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Hierarchical Zeolites with Enhanced Textural and Catalytic Properties Synthesized from Organofunctionalized Seeds

David P. Serrano,* José Aguado, José M. Escola,
José M. Rodríguez, and Ángel Peral

Department of Chemical and Environmental Technology,
ESCET, Rey Juan Carlos University,
28933 Móstoles, Madrid, Spain

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Zeolites are microporous crystalline metallosilicates featured by exhibiting molecular sieve and shape selective properties, which have found widespread applications in catalytic, adsorption, and ion exchange processes.[1] Zeolites have usually been synthesized with crystal sizes in the micrometer range and, therefore, with negligible external surface area. These properties impose severe limitations for their use in the conversion of bulky compounds.[2] A huge interest has emerged recently for the synthesis of new zeolitic materials with enhanced accessibility: nanozeolites,[3] hybrid zeolitic-ordered mesoporous materials,[4,5] delaminated zeolites,[6] and zeolites with a secondary porosity prepared by steaming,[7] by desilication,[8] or according to the confined space synthesis.[9,10] The term hierarchical zeolites has been applied for designating zeolites containing a bimodal porosity and showing reduced steric and diffusional restrictions.[11]

In the present work, a novel strategy has been designed for the synthesis of hierarchical zeolites with enhanced surface area, porosity, and catalytic activity. The method is based on perturbing the growth of zeolite crystals by silanization of the zeolitic seeds to hinder their further aggregation (see Supporting Information for experimental details of the syntheses). Organic-functionalized molecular sieves have been prepared earlier by addition of organosilanes to the raw gel, which caused their incorporation within the zeolite micropores.[12] However, in the method here outlined the silylating agent is added once the first zeolite entities are formed. This strategy has been successfully applied to the synthesis of both ZSM-5 and beta zeolites, using phenylaminopropyl−trimethoxysilane (PHAPTMS) as the silylating agent.

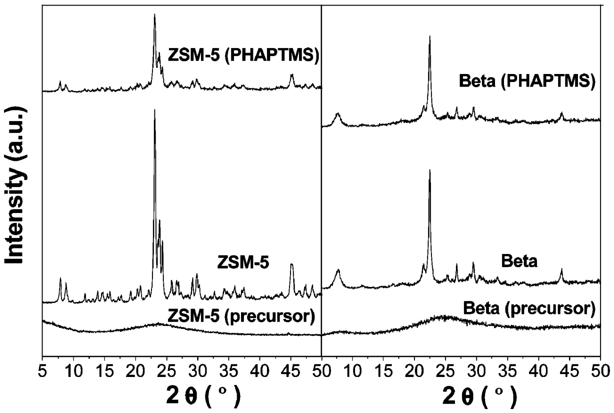

Figure 1. XRD spectra of as-synthesized samples compared to those of the precursor materials recovered after the precrystallization step.

Table 1. Physicochemical and Catalytic Properties of the Samples

sample	Si/Al	S_{BET} (m^2/g)	S_{MIC} [a] (m^2/g)	S_{EXT} [a] (m^2/g)	V_{MIC}[a] (cm^3/g)	PP Cv[b] (%)
ZSM-5	40	459	365	94	0.157	27.3
ZSM-5 (PHAPTMS)	45	586	272	314	0.117	100
beta	36	590	568	22	0.258	3.8
beta (PHAPTMS)	47	769	649	120	0.287	19.7

[a] Determined by applying the *t*-plot method. [b] PP cracking conversion (360 °C, 3 h, PP/zeolite = 50, w/w).

As illustrated in Figure 1, the samples obtained after the final hydrothermal treatment are highly crystalline. For the materials prepared with the silylating treatment, the peaks are less intense compared to those of the conventional zeolites, suggesting that the former present smaller crystalline domains. All zeolite samples possess significant Al amounts (Table 1), although the crystallization from silylated seeds causes a slight reduction in the Al content.

