polymer was 25 000, and silylation was carried out by reaction with (3-glycidoxypropyl)trimethoxysilane at a Si/NH molar ratio of 1.0:5.0. Included for comparison are the isotherms for ZSM-5 zeolite prepared under equivalent conditions in absence of the silylated porogen.

incorporated polymer becomes phase-segregated from the zeolite matrix, forming an intracrystal polymer network that is covalently linked to the zeolite framework. Calcination of the composite crystals removes the polymer porogen and forms a zeolite with uniform intracrystal mesopores.

Verification of the above synthetic scheme was obtained using a silane-fuctionalized polyethylenimine as the mesoporogen for the preparation of mesoporous forms of zeolite ZSM-5. The silylated polymer, formed from the reaction of (3-glycidoxypropyl)trimethoxysilane and polyethylenimine PEI at a Si/NH ratio of 0.20, was combined with tetraethylorthosilicate and aluminum tri-*sec*-butoxide to form a reaction mixture with the molar oxide composition $1.00\,Al_2O_3{:}100\,SiO_2{:}18.5\,[TPA]_2O{:}2000\,H_2O{:}10\,SiO_2$ as silylated PEI. Digestion of the mixture at 150 °C, followed by calcination at 600 °C to remove both the framework template and the mesoporogen yielded the final mesoporous zeolite, denoted MSU-MFI.

Figure 1 provides the nitrogen adsorption/desorption isotherms for a representative mesoporous ZSM-5 made from a silylated form of PEI with an initial molecular weight of 25 000. Included for comparison are the isotherms for conventional ZSM-5 prepared under equivalent conditions in the absence of silylated polymer. The near-linear uptake of nitrogen by MSU-MFI over the range $P/P_0 = 0.10$ to 0.60 is indicative of the presence of small mesopores. The conventional form of MFI lacks this adsorption feature. Direct evidence for the presence of intracrystal mesopores is provided by the TEM images shown in Figure 2 for whole-particle and thin-sectioned specimens. Each particle is permeated by randomly oriented small mesopores of nearly the same size. Higher resolution images reveal lattice fringes that extend over the entire particle, thus indicating that each particle is a single crystal and not an aggregate of nanocrystals.

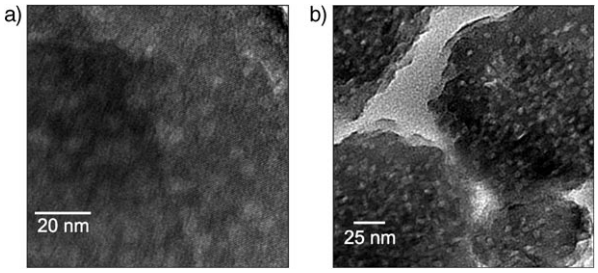

Figure 2. TEM images of the MSU-MFI zeolite prepared in the presence of silylated polyethylenimine with an initial molecular weight of 25 000: a) whole-particle specimen; b) thin-sectioned sample. The light contrast areas are intracrystal mesopores.

Figure 3 provides the mesopore size distributions and corresponding mesopore volumes for MSU-MFI zeolites prepared in the presence of PEI polymers with initial molecular weights of 600, 1800, and 25 000. For each derivative, the pore size distribution is confined to values below 8 nm, and the distribution of pores is centered between 2.0 and 3.0 nm with a width at half maximum less than 1.5 nm. These mesopore size distributions, which are in the range anticipated for selective polymer cracking, are unprecedented among all previously reported mesoporous forms of ZSM-5 or any other zeolite structure type. Also, the corresponding mesopore volumes for these new ZSM-5 derivatives (0.07–0.11 cm^3g^{-1}) compare favorably with the micropore volume of the zeolite framework (0.12 cm^3g^{-1}).

