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## Two Kinds of Framework Al Sites Studied in BEA Zeolite by X-ray Diffraction, Fourier Transform Infrared Spectroscopy, NMR Techniques, and V Probe

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The dealumination of BEA zeolite by treatment with concentrated nitric acid is evidenced by X-ray diffraction (XRD) and Fourier Transform Infrared (FTIR) spectroscopy. Two-dimensional <sup>27</sup>Al 3Q and 5Q magic-anglespinning (MAS) NMR allow the detection of two kinds of tetrahedral Al atoms whose relative amounts depend on the Si/Al ratio and which correspond to two specific T-sites. <sup>29</sup>Si MAS NMR and <sup>1</sup>H MAS NMR measurements confirm these results. <sup>29</sup>Si MAS NMR spectra evidence two resonances at around -114 and -111 ppm ascribed to Si sites of the Si(OSi)<sub>4</sub> environment of two different crystallographic sites. Moreover, the presence of Si atoms associated with hydroxyl groups is confirmed by a resonance at -102 ppm when  $^{1}H^{-29}Si$  CP is applied. The Brønsted and Lewis acidic sites in dealuminated BEA zeolites are evidenced by FTIR spectra of adsorbed pyridine which show two kinds of bridging hydroxyl groups (Si-O(H)-AI) of different acid strength. <sup>51</sup>V MAS NMR confirms the incorporation of vanadium atoms into vacant T-atom sites of a fully dealuminated SiBEA zeolite leading to two kinds of tetrahedral V(V) sites ( $\delta_{iso} = -708$  and -766 ppm), with a V=O double bond and linked by V-OSi bonds to the framework. The two types of tetrahedral V(V) sites are in line with the two kinds of tetrahedral Al sites initially present in the zeolite. Moreover, the two bands at 3620 and 3645 cm<sup>-1</sup> suggest that VSiBEA also contains V(V) sites with V(V)O-H groups, which exhibit Brønsted acidic character as shown by FTIR of adsorbed pyridine. Possible ways for the formation of tetrahedral V(V) in the BEA structure are proposed.

#### Introduction

Zeolites are used in many catalytic applications because of their stability, activity, and high selectivity.<sup>1–9</sup> Zeolites are often modified to tune their catalytic properties. This is often performed by dealumination, and different methods such as steaming and/or acid treatment<sup>10–12</sup> lead to partially dealuminated zeolite with particular acidic properties. The extent of dealumination cannot be judged solely on the basis of bulk elemental analysis because extra-framework aluminum usually forms during dealumination.<sup>10–14</sup> Therefore, spectroscopies such as Fourier Transform Infrared Spectroscopy (FTIR) and magic-angle-spinning (MAS) NMR<sup>10–21</sup> are often used to evidence the type and number of hydroxyl groups in zeolites and their role in heterogeneous catalysis.

It is well established that the activity of zeolites in Brønsted acid-catalyzed reactions is related to the number and intrinsic properties of protons associated with tetrahedral framework Al.<sup>1</sup> The favorable influence of dealumination on the catalytic

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properties of zeolites has been recognized very early and often related to heterogeneity of the Brønsted acidic strength.<sup>12,13,17</sup> The activity, selectivity, and stability of the material strongly depend on the chemical and/or thermal treatment, as well as the type of zeolite.

In the last twenty years, many teams investigated the large pore BEA zeolite because of its high activity in industrial-type reactions, such as catalytic cracking,<sup>22</sup> isomerization,<sup>23,24</sup> aromatic alkylation with alkenes,<sup>25</sup> or isobutane alkylation with *n*-butene.<sup>26</sup> The acidic properties of BEA zeolite have been studied mostly by IR.<sup>15–17,27–29</sup> The presence of very strong Brønsted acidic sites has been reported.<sup>13,17,19,28</sup> The strongest acidic sites were reported to be located in well crystallized areas, and the weakest in poorly crystallized areas.<sup>13</sup> Pazè et al.<sup>19</sup> have identified weak Brønsted acidic bridging hydroxyls perturbed by H-bond interaction with the zeolite framework characterized by a broad IR band (3600–3200 cm<sup>-1</sup>).