The effective incorporation of the organosilanes into the zeolites occurs with proportions close to that of the synthesis gel, being checked by a number of techniques (CHN, thermogravimetric analysis (TGA), ^{29}Si magic-angle spinning (MAS) NMR). No significant changes are observed in the content of the silylating agent before and after the final hydrothermal treatment or along the synthesis time, showing the stability of its links to the zeolite seeds. Both the structure directing agent (SDA) and organosilane are removed during the calcination treatment, which causes the space occupied by these molecules to become accessible for adsorption and catalysis. The weight loss associated with the silylating agent occurs at lower temperature than in the case of the SDA, suggesting that the former is located mainly on the external surface of SDA-containing particles.

Figure 2 shows that the ZSM-5 sample obtained omitting the silanization treatment is formed by 40−60 nm sized nanocrystals. However, the ZSM-5 sample crystallized from silanized seeds consists of particles of about 300−400 nm, which are formed by aggregates of ultrasmall primary units

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* To whom correspondence should be addressed. Fax: (+34) 91 4887068.

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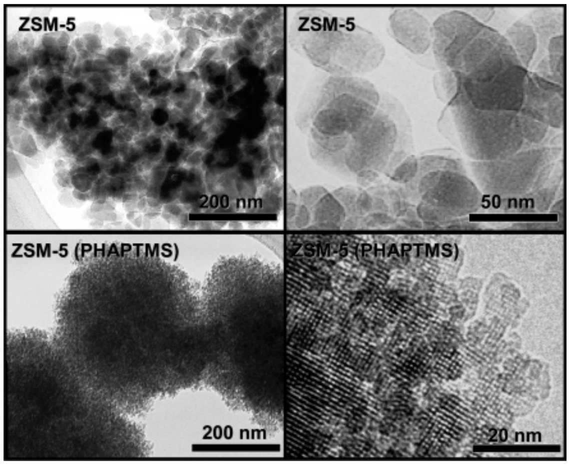

Figure 2. TEM micrographs of the ZSM-5 samples.

with sizes even below 10 nm. The crystalline nature of the latter is clearly demonstrated by the lattice fringes observed in the transmission electron microscopy (TEM) images despite their extremely small size. These nanocrystals exhibit sizes close to that of the nanoparticles elsewhere detected in the precursor solution.[13] The material so obtained must be considered as being polycrystalline rather than consisting in mesoporous single crystals. However, it is interesting to note that adjacent nanocrystals exhibit the same crystalline orientations, which suggests that they present a significant degree of intergrowth. This fact has been also observed in the crystallization of other nanozeolites,[14] and it may explain the relatively well-defined X-ray patterns corresponding to these samples. In a previous work,[15] we have shown that ZSM-5 consisting of nanocrystal aggregates can be also obtained when carrying out the synthesis at low temperature and atmospheric pressure. However, under these conditions very low synthesis yields are obtained (around 20% in regards to the raw silica), which is in contrast with the yields over 90% corresponding to the crystallization at high temperature from silanized seeds.

According to the TEM images (see Supporting Information), the beta sample obtained omitting the silanization treatment is formed by particles with sizes around 400−600 nm. Inspection of these micrographs with high magnifications reveals the polycrystalline nature of these particles, as they seem to be formed by a tight packing of grains. In the beta sample prepared from silylated seeds, the macroparticles exhibit a lower defined shape, while the grains are more clearly visible.

As shown in Figure 3, the materials prepared from silylated seeds exhibit significant higher N_2 adsorption compared to the samples obtained omitting the silanization treatment. For the ZSM-5 zeolite, this enhanced adsorption is originated by the presence of mesopores between the nanocrystals (maximum at 4.5 nm). However, for the beta zeolite the increase in the N_2 adsorption occurs mainly at relative pressures below 0.2, showing the presence of a secondary porosity within the supermicropore region (maximum at 1.6 nm). The data in Table 1 indicate that the materials obtained from organo-functionalized seeds present enhanced BET and external surface areas. Thus, the BET surface area of the ZSM-5 prepared from silylated seeds (586 m^2/g) is exceptionally high for MFI zeolites, while its external surface area accounts for more than 50% of the overall surface area. For the beta zeolite, the seed silanization causes also an increase in the micropore volume, which confirms the presence of a secondary microporosity.

