

Hybrid Organic–Inorganic Solids That Show Shape Selectivity

Yuriy Román-Leshkov,[†] Manuel Moliner,[†] and Mark E. Davis*

Chemical Engineering, California Institute of Technology, Pasadena, California 91125. [†] Contributed equally to this work.

Received January 12, 2010. Revised Manuscript Received February 17, 2010

Hybrid organic–inorganic solids featuring millimolar/gram concentrations of intracrystalline organic moieties and shape-selectivity are synthesized. Pure-silica zeolite beta crystals are coated with zirconia and treated in aqueous sodium hydroxide to create defects and mesoporosity within the crystalline structure. Aminopropyl organic groups are subsequently grafted onto the generated intracrystalline silanol groups. After grafting, characterization data indicate a high organic concentration localized primarily within the intracrystalline voids. Specifically, thermogravimetric analysis shows an organic loading of 0.7 mmol of NH₂/g, ²⁹Si solid-state nuclear magnetic resonance (NMR) spectra display a quantitative decrease in Q³ silicon atoms with a corresponding resharpening of the Q⁴ resonances, and N₂ adsorption data show a decrease in micropore volume to 0.10 cm³/g. Knoevenagel condensation reactions are catalyzed by the aminopropyl-functionalized materials using differently sized aldehydes and the results show that the zirconia-protected functionalized solid have shape selective properties.

1. Introduction

The incorporation of single or multiple organic functional groups onto inorganic supports leads to hybrid organic–inorganic materials with tailored physicochemical properties useful in many applications including catalysis, separation processes, medicine, microelectronics, and bioengineering.¹ To date, the most studied hybrid materials have been synthesized using mesoporous (2–50 nm) siliceous supports that have large surface areas, high silanol contents, and large pore diameters.² However, low hydrothermal stability and lack of shape selectivity can limit some of the potential applications of these materials. Thus, the incorporation of organic groups into more stable and shape-selective matrixes is of great interest.

Zeolites are crystalline solids composed of metal oxides arranged in a three-dimensional network of uniformly shaped micropores (<2 nm) that act as molecular sieves. Although incorporating organic moieties into the structure of zeolites can give rise to materials with unprecedented properties, few examples of such organo-zeolites exist in the literature. Corma et al. and Cauvel et al. incorporated organic groups into Y-zeolite subjected to an alkaline treatment and steaming, respectively, leading to novel hybrid organic–inorganic crystalline solids.^{3,4} However, these materials did not preserve shape-selective

properties due to organic groups being mainly grafted on the large external surface generated by the post-treatment. Recently, Tatsumi et al.^{5,6} and Corma et al.⁷ synthesized microporous, organic–inorganic materials containing framework methylene or ethylene groups while preserving the structure of the parent zeolites. These types of materials are very limited in the structure type and organic group that can be prepared. Jones et al. first incorporated terminal organic functional groups into zeolites by direct synthesis, introducing different organosilanes into the synthesis media during the crystallization of zeolite beta.⁸ It was shown that shape selectivity was maintained by reacting aldehydes of different sizes with aminopropyl- and sulfonic-acid-functionalized zeolites to form imines and acetals, respectively.^{9–11} However, the introduction of terminal functional groups into zeolites by direct synthesis is also quite limited in the type and amount of organic group (less than 2.8 atom % silicon substituted by organic groups), as the organic precursors used in the synthesis and their amounts must be compatible with the synthesis process. Additionally, zeolites that can be prepared in the absence of a structure directing agent (SDA) or with an SDA that can be removed by

*Corresponding author. E-mail: mdavis@cheme.caltech.edu.

- (1) Davis, M. E. *Nature* **2002**, *417*, 813.
- (2) Hoffmann, F.; Cornelius, M.; Morell, J.; Fröba, M. *Angew. Chem., Int. Ed.* **2006**, *45*, 3216.
- (3) Corma, A.; Iglesias, M.; del Pino, C.; Sanchez, F. *J. Chem. Soc., Chem. Commun.* **1991**, 1253.
- (4) Cauvel, A.; Brunel, D.; DiRenzo, F.; Moreau, P.; Fajula, F. *Stud. Surf. Sci. Catal.* **1995**, *94*, 286.
- (5) Yamamoto, K.; Tatsumi, T. *Chem. Mater.* **2007**, *20*, 972.
- (6) Yamamoto, K.; Sakata, Y.; Nohara, Y.; Takahashi, Y.; Tatsumi, T. *Science* **2003**, *300*, 470.
- (7) Diaz, U.; Vidal-Moya, A.; Corma, A. *Microporous Mesoporous Mater.* **2006**, *93*, 180.
- (8) Jones, C. W.; Tsuji, K.; Davis, M. E. *Nature* **1998**, *393*, 52.
- (9) Jones, C. W.; Tsuji, K.; Davis, M. E. *Microporous Mesoporous Mater.* **1999**, *33*, 223.
- (10) Jones, C. W.; Tsapatsis, M.; Okubo, T.; Davis, M. E. *Microporous Mesoporous Mater.* **2001**, *42*, 21.
- (11) Tsuji, K.; Jones, C. W.; Davis, M. E. *Microporous Mesoporous Mater.* **1999**, *29*, 339.

