

Organic-functionalized molecular sieves (OFMSs) I. Synthesis and characterization of OFMSs with polar functional groups

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Received 5 October 1998; accepted 10 December 1998

Abstract

Organic-functionalized molecular sieves that contain polar functional groups are synthesized and characterized. Small, uniform-sized crystals with the BEA topology are obtained when tetraethylammonium fluoride is used as a structure-directing agent and added at the initiation of tetraethylorthosilicate/organosilane hydrolysis. An aminopropyl-functionalized material with the BEA topology is prepared and characterized by X-ray diffraction, solid-state NMR spectroscopy, Raman spectroscopy and diffuse reflectance ultraviolet–visible spectroscopy. The results indicate that the aminopropyl groups are located within the intracrystalline void space and that they can be reacted with aldehydes to form occluded imines. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Aminopropyl group; Functional groups; Molecular sieves; Zeolite beta

1. Introduction

Organic functionalities have been incorporated onto and into amorphous silica and other solid phases for chromatographic and catalytic purposes for many years. The discovery of the periodic, mesoporous structures such as the MCM-41/MCM-48 type materials [1] added a higher degree of regularity to materials that could be functionalized by organic moieties. Organic functionality has been incorporated into these materials via two routes. First, organosilanes can be grafted onto preformed materials [2,3]. The second route to functionalized mesoporous materials is to synthe-

size the material with an organosilane in the synthesis gel. This approach, pioneered by Burkett, Mann and coworkers [4,5] has subsequently been used by a number of research groups. Several recent reviews discuss these materials [6–8].

In contrast, there has been little success in the functionalization of microporous materials with organosilanes. Corma and coworkers first functionalized zeolites with organic species by grafting organic groups into the mesoporous region of USY (ultra-stable Y) zeolites [9–12]. The grafted silanes were then used as ligands for the heterogenization of metal complex catalysts. Cauvel et al. also investigated the grafting of organosilanes onto a series of Y zeolites with varying mesopore content (mesopores introduced via steaming) [13]. They found that the grafting efficiency increased

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with the mesopore (and hence silanol) content. This result indicates that the majority of functionalization occurs on the external surface or in the mesopores, not in the micropores. Similar results have been obtained in our laboratory [14].

Organic-functionalized, microporous aluminophosphonates have been synthesized by Maeda et al. [15–18]. The organic functionality is introduced by using methylphosphonic acid in the synthesis. Unlike the inorganic/organic hybrid materials described above, which have a Si–C inorganic/organic linkage, the aluminophosphonates have a P–C inorganic/organic linkage. In addition, the only organic group reported is a methyl group, which cannot act as a catalytically active site, nor can it be further functionalized to behave as one.

Recently, we reported the first synthesis of a shape-selective OFMS [19]. In that initial study, an OFMS with the BEA topology that contained a tethered sulfophenethyl group was prepared. Here, we report the syntheses and characterizations of OFMS and detail the case for a polar functional groups; namely, an aminopropyl-functionalized, pure-silica beta molecular sieve.

2. Experimental section

2.1. Synthesis of OFMS

The materials that have the BEA topology were synthesized by modifying the method reported by Cambor et al. [20]. The gel composition of the reaction mixture was x R–Si/ 1 SiO₂/0.54(1 + x) TEAF/ 7 H₂O where R–Si denotes an organosilane, TEAF is tetraethylammonium fluoride and $0 < x < 0.1$. A typical synthesis procedure is as follows for the case of aminopropyl-tethered BEA. An aminopropyltrimethoxysilane (APTMS) (0.162 g, 0.9 mmol, Gelest) was added to a 100 ml flask that contained tetraethylorthosilicate (TEOS) (6.38 g, 30 mmol, 98% Aldrich) and a stir bar. A solution of tetraethylammonium fluoride (TEAF) (3.04 g, 16.5 mmol, % Aldrich) in water (15 ml) was added to the APTMS/TEOS mixture with stirring. The reaction contents were agitated

overnight to obtain a white slurry. The generated ethanol and excess water were removed by evaporation at 50°C. Water was added to the resultant wet solid to adjust the water content. The final gel composition was as follows:

0.03 Aminopropylsilaneoxide/ 1 SiO₂/ 0.56 TEAF/ 7 H₂O

The whole was transferred to a Teflon-lined autoclave and heated at 140°C with rotation (about 60 rpm). The product was recovered by filtration and washed with water and acetone and dried at room temperature.

2.2. Extraction of TEAF and pretreatment of aminopropyl-tethered BEA

An as-synthesized, aminopropyl-tethered beta (0.5 g) was heated at 80°C with gentle stirring in a mixture of pyridine (30 ml) and 1 N HCl(aq) (50 ml) for 24 h. The solid was recovered by filtration and washed with water and acetone. The whole extraction procedure was repeated to obtain a completely extracted material (confirmed by thermogravimetric analysis (TGA)). The resultant solid was added to a mixture of 28% NH₃(aq) (5 ml) and methanol (15 ml) and aged for 12 h. Filtration and washing with water and acetone gave a white solid. The solid was dried under vacuum at 150°C for 12 h.

2.3. Preparation of imines from aminopropyl groups

Condensation reactions of aminopropyl-functionalized materials (aminopropyl-functionalized beta and aminopropyl-functionalized silica (Aldrich)) with aldehydes were carried out to form imines. At least a five times excess 4-(dimethylamino)benzaldehyde (Aldrich, designated as DMBA) and 4-dimethylamino-1-naphthaldehyde (Aldrich, designated as DMNA) were used relative to the amount of amino groups in the materials. For the case of the reaction of aminopropyl-tethered beta with DMBA, the specific procedure is provided below.

