Synthesis of Macroporous Materials with Zeolitic Microporous Frameworks by Self-Assembly of Colloidal Zeolites

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This study reports a novel and flexible technique to synthesize bimodal porous materials with ordered macropores whose walls are composed of microporous zeolites by self-assembly of nanocrystals of silicalite-1 and ZSM-5. The materials prepared by this novel technique are well crystalline and possess uniform macropores interconnected in three dimensions through windows.

Materials with bimodal pore structures have attracted considerable research enthusiasm due to their technological promise in many important applications, such as adsorption, separation and catalysis.[1-3] Most of previous reports focused on the meso/macroporous system with the walls exhibiting no crystalline domains.[3~5] Some authors have tried to prepare bimodal pore materials with zeolitic walls.[6,7] However, only embryo of tectosilicate was detected in the walls of MCM-41[7] because of its thin walls (0.9–1.5 nm) which can contain one layer of typical zeolite unit cells at most. Recently, Holland et al.[8] first prepared micro/macroporous materials with silicalite-l walls by employing the pseudo-solid-state transformation of preformed macroporous amorphous silica formed by the rigid-colloid templating method.[9] This kind of material was expected to improve reaction efficiencies because of the co-existence of the zeolitic micropores in the walls and the macropores, which provide an easier access to the active sites. However, it seems that there are two potential limitations in this method. Firstly, it is difficult to ensure that the amorphous silica pre-filled in the voids between PS (polystyrene) spheres is fully crystallized. Secondly, only few types of zeolites could be crystallized below the glass transition temperature of the PS sphere ($T_g \approx 3\ 77$ K), above which PS sphere will soften and the orderness of the macropores in the product might be damaged, though using the pseudo-solid-state transformation method seems to solve this difficulty to a certain extent.[8]

Recently, nanozeolites have been widely studied and a variety of nanozeolites including silicalite-1, NaZSM-5, TS-1, sodalite A, Y, ZSM-2 and $AlPO_4$-5 have been synthesized.[10] It is reported that colloidal zeolites can form aggregations by the condensation reaction of hydroxyl bond between nanozeolite particles under certain conditions.[11] By a combination of this property of nanozeolites and the close-packed PS spheres as templates, we developed a more flexible method to synthesize micro/macroporous materials by self-assembly of pre-synthesized nanozeolites in room temperature. The products fabricated by this method are proved to possess ordered interconnecting macropores with well crystalline zeolitic walls.

Colloidal silicalite-1 and ZSM-5 were prepared with the initial molar composition 9 TPAOH: 25 SiO_2: 480 H_2O: 100 EtOH (EtOH = ethanol) and 9 TPAOH : 25 SiO_2: 0.25 Al_2O_3: 480 H_2O: 100 EtOH, respectively, according to methods given in the literature.[10,12] The products were purified by repeated centrifugation (15000 rpm) and washing, then resuspended in distilled water to form a stable colloidal zeolite suspension with a concentration of approximately 4.0 wt%.

The macroporous silicalite-1 was prepared as follows: 2.0 ml of PS sphere (2600 ± 100 nm, dispersed in ethanol with a concentration of 20 wt%) suspension was placed on micropore filter membrane (pore size < 0.1 µm) in a Büchner funnel and filtered to form disc-shaped close-packed arrays by suction, to which 1.0 mL of colloidal silicalite-1 suspension was then added dropwise while vacuum was still applied. In such a case, colloidal zeolites were permeated into the voids between close-packed PS spheres. After being dried at 373 K overnight and calcined at 823 K (heating rate = 10 K min^{-1}) for 8 h in air to remove the organic components, the macroporous silicates (labeled as MaS-1) monolith with a disc-shape was obtained. In the same manner, macroporous ZSM-5 (labeled as MaZSM-5) is made by self-assembly of colloidal ZSM-5 within the voids between close-packed PS spheres (2400 ± 100 nm). For comparison, nanophase silicalite-1 and ZSM-5 are obtained by freeze-drying a portion of the above colloidal zeolites suspension followed by calcination in air at 823 K.

The powder X-ray diffraction (XRD) patterns of calcined MaS-1 and MaZSM-5 are well matched with that of zeolites with MFI-type structure, except that the diffraction lines are broadened as a result of the small crystal size. The average crystal sizes of MaS-1 and MaZSM-5 samples are 40–70 nm and 60–95 nm, respectively, calculated by the XRD line broadening of (011) and (200) reflections using the Scherrer equation and KBr powder as an internal reference.