The aim of the present study is to improve our understanding of the nature and acidic properties of aluminum species in BEA zeolite, in which transition metal ions can be incorporated by a two-step post-synthesis method.<sup>30–34</sup> The latter consists first of the dealumination of a tetraethylammonium (TEA) BEA zeolite by a nitric acid treatment leading to vacant T-atom sites in which transition metal ions are incorporated. As shown earlier,<sup>30–34</sup> different kinds of framework metal sites are distinguished in VSiBEA<sup>30–32</sup> and CoSiBEA<sup>33,34</sup> prepared by this method,

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TABLE 1: Composition and Structure Characteristics of BEA Samples (Chemical Analysis, XRD)

dealumination procedure							
sample	calcination temp/time	HNO <sub>3</sub> conc/time	Si/Al (bulk)	Al extracted (%)	d <sub>302</sub> (Å)	XRD relative crystallinity $(\%)^b$	
$BEA(11)^a$	823K/15 h	not treated	11	0	3.955	100	
BEA(46)	not calcined	8 M/4 h	46	73	3.939	98	
BEA(87)	not calcined	13 M/0.1 h	87	85	3.929	96	
BEA(135)	not calcined	13 M/0.5 h	135	90	3.922	95	
BEA(1240)	not calcined	13 M/4 h	1240	$\sim 100$	3.920	94	
BEA(1500)	not calcined	13 M/5 h	1500	$\sim 100$	3.920	92	

<sup>*a*</sup> The parent TEABEA zeolite (Si/Al = 11) was calcined in flowing air at 823 K for 15 h to remove the tetraethylammonium (TEA) template. <sup>*b*</sup> Relative crystallinity of the samples using the (302) peak intensity from XRD patterns and considering the parent zeolite as100% crystalline.

suggesting that different kinds of framework Al sites exist in the initial TEABEA zeolite.

To improve our understanding of the nature and kind of framework Al atoms present in BEA zeolite, we have investigated samples with different Si/Al ratios (11–1240) obtained by dealumination by nitric acid treatment using FTIR and two-dimensional (2D) <sup>27</sup>Al 3 and 5 Quantum (3Q and 5Q) MAS NMR.<sup>35–38</sup>

#### **Experimental Section**

**Materials.** The TEABEA zeolite (Si/Al = 11) provided by RIPP-China is separated into two fractions. The first fraction is calcined in flowing air at 823 K for 15 h to remove the TEA template and obtain the organic-free HBEA (Si/Al = 11),<sup>30,39,40</sup> labeled BEA(11). The second fraction is treated in a 8 N HNO<sub>3</sub> solution with stirring at 353 K, according to the procedure described earlier.<sup>30,31</sup> Upon treatment for 4 h the partly dealuminated BEA is obtained with an atomic Si/Al ratio of 46. This sample is labeled BEA(46). Dealumination with 13 N HNO<sub>3</sub> for 0.1, 0.5, and 4 h leads to BEA(87), BEA(135), and BEA(1240), respectively. Table 1 gives the nomenclature of the samples and the structural characteristics.

The fully dealuminated SiBEA (Si/Al = 1500) siliceous sample obtained by treatment with 13 N HNO<sub>3</sub> for 5 h, labeled BEA(1500), is then contacted with an aqueous solution of ammonium metavanadate (NH<sub>4</sub>VO<sub>3</sub>) ( $\sim 10^{-2}$  mol L<sup>-1</sup>) at pH = 2.5. The corresponding NH<sub>4</sub>VO<sub>3</sub> aqueous solution is expected to mainly contain mononuclear V species.<sup>41</sup> Two concentrations are used (1.3 and 2.9 10<sup>-2</sup> mol L<sup>-1</sup>) to vary the V content. The suspensions are left for 3 days at room temperature without stirring. The solids are recovered by centrifugation and dried at 353 K overnight. The resulting VSiBEA samples with 0.8 and 1.8 V wt % are labeled V<sub>0.8</sub>SiBEA and V<sub>1.8</sub>SiBEA, respectively.

**Techniques.** Nitrogen adsorption–desorption isotherms are obtained at 77 K using a Micromeritics ASAP 2010 apparatus. The samples are initially outgassed at 298 K for 1 h and then at 623 K for 3 h to a pressure <0.2 Pa. Pore size distributions are obtained by a single point t-plot procedure.<sup>42</sup> Microporous volumes are calculated using the Barrett, Joyner, and Halenda equation.<sup>42</sup>

X-ray diffractograms are recorded on a Siemens D5000 using the Cu K $\alpha$  radiation ( $\lambda = 154.05$  pm).