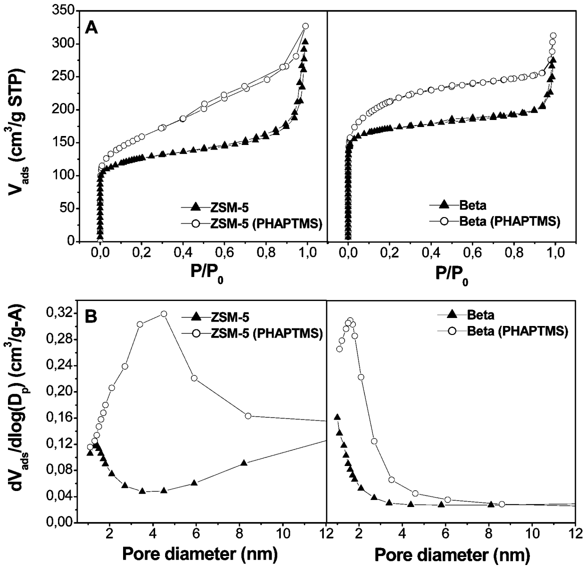

Figure 3. N_2 adsorption−desorption at 77 K of the calcined samples: (A) isotherms and (B) pore size distributions.

The effect of the drastic changes induced in the zeolite properties by the seed silanization treatment on their catalytic behavior has been evaluated using the cracking of polypropylene (PP) as a test reaction (Table 1), which is known to be very sensitive to variations in the zeolite external surface.[16] For both zeolites, the sample prepared from silylated seeds leads to a PP conversion very superior to that of the standard one. These results show the significant effect of the presence of high external surface area and secondary porosity in the zeolites obtained from silylated seeds, which lower the steric and diffusional hindrances.

The protozeolitic nature of the precursor materials obtained in the precrystallization step, prior to the silanization treatment, has been confirmed by different techniques (see Supporting Information). X-ray diffraction (XRD) spectra (Figure 1) indicate that they are X-ray amorphous, although their Fourier transform infrared (FTIR) spectra present a clear shoulder in the region of the zeolitic framework vibrations (500−600 cm^{-1}).[14] Likewise, CHN and TGA measurements show that they contain significant amounts of the zeolite SDAs. Thus, TGA of the ZSM-5 precursor exhibits a weight loss at 400 °C, originated from tetrapropylammonium (TPA^+) cations strongly retained in the solid, whereas its N_2 adsorption−desorption isotherm is typical of microporous solids, showing that a part of the TPA^+ cations are occluded within micropores.

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As a summary, the following mechanism is proposed for the synthesis of hierarchical zeolites from silanized seeds:

(i) Formation of the zeolite nuclei occurs during the precrystallization step. These nuclei must be considered as pseudocrystalline entities, because they present properties intermediate between those of amorphous aluminosilicates and those of zeolites.

(ii) Anchoring of the silylating agent on the external surface of the zeolite nuclei takes place during the silanization step, as the microporosity is filled by the SDA.

(iii) Hydrothermal crystallization of the functionalized seeds occurs, which leads to materials with macroscopic crystalline features and hierarchical porosity, because the presence of the silylating agent hinders the aggregation and densification of the nanounits.

In conclusion, a novel synthesis method has been developed for the preparation of hierarchical zeolites with unique properties. This new strategy can be considered as a general method, as it has been successfully applied to the crystallization of different structures. Moreover, the availability of a large variety of silylating agents, varying in size and chemical nature, provides great opportunities for altering and tailoring the zeolite properties.

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Supporting Information Available: Details of the zeolite synthesis and characterization techniques, ^{29}Si MAS NMR spectra of the hierarchical zeolites, TEM images of the beta samples, and FTIR spectra and TGA of ZSM-5 samples (PDF). This material is free of charge via the Internet at http://pubs.acs.org.

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