An aminopropyl-functionalized beta (0.1 g, extracted) and DMBA (0.1 g) were added to a

vial that contained molecular sieve 3A beads (EM Science, 8–12 mesh, 8 g). 10 ml of methanol was added and the whole was shaken for 12 h. The beads were removed by sieving and the remaining solid was recovered by filtration, washed with 300 ml of methanol and dried under vacuum at room temperature for 8 h.

2.4. Analytical procedures

X-ray powder diffraction (XRD) patterns were collected on a Scintag XDS 2000 diffractometer equipped with a liquid-nitrogen-cooled Ge detector using Cu K α radiation. TGA was carried out on a Du Pont 951 thermogravimetric analyzer. The samples were heated in air and the temperature ramp was 10°C min⁻¹. Solid-state NMR spectroscopy was performed on a Bruker AM 300 spectrometer equipped with a high power assembly for solids. Samples were packed into 7 mm ZrO₂ rotors and spun in air. ¹H–²⁹Si CP/MAS NMR spectra were measured with ¹H decoupling at magic angle spinning (MAS) of 4.0 kHz using a 7 μ s ¹H pulse (¹H 90°), ²⁹Si contact times of 2.5 ms, and recycle times of 5 s. Tetrakis(trimethylsilyl)silane was used as the reference material for ²⁹Si NMR chemical shift determinations, and all chemical shifts are reported in ppm relative to external TMS. Scanning electron microscopy (SEM) images were recorded on a Camscan 2-LV scanning electron microscope operating with an accelerating voltage of 15 kV. UV–VIS spectra were acquired on Varian Cary 3G UV–Visible spectrophotometer equipped with diffuse reflectance accessory. Raman spectra were obtained on a Nicolet Raman 950 Stand Alone FT-Raman Accessory using Happ–Genzel Apodization. The instrument was equipped with 1 mW He–Ne laser (633 nm). Data were obtained at a resolution of 1.928 cm⁻¹. Nitrogen adsorption isotherms were collected at liquid nitrogen temperature (77 K) on a Omnisorp 100 analyzer. The cyclohexane adsorption amounts were analyzed using McBain–Bakr balance at 24 mmHg at room temperature. The samples were dehydrated under vacuum at 150°C for 4 h before dosing cyclohexane.

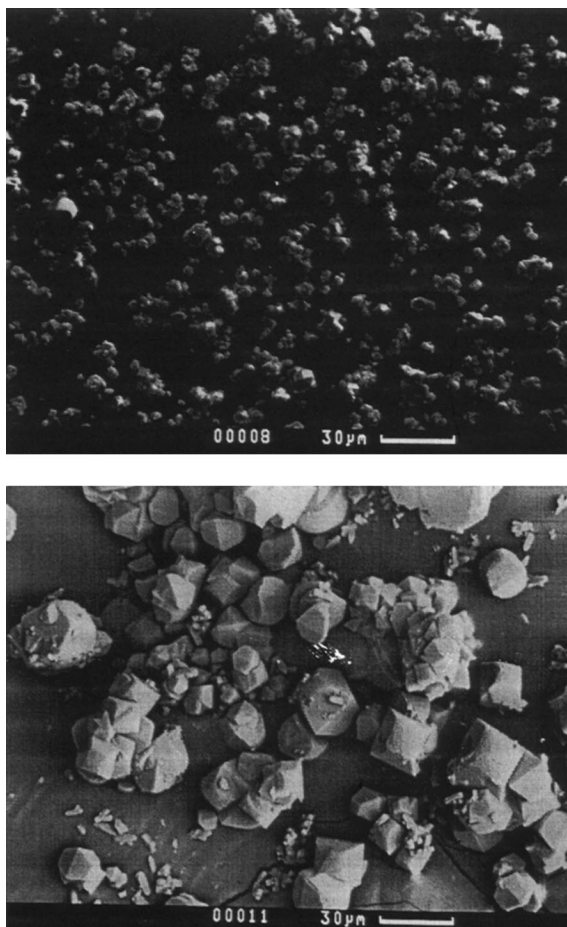


Fig. 1. SEM images of as-synthesized, pure-silica beta. Top: synthesized using TEAF. Bottom: synthesized using TEAOH + HF.

3. Results and discussion

3.1. Synthesis of organic-functionalized molecular sieves

Fig. 1 shows SEM images of the pure-silica molecular sieves with the BEA topology obtained with tetraethylammonium fluoride (TEAF) as structure-directing agent (SDA) (top) and with tetraethylammonium hydroxide (TEAOH) and hydrofluoric acid (HF) (bottom). The dispersion in the crystal sizes is large (1–30 μ m) when using TEAOH + HF while the use of TEAF alone from the beginning of the hydrolysis yields a product that has relatively uniform-sized crystals (1–5 μ m).