Transmission FTIR spectra of self-supported wafers (20 mg) are recorded at 298 K on a Bruker IFS 66 V spectrometer, with a resolution of 2 cm<sup>-1</sup>. Before measurements, the wafers are dehydrated in flowing oxygen (120 mL/min) to 773 K (heating rate of 100 K/h), kept at this temperature for 8 h, and finally evacuated for 6 h at 573 K in the IR cell. Gaseous pyridine is introduced on dehydrated wafers by opening a connection

between the cell and the compartment containing liquid pyridine. Physisorbed pyridine is outgassed at 423 K for 1 h ( $10^{-3}$  Pa).

Solid state MAS NMR experiments are performed with a Bruker AVANCE 400 spectrometer at 9.4 T and 4 mm zirconia rotors. Two-dimensional (2D) <sup>27</sup>Al 3 and 5 Quantum (3Q) and 5Q MAS NMR spectra are acquired with the multiplex SPAM MQMAS sequence.<sup>43,44</sup> For the two first pulses P1 and P2, the applied RF field is about 135 kHz and for the third pulse P3 about 10 kHz. The multiplex spectra are acquired at a spinning rate of  $v_{\text{Rot}} = 10$  kHz, with a 0.5 s recycle delay. Chemical shifts,  $\delta$ , are reported relative to 1 N Al(NO<sub>3</sub>)<sub>3</sub> aqueous solution. For 3Q MAS experiments, the pulse durations P1, P2, and P3 are set empirically at 3.5, 1.5, and 6.5  $\mu$ s, respectively. We use 48 t<sub>1</sub> increments of 50  $\mu$ s for F1 dimension acquisition. For 5Q MAS experiments, we fixed P1, P2, and P3 pulses durations at 4.5, 1.75, and 7.5  $\mu$ s, respectively, with 80 t<sub>1</sub> increments of 2  $\mu$ s. Data processing is performed using the "MSM" program.<sup>44</sup> Shearing transformation and scaling of the F1 axis is realized with the "xfshear" program.<sup>45</sup> The quantification of the concentration of the two tetrahedral Al is performed by fitting the corresponding 1D MAS spectra using the quadrupolar product and isotropic chemical shift determined in the MQMAS experiment.

<sup>29</sup>Si spectra are recorded at 79.5 MHz with cross-polarization (<sup>1</sup>H–<sup>29</sup>Si CP-MAS NMR) and without (<sup>29</sup>Si MAS NMR). Chemical shifts of silicon are measured by reference to tetramethylsilane (TMS). <sup>29</sup>Si MAS NMR spectra are obtained with 4 kHz spinning speed, 2.5  $\mu$ s excitation pulse, and 10 s recycle delay. Polydimethylsilane (PDMS) is used for setting the Hartmann–Hahn condition. The proton  $\pi/2$  pulse duration, the contact time, and the recycle delay are 6.8  $\mu$ s, 5 ms, and 5s, respectively.

<sup>1</sup>H MAS NMR spectra are performed with a 90° pulse duration of 3  $\mu$ s and a recycle delay of 6 s. The MAS equipment for rotation (12 kHz) was carefully cleaned with ethanol to avoid spurious proton signals. The probe signal was subtracted from the total FID.

<sup>51</sup>V MAS NMR experiments are performed at 105.1 MHz using a 4 mm (external diameter) zirconia rotor. MAS spectra are obtained using a multi pulse sequence with pulse duration of 1.2  $\mu$ s, a pulse delay of 0.5 s, and a rotor spinning rate of 14.5 kHz. All chemical shifts are measured by reference to NH<sub>4</sub>VO<sub>3</sub> solution (0.1 mol L<sup>-1</sup>,  $\delta = -570$  ppm).

#### **Results and Discussion**

Evidence of Aluminum Removal from the Framework. Porosity and crystallinity of BEA zeolite are preserved upon calcination in flowing air and dealumination of the parent TEABEA zeolite by  $HNO_3$  treatment. As a matter of fact, BEA(11), BEA(46), BEA(87), BEA(135), and BEA(1240)



**Figure 1.** X-ray diffractograms of BEA(11), BEA(46), BEA(87), BEA(135), and BEA(1240) recorded at room temperature and ambient atmosphere.

present similar X-ray diffraction (XRD) patterns (Figure 1) and no mesoporosity in the histograms of pore sizes (results not shown). The diffractograms do not show any evidence of either extra lattice crystalline compounds or long-range amorphization of the zeolite.