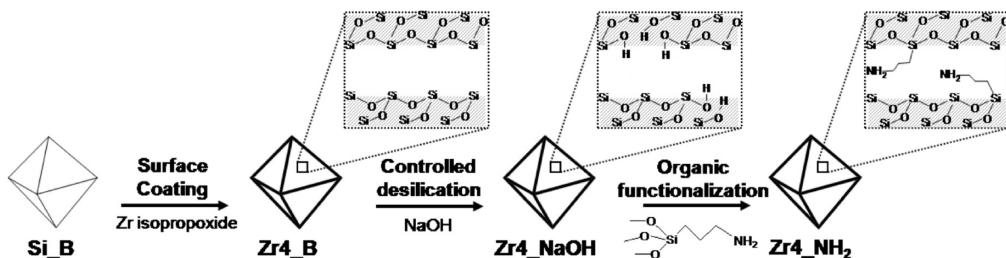


Figure 1. Schematic representation depicting the methodology used to synthesize hybrid, organic–inorganic solids with high organic content and shape selectivity.

extraction are necessary to create the organic-functionalized molecular sieve.

Here, we present a new methodology for the introduction of organic functional groups into molecular sieves by a postsynthetic route that generates materials containing higher organic concentrations and that preserves the shape selectivity of the parent zeolite. A schematic representation of the rationale behind this technique is depicted in Figure 1. Amorphous siliceous supports, such as MCM-41 or SBA-15, have a large number of silanol groups available for grafting organosilanes. In contrast, zeolites that contain primarily tetrahedrally coordinated silicon atoms have a low number of intracrystalline silanol groups (framework defects). Therefore, a procedure is required to increase the number of silanol groups available for silane functionalization by removing atoms from the framework, i.e., artificially creating framework defects, that usually involves steaming and acid or alkaline treatments. Indeed, the fact that Si–O–Si bonds are readily hydrolyzed in the presence of alkaline ions at low temperatures has led to many studies detailing the variables and conditions affecting the silicon removal process from molecular sieves.^{12–14} For example, kinetic studies on alkaline-induced desilication of zeolites have shown that the rate of hydrolysis of Si–O–Si bonds is increased in the vicinity of Si–OH groups and hindered in the presence of heteroatoms such as Al³⁺.^{15,16} This result suggests that a pure-silica zeolite undergoing an alkaline treatment would be desilicated preferentially from the surface (where terminal Si–OH groups are found), creating defects on the surface rather than within the zeolite pores. In order to avoid this outcome, we protected the zeolite's surface with zirconia, which is known to possess excellent resistance to alkaline environments,¹⁷ thus allowing the selective formation of defects within the zeolite pores upon alkaline treatment. Consequently, functional groups grafted on these defects were primarily localized within the zeolite pores. This new method for creating hybrid organic–inorganic molecular sieves that can show shape selectivity opens avenues for functionalizing

molecular sieves regardless of zeolite topology or organic group type.

2. Experimental Section

2.1. Synthesis of Pure-Silica Beta Zeolite. In a typical synthesis of pure-silica beta zeolite, 15.02 g of Ludox AS-40 (40 wt %, Sigma-Aldrich) was added to a solution of tetraethylammonium fluoride (TEAF) (8.05 g, Sigma-Aldrich) in water (4.04 g). The contents were stirred vigorously until a homogeneous gel was obtained with a final molar composition of 1 SiO₂/0.54 TEAF/7.3 H₂O. Next, the gel was loaded into a Teflon-lined stainless steel autoclave and heated in a convection oven at 150 °C for 10 days. The product was recovered by filtration, washed with water and acetone, and dried at 100 °C overnight. When required, the organic structure directing agent was removed by calcination at 540 °C in flowing air.

2.2. Zirconia Coating Procedure. The surface of pure-silica beta zeolite crystals was coated with zirconia using the following procedure: in a typical coating cycle, approximately 1 g of as-prepared pure-silica beta was dried under vacuum at 130 °C for 4 h. The powder was allowed to cool down to room temperature under an inert atmosphere, and then 20 mL of dry *n*-hexane was added under stirring. Next, 0.25 g of zirconium isopropoxide (Sigma-Aldrich, 70–75% in heptane) was added slowly by syringe to the dispersion and the mixture was stirred for 30 min to allow for surface hydroxyl groups to react with the zirconium-containing complex. The mixture was then filtered and washed with 500 mL of *n*-hexane (2 × 250 mL), followed by 500 mL of acetone (2 × 250 mL), and 500 mL of water (2 × 250 mL). This cycle was repeated 3 more times for the Zr4 sample. Finally, samples were calcined at 540 °C for 4 h under flowing air.

2.3. Desilication Procedure. Desilication of the zeolite framework was performed using the following procedure: typically, 1 g of zeolite was added to 50 mL of a 0.25 M sodium hydroxide aqueous solution. The mixture was then placed in an oil bath set at 60 °C and stirred for 15 min. Next, the powder was filtered and washed with water until the filtrate and the water used for washing had the same pH.

