

## A New Route for the Synthesis of Uniform Nanozeolites with Hydrophobic External Surface in Organic Solvent Medium

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Nanosized zeolite crystals (nanozeolites) with narrow particle-size distributions and sizes less than 100 nm have received much attention because of their great potential applications in catalysis and adsorption. The decrease in the crystal sizes results in high external surface areas, reduced diffusion path lengths, and more exposed active sites. For example, small Y-type zeolite crystals have been reported to increase catalytic activity and improve the selectivity of intermediate cracked products such as gasoline and light gas oil in catalytic cracking of heavy gas oil. This catalyst exhibited lower deactivation rates since the coke formation was suppressed.<sup>1</sup> Moreover, nanozeolites can be used as “building units” for constructing hierarchical materials. Zeolite nanoclusters have been employed for assembling mesoporous aluminosilicates.<sup>2</sup> Materials with semicrystalline zeolitic mesopore walls<sup>3</sup> and nanozeolite coated mesoporous aluminosilicates<sup>4</sup> were reported by our group. Recently, zeolites with intracrystal mesopores and strong acidity were also synthesized.<sup>5</sup> The resulting materials are considered of potential for application in catalysis and separation, owing to easier transport of guest molecules through the mesopores and shorter diffusion pathways in the zeolitic walls.

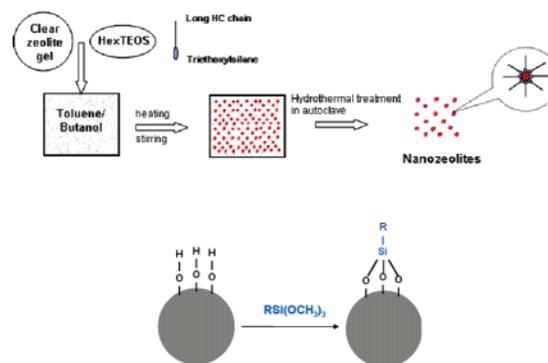
Syntheses of nanozeolites are often carried out in the aqueous phase. During the crystallization, once the nanozeolite precursors are formed, the aqueous phase acts as an effective environment for the incorporation of soluble aluminosilicate species and the aggregation of zeolite crystals. This could lead to the formation of large crystals and aggregates.<sup>6</sup> Direct synthesis using a clear gel solution of aluminosilicates can also produce nanozeolites by careful control of the gel composition and crystallizing conditions.<sup>7</sup> Another method, which is called confined space synthesis, has been developed for the preparation of nanosized zeolite crystals. The synthesis is conducted within an inert matrix such as porous carbon matrices,<sup>8</sup> thermoreversible polymer hydrogels, or microemulsions<sup>9</sup> which provides a steric hindered space for zeolite crystal growth.

Several synthetic routes have been reported for the preparation of nanocrystalline zeolites. However, none of these attempts has produced an easy means of controlling the small size. Furthermore, the external surface of nanocrystalline zeolites is hydrophilic and thereby has mostly silanol groups that limit catalytic reactivity to the internal pore surface.<sup>6</sup>

Serrano et al.<sup>10</sup> have recently reported the use of organosilane as growth inhibitor. In this study, MFI and  $\beta$  zeolites were synthesized in the aqueous medium, using phenylaminopropyl-trimethoxysilane (PHAPTMS). The synthesis is based on reducing the growth of zeolite crystals by silanization of the zeolitic seeds to hinder their further aggregation. However, as investigated by TEM analysis, the obtained MFI sample consisted of particles of about 300–400 nm which were formed by the aggregation of ultrasmall units of 10 nm. Having that large size, the sample was hardly considered as true nanozeolite.