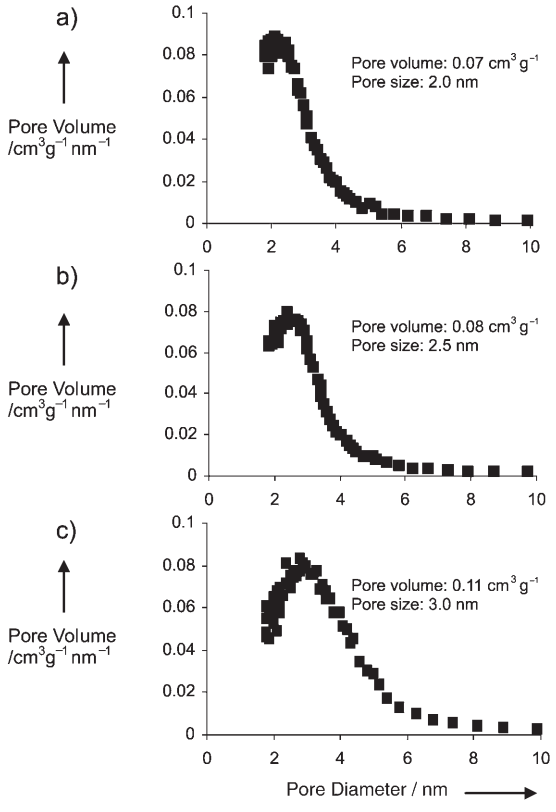

Figure 3. BJH mesopore size distributions, obtained from nitrogen adsorption isotherms, for MSU-MFI zeolites prepared from polyethylenimine polymers with initial molecular weights of a) 600, b) 1800, and c) 25 000. For each silylated porogen the Si/N ratio was 1.0:5.0. The mesopore volumes are reported for the corresponding mesopore size distributions.

The 50% increase in average mesopore size observed upon increasing the polyethylenimine molecular weight from 600 to 25 000 is substantially lower than the approximately 3.4-fold increase expected for a 40-fold increase in polymer molecular weight. This latter observation indicates the zeolite matrix greatly alters the solvation and conformation of the phase-segregated polymer embedded in the crystal. Further evidence for confinement effects on the polymer is provided by a comparison of the hydrodynamic radius of the free polymer with the pore sizes of the templated material. For example, the hydrodynamic radius of polyethylenimine with molecular weight of 25 000 is around 6.6 nm,[16] whereas the average radius of the mesopores templated by the silylated form of this polymer is about 1.5 nm.

Non-silylated forms of polyethylenimine do not inhibit zeolite nucleation nor do they act as intracrystal mesoporogens. Thus, silylation is essential for effective incorporation of the polymer into a growing zeolite matrix. However, also the degree of polymer silylation is important in forming intracrystal mesopores. For example, silylated polyethylenimines formed from a Si/NH ratio of 1:1 in the reaction mixture are ineffective in templating intracrystal mesopores. Instead, fully silylated PEI derivatives limit crystal growth to the sub-micrometer size domain, thus giving rise to zeolites with interparticle mesopores far larger than the intracrystal mesopores formed at a Si/NH ratio of 1.0:5.0 in the reaction mixture. Even simple organosilanes of the type $RSi(OR)_3$ are known to limit the growth of zeolites crystals,[17] but none have resulted in zeolites with intracrystal mesopores.

Finally, our molecular approach to the formation of zeolites with small and uniform mesopores is not limited to MFI framework structures. We have been successful in forming intracrystal mesopores also in FAU frameworks, particularly zeolite Y, which also is an important zeolite for the catalytic cracking of large polymers. Further, other forms of silylated polymers are showing promise as intracrystal mesoporogens in zeolite synthesis, thus indicating that our approach is quite general and not limited to one zeolite structure type nor to one type of silylated polymer.

Experimental Section

The silylated polymer was formed by reaction of (3-glycidoxypropyl)trimethoxysilane with polyethylenimine PEI at a Si/NH ratio of 0.20. The epoxide ring opening and the formation of hydrolytically stable C–N bonds was completed within 24 h at 80 °C. The transparent polymer gel was evacuated under vacuum to remove ethanol and then stored in a sealed vial to prevent hydrolysis of the Si-OCH_3 groups in the polymer. The silylated polymer in tetrapropylammonium hydroxide solution was combined with tetraethylorthosilicate and aluminum tri-*sec*-butoxide to form a reaction mixture with the molar oxide composition $1.00\,Al_2O_3$:100 SiO_2:18.5 $[TPA]_2O$:2000 H_2O:10 SiO_2 as silylated PEI. The mixture was heated at 150 °C for 48 h to form the zeolite–silylated PEI composite. ^{29}Si MAS NMR spectroscopy verified the presence of Q^4 SiO_4 groups characteristic of the zeolite lattice (100–120 ppm) and of T^3 and T^2 SiO_3 moieties indicative of silylated PEI (65–75 ppm). Essentially all the silylated polymer was incorporated into the zeolites matrix, as judged from the relative intensities of the Q and T resonances.

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