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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.[1−5] 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 alumosilicate foams (zeolite-coated MCF) were synthesized by a two-step procedure. The first step consists of the preparation of the mesocellular alumosilicate 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 N_2 adsorption/desorption isotherms and BdB-FHH cell size distributions calculated from the adsorption branch of the isotherm for the MCF sample before and after coating using a clear ZSM-5 gel solution.[11] Table 1 summarizes for the same samples the BdB-FHH spherical cell sizes along with the BET surface areas and pore volumes. Significant decreases in surface area, spherical cell size, and pore volume clearly indicate that zeolite nanoclusters were located inside the mesopore channels. XRD diagrams of the coated samples show no peaks in the 2θ range of 10−50°, indicating that the coating contains no crystals having diameters above ∼50 Å. Figure 2 shows the TEM images of the parent MCF and ZSM-5-coated MCF samples. The parent sample presents a typical strutlike MCF structure (Figure 2A). For the coated sample, slight deformation of the spherical cells was observed. However, some spots of ∼30 Å in size (due to a higher density of zeolite particles as compared to the amorphous mesopore walls) become visible as distributed homogeneously over the coated sample (Figure 2B).

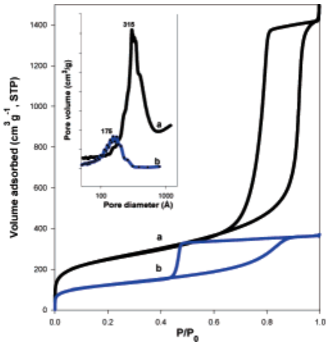

Figure 1. N_2 adsorption/desorption isotherms at −196 °C and BdB-FHH pore diameter distributions calculated from the adsorption branch of the isotherm (inset) for (a) parent MCF and (b) ZSM-coated MCF.

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

materials	Si/Al[a] (atom)	S_{BET} (m^2/g)	meso vol (cm^3/g)	spherical cavity diameter (Å)[b]
PMCF	200	875	2.35	315
ZSM-5-coated MCF	125	435	0.70	175
NaY-coated MCF	115	455	0.55	155

[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).

A blank experiment consisting of heating the parent MCF sample in glycerol 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, ^{129}Xe 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 ^{29}Si MAS spectrum of the parent MCF sample exhibited two broad resonances at −110 ppm for a Q^4 environment and at −100 ppm for a Q^3 environment together with a shoulder at 90 ppm ascribable to Q^2 species. However, the spectra of the coated MCF samples show a main Q^4 peak at −108.5 ppm and a small Q^3 shoulder peak at ∼ −98 ppm, and essentially no Q_2 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 ^{27}Al MAS and

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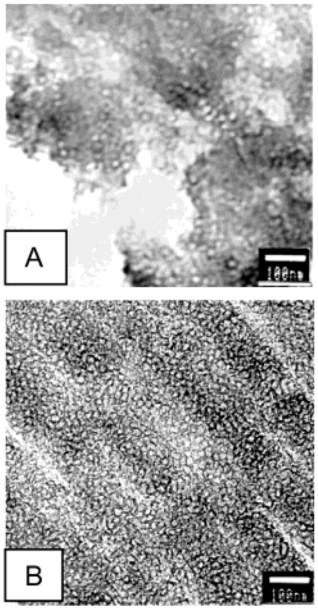

Figure 2. TEM image of (A) parent MCF and (B) ZSM-5-coated MCF.

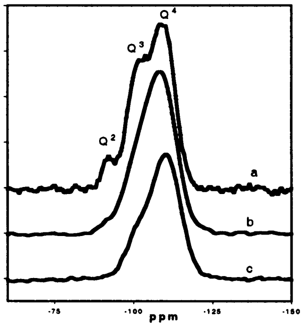

Figure 3. ^{29}Si MAS NMR spectra of (a) parent MCF, (b) NaY-coated MCF, and (c) ZSM-5-coated MCF.

MQMAS (750 MHz for ^{1}H) NMR.[12] For the parent MCF sample, two distinct aluminum environments were detected; a broad peak is a typical tetrahedral aluminum in amorphous materials, and the second is an extraframework aluminum species. However, the coated samples (e.g., ZSM-5- and NaY-coated MCF) show an additional sharp peak, which is characteristic of the tetrahedral aluminum in the zeolite framework.[12,13] The combination of these results suggests that zeolite nanoparticles were located within the mesopore channels. The actual decrease in spherical cavity diameter (Table 1) indicates that this coating encompasses more than one monolayer of nanoparticles.