2.4. Grafting of Organosilanes. Aminopropyl-functionalized materials were created postsynthetically using the following procedure: 1 g of solid was dried under vacuum at 130 °C for 4 h before adding 50 mL of dry toluene. Next, the proper amount of the (3-aminopropyl)trimethoxy silane (Sigma-Aldrich, 97%) was added by

- (12) Perez-Ramirez, J.; Christensen, C. H.; Egeblad, K.; Christensen, C. H.; Groen, J. C. *Chem. Soc. Rev.* **2008**, *37*, 2530.
- (13) Groen, J. C.; Moulijn, J. A.; Perez-Ramirez, J. *J. Mater. Chem.* **2006**, *16*, 2121.
- (14) Jacobsen, C. J. H.; Madsen, C.; Houzicka, J.; Schmidt, I.; Carlson, A. *J. Am. Chem. Soc.* **2000**, *122*, 7116.
- (15) Groen, J. C.; Peffer, L. A. A.; Moulijn, J. A.; Perez-Ramirez, J. *Chem.—Eur. J.* **2005**, *11*, 4983.
- (16) Cizmek, A.; Subotić, B.; Aiello, R.; Crea, F.; Nastro, A.; Tuoto, C. *Microporous Mater.* **1995**, *4*, 159.
- (17) Jung, T. H. *J. Mater. Res.* **1994**, *9*, 1006.

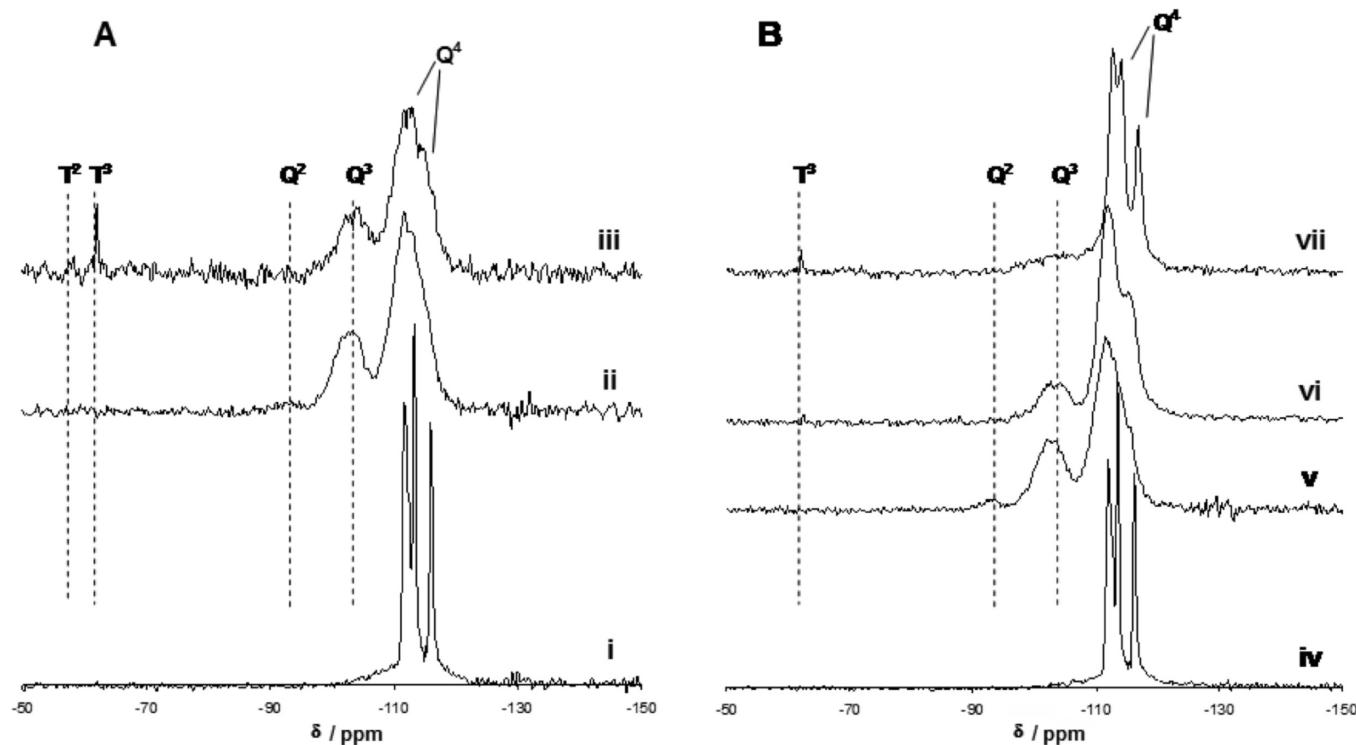


Figure 2. ^{29}Si MAS NMR spectra of (A) pure-silica beta zeolite samples as follows: (i) Si_B (calcined material), (ii) B_NaOH (after desilication treatment with NaOH), (iii) B_NH_2 (after functionalization with aminopropyltrimethoxysilane). (B) Pure-silica beta zeolite samples coated four times with zirconia as follows: (iv) Zr_4B (parent material), (v) Zr_1NaOH (after desilication treatment with NaOH of a material coated only one time with zirconia), (vi) Zr_4NaOH (after desilication treatment with NaOH), and (vii) Zr_4NH_2 (after desilication treatment and subsequent functionalization with aminopropyltrimethoxysilane).

