Zeolite-Coated Mesostructured Cellular Silica Foams

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Recent effort has been focused on improving both the acidity and the hydrothermal stability of mesoporous aluminosilicates through the use of zeolite seeds to construct the walls of mesoporous materials.1–3 For example, zeolite colloidal gels of ZSM-5, TS-1 (MFI), beta (BEA), and faujasite (FAU) were autoassembled to form steam-stable mesostructured material.2,3 Mesoporous materials (UL-zeolites) with semicrystalline zeolitic mesopore walls were also prepared using a templated solid-state crystallization method. Bright- and dark-field TEM images of UL-zeolites indicated that nanocrystals were embedded in the continuous amorphous inorganic matrix to form semicrystalline wall structures.4 Recently, we have described a new concept exemplified by the production of unusual ZSM-5-coated mesoporous aluminosilicate SBA-15 using a diluted clear solution containing primary zeolite units. Steam-ultrastable and highly acidic materials were achieved due to the nanocrystalline zeolitic nature of their pore wall surface.5 Unlike MCM-41 and SBA-15, which have monodimensional mesopore structures leading to serious mass transfer limitations, 6,7 mesostructured cellular silica foams (MCF) are composed of uniformly sized, large spherical cells (up to 500 Å) with high surface areas that are interconnected by uniformly sized windows to create a continuous 3-D pore system.8 It would therefore be also of interest to impart to these new larger pore materials the high hydrothermal stability already obtained by zeolite coating of SBA-15. Our objective here is thus to prepare a new type of zeolite-coated MCF using clear ZSM-5 (MFI) and faujasitic zeolite type Y (FAU) gel solutions.

Zeolite-coated mesocellular aluminosilicate foams (zeolite-coated MCF) were synthesized by a two-step procedure. The first step consists of the preparation of the mesocellular aluminosilicate foam precursor (MCF) according to the method described in ref 8 and the desired clear zeolite gel solution containing primary zeolite seeds (NaY and ZSM-5).9,10 The second step is a coating of nanozeolite seeds on the MCF surface using the diluted clear zeolite gel. The detailed synthesis procedure is better described in the Supporting Information.

Figure 1 shows the N2 adsorption/desorption isotherms and BdB-FHH pore diameter distributions calculated from the adsorption branch of the isotherm (inset) for (a) parent MCF and (b) ZSM-coated MCF.

Table 1. Physicochemical Properties of the Parent Mesocellular Alumosilica Foam (PMCF) and Zeolite-Coated Mesocellular Foam (Zeolite-MCF) Samples

<table>
<thead>
<tr>
<th>materials</th>
<th>Si/Al (atom)</th>
<th>S BET (m2/g)</th>
<th>meso vol (cm3/g)</th>
<th>spherical cavity diameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMCF</td>
<td>200</td>
<td>875</td>
<td>3.25</td>
<td>315</td>
</tr>
<tr>
<td>ZSM-5-coated MCF</td>
<td>125</td>
<td>435</td>
<td>0.70</td>
<td>175</td>
</tr>
<tr>
<td>NaY-coated MCF</td>
<td>115</td>
<td>455</td>
<td>0.53</td>
<td>155</td>
</tr>
</tbody>
</table>

*a Atomic Si/Al ratios obtained by atomic adsorption spectroscopy. b Cell diameter determined according to the BdB-FHH method using the spherical pore model (ref 11).

walls) become visible as distributed homogeneously over the coated sample (Figure 2B).

A blank experiment consisting of heating the parent MCF sample in glyceral without a treatment with the clear ZSM-5 gel yielded a material which did not show these spots. The formation of ~30 Å particles is in agreement with the initial stage of the ZSM-5 crystal growth mechanism reported in the literature.9,10

Furthermore, 129Xe NMR was also used as a sensible probing technique for studying the internal pore structure of these materials. A weak band at ~174 ppm, which is characteristic of xenon adsorbed in the ZSM-5 micropore channels, was observed for the ZSM-5-coated sample. Such a band was indeed not present in the parent MCF sample.12 Similar trends were also observed for the NaY-coated MCF sample (Table 1 and Figure S1). The 27Si MAS spectrum of the parent MCF sample exhibited two broad resonances at ~110 ppm for a Q<sup>4</sup> environment and at ~100 ppm for a Q<sup>3</sup> environment together with a shoulder at 90 ppm ascribable to Q<sup>2</sup> species. However, the spectra of the coated MCF samples show a main Q<sup>4</sup> peak at ~108.5 ppm and a small Q<sup>3</sup> shoulder peak at ~~98 ppm, and essentially no Q<sup>2</sup> peak was found (Figure 3). These reflect a lower OH concentration in the coated samples, which indicates the coating procedure led to grafting nanoclustered zeolite particles on the mesopore surface by the condensation reaction of silanol groups at the interface. Aluminum environments in these materials were also quantified by ultrahigh field 27Al MAS and
MQMAS (750 MHz for $^1$H) NMR. For the parent MCF sample, the mesopore walls. The order of the acid site density is HY-coated attributed to secondary building units characteristic of zeolite within corresponding MCF sample (Figure S2). The higher acidity can be attributed to the zeolite seeds coated on the mesopore surface, which create valence bonds with the precursor and heal defect sites, reducing consequently the concentration of silanol groups. It can be concluded that zeolite-coated MCF are promising as new acid catalysts for the conversion of bulky molecules at high temperature. The methodology of coating zeolite seeds into the wall surface of mesoporous aluminosilicates as a means of improving hydrothermal stability and acidity is quite simple, general, and applies to various kinds of zeolite guests and mesoporous materials hosts.

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Supporting Information Available: Figures S1–S3 and synthesis procedure (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References


JA028656A
Fig. S1: \( \text{N}_2 \) adsorption/desorption isotherms at -196\(^\circ\)C for: a) parent MCF and b) NaY coated MCF.
**Fig. S2:** FT-IR spectra of pyridine adsorbed on the protonated samples in the 1350-1600 cm⁻¹ range after pyridine adsorption and then desorption at 150ºC: a) parent MCF in H-form, b) H-ZSM-5 coated MCF, c) HY coated MCF and d) H-ZSM-5.
Fig. S3: $\text{N}_2$ adsorption/desorption isotherms for (A) parent MCF sample, (B) ZSM-5 coated MCF and (C) NaY coated MCF a) before and b) after steaming with 20% H$_2$O in N$_2$ at 800ºC for 2 h.