This is probably due to the increased homogeneity of the reaction components in the synthesis gel when using TEAF. When using TEAOH+HF, addition of about half of the required amount of HF to the solution of silica and TEAOH in water forms a solid and it becomes impossible to magnetically stir the whole mixture. Thus, it is necessary to stir by hand after the mixture becomes solid and the resultant gel appears to be nonhomogeneous. Therefore, it is advantageous to use TEAF instead of TEAOH+HF in order to obtain uniform-sized crystals. Also, the use of TEAF enables the hydrolysis reaction to occur at neutral pH. This feature is also preferred, as the organosilane and TEOS tend to hydrolyze at distinctly different rates in alkaline media [21]. Thus, unless otherwise noted, TEAF is used in the synthesis studies of organic-functionalized molecular sieves reported below.

Table 1 shows the results of pure-silica beta syntheses using various organic trimethoxysilanes. The ratio of organosilane to TEOS in these experiments was R-Si/Si=0.02. Well-crystallized beta materials are obtained in all the cases (from XRD analysis) and the crystals are similar to the pure-silica beta obtained without organosilanes (Fig. 1, top). It is observed that longer crystallization times are required with the bulkier functional groups.

3.2. Extraction of SDA from as-synthesized molecular sieves

In order to use an organic-functionalized molecular sieve as a catalyst or for separations, it is

necessary to remove the SDA that fills the pores of the as-synthesized material. Several methods were examined for the extraction of the TEAF from as-synthesized, pure-silica beta (not functionalized with organic groups). The results are summarized in Table 2. The best extraction is obtained using a mixture of acetic acid and water at 120°C. However, if the temperature is increased to 140°C, a loss in the degree of crystallinity is observed by XRD for the cases of acetic acid/water, methanol/water and acetonitrile/water mixtures. This is likely caused by acidity originating from either the solvent or the HF generated during extraction. Extracting solvents such as a mixture of methanol/water become acidic after the extraction. However, this is not the case for a basic solvent (the degree of crystallinity is similar to that of the as-synthesized material). The addition of small amount of HCl accelerates the extraction without loss of crystallinity. Thus, a mixture of pyridine and 1 N HCl(aq) is the best solvent system for the general extraction among the conditions employed here. All extractions on the OFMS materials were performed by the pyridine/HCl(aq) solvent as described in Section 2.

3.3. Characterization

Fig. 2 shows the XRD patterns of as-synthesized and extracted beta that contain the aminopropyl functionality. In the pattern of extracted BEA, two peaks at 13.5 and 14.6° are intensified when compared with those of the as-synthesized mate-

Table 1
Results of BEA syntheses using various organic silanes

Organosilane	Time (days)
None (pure silica)	5
2-Cyanoethyltrimethoxysilane	15
3-Iodopropyltrimethoxysilane	15
Allyltrimethoxysilane	17
3-Bromopropyltrimethoxysilane	17
3-Aminopropyltrimethoxysilane	18
<i>N,N</i> -Dimethyl-3-aminopropyltrimethoxysilane	21
Phenethyltrimethoxysilane	27
2-(4-Chlorosulfonylphenyl)ethyltrimethoxysilane	28
3-Mercaptopropyltrimethoxysilane	47

Table 2
Extraction of TEAF from as-synthesized pure-silica BEA^a

Solvent	Temperature (°C)	Time (h)	Efficiency ^b (%)
H ₂ O	120	24	36
CH ₃ OH/H ₂ O (1:1)	120	24	34
CH ₃ CN/H ₂ O (1:1)	120	24	42
CH ₃ COOH/H ₂ O (1:1)	120	24	90
Pyridine/H ₂ O (1:1)	120	24	43
Pyridine/1 N HCl(aq) (1:1)	120	24	72
Under vacuum	200	12	48

^a 0.05 g of sample were treated in 3 ml of solvent.

^b Percentage of TEAF removed.

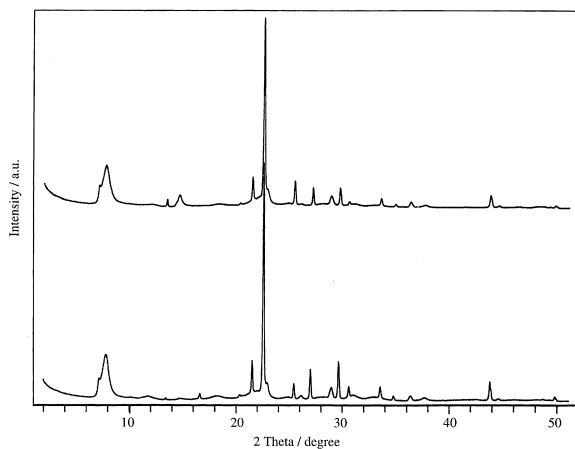


Fig. 2. XRD patterns of aminopropyl-beta. Top: extracted. Bottom: as synthesized.

rial. This is also a characteristic feature of the calcined beta and suggests that the SDA is removed from the material. The ^{29}Si CP-MAS NMR spectrum of the extracted aminopropyl-tethered beta is shown in Fig. 3. There is a resonance at -68 ppm that corresponds to the Si atom covalently bonded to carbon and three framework oxygens [22]. This result confirms that the Si–C bond exists in the extracted material and this bond is stable under the synthesis and extraction conditions. There is a broad shoulder around -100 ppm that corresponds to $\text{Si}(\text{OSi})_3\text{-X}$ (Q_3). Thus, it is likely that one framework Si–O–Si linkage in the