A narrow diffraction peak near 22.6° is generally taken as evidence of lattice contraction/expansion of the  $\beta$  structure.<sup>46,47</sup> Figure 1 shows that the position of this main diffraction peak significantly changes as a function of the Si/Al ratio. The corresponding d<sub>302</sub> spacing decreases from 3.955 (BEA(11); 2 $\theta$  = 22.55°) to 3.939 (BEA(46); 2 $\theta$  = 22.57°), 3.929 (BEA(87); 2 $\theta$  = 22.63°), 3.922 (BEA(135); 2 $\theta$  = 22.69°) and finally to 3.920 Å (BEA(1240); 2 $\theta$  = 22.71°) (Figure 1, Table 1).

The FTIR spectrum of activated BEA(11) exhibits five IR bands (Figure 2) attributed to Al–OH groups (3781 and 3665 cm<sup>-1</sup>), bridging acidic hydroxyls Al–O(H)Si (3609 cm<sup>-1</sup>),<sup>48,49</sup> Si–OH groups with a narrow band at 3741 cm<sup>-1</sup>, indicating that they are isolated, and a broad band at 3520 cm<sup>-1</sup>, showing that they are H-bonded.<sup>39,50</sup> Upon dealumination, the three bands attributed to Al–OH groups are successively eliminated, when the Si/Al ratio increases, suggesting that aluminum is removed. The appearance of IR bands related to isolated silanol groups at 3736 and 3708 cm<sup>-1</sup> and an intense broad band of H-bonded Si–OH groups at 3520 cm<sup>-1</sup> in BEA(46), BEA(87), BEA(135), and BEA(1240) (Figure 2) reveals the creation of vacant T-atom sites associated with silanol groups upon elimination of framework aluminum (Scheme 1), as shown earlier.<sup>39</sup>

Evidence of Two Kinds of Framework Aluminum Atoms. It is well-known,  $^{11,18,20,21,51}$  that  $^{27}$ Al MAS NMR spectroscopy provides information on the state of aluminum in zeolites. Framework aluminum atoms in tetrahedral coordination (Al<sub>Td</sub>) exhibit a signal at 50–60 ppm while extraframework aluminum atoms in octahedral coordination (Al<sub>Oh</sub>) usually give a signal at  $\sim$ 0 ppm.

1D <sup>27</sup>Al MAS NMR spectra of BEA(11), BEA(46), and BEA(135) exhibit two main signals at  $\sim$ 54–58 and 0 ppm



**Figure 2.** FTIR spectra recorded at room temperature of BEA(11), BEA(46), BEA(87), BEA(135), and BEA(1240) samples dehydrated in flowing oxygen (120 mL/min), at 773 K for 8 h, then outgassed for 6 h at 573 K ( $10^{-3}$  Pa).





(Figure 3) assigned to  $Al_{Td}$  and  $Al_{Oh}$  atoms, respectively. The signal at ~54 ppm and the shoulder near ~58 ppm suggest the presence of two kinds of different  $Al_{Td}$  sites. Note that second-order quadrupolar interactions reduce the resolution. The position of the central resonance at ~54 ppm is shifted and the powder patterns are broad. The absolute signal intensity decreases with increasing Si/Al ratio, as expected while the shoulder near ~58 ppm is still present at high Si/Al ratio.

2D MQ MAS NMR, developed by Frydman and Harwood,<sup>35</sup> is used to remove anisotropic line broadening, helping identify



**Figure 3.** 1D <sup>27</sup>Al MAS NMR spectra recorded at room temperature of BEA(11), BEA(46), and BEA(135) in 4 mm (external diameter) zirconia rotor.



**Figure 4.** 2D 3Q MAS (A) and 5Q MAS (B) multiplex SPAM NMR spectra recorded at room temperature of BEA(11) in 4 mm (external diameter) zirconia rotor. The top spectrum is the 1D <sup>27</sup>Al MAS NMR spectrum, and the projection along the F1 axis is the isotropic spectrum. The inset shows a magnification of the tetrahedral region.

species with close isotropic chemical shifts ( $\delta_{iso}$ ) but different quadrupolar products ( $C_{Q\eta}$ ). In this work, we use the soft-pulseadding-mixing (SPAM) MQ MAS sequence proposed by Malicki et al.<sup>43</sup> which allows one to combine the multiplex phase cycling approach<sup>52</sup> with SPAM method<sup>53,54</sup> and to better resolve the spectra.