Herein, we demonstrate a new route for the synthesis of controlled uniform size nanozeolites with the hydrophobic external

**Scheme 1.** Schematic Representation of the Single-Phase Synthesis Method

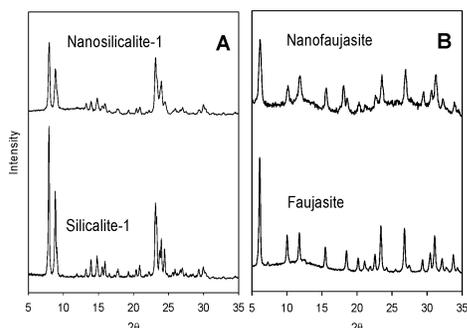


surface. An organic solvent is used as the medium for crystallization instead of water. The zeolite precursors are functionalized with organic silane groups. They thus become hydrophobic and highly dispersed in the organic solvent. Because the crystallization occurs in the organic phase and the zeolite precursors are protected by functional groups, catastrophic aggregation can be prevented hence, resulting in small and uniform nanozeolites with hydrophobic external surface.

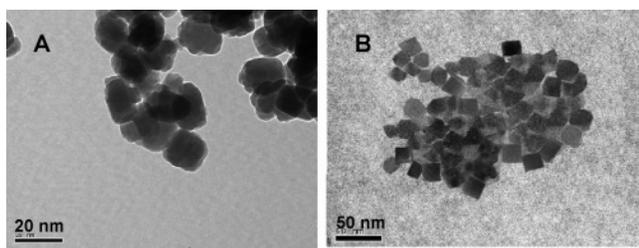
The MFI and faujasite zeolites were selected to illustrate our approach, because they are widely recognized for their unique properties as catalysts. As seen in Scheme 1, this approach is simple and was found to be reproducible when using hexadecyltrimethoxysilane as organosilane agent and the mixture of toluene and *n*-butanol as organic medium.

The XRD patterns of the as-made nanozeolite samples prepared from silylated seeds are shown in Figure 1. Samples prepared by the conventional method in aqueous medium from the same clear zeolite gel solution without organosilane were used as references. The XRD pattern of the nanosilicalite-1 sample is identical to that of the reference, indicating the MFI structure of this nanosilicalite-1 sample. However, there is a clear broadening of the reflections, which is attributed to small crystals. In addition, no significant peak at  $2\theta = 20\text{--}30^\circ$  which is characteristic of amorphous phase was observed, indicating a relatively high crystallinity of this sample. A similar trend was also observed for the nanofaujasite sample (Figure 1B). Furthermore, the FTIR spectra of both as-made nanosilicalite-1 and nanofaujasite match well with the typical FTIR peaks assigned to silicalite-1 and zeolite Y, respectively (not shown).<sup>11</sup>

Representative TEM micrographs of the as-made silylated zeolite samples are shown in Figure 2 and exhibit very uniform nanocrystal sizes mostly with spherical and cubic shaped particles for silicalite-1 and zeolite Y, respectively. The particle size is about 21 nm for silicalite-1 and 27 nm for faujasite. The standard deviation established from the analysis of more than 1500 particles in representative TEM pictures of each sample showed a standard



**Figure 1.** XRD patterns of the as-made silylated zeolite and zeolite samples prepared from the same zeolite gel in solvent medium in the presence of organosilane and in aqueous medium in the absence of organosilane, respectively: (A) silicalite-1; (B) faujasite.



**Figure 2.** TEM images of the as-made samples: (A) silylated nanosilicalite-1, (B) silylated nanofaujasite.

deviation of less than 10% (Supporting Information (SI) Table 1). Interestingly, the samples are composed of discrete particles rather than aggregates. Owing to the organosilane being grafted on the zeolite precursor, the nanoparticles remain highly dispersed in the organic medium and protected against drastic aggregation during crystallization.