syringe to the dispersion, and the mixture was allowed to stir at room temperature for 24 h before the temperature of the oil bath was increased to 120 °C, causing the toluene to reflux (the organic content of the functionalized materials is reported in Table 3). The grafting procedure at 120 °C was allowed to proceed for 24 h. Grafted solids were collected by filtration and washed subsequently with 1 L of toluene (4 × 250 mL) and 1 L of ethanol (4 × 250 mL). The washed samples were dried overnight at 100 °C.

2.5. Imine Formation. Condensation reactions between aminopropyl-functionalized materials and aldehydes were performed to form imines in magnetically stirred thick-walled glass reactors (Alltech Corp.). Prior to starting the experiments, benzaldehyde (Sigma-Aldrich, 99.9%, hereafter designated as BA) was redistilled and stored under argon, while naphthaldehyde (Sigma-Aldrich, 97%, hereafter designated as NA) was recrystallized from hot isopropanol in order to remove trace acidic impurities. The proper amount of a 0.05 M solution of either BA or NA in diethyl ether was added to a vial containing 25 mg of aminopropyl-functionalized material to achieve a 2:1 aldehyde/amine molar ratio. Next, 0.25 g of activated molecular sieve 3A beads (Sigma-Aldrich) were added to the vial and the mixture was stirred for 24 h at room temperature. Next, after removal of the beads by sieving, the catalyst was filtered, washed with 100 mL of diethyl ether, and dried under vacuum for 24 h. The amount of aldehyde reacted was quantified by gas chromatography with mass spectrometry (GC/MS), and

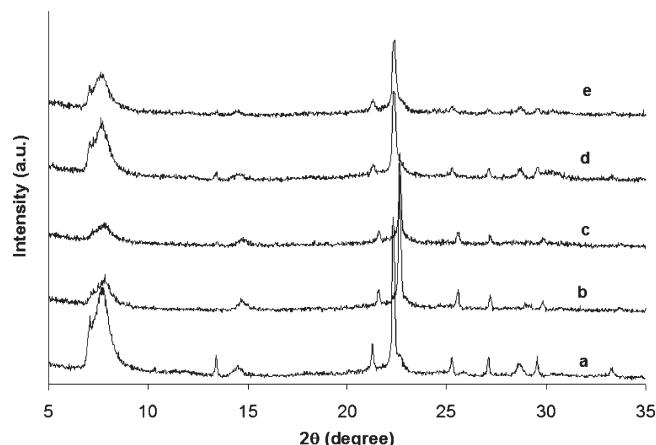


Figure 3. XRD patterns of synthesized samples: (a) Si_B , (b) B_NaOH , (c) Zr_1NaOH , (d) Zr_4NaOH , and (e) Zr_4NH_2 .

the dried solid samples were subjected to Raman spectroscopy to track imine formation on the solid.

2.6. Catalytic Test. Knoevenagel condensations between benzaldehyde or naphthaldehyde and ethylcyanoacetate (Sigma-Aldrich, 99.9%, hereafter designated as ECA) were conducted in magnetically stirred thick-walled glass reactors at 70 °C. The reactor was charged with 1 mL of toluene, 0.1 mmol of BA, 0.1 mmol of NA, 0.2 mmol of ECA, and 7 mg of catalyst. For the experiments conducted using the SBA_NH_2 catalyst, the amount of catalyst was adjusted to 6 mg in order to match the number of sites used in the Zr_4NH_2 experiments. Samples were taken periodically using a syringe