As shown in Figures 4, 5, and 6, the resolution of the broad peaks observed in 1D  $^{27}$ Al MAS NMR spectra at  $\sim$ 54 ppm improves in the 2D 3Q MAS (A) and 5Q MAS (B) NMR spectra of BEA(11), BEA(46), and BEA(135). Two distinct framework Al species, labeled Al<sub>Td</sub>(2a) and Al<sub>Td</sub>(2b), can be seen in the



**Figure 5.** 2D 3Q MAS (A) and 5Q MAS (B) multiplex SPAM NMR spectra recorded at room temperature of BEA(46) in 4 mm (external diameter) zirconia rotor.



**Figure 6.** 2D 3Q MAS (A) and 5Q MAS (B) multiplex SPAM NMR spectra recorded at room temperature of BEA(135) in 4 mm (external diameter) zirconia rotor.

tetrahedral region and a third one, Al<sub>Oh</sub>(1), in the octahedral region at ~0 ppm for BEA(11) and BEA(46). The isotropic projection of the aluminum spectrum of these samples shows two main peaks with  $\delta_{iso}$  around ~58 and 54 ppm (Table 2).

 TABLE 2: NMR Parameters and Relative Al Content Corresponding to Two Kinds of Tetrahedral Sites Determined by 2D

 <sup>27</sup>Al MQ MAS NMR of BEA Samples

		Al <sub>Td</sub> (2b)		Al <sub>Td</sub> (2a)			
sample	$\delta_{ m iso}$ (ppm)	$C_{Q\eta}$ (MHz)	Al content (%)	$\delta_{ m iso}$ (ppm)	$C_{Q\eta}$ (MHz)	Al content (%)	
$BEA(11)^{a}$	58.4	2.4	61	54.1	1.5	39	
BEA(46)	58.2	2.3	52	54.2	1.5	48	
BEA(135)	58.0	2.4	41	53.9	1.8	59	

<sup>*a*</sup> The parameters  $\delta_{iso}$ ,  $C_{Q\eta}$ , and Al content are the isotropic chemical shift, the quadrupolar products, and the relative aluminum content Al, respectively.



**Figure 7.** <sup>29</sup>Si MAS NMR spectra recorded at room temperature of BEA(11), BEA(46), BEA(135), and BEA(1240) in a 7 mm (external diameter) zirconia rotor.

The Al<sub>Td</sub>(2a) peak with isotropic chemical shift at  $\sim$ 54 ppm is assigned to aluminum in T1 and T2 sites in the BEA framework, while the peak Al<sub>Td</sub>(2b) at  $\sim$ 58 ppm corresponds to aluminum in positions T3-T9 sites, in line with an earlier report.<sup>18</sup> Table 2 compares the relative aluminum content corresponding to two kinds of aluminum tetrahedral sites, that is, Al<sub>Td</sub>(2a) and Al<sub>Td</sub>(2b) sites for BEA(11), BEA(46), and BEA(135). The relative aluminum content corresponding to Al<sub>Td</sub>(2a) sites increase with the Si/Al ratio from 39% for BEA(11) to 59% for BEA(135), suggesting that there is a nonrandom distribution of aluminum atoms in the BEA framework. The aluminum atoms in T1 and T2 sites appear to be more resistant to dealumination by nitric acid treatment than those in T3-T9 sites, probably because they are in four-membered rings, which exhibit the largest strain with the largest T-O-T angle.18

The presence of two kinds of Al<sub>Td</sub> sites is confirmed by <sup>29</sup>Si MAS NMR: the spectra of BEA(11), BEA(46), BEA(135), and BEA(1240) exhibit two resonances at around -114 and -111 ppm (Figure 7) ascribed to two different crystallographic Si sites in Si(OSi)<sub>4</sub> environments (Q<sup>4</sup> sites).<sup>55</sup> The relative intensity of the peaks at -114 and -111 ppm changes with dealumination of BEA zeolite: the former decreases upon dealumination more rapidly than the latter, a characteristic very similar to that observed for the two <sup>27</sup>Al MAS NMR peaks at  $\sim$ 58 and 54 ppm corresponding to two kinds of Al<sub>Td</sub> sites. The <sup>29</sup>Si MAS NMR spectra also show a peak at around -102 ppm whose intensity strongly increases upon cross polarization (Figure 8). It suggests that this band can be attributed to Si atoms in Si(OH)(OSi)<sub>3</sub> environments (Q<sup>3</sup> sites). Moreover, a small <sup>29</sup>Si CP-MAS NMR signal at -91 ppm (Figure 8) suggests the presence of a small amount of Si atoms in  $Si(OH)_2(OSi)_2$  environments (Q<sup>2</sup> sites).



