

## Zeolite Nanoclusters Coated onto the Mesopore Walls of SBA-15

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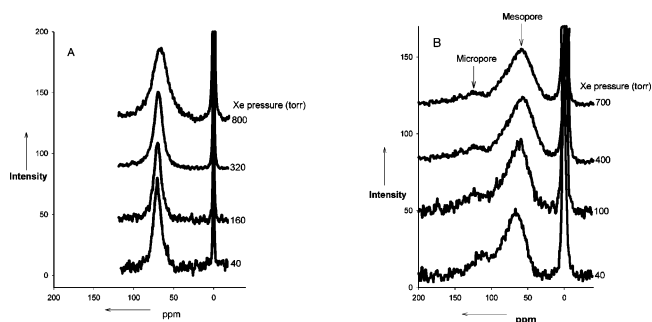
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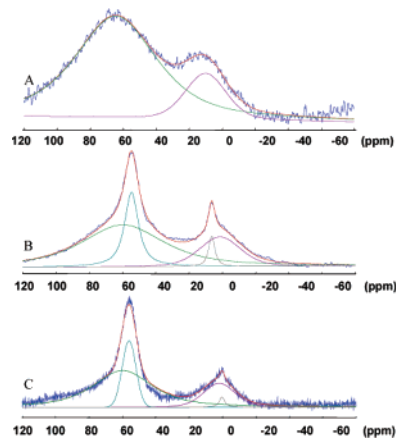
Hydrothermal stability and acidity are both essential for the application of mesoporous materials in catalysis.<sup>1,2</sup> Several approaches have been aimed at improving these properties;<sup>3–8</sup> for example, hydrothermally stable and strongly acidic mesoporous aluminosilicates have been assembled using protozeolitic seeds.<sup>5,6</sup> A recent study from our group showed that the coating of protozeolitic nanoclusters onto the surface of preformed mesostructured aluminosilicates greatly improved both their acid strength and hydrothermal stability.<sup>7,8</sup> These resulting zeolite-coated mesoporous aluminosilicates (noted ZCMeso-AS) were found to be stable to exposure to 20% water vapor for 24 h at 800 °C and in boiling water at 100 °C for at least 5 days and to exhibit acidities comparable to those of zeolites. It is thought that these properties of the highly acidic ZCMeso-AS are due to the zeolitic nature of their mesopore wall surfaces.<sup>7</sup> These features overcome the limitations of conventional zeolites and mesoporous materials as catalysts.

In a previous paper,<sup>7</sup> we have shown that there are significant decreases in mesopore diameter (from 70 to 54 Å), in surface area (from 800 to 465 m<sup>2</sup> g<sup>-1</sup>), and in mesopore volume (from 1.56 to 0.78 cm<sup>3</sup> g<sup>-1</sup>) of a mesoporous aluminosilicate SBA-15 sample (designated as PMesoAS in ref 7, atomic Si/Al = 65) after coating with ZSM-5 seeds (designated as ZCMesoAS,<sup>7</sup> atomic Si/Al = 50). The coated sample shows a FTIR band at ~550 cm<sup>-1</sup> (characteristic of the five-membered ring units in the pentasils) which is not present in the parent SBA-15 sample. Taken together, these observations indicated that zeolite nanoclusters were located inside the mesopore channels.<sup>7</sup> However, no micropore volume of zeolite was detected by nitrogen adsorption isotherms. XRD diagrams of the coated samples show no zeolite peaks in the 2θ range of 10–50°, indicating that the coating contains no crystals with dimensions greater than ~50 Å. Similarly, no XRD reflections characteristic of zeolite crystals were observed for the materials assembled from zeolite seeds.<sup>5,6</sup> In the present paper, we provide additional evidence which confirms that zeolite nanoclusters are coated on the mesopore surface of the host, using <sup>129</sup>Xe NMR as a sensitive technique for probing the internal pore structure<sup>9</sup> as well as ultrahigh-field <sup>27</sup>Al MAS and MQMAS (750 MHz for <sup>1</sup>H) NMR for quantifying the multiple aluminum environments in these materials.<sup>10</sup>

The <sup>129</sup>Xe NMR spectra of the parent SBA-15 sample (e.g., PMesoAS) at various pressures show two lines at ~70 and 0 ppm corresponding to the xenon in the mesopore channels and in the gas phase, respectively (Figure 1A). The chemical shift of the line from the adsorbed xenon slightly decreases as it is the case for Xe adsorbed in mesoporous systems (ca. 3 ppm as the xenon pressure changes from 40 to 820 Torr).<sup>9</sup> However, the ZSM-5-coated sample (e.g., ZCMesoAS) shows an additional signal at higher chemical