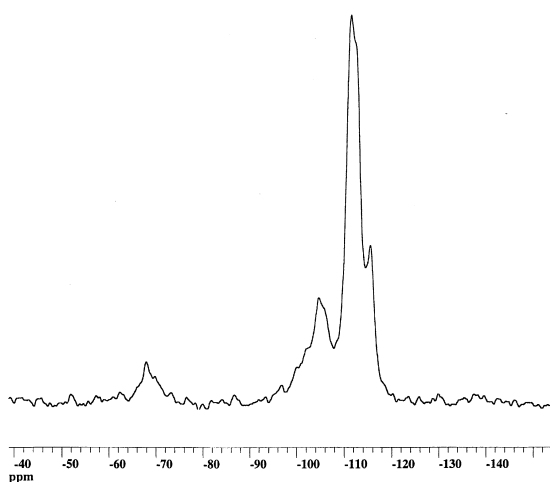


Fig. 3. ^{29}Si CP-MAS NMR spectrum of aminopropyl-beta.

pure-silica beta is substituted by a T_3 silicon attached to the carbon of the organic moiety and a Q_3 silicon yielding a silanol group. The results of TGA analyses of the as-synthesized and the extracted aminopropyl-beta materials are given in Fig. 4 with the results of calcined pure-silica beta. The TGA curve of as-synthesized aminopropyl-beta (Fig. 4, curve a) is very similar to the as-synthesized beta without any organic functional groups (not shown). There is a large weight loss from 200 to 400°C and this is the typical temperature region for the combustion of the SDA. However, almost no weight loss is observed from 150 to 300°C for extracted aminopropyl-beta and there is a loss due to the adsorbed water at under 150°C (Fig. 4, curve b). The 2.4% weight loss observed in the range $300\text{--}700^\circ\text{C}$ can be attributed to the loss of aminopropyl groups from the material as there is almost no loss in the calcined pure-silica beta over this same temperature range (Fig. 4, curve c). The number of aminopropyl groups calculated from this weight loss data is $\text{R-Si/SiO}_2 = 0.027$ and compares well with the number in the starting gel (0.03). Elemental analyses of the extracted aminopropyl-beta (C: 1.3%, N: 0.2% and Si: 42%) agrees reasonably well with the TGA results (R-Si/SiO_2 calculated from carbon to silicone ratio is 0.024).

It is clear that the organic moieties exist in

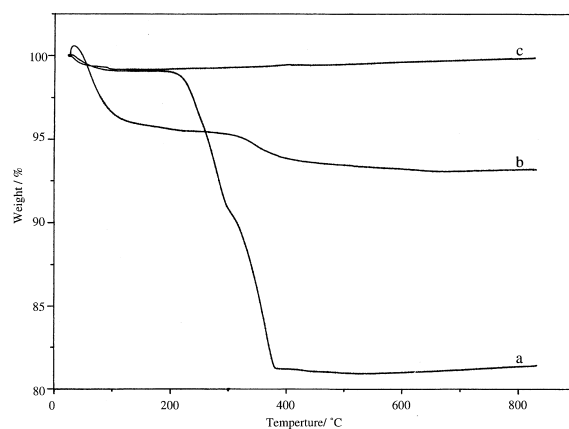
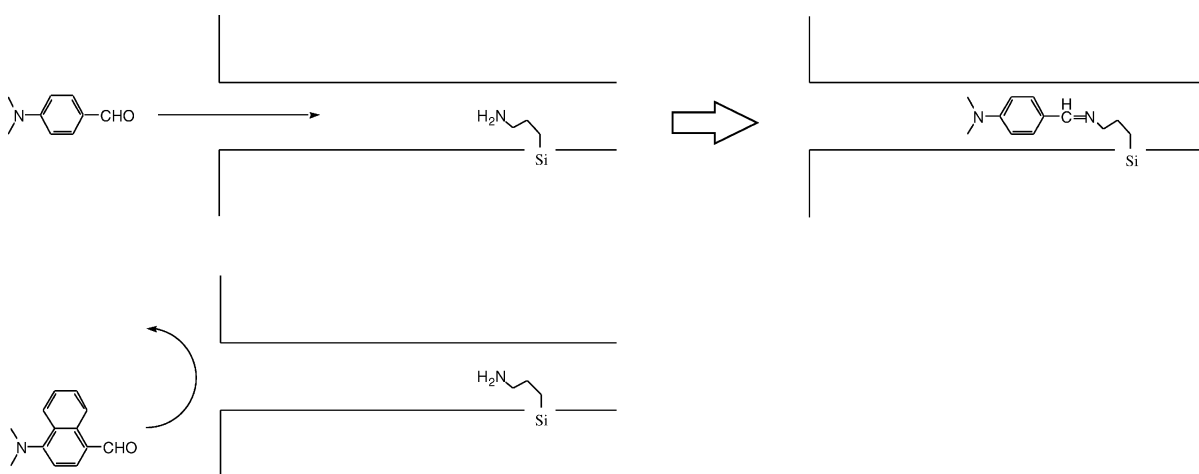


Fig. 4. TG curve of the aminopropyl-beta: curve a, as-synthesized aminopropyl-beta; curve b, extracted aminopropyl-beta; curve c, calcined beta. (Slight weight gain illustrated is from improper buoyancy corrections in the TGA.)