The IR spectra of pyridine adsorbed on protonated samples in the region 1600−1400 cm^{-1} after evacuation at different temperatures show that both Brönsted and Lewis acid sites of the coated samples are in much higher concentration than those of the corresponding MCF sample (Figure S2). The higher acidity can be attributed to secondary building units characteristic of zeolite within the mesopore walls. The order of the acid site density is HY-coated MCF > H-ZSM-5-coated MCF ≫ parent MCF. The higher acid site density of the HY-coated sample could be due to the high aluminum loading in the faujasite gel (Si/Al = 10) as compared to that in ZSM-5 gel (Si/Al = 50). Figure S3 shows the N_2 adsorption/desorption isotherms for the parent MCF and ZSM-5- and NaY-coated samples before and after exposure to 20% steam at 800 °C for 2 h. The mesopore structure of the parent sample had collapsed after this treatment. By contrast, no significant change in the mesopore structure under the same treatment conditions indicates that the coated samples are much more hydrothermally stable than is the parent MCF sample. This could 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.

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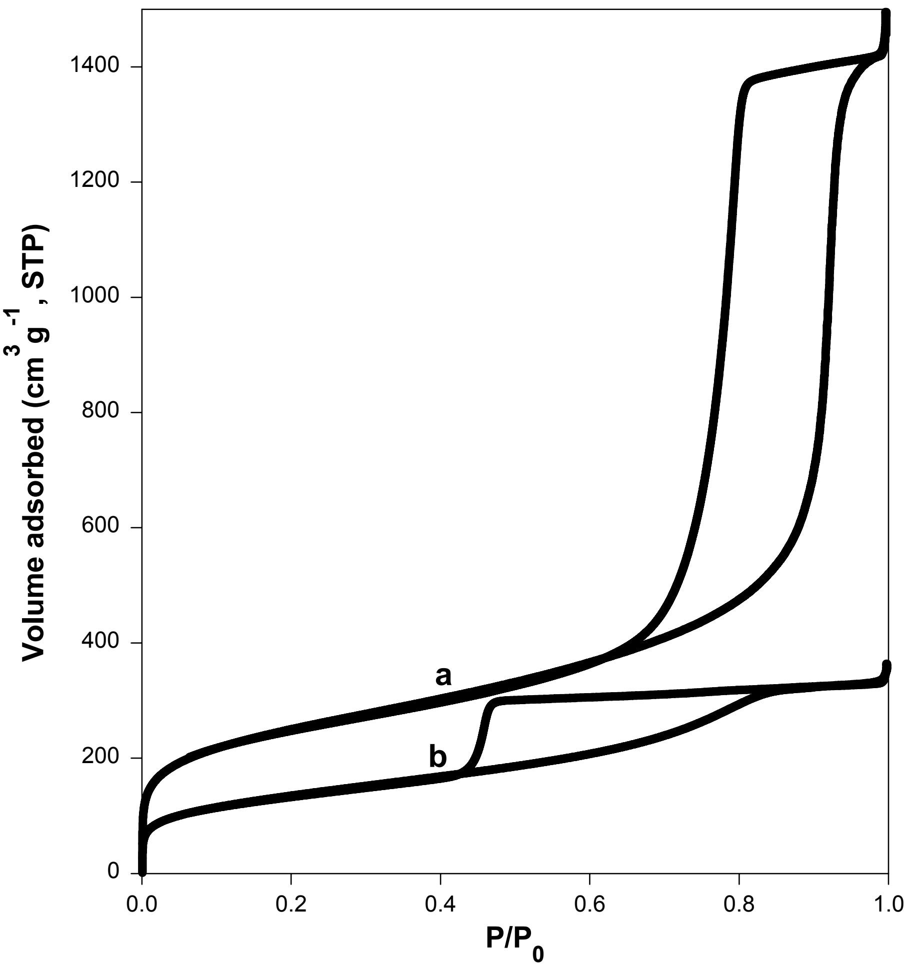

Fig. S1: N_2 adsorption/desorption isotherms at -196ºC for: a) parent MCF and b) NaY coated MCF.