The  $^{29}\text{Si}$  MAS NMR spectra of the as-made samples, silicalite-1 and silylated silicalite-1, prepared from the same zeolite gel solution were investigated (SI Figure 1A). The NMR spectrum of the as-made silicalite-1 sample shows a main resonance at ca.  $-110$  ppm and a weak resonance peak at ca.  $-100$  ppm which are attributed to  $\text{Si}(\text{OSi})_4$ ,  $\text{Q}^4$  and  $\text{Si}(\text{OSi})_3\text{OH}$ ,  $\text{Q}^3$  species, respectively. For the as-made silylated silicalite sample, only one resonance peak at ca.  $-110$  ppm attributable to  $\text{Q}^4$  species was observed; however, an additional peak at  $-65$  ppm assigned to R-C-Si-(OSi) $_3$  species is present.<sup>11</sup> This additional peak is the result of the reaction between the silicon in the organosilane and the silanol groups of zeolite nuclei during the synthesis. This also suggests the silanization on the external surface of nanosilicalite-1, which acts to heal defect sites (e.g., silanol groups) in the zeolite surface. Furthermore this calcined sample also shows essentially a single resonance peak  $\text{Q}^4$  at ca.  $-110$  ppm (SI Figure 1A). Thus, it can be concluded that the presence of only one resonance  $\text{Q}^4$  even after calcination of the silylated silicalite-1 sample suggests its hydrophobic surface character. Similar results were also obtained for the silylated faujasite sample (SI Figure 1B). For the silylated faujasite sample, besides the resonance peaks at  $-88$ ,  $-95$ ,  $-100$ , and  $-103$  ppm corresponding to  $\text{Si}(3\text{Al})$ ,  $\text{Si}(2\text{Al})$ ,  $\text{Si}(1\text{Al})$ , and  $\text{Si}(0\text{Al})$ , respectively,<sup>11</sup> the peak attributed to R-C-Si-(OSi) $_3$  species at  $-65$  ppm was also observed. This peak at  $-65$  ppm is absent in the faujasite sample prepared in aqueous medium in the absence of organosilane. For the silylated faujasite sample,  $\text{Q}^4$  signals became much broader

with higher intensity as compared to those of the faujasite one. This means that the silanization led to the transformation of  $\text{Q}^3$  to  $\text{Q}^4$  silicon species during the synthesis.

The physicochemical properties and crystal size of the nanozeolite samples are presented in SI Table 1 and SI Figure 2. The crystal sizes determined using the Scherrer equation correspond reasonably well to those estimated from the TEM pictures. The BET surface area is 570 and 545  $\text{m}^2/\text{g}$  for the nanosilicalite-1 and nanofaujasite samples, respectively. The external surface area based on  $t$ -plot calculation is 150 and 96  $\text{m}^2/\text{g}$ , in that order. This high external surface value also indicates the small crystal size of the sample. Detailed studies of the sorption behavior and catalytic properties are underway.

In conclusion, a new approach has been developed for the synthesis of uniform zeolite nanocrystals with hydrophobic external surface. We anticipate that with this approach the syntheses of other types of nanozeolites should also be possible. Furthermore, a large variety of silylating agents allows also the tailoring of nanozeolite properties such as crystal size and chemical nature of the surface.

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**Supporting Information Available:** Experimental procedure, SI Figures 1–3, SI Table 1. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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## Supporting information:

**Synthesis:** The synthesis of nanozeolites involves two steps: (i) In the first step, clear zeolite gel solutions were prepared with molar composition of 2.5 TPAOH: 10 SiO<sub>2</sub> : 250 H<sub>2</sub>O and 0.07 Na<sub>2</sub>O : 2.4 (TMA)<sub>2</sub>O : Al<sub>2</sub>O<sub>3</sub> : 4 SiO<sub>2</sub> : 264 H<sub>2</sub>O for silicalite-1 and faujasite, respectively. In a typical silicalite-1 gel synthesis, 35g of 20% aqueous solution of TPAOH was added to 19.5 g of TEOS in 25 g of water. The resulting clear solution was stirred for 24 h at room temperature. These gel solutions were then heated at 80°C for 24 h to speed up the formation of protozeolitic species (known as zeolite seeds). (ii) In the second step, 10 g of gel solution was added to 500 ml of a solution of toluene containing n-butanol (30% wt) and a proper amount of hexadecyltrimethylsilane. The organosilane was in a proportion of less than 10 mol% in regards to the silica content in the gel. Toluene is a suitable medium for the modification of zeolite with organosilane and n-butanol acts as a surfactant. The functionalization reaction was carried out batchwise in a glass reactor under stirring at 60°C for 12 h and reflux. After 12 h of stirring, a mixture of only one clear liquid phase was observed. This mixture was then transferred to an autoclave for further hydrothermal treatment at 150°C for 3 days, and 180°C for 5 days for faujasite and silicalite-1 respectively. After the crystallization, the crude solution of nanozeolite product was precipitated with ethanol and further isolated by centrifugation and then washed with ethanol for several times. The product was then dried at 100°C for 24 hours and calcined at 550°C for 5 hours.