OFMS but the integrity of the functional groups and their locations need to be determined. In order to address these points, an extracted sample is used to demonstrate the existence of amino groups and to obtain information concerning their locations. Attempts to identify the small number densities of amines in these materials by infra red (IR) and Raman spectroscopies proved inconclusive. It has been reported that $\nu_{\text{N=H}}$ bands are sometimes undetectable by Raman spectroscopy when a He–Ne laser is used [23]. Therefore, the sample was reacted with aldehydes to transform the amino groups to imines. The imines have strong bands, as described in the text below (individual bands assigned based on [23]), that are easy to follow via Raman spectroscopy. 4-(Dimethylamino)-benzaldehyde (DMBA) and 4-dimethylamino-1-naphthaldehyde (DMNA) were used for these reactions. While DMBA is small enough to migrate into the pores of the BEA structure, DMNA is not. Therefore, the reactions with these aldehydes can be used to determine whether the amino groups are located inside the pore structure or outer surface of the material (see Scheme 1). Fig. 5 shows the Raman spectra of aminopropyl-grafted silica purchased from Aldrich (aminopropyl-silica) before and after reaction with DMBA and DMNA. In the spectrum of pure aminopropyl-silica (bottom), a small peak indicative of the amino group is observed at 3310 cm^{-1} ($\nu_{\text{N-H}}$) and

there are also several bands from CH_2 groups at $2830\text{--}3000\text{ cm}^{-1}$ (ν_{CH_2}). These bands are good indications of the aminopropyl group. Once this material is contacted with aldehydes, the peak at 3310 cm^{-1} disappears and new bands appear. The most important peak to note is that of imine that appears at 1640 cm^{-1} ($\nu_{\text{C=N}}$). Although aromatic aldehydes also have an absorption at $1650\text{--}1670\text{ cm}^{-1}$ ($\nu_{\text{C=O}}$), these peaks are distinguishable from the imine band (the shoulders at 1680 cm^{-1} in Fig. 5, middle and top, are likely due to the unreacted (adsorbed) aldehydes). The band at 1640 cm^{-1} is observed in samples contacted either DMBA or DMNA. These results indicate that the amorphous silica material containing aminopropyl group forms imines with both DMBA and DMNA (since both aldehydes can access the amino group). Fig. 6 shows the Raman spectra of aminopropyl-tethered beta (aminopropyl-beta). The sample of aminopropyl-beta is treated with ammonia and dried at 150°C under vacuum before contacting the aldehydes in order to make sure that the tethered amine are not protonated. From the bottom, the spectra are shown for the aminopropyl-beta before the contact, after the contact with DMNA and after the contact with DMBA, respectively. Since there are bands around $2830\text{--}3000\text{ cm}^{-1}$ in the spectrum before contact with aldehydes, it is apparent that this material has CH_2 groups. The peak at 3310 cm^{-1} exists



Scheme 1

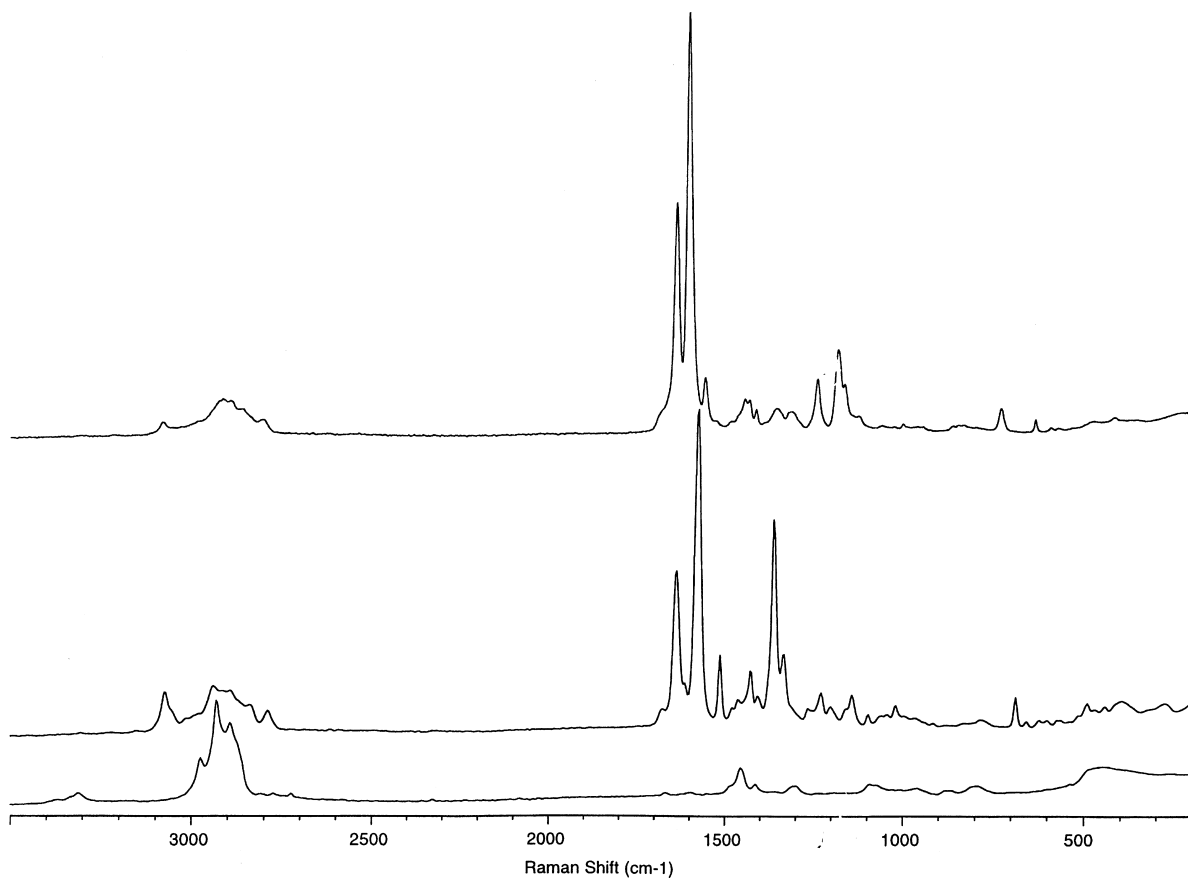


Fig. 5. Raman spectra of aminopropyl-silica (Aldrich). From the bottom: before the reaction, after the contact with DMNA and after the contact with DMBA.