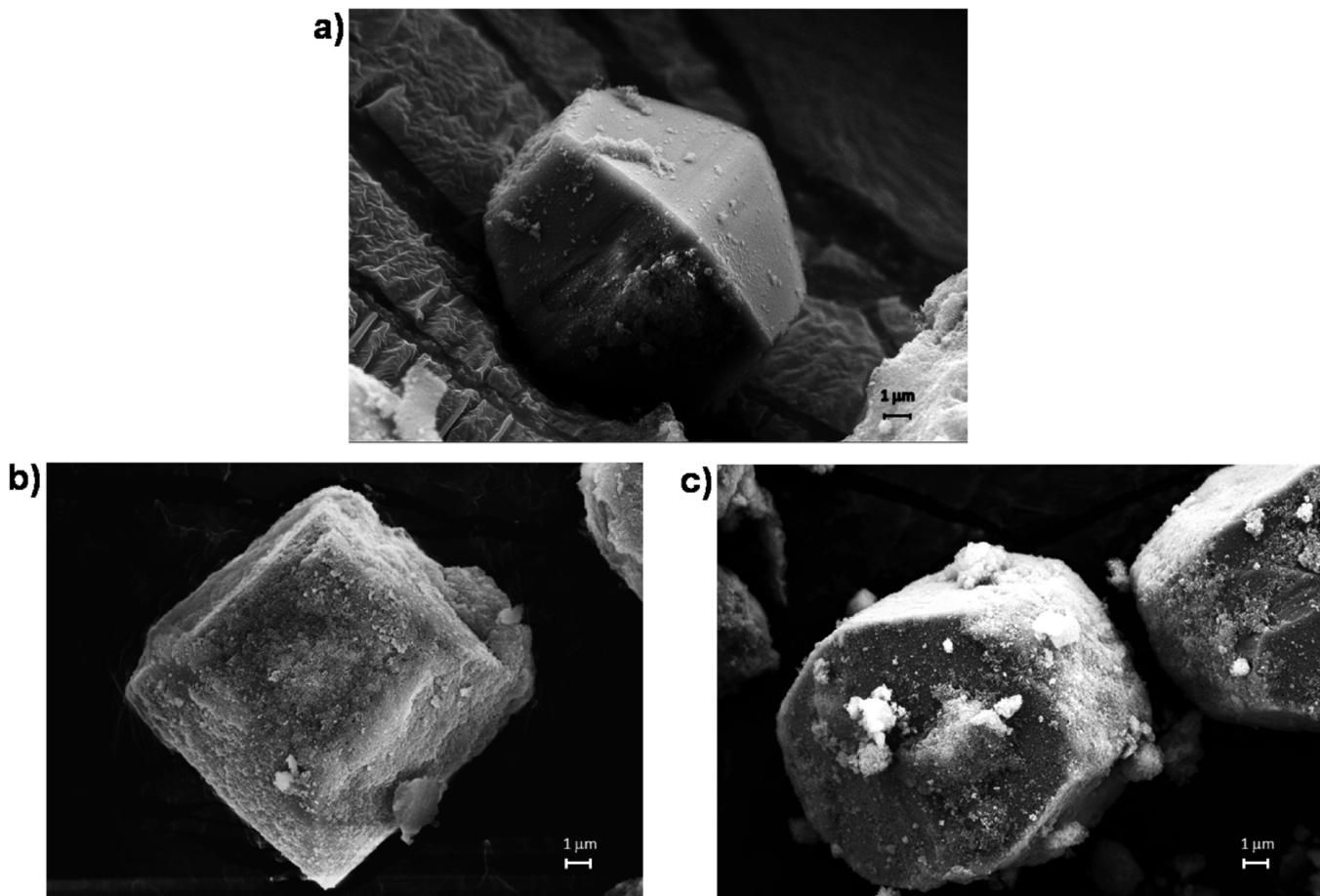


Figure 4. SEM images of synthesized materials: (a) Si-B, (b) B_NaOH, (c) Zr4_NaOH. The unprotected sample B_NaOH shows clear signs of structural damage upon being subjected to the alkaline treatment, whereas sample Zr4_NaOH seems to preserve its external structural integrity.

and quantified with GC/MS using dodecane as an internal standard.

2.7. Characterization. Single pulse ^{29}Si solid-state magic angle spinning nuclear magnetic resonance (MAS NMR) measurements were carried out on a Bruker DSX 200 spectrometer at 39.5 MHz, with a pulse length of 4 μs , a recycle delay time of 300 s, a spinning rate of 4 kHz, and approximately 300 scans. Cross-polarization ^{29}Si solid-state MAS NMR spectra were recorded at 39.5 MHz, a pulse interval of 2 s, a contact time of 4 ms, a spinning rate of 4 kHz, and approximately 5000 scans using a 7 mm zirconia rotor. Powder X-ray diffraction patterns were collected by using a Scintag XDS 2000 diffractometer using Cu $\text{K}\alpha$ radiation. Organic content was determined by thermogravimetric analysis (TGA) using a Netzsch STA 449 C apparatus with alumina crucibles heated in air at 10 $^{\circ}\text{C}/\text{min}$. Nitrogen adsorption was carried out on a Micromeritics ASAP 2010 instrument at liquid nitrogen temperature (77 K). Scanning electron microscopy images were recorded on a LEO 1550 VP field emission scanning electron microscopy (FE SEM) at an electron high tension (EHT) of 10 kV using samples that were coated (using a metal sputtering coater) with 5 nm of Pt to minimize the effects of charging. Raman spectra were obtained using a Renishaw M-1000 micro-Raman spectrometer, equipped with a Ar ion laser operating at 514.5 nm. GC/MS was performed using an HP 5890

series II apparatus equipped with a mass spectrometer and an HP-1 capillary column (12 m \times 0.2 mm \times 0.33 μm).