In the IR spectra of all calcined samples, the bands ascribed to PS or the template molecules disappeared, indicating they were totally removed from the samples. Being different from those of micrometer-sized zeolites, the framework vibration at 550 cm^{-1}, characteristic band of MFI-type zeolites, appears as a doublet (548 cm^{-1} and 560 cm^{-1}) which has been observed in nanophase silicalite-1.[10] For the as-synthesized samples, there is an intense band at 960 cm^{-1}, which is ascribed to silanol groups associated with the Q^3 silicon species.[10] This band disappears after the calcination, implying that the condensation of surface Si-OH groups on nanozeolites happened during calcination. This phenomenon was also observed in the spectra of ^{29}Si MAS NMR. The integrated intensity of the peak at -l04 ppm, assigned to Q^3 silicons from surface hydroxyl groups or to an amorphous component,[13] decreased from 19.85% for the as-synthesized nanophase silicalite-1 to 4.7% for the calcined MaS-1 sample. Hence, we can expect the macroporous structures were reinforced by further condensation reaction between nanozeolite particles during the period of calcination.

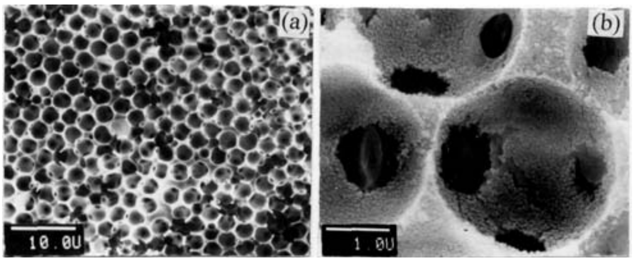

Figure 1. SEM images for cross-sections of the calcined MaS-1 samples under different magnifications: (a) 2 000 and (b) 20000 times.

The scanning electron micrograph (SEM) images in cross-sections of the calcined MaS-1 and MaZSM-5 samples show ordered spheroidal voids with uniform diameters. The SEM images of MaS-1 sample under different magnifications are shown in Figure 1. Being different from the reports in literature,[8] the diameters of the voids are nearly the same as that of the PS spheres used, showing that there is little shrinkage and/or deformation of the macropores during the period of drying and calcination, which might be contributed by the facts that the macroporous skeleton has formed at room temperature and little deformation will happen upon the further heat treatment because of the "hardness" of zeolite particles. At a magnification of 20000, we can clearly observe that the walls of the macropores are made up of nanocrystals and the macropores are interconnected in three dimensions through windows whose diameters typically exceed 500 nm. Based on the SEM observation we can expect the novel materials to be of benefit to the diffusion of the reactant.

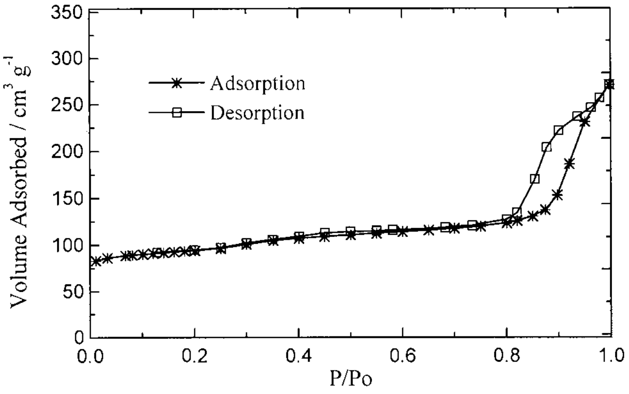

Figure 2. Nitrogen sorption isotherms of MaS-1 sample.

The N_2 sorption isotherms of calcined MaS-1 and MaZSM-5 samples have a similar shape. Figure 2 depicts the isotherms of MaS-1 sample, from which we can observe three adsorption steps. The first step at very low partial pressures indicated filling of intracrystalline micropore system, the second adsorption step at P/Po of ca. 0.27 may be explained by N_2 condensation in intercrystalline voids present between the nanophase crystalline particles[10] and the third upward turn of the isotherm at higher P/Po indicated filling of larger interparticle spaces. The detailed N_2 sorption data are summarized in Table 1. The well-crystallized walls of the macropores are evidenced by nearly identical micropore surface areas of MaS-1, MaZSM-5 and their original nanophase zeolites. However, the external surface areas of MaS-1 and MaZSM-5 are relatively lower than their original nanophase zeolites, which can be explained by the condensation procedure during calcination as proposed above.

Table 1. Summary of the N_2 sorption data of the macroporous materials and the nanophase zeolites

Samples	Specific surface area BET /m^2 g^{-1}	Specific surface area Langmuir /m^2 g^{-1}	External surface area[a] /m^2 g^{-1}	Micropore surface area[b] /m^2 g^{-1}
MaS-1	316	421	51	265
silicalite-1	358	476	97	261
MaZSM-5	339	453	37	302
ZSM-5	347	460	51	296

[a]t-plot according to the method of Lipens and de Boer.[14]
[b]subtract external surface area from specific surface area (BET).

This study has demonstrated that macroporous materials can be made by self-assembly of colloidal zeolites within the voids between close-packed PS spheres. Currently, detailed studies are in progress to determine the sorption behavior, thermal stability, and catalytic reactivities.

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