**Figure 1.** <sup>129</sup>Xe NMR spectra of (A) parent SBA-15 and (B) ZSM-5-coated SBA-15 at various xenon pressures.



**Figure 2.** <sup>27</sup>Al MAS NMR spectra at 208.43 MHz (18.8 T, 800 MHz for protons) of: A) parent SBA-15, B) ZSM-5 coated SBA-15 after calcination, (C) NaY-coated SBA-15. Pulse angles of approximately 12° were used to ensure even excitation of all the nuclei.

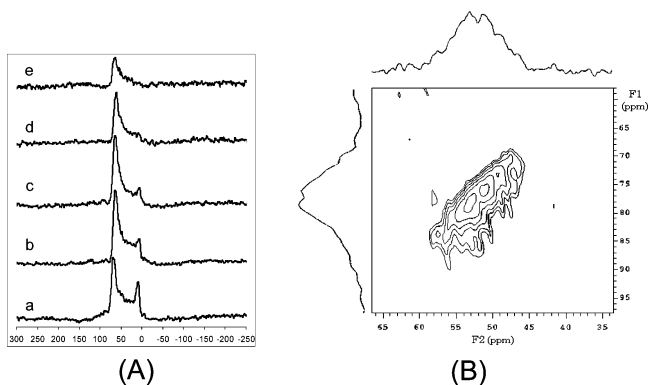
shift increasing from 109 to 125 ppm for the same pressure range as above, which is attributed to the xenon adsorbed in the microporous channels of ZSM-5 (Figure 1B). This intensity corresponds to ~2 wt % of zeolite ZSM-5. Figure 1a,b, shows that increasing the Xe pressure yields broader resonance signals, an effect which is ascribed to an increased exchange between Xe populations  $N_{\text{gas}}$ ,  $N_{\text{meso}}$ , and  $N_{\text{micro}}$ .

As shown by the spectra and deconvolutions in Figure 2, various aluminum environments in these samples are detected by ultrahigh-field <sup>27</sup>Al MAS NMR spectroscopy. NMR experiments were carried out at 750 and 800 MHz for <sup>1</sup>H on spectrometers at the Pacific Northwest National Laboratory, Richland, Washington.<sup>10</sup> For the parent sample, (Figure 2A), two distinct aluminum environments are present: a broad peak at 64.4 ppm typical of tetrahedral aluminum in amorphous materials (considering that the high-field yields lower experimental shifts by partially removing the quadrupolar interaction of <sup>27</sup>Al) and a second broad peak at 9.9 ppm due

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**Figure 3.** (A)  $^{27}\text{Al}$  MAS NMR spin-echo spectra at 208.43 MHz (18.8 T, 800 MHz for protons) of the ZSM-5-coated SBA-15 in Figure 2b recorded at tau values of (a) 0.15, (b) 0.30, (c) 0.60, (d) 1.2, (e) 2.4 ms. (B)  $^{27}\text{Al}$  MQMAS NMR spectra at 195.40 MHz (17.6T, 750 MHz for protons) with a two-pulse nutation sequence on a Varian Inova system using a similar probe and stator assembly of ZSM-5-coated SBA-15.

to octahedral aluminum, again in an amorphous environment. However, the calcined ZSM-5-coated sample (Figure 2B) shows two additional sharper peaks centered at 54.5 and 6.3 ppm. The former is characteristic of an additional tetrahedral environment,<sup>10</sup> and is at a chemical shift value similar to that of the Al in ZSM-5 at this field. However, it is broader than the corresponding resonance from the bulk of perfectly crystalline ZSM-5 (9.9 ppm vs 4.8 ppm), in agreement with its being present in the less highly ordered environment of nanoclusters as proposed. The appearance of the small, sharper octahedral resonance is consistent with the effect of calcinations on ZSM-5. The spectrum of the uncalcined material is similar, but this octahedral resonance is absent. Similar results are obtained for materials coated with nanoclusters of zeolite Y, Figure 2C. In this case, there is more aluminum present in the zeolite nanoseeds, and the relative intensities of the resonances from the framework are reduced. Again, the sharper signal at 55.9 ppm is due to tetrahedral aluminum in the zeolite seeds and is at a chemical shift value similar to that of the tetrahedral aluminum in the macroscopic zeolite crystals of zeolite Y, but again is broader (9.7 ppm vs 2.2 ppm), consistent with it being in a similar but less highly ordered environment. An important advantage of solid-state NMR in the characterization of these materials is that it detects the immediate environments of the nuclei and is unaffected by particle dimensions or the long-range ordering.