3. Results and Discussion

Pure-silica zeolite beta prepared in fluoride media was used in this study because it contains a remarkable low number of framework defects,¹⁸ thereby allowing for the clear detection and study of defect evolution during postsynthetic treatments. The solid-state ^{29}Si MAS NMR spectrum of the parent material shows the exclusive presence of Q⁴ peaks (between -110 and -117 ppm) due to Si atoms connected via siloxane bonds to four other Si atoms (see Figure 2i). Powder X-ray diffraction (XRD) verifies that the calcined material has the *BEA framework topology with a high degree of crystallinity (see Figure 3a). Scanning electron microscopy (SEM) images and N₂ adsorption measurements indicate the presence of uniformly shaped octahedral crystals of $\sim 15\ \mu\text{m}$ with a micropore volume of $0.19\ \text{cm}^3/\text{g}$ (see Figure 4 and Table 1).

Substantial differences were observed between zirconia-protected and unprotected samples subjected to the NaOH treatment. Characterization data suggest that the zirconia protection successfully prevents progressive

(18) Cambor, M. A.; Corma, A.; Valencia, S. *Chem. Commun.* **1996**, 20, 2365.

crystal dissolution from the external surface, thereby maintaining the zeolite's structural integrity while creating controlled mesoporosity within the pores. Specifically, data from various characterization techniques revealed the following: (1) Although XRD patterns show that all samples lose crystallinity with respect to the parent compound (due to framework desilication), the sample coated four times with zirconia ($\text{Zr}_4\text{-NaOH}$) shows a much lower degree of peak broadening. This suggests that crystallinity is better preserved in the protected sample in comparison to the unprotected (B-NaOH) and the once-coated ($\text{Zr}_1\text{-NaOH}$) samples (see Figure 3). (2) ^{29}Si MAS NMR spectra show that Q^3 peaks (~ 100 ppm), indicative of $\text{Si}(\text{OSi})_3\text{OH}$ bonds (i.e., framework defects), appear in all samples after the NaOH treatment; however, sample $\text{Zr}_4\text{-NaOH}$ presents better defined Q^4 peaks and no Q^2 peaks (see Figure 2ii,v, vi). NMR quantification of the total number of silanol groups yields 2.7 mmol of OH/g and 4.6 mmol of OH/g for the $\text{Zr}_4\text{-NaOH}$ and B-NaOH samples, respectively (see Table 2). (3) SEM image clearly show that the unprotected sample suffers from severe surface structural damage after the NaOH treatment, while sample

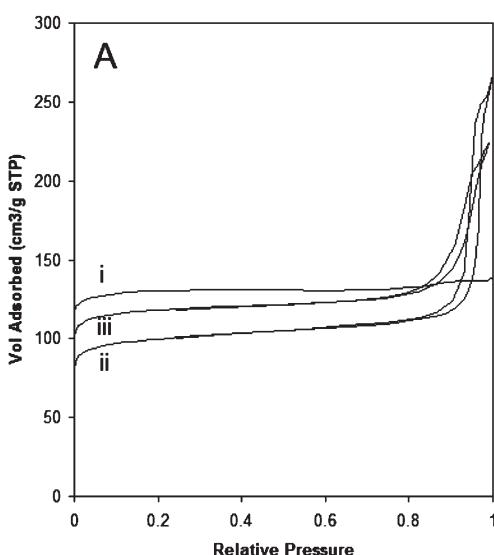
Table 1. Summary of N_2 Adsorption Data

	micropore volume (cm^3/g)	total pore volume (cm^3/g)
Si_B	0.19	0.21
B_NaOH	0.13	0.39
Zr4_NaOH	0.16	0.32
Zr4_NH ₂	0.10	0.19

Table 2. Summary of Quantification Results from ^{29}Si MAS NMR Data

sample	Zr/Si ^a (% wt)	Q^4 (%)	Q^3 (%)	Q^2 (%)	mmol of OH/g
Si_B	0	100	0	0	0
B_NaOH	0	71.4	26.4	2.2	4.6
Zr1_NaOH	0.5	70.3	27.2	2.5	4.8
Zr4_NaOH	2.5	81.6	18.4	0	2.7

^a Calculated from ^{29}Si MAS NMR data.



$\text{Zr}_4\text{-NaOH}$ retains its surface structural integrity to a much high degree (see Figure 4). (4) N_2 adsorption data indicate a significant increase in nonmicropore volume for the B-NaOH sample in comparison with the lower increase in the protected $\text{Zr}_4\text{-NaOH}$ sample (see Table 1 and Figure 5A). These results suggest that the zirconia protection successfully prevents progressive crystal dissolution from the external surface, thereby maintaining the zeolite's structural integrity while creating defects within the pores.