although it is very weak. Thus, the aminopropyl group is verified by Raman spectroscopy. Unlike the case of aminopropyl-silica, a difference in the reactivity of the aldehydes is observed with the aminopropyl-beta. The spectrum of the aminopropyl-beta contacted with DMBA (Fig. 6, top) has an intense band at 1640 cm^{-1} whereas this peak is hardly observed after the contact with DMNA (Fig. 6 middle). There also may exist a difference in the region for $\nu_{\text{N-H}}$. The band at 3310 cm^{-1} disappears from the spectrum of the beta contacted with DMBA while a small 'hump' is observed in the spectrum of the sample exposed to DMNA. Therefore, the aminopropyl groups in the beta appear to be accessible to DMBA and not to DMNA. The obvious location at the aminopropyl groups is inside the pore of the BEA structure. If

such is the case, a loss in micropore volume should be observed. Indeed, a loss of N_2 capacity is observed as is shown in Fig. 7. The N_2 uptake of aminopropyl-beta is less than that of calcined aminopropyl-beta (calcined at 600°C). This is also the case of cyclohexane adsorption; the amount adsorbed on aminopropyl-beta is 0.226 ml g^{-1} of sample whereas calcined aminopropyl-beta adsorbs 0.261 ml g^{-1} of sample. If the density of aminopropyl group is assumed to be similar to 1-propylamine (0.719 g ml^{-1}), the amount of aminopropyl groups within the aminopropyl-beta material calculated from these data is $\text{R-Si/SiO}_2 = 0.025$. This agrees very well with the results of TGA (0.027) and elemental analyses (0.024).

The imines produced by the reaction of the aminopropyl group and aldehydes are relatively

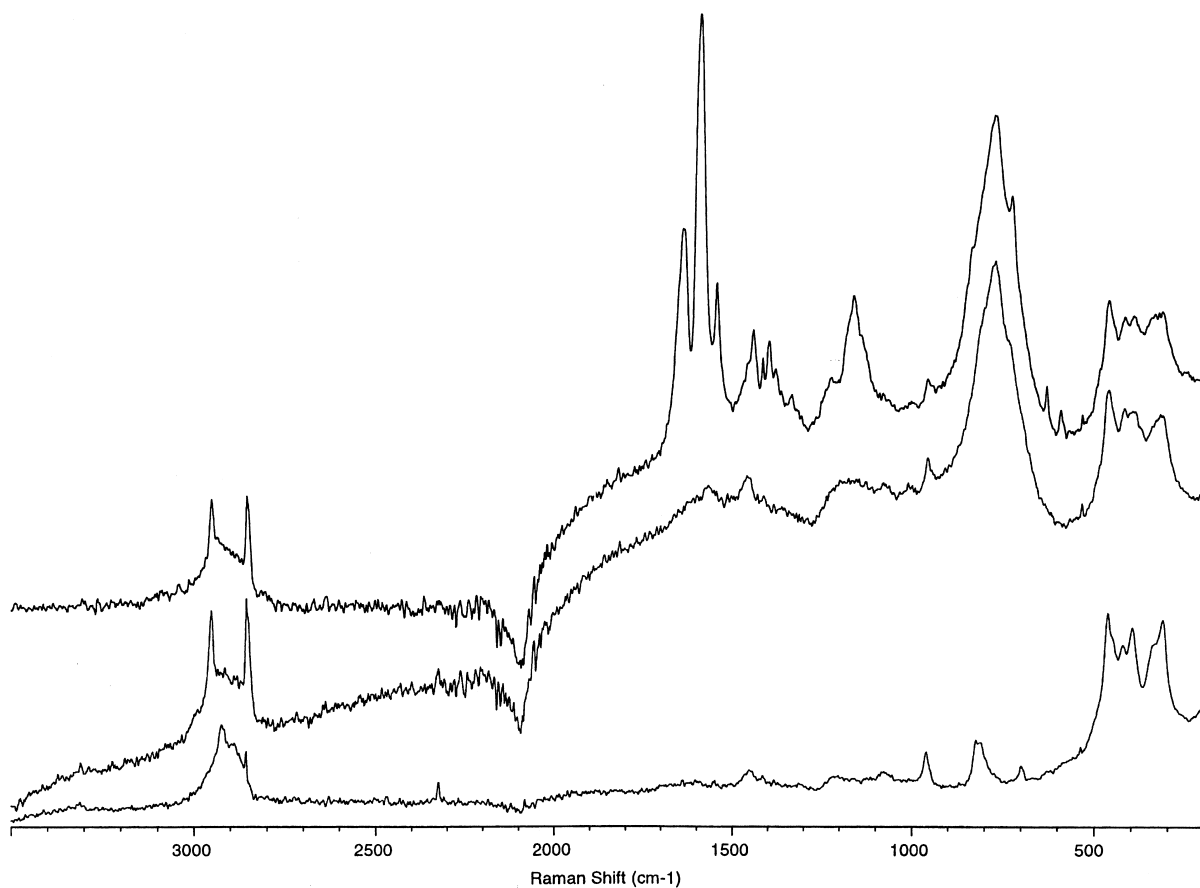


Fig. 6. Raman spectra of aminopropyl-beta. From the bottom: before the reaction, after the contact with DMNA and after the contact with DMBA.