It was thought that the higher degree of ordering of the nanoclusters compared to that of the amorphous framework might result in their aluminum nuclei having longer  $T_2$  values than those in the framework and that this might make it possible to easily differentiate them, even in cases where there was severe overlap. Figure 3A shows a series of spectra obtained with a 90- $\tau$ -180- $\tau$ -acquire spin-echo pulse sequence for the different  $\tau$  values indicated, for the calcined ZSM-5 coated material corresponding to Figure 2B. As anticipated, the signals due to the framework decrease rapidly in relative intensity as  $\tau$  becomes longer, followed by the sharper octahedral peak due to nonframework aluminum until at a tau value of 2.4 ms, only the resonance due to the nanozeolite framework tetrahedral aluminum remains.

Figure 3B shows the  $^{27}\text{Al}$  MQMAS spectrum of the ZSM-5-coated sample at 750 MHz. Only two partially resolved signals at 55 and 52 ppm (F2) are observed which are assigned to tetrahedral aluminum species in the nanozeolite framework.<sup>10</sup> These signals may be hypothesized to correspond to surface and bulk Al in the zeolite nanoclusters. No signals are seen for the tetrahedral and octahedral environments in the amorphous mesostructure. This is in agreement with the observations presented above from the spin-

echo sequence since the MQMAS experiment is a 2D experiment where each individual experiment in the series also generates an echo, and in general, these experiments may also be expected to discriminate in favor of more highly ordered environments in these composite materials. The increased hydrothermal stability and acidity of the coated sample, as reported in the previous paper,<sup>7</sup> were attributed to the coating of nanosized ZSM-5 seeds on the walls of the parent SBA-15. Figure S1 shows the  $^{29}\text{Si}$  MAS spectra of the parent and coated SBA-15 samples. A much higher  $Q^4/Q^3$  ratio is observed in the coated sample compared to that of the parent SBA-15, which reflects the transformation of the hydrophilic surface of the parent sample into a more hydrophobic one upon seed coating. This also indicates the coating procedure leads to the grafting of the zeolite nanoclusters onto the mesopore surface by the condensation reactions of silanol groups at the interface. It is worth recalling that a blank experiment, in which the parent SBA-15 was suspended for 24 h in glycerol at 130 °C, did not lead to any improvement in hydrothermal stability of this material. Thus, all of the experimental data presented above are in agreement with the zeolite nanoclusters being located within the mesopore channels of SBA-15 and bonded to these surfaces. Figure S2 gives a schematic presentation of the hexagonal structure before and after the coating procedure, showing the proposed arrangement of the zeolite nanoclusters within the cylindrical channels.

Combined  $^{129}\text{Xe}$  NMR and ultrahigh-field  $^{27}\text{Al}$  MAS and MQMAS NMR are useful tools for the detection of zeolite nanoclusters and different aluminum environments in nanozeolite/mesoporous aluminosilicate composites, which are very difficult or even impossible to detect by conventional diffraction techniques. Such techniques will be useful in characterizing the numerous other materials prepared from nanoclustered zeolite seeds as framework precursors, such as MSU-S, MAS-5, MSU-S/H, MAS-7 and MSU-S/F.<sup>2-6</sup>