**Figure 8.** <sup>1</sup>H-CP <sup>29</sup>Si MAS NMR spectra recorded at room temperature of BEA(11), BEA(135), and BEA(1240) in a 7 mm (external diameter) zirconia rotor.

Evidence of Two Kinds of Bridged Brønsted Acidic Sites. The strong difference of isotropic chemical shifts of the two kinds of tetrahedral aluminum  $Al_{Td}$  sites in BEA zeolite suggests at least two different kinds of Brønsted acidic sites.

Indeed, the <sup>1</sup>H MAS NMR spectrum of BEA(11) recorded at room temperature (Figure 9) evidence a broad peak at 4.6 ppm due to protons of bridged Si-O(H)-Al Brønsted groups and a small peak at 1.3 ppm due to silanol protons, in line with earlier data.<sup>19</sup> The broad character of the 4.6 ppm peak seems to indicate that at least two kinds of protons related to bridged Si-O(H)-Al Brønsted groups are present in BEA(11). This is confirmed by the <sup>1</sup>H MAS NMR spectrum of BEA(46) which exhibits two bands at about 4.9 and 3.8 ppm probably because of protons of two kinds of bridged Si-O(H)-Al Brønsted groups and the intense peak at 1.3 ppm due to protons of silanols (Figure 9). The latter peak, more intense than that of the initial BEA(11) sample, is related to the presence of vacant T-atom sites associated with silanol groups, formed upon dealumination (Scheme 1).

Because the calculated proton affinity of the site decreases with the T–O–T angle from 155° for  $Al_{Td}$  in T1 and T2 sites to 150° for  $Al_{Td}$  in T3–T9 sites,<sup>56</sup> the  $Al_{Td}(2a)$  site at ~54 ppm observed by <sup>27</sup>Al MAS NMR is assigned to more acidic Brønsted sites (4.9 ppm peak in <sup>1</sup>H MAS NMR spectrum), while the  $Al_{Td}(2b)$  site at ~58 ppm corresponds to less acidic sites (3.8 ppm peak in <sup>1</sup>H MAS NMR spectrum).

To evaluate the acid strength of OH groups, pyridine was adsorbed on the samples. Figure 10 shows the FTIR spectra of BEA(11), BEA(46), BEA(87), BEA(135), and BEA(1240) of pyridine adsorbed at room temperature and after its desorption at 423 K. It can be seen (Figure 2) that all Si–O(H)–Al and Al–OH groups at 3609 and 3781 cm<sup>-1</sup>, respectively, disappear as a result of their interaction with pyridine (pyridinium ions



**Figure 9.** <sup>1</sup>H MAS NMR spectra recorded at room temperature of BEA(11) and BEA(46) in a 4 mm (external diameter) zirconia rotor.

PyH<sup>+</sup> are formed). Moreover, for BEA(11), two bands at around 3250 cm<sup>-1</sup> appear which are related to the red shift of strongly acidic Si-O(H)-Al groups. The absence of the latter band in the IR spectra of dealuminated samples (Figure 10) confirms that the bands at around 3250 cm<sup>-1</sup> originate from acidic Si-O(H)-Al groups and are due to vibration of pyridinium ions.

The band at ~3250 cm<sup>-1</sup> for BEA samples (Figure 10) involves in fact two bands at 3270 and 3247 cm<sup>-1</sup>, probably corresponding to the red shifts of two kinds of bridged Si-O(H)-Al with different Brønsted acidity. The high O-H stretching frequency shift for the both kinds of bridged Si-O(H)-Al groups,  $\Delta\nu(OH)$  of ~ 339 and 362 cm<sup>-1</sup>, respectively, indicates that they have a very strong Brønsted acidic character. The intensity of these bands decreases with increasing Si/Al ratio as shown in Figure 10, the band at 3270 cm<sup>-1</sup> decreasing, however, more than that at 3247 cm<sup>-1</sup>. It suggests that the less acidic Si-O(H)-Al groups related to the Al<sub>Td</sub>(2b) site are removed more easily from the BEA zeolite than that of the more acidic one related to the Al<sub>Td</sub>(2a) site.

Moreover, the adsorption of pyridine on BEA samples leads to a band at 1454 cm<sup>-1</sup> (besides the 1545 cm<sup>-1</sup> band due to PyH<sup>+</sup>), characteristic of pyridine bonded to Lewis acid sites, PyL. Dealumination of BEA zeolite results in the reduction of