stable Schiff bases and DMBA has been used to detect trace amounts of nitrogen compounds since the resultant imines usually are colored [24]. This is the case for aminopropyl-tethered silicate materials. Both aminopropyl-silica and aminopropyl-beta turn yellow (from white) after exposure to DMBA. For contact with DMNA, aminopropyl-silica becomes yellow while aminopropyl-beta becomes very weakly colored. Such a slight color change is observed on the calcined pure-silica beta after contact with DMNA since DMNA itself is yellow. The UV-VIS spectra of these materials are shown in Figs. 8 and 9. The aminopropyl-silica contacted with DMBA and DMNA have intense absorptions below 500 nm (Fig. 8, curve c, and Fig. 9, curve c) as expected. This intense peak is

also observed in the spectrum of aminopropyl-beta contacted with DMBA (Fig. 8, curve b, λ_{\max} is around 350 nm). However, aminopropyl-beta does not have such an intense absorption after contact with DMNA, but rather small absorptions at 250 and 380 nm with a shoulder at 470 nm (Fig. 9, curve b). Since the former two bands are also observed in the pure-silica beta contacted with DMNA (Fig. 9, curve a), they are probably due to the DMNA adsorbed on the surface of beta that makes these materials slightly yellow. However, there is an additional shoulder at 470 nm in the spectrum of the aminopropyl-beta contacted with DMNA that is not seen in calcined beta. This band is also observed in the aminopropyl-silica contacted with DMNA. Thus, a trace amount of

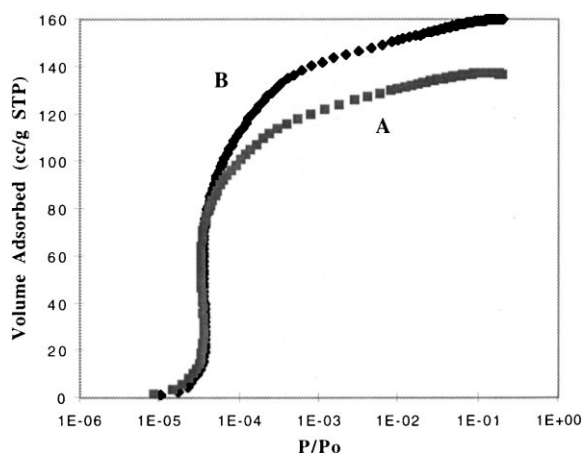


Fig. 7. Nitrogen adsorption isotherm at 77 K for aminopropyl-beta: curve A, extracted aminopropyl-beta; curve B, calcined aminopropyl-beta.

imine might be generated by contacting the aminopropyl-beta with DMNA. This imine formation with DMNA could occur if some of the aminopro-

pyl groups are located near the outer surface. This is probably the case because the contact of DMNA to the as-synthesized, aminopropyl-beta does not generate this absorption. The color and the spectrum of the material obtained by the reaction of extracted aminopropyl-beta (without pretreatment with ammonia) with DMBA are similar to those of the ammonia-treated aminopropyl-beta (yellow), while the acid-treated aminopropyl-silica gives a red product that has a different UV–VIS spectrum (Fig. 8, curve d). Since it has been reported previously that protonation of imine compounds gives intense absorption bands at long wavelengths [25], the aminopropyl groups in the extracted material may not be protonated and ammonia pretreatment may not be necessary.

4. Summary

Addition of small amounts of organic species to a zeolite synthesis mixture can have an extreme