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**Supporting Information Available:** Figures S1 and S2 and synthesis procedure. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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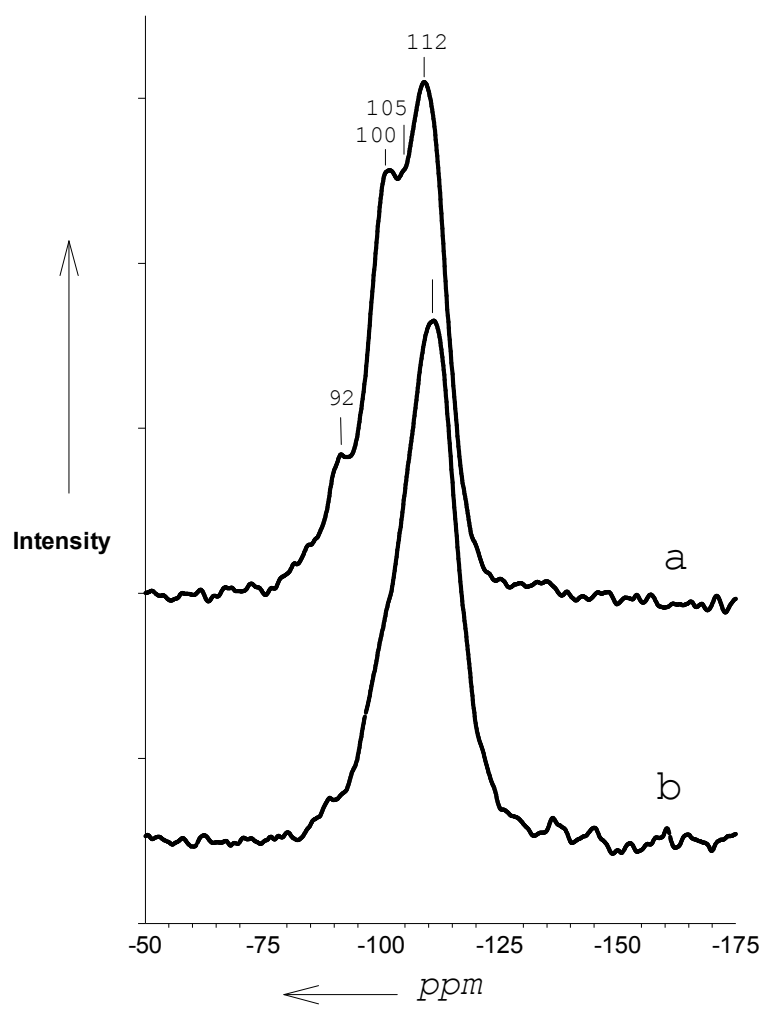
Do Trong On, Andrei Nossov, Marie-Anne Springuel Huet, Celine Schneider, Jeremy L. Bretherton, Colin A. Fyfe, and Serge Kaliaguine

### *Experimental section*

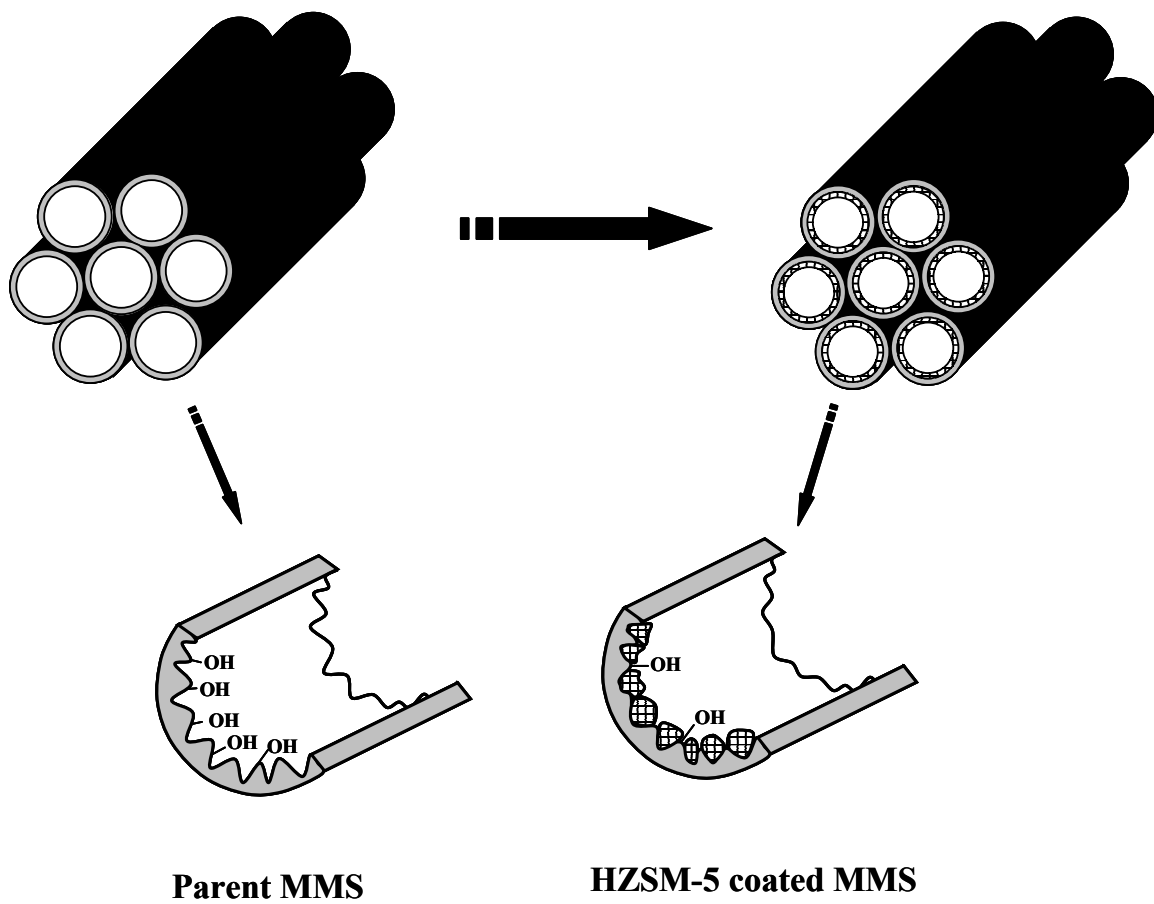
*Synthesis:* The synthesis of zeolite coated mesoporous materials involves two steps: the first step consists in the preparation of the mesoporous aluminosilicate precursor (SBA-15) and of the desired clear zeolite gel.<sup>[7]</sup> Clear zeolite gel solutions were prepared with molar composition of 2.5TPAOH : 0.1Al<sub>2</sub>O<sub>3</sub> : 10SiO<sub>2</sub> : 250H<sub>2</sub>O for ZSM-5 and 0.15Na<sub>2</sub>O : 5.5(TMA)<sub>2</sub>O : 0.5Al<sub>2</sub>O<sub>3</sub> : 10 SiO<sub>2</sub> : 570 H<sub>2</sub>O for faujasite. In a typical ZSM-5 gel synthesis (atomic Si/Al=50), 35 g of 20% aqueous solution of TPAOH was added to 19.5 g of TEOS. To the resulting clear solution, a solution of 0.216 g sodium aluminate (46.78% Al<sub>2</sub>O<sub>3</sub>, 28.43% Na<sub>2</sub>O) in 25 g of distilled water was added. The resulting clear solution was stirred for 24 h at room temperature to form protozeolitic species (known as zeolite seeds) and was finally diluted by distilled water to a volume of 600 ml.