The conventional synthesis of the zeolites in aqueous medium was carried out according to the procedure described in the literature.<sup>7</sup> For the synthesis of silicalite-1, the temperature was 150°C and the crystallization time was 3 days, whereas, for that of FAU zeolites, the temperature and crystallization time were 100°C and 5 days.

**Characterization:** The FTIR spectra were recorded using a Biorad FTS-60 spectrometer on sample wafers. Powder XRD patterns of the materials were recorded on a Philips X-ray diffractometer (PW 1010 generator and PW 1050 computer assisted goniometer) using nickel-filtered CuKα ( $\lambda = 1.5406$

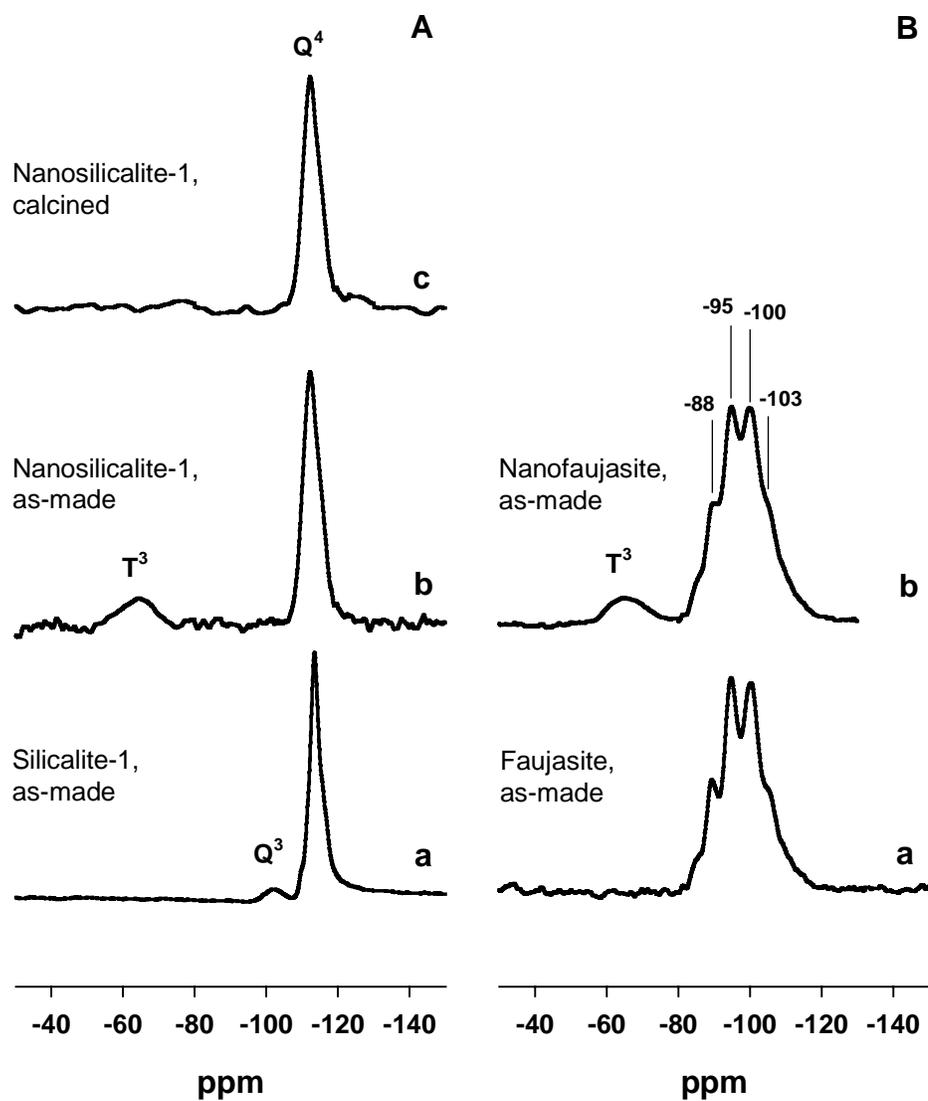
Å) radiation, 0.0258 step size and a 1 s step time. The crystal size of the zeolites was estimated from the broadening of the XRD peaks using the Scherrer equation:  $d = 0.9\lambda / (w-w_1) \cos \theta$  ; where d is the crystal diameter, w and  $w_1$  are the half-intensity width of the relevant diffraction peak and the instrumental broadening, respectively,  $\lambda$  is the X-ray wavelength and  $\theta$  is the angle of diffraction. The following reflections were used for the crystal size determination: for silicalite-1, [501] and [151] plans corresponding to the  $2\theta$  peaks at 23.10 and 23.75°; and for faujasite, [440] and [733] planes corresponding to those at 20.30 and 29.55°.