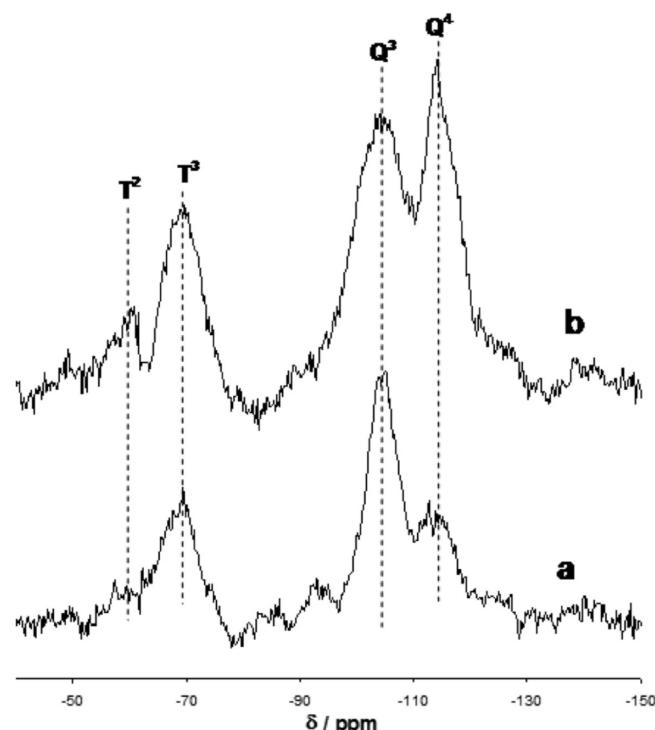


Figure 6. ^{29}Si CP MAS NMR of synthesized samples: (a) B-NH_2 and (b) $\text{Zr}_4\text{-NH}_2$. T^2 and T^3 resonances are clearly seen near -60 and -70 ppm, respectively, indicative of $\text{C-Si}[\text{OSi}]_x[\text{OH}]_{(3-x)}$ bonds, where x is from T^x .

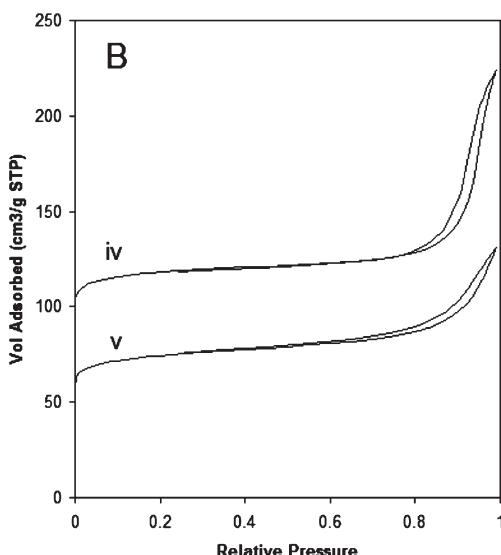


Figure 5. Nitrogen adsorption/desorption isotherms at 77 K for (A) calcined Si_B (i), B_NaOH (ii), and Zr4_NaOH (iii); (B) Zr4_NaOH (iv) and Zr4_NH2 (v).

Table 3. Content of NH₂ Functional Groups

	theoretical (mmol of NH ₂ /g of solid)	measured (mmol of NH ₂ /g of solid)
SBA_NH ₂	1.2	1.1
B_NH ₂	1.4	1.1
Zr4_NH ₂	0.8	0.7

Aminopropyl-functionalized zeolites were created by grafting (3-aminopropyl)trimethoxysilane onto the defect sites of the alkaline-treated zeolites. ²⁹Si CP MAS NMR data confirm the silicon–carbon connectivity between the organic groups and the inorganic framework by the appearance of a T³ peak at -69 ppm that indicates the presence of a C–Si–(OSi)₃ bond (see Figure 6). Upon functionalization, ²⁹Si MAS NMR of the Zr4_NH₂ sample shows a dramatic decrease of the Q³ peak with a corresponding reshaping of the Q⁴ peaks, whereas the nonprotected B_NH₂ sample shows only a slight improvement in the definition of the Q⁴ bands (see Figure 2iii,vii). Thus, it appears that the grafting process heals a sufficient number of defects in the framework of the alkaline-treated protected sample by substituting silanol groups with tetrahedrally coordinated Si atoms to recover a high degree of ordering that is observable by ²⁹Si NMR. The presence of aminoalkyl groups inside the pore space of the zeolite decreases the micropore and mesopore volume (see Table 1 and Figure 5B), indicating that the functional groups are mostly occupying space inside the intracrystalline space. The total organic content in the Zr4_NH₂ material is approximately 0.7 mmol of

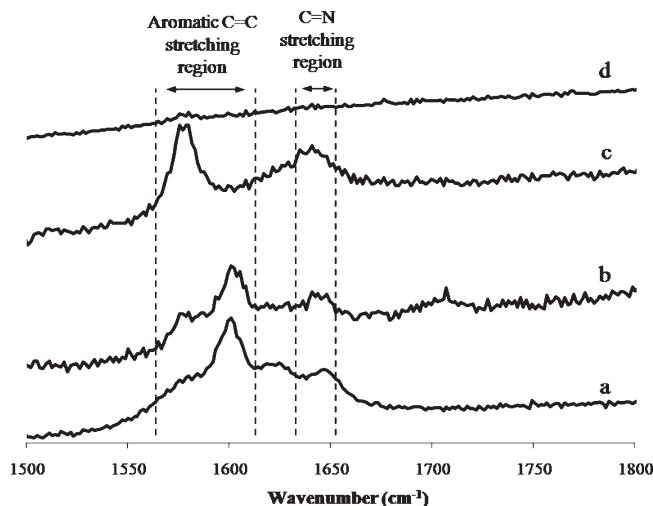


Figure 7. Raman spectra of materials following condensation reactions with benzaldehyde (BA) and naphthaldehyde (NA) to form the corresponding imines: (a) SBA_NH₂ sample contacted with BA, (b) Zr4_NH₂ sample contacted with BA, (c) SBA_NH₂ contacted with NA, and (d) Zr4_NH₂ sample contacted with NA.