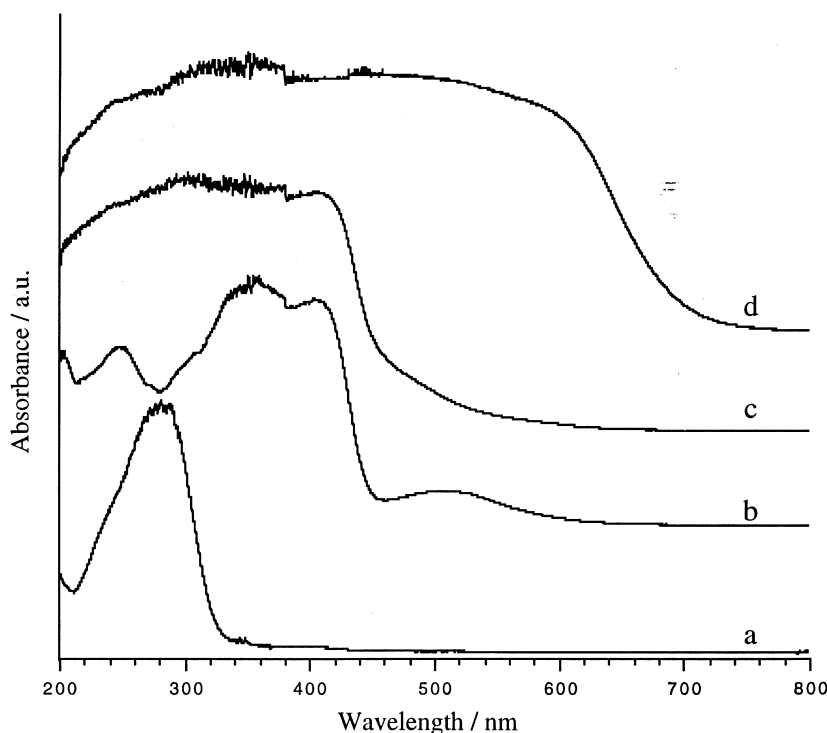


Fig. 8. UV–VIS spectra of materials contacted DMBA: curve a, calcined pure-silica beta; curve b, aminopropyl-beta; curve c, aminopropyl-silica; curve d, acid-treated aminopropyl-silica contacted with DMBA.

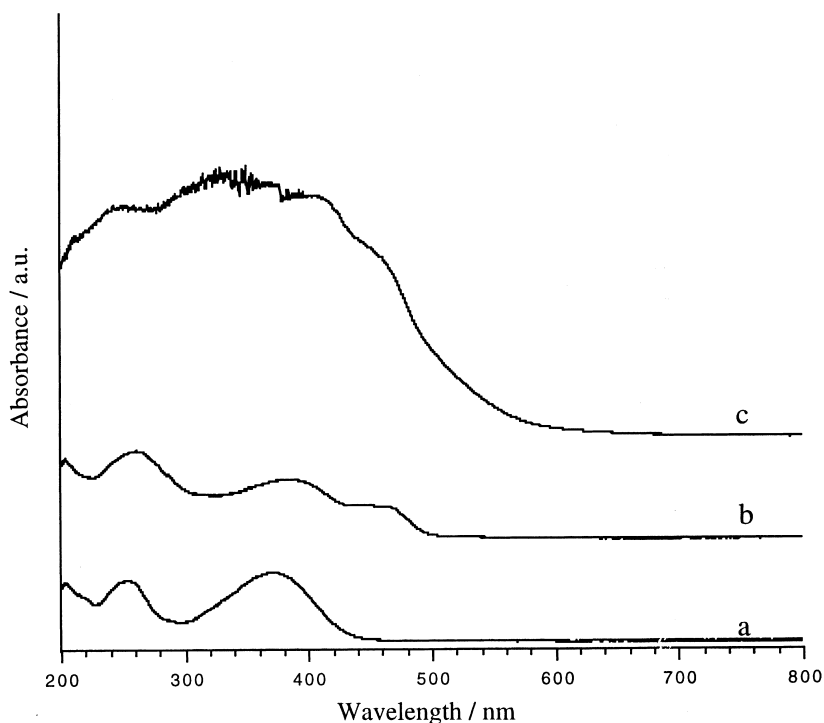


Fig. 9. UV-VIS spectra of materials contacted DMNA: curve a, calcined pure-silica beta; curve b, aminopropyl-beta; curve c, aminopropyl-silica contacted with DMNA.

influence on the synthesis. Often, a mixture of crystalline phases is obtained, or no crystalline phase results. In syntheses free of an organic SDA, the organosilane often phase separates from the zeolite synthesis gel and the organic functionality is not incorporated when a zeolite is formed. When performing syntheses that require an organic SDA, there is an additional requirement that the SDA must be extracted in order to obtain porosity. These severe requirements limit the scope of synthesizing molecular sieves with organic functionalities. The synthesis method used to obtain the pure-silica analogue of zeolite beta with TEAF by Cambor et al. [20] allows the circumvention of these problem. Cambor's synthesis method has desirable features that allow it to be adapted to the synthesis of OFMSs. The reaction gel appears to be sufficiently hydrophobic so that an organosilane does not phase-separate from the other components and the TEAF that is used as the SDA is small enough compared with the pore opening of the BEA structure to be extracted. As we pre-

viously reported [19], this system successfully prepares beta with organic functionalities such as phenethyl groups. The phenethyl-functionalized material contains intracrystalline phenethyl groups as revealed by catalytic tests [19]. The success of this synthesis can be attributed to the hydrophobic nature of the phenethyl group that prevents disruption of the beta synthesis. We hypothesized that polar functional groups may behave similarly to SDAs and disturb the formation of zeolites. However, this is not the case as demonstrated here. Well-crystallized beta is obtained with a variety of polar organosilanes. Although details proving organic incorporation are not provided for all cases, the aminopropyl group is used as a model to demonstrate that it is so. The aminopropyl groups are shown to be intrazeolitic by noting the difference in the reactivity of the aminopropyl group with large and small aldehydes. Additionally, the aminopropyl group is able to be transformed to other functional groups such as an imine by common organic synthetic methods (in

the previous reports, the phenethyl group was reacted to sulfophenethyl by SO_3 [19]. Thus, the methodologies illustrated here are useful for synthesizing organic-functionalized beta that has functional groups inside the pore system independent of whether the organic functional groups are polar or not. Finally, it is notable that the use of TEAF as an SDA leads to the formation of the product with relatively small, uniform-sized crystals, since it is often advantageous to have smaller crystals for the catalysis or separation applications.

Acknowledgements

Financial support for the work was provided by Akzo Nobel. The authors thank Osamu Chiyoda for performing the cyclohexane adsorption experiments. K.T. thanks Showa Denko K.K. for the opportunity to study at Caltech.

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