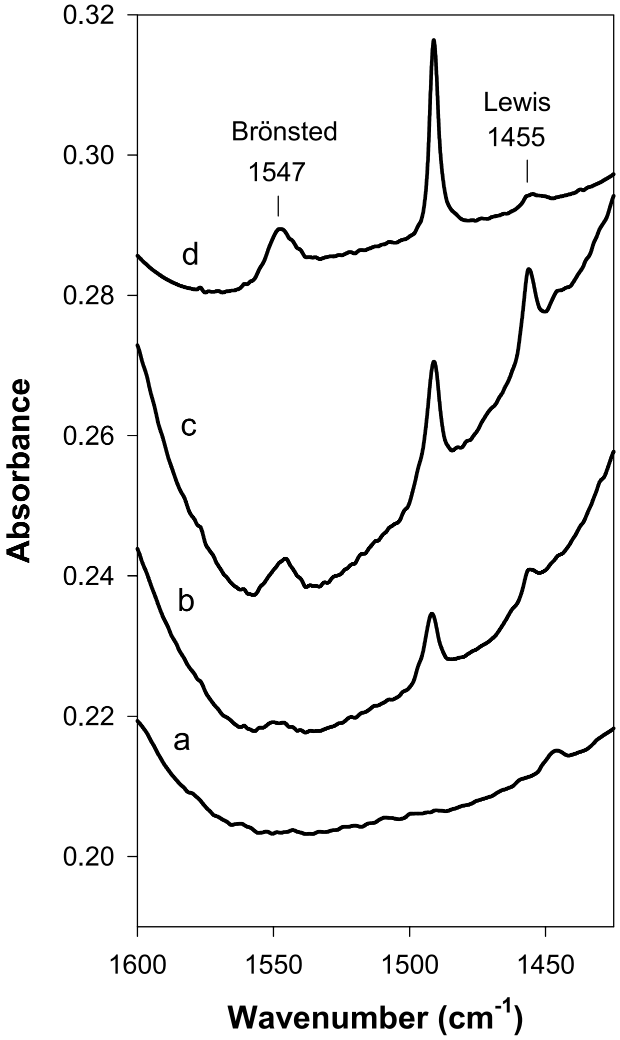

Fig. S2: FT-IR spectra of pyridine adsorbed on the protonated samples in the 1350-1600 cm^{-1} range after pyridine adsorption and then desorption at 150ºC: a) parent MCF in H-form, b) H-ZSM-5 coated MCF, c) HY coated MCF and d) H-ZSM-5.

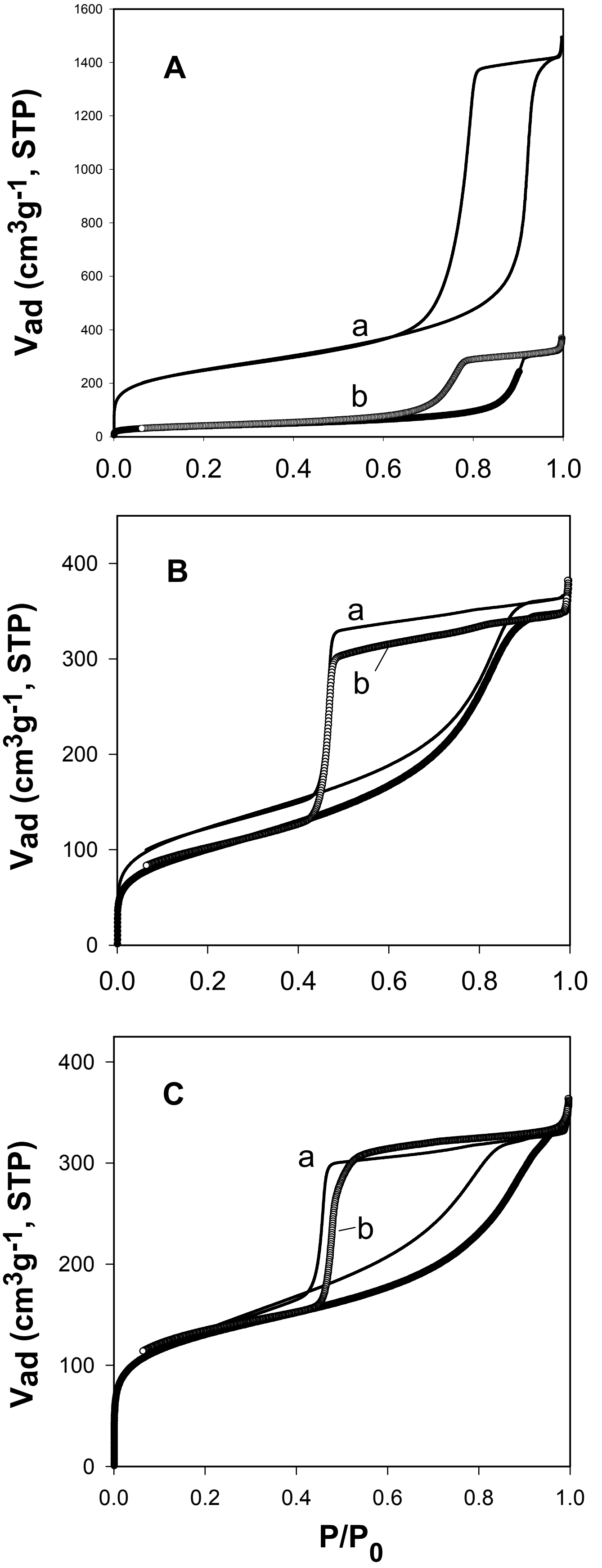

Fig. S3: N_2 adsorption/desorption isotherms for (A) parent MCF sample, (B) ZSM-5 coated MCF and (C) NaY coated MCF a) before and b) after steaming with 20% H_2O in N_2 at 800ºC for 2 h.