In the second step, 20 g of the calcined mesoporous aluminosilicate precursor (SBA-15) was contacted with 600 ml of the diluted ZSM-5 gel prepared above under vigorous stirring at room temperature for 1 h. The solid sample was filtered, washed with distilled water, dried at 80°C. The resulting solid was subsequently suspended in 50 ml glycerol and the mixture was then transferred into Teflon lined autoclave and heated at 130°C for 24 hours. Glycerol was used as the medium for crystallization because due to the low solubility of silica in this medium, the framework was better retained during crystallization. Finally the solid product was filtered, washed with distilled water, dried at 80°C and calcined at 550°C.

*Characterization:* <sup>129</sup>Xe NMR spectra were recorded at 293 K with a Bruker MSL-300 instrument operating at 83.0 MHz. The samples were packed in an NMR tube equipped with a re-sealable valve suited for attachment to a vacuum line, then dehydrated in vacuum at 573 K for 5 h before xenon adsorption at room temperature. The samples were equilibrated at different xenon pressures before the NMR tube was sealed. The relaxation delay of 0.5 s was used to get the spectrum.<sup>9</sup> The chemical shifts were expressed relative to that of xenon gas extrapolated to zero pressure. <sup>27</sup>Al spectra were obtained at 208.43 MHz (18.8 T, 800 MHz for protons) using home-built MAS probes incorporating a Doty scientific 5mm “SuperSonic” stator assembly on a Varian Inova system at the Pacific Northwest National Laboratory, Richland, Washington. Spinning rates were ca. 15 kHz. MAS experiments were conventional and 12° pulse lengths of 1 μs were used for the single pulse experiments. Echo experiments used a rotor synchronized “90°-τ-180°-τ-acquire” sequence with pulse lengths of 1.7 (90°) and 3.4 μs (180°) and τ = 0.15, 0.30, 0.60, 1.2, 2.4 ms. <sup>27</sup>Al MQMAS experiments were run at 195.40 MHz (17.6T, 750 MHz for protons) with a two-pulse nutation sequence on a Varian Inova system using a similar probe and stator assembly.<sup>10</sup>



**Figure S1:**  $^{29}\text{Si}$  MAS NMR spectra of: a) parent MesoAS, b) ZSM-5 coated MesoAS at 59.61 MHz



**Figure S2:** A schematic presentation of the hexagonal SBA-15 structure before and after nanozeolite seed coating.