Nitrogen adsorption/desorption isotherms at -196°C were established using an Omnisorp-100 apparatus. The specific surface area ( $S_{\text{BET}}$ ) was determined from the linear part of the BET equation ( $P/P_0 = 0.05 - 0.15$ ). High-resolution TEM images were obtained on a JEOL 200 CX transmission electron microscope operated at 120 kV. The samples for TEM were prepared by dispersing the fine powders of the products in slurry in ethanol onto honeycomb carbon copper grids. Solid-state  $^{29}\text{Si}$  MAS NMR spectra were recorded at room temperature on a Bruker ASX 300 spectrometer.

*S-Table 1.* Physicochemical properties of the calcined silylated nanozeolite and zeolite samples prepared from the same zeolite gel, in solvent medium in the presence of organosilane, and in aqueous medium in absence of organosilane, respectively.

Sample	$S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )	$S_{\text{EXT}}$ ( $\text{m}^2/\text{g}$ )	$S_{\text{MIC}}$ ( $\text{m}^2/\text{g}$ )	$V_{\text{MIC}}$ ( $\text{cm}^3/\text{g}$ )	$V_{\text{MESO}}$ ( $\text{cm}^3/\text{g}$ )	$R_{\text{PORE}}$ (nm)	Crystal size (nm)-TEM	Crystal size* (nm)-XRD
Nanosilicalite-1	570	150	420	0.154	0.230	3.7	21±2	23 ±1
Silicalite-1	512	15	479	0.162	-	-	~300	-
Nanofaujasite	545	96	449	0.149	0.195	6.5	27 ±2	24 ±1
Faujasite	479	19	460	0.173	-	-	~400	-