NH₂/g (see Table 3), which corresponds to 5.5 atom % of silicon substituted by the organosilane. Importantly, we note that this value is almost twice as high as the highest value previously reported by direct synthesis.⁸

Two separate tests involving aldehyde condensation reactions catalyzed by the aminopropyl-functionalized materials with differently sized aldehydes confirmed that the Zr4_NH₂ sample maintained shape-selectivity. In the first test, benzaldehyde (BA) and naphthaldehyde (NA) solutions were contacted with Zr4_NH₂ and mesoporous aminopropyl-functionalized SBA-15 (SBA_NH₂) samples (the latter used as a nonshape selective control), and the characteristic adsorption bands produced by the resulting imines were tracked with Raman spectroscopy. Peaks in the 1640 cm⁻¹ and in the 1550–1610 cm⁻¹ regions (corresponding to the presence of C=N and aromatic C=C bonds, respectively) were found when SBA_NH₂ was contacted with either BA or NA (see Figure 7). However, when the Zr4_NH₂ sample was contacted with both aldehydes, adsorption bands were only observed for the BA case. Quantification of the aldehydes remaining in solution following condensation revealed that 81% of BA and 99% of NA was recovered after contact with Zr4_NH₂, while 42% BA and 46% NA were recovered after contact with SBA_NH₂ (see Table 4). Thus, although NA can easily fit into the pores of an SBA-15 material (~ 65 nm), it is highly restricted from migrating into the pores of the aminopropyl-functionalized solid. The second test was the Knoevenagel condensation of BA or NA with ethylcyanoacetate (ECA) (see Table 5). For the Zr4_NH₂ sample, after 60 min at 70 °C, the BA and NA conversion values were 51% and 3%, respectively. In contrast, for the SBA_NH₂ sample, after 5 min, BA and NA conversion values were 80% and 65%, respectively. The small amount of NA reactivity observed with the Zr4_NH₂ material can be attributed to active groups located outside the channel

Table 5. Knoevenagel Condensation Results^a

time (min)	conversion (%)			TON ^b	
	ECA	BA	NA	BA	NA
Si_SBA	60	0	0	0	0
SBA_NH ₂	5	76	80	36.7	29.8
	10	84	95	43.5	35.8
Zr4_NaOH	60	0	0	0	0
Zr4_NH ₂	60	27	51	26.7	1.6
	120	33	63	33.0	4.7

^a Reaction conditions: 0.33 mmol of each BA and NA, 0.66 mmol of ECA, using toluene as solvent at 70 °C. ECA, ethylcyanoacetate; BA, benzaldehyde; NA, naphthaldehyde. ^b TON, turn over number, defined as millimoles of aldehyde/millimoles of NH₂. The number of NH₂ groups used for the TON calculation is shown in Table 3.

Table 4. GC Quantification of Remaining Aldehydes in Solution after Contacting with Aminopropyl-Functionalized Materials^a

sample	catalyst amount (mg)	loading (mmol of NH ₂ /g)	aldehyde remaining (%)	sites reacted w/aldehydes (%)
Zr4_NH ₂ + BA	50.1	0.7	80.7	27.1
Zr4_NH ₂ + NA	49.9	0.7	98.9	1.4
SBA_NH ₂ + BA	30.1	1.2	41.5	75.0
SBA_NH ₂ + NA	30.2	1.2	46.0	81.2

^a Reaction conditions: 1 mL of 0.05 M solution of aldehyde in diethylether, stirring at room temperature for 24 h.

system or to the effective diffusion of NA molecules into the pores of beta after prolonged exposure to the material at 70 °C. Two blank experiments were performed with pure silica SBA-15 and zirconia-protected beta after alkaline treatment to show that no reactivity is present in the absence of the organic functional group (see Table 5).

4. Conclusions

In conclusion, we have synthesized hybrid, organic–inorganic solids that feature high concentrations of intracrystalline organic moieties and shape-selectivity.

Protecting the zeolite's surface with a zirconia coating is critical to selectively creating defects within the intracrystalline pore space. Grafting organic alkoxy silanes onto these defects produced hybrid, organic–inorganic materials with high organic content that maintained shape selectivity. We are currently investigating the cooperative effects of incorporating different functional groups into various zeolite topologies.

Acknowledgment. Financial support for the work was provided by British Petroleum. M.M acknowledges the Fundación Ramón Areces Postdoctoral Research Fellowship Program for financial support.