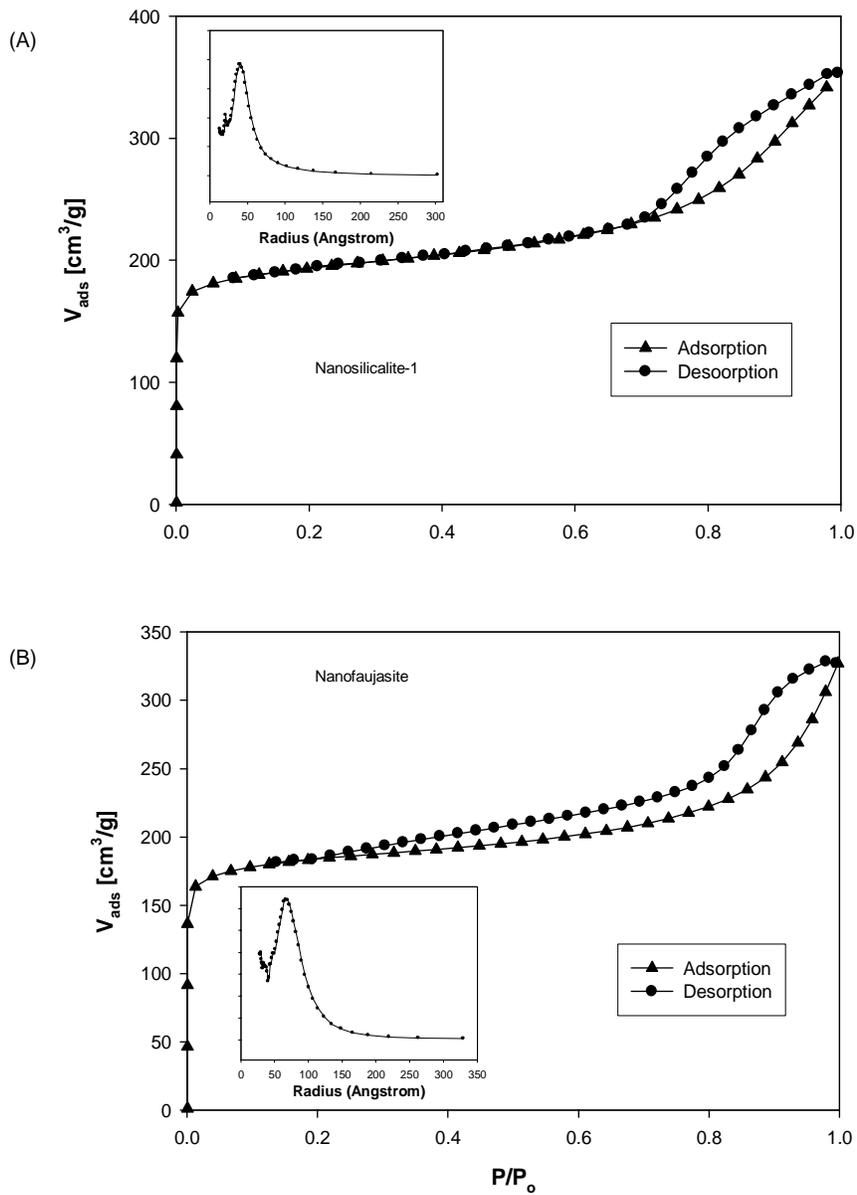
\* The crystal sizes were calculated by applying the Scherrer's equation to the XRD reflections of [501] [151] planes for nanosilicalite-1 and those of [440], [733] planes for nanofaujasite.



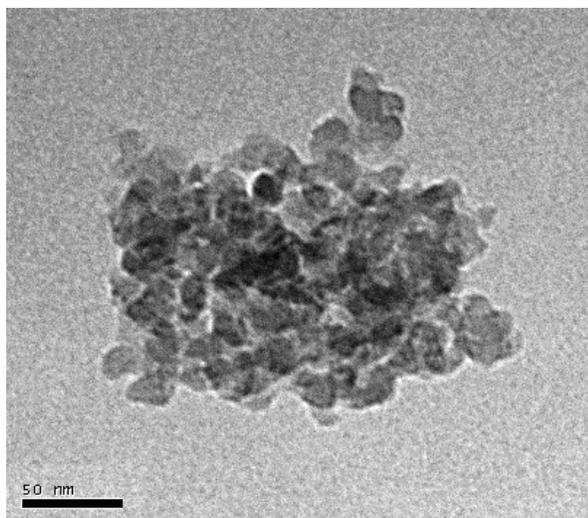
*S-Figure 1.*  $^{29}\text{Si}$  MAS NMR spectra of the as-made silylated samples prepared from the same zeolite gel, in solvent medium in the presence of organosilane, and in aqueous medium in absence of organosilane, respectively.

(A) **silicalite-1:** a) as-made silicalite-1, b) as-made nanosilicalite-1, c) calcined nanosilicalite-1.

(B) **faujasite:** a) as-made faujasite, b) as-made nanofaujasite.



**S-Figure 2.** Nitrogen adsorption/desorption isotherms and BJH pore radius distribution (inset) of the calcined nanosilicalite-1 and nanofaujasite samples



*S-Figure 3.* TEM image of the calcined silylated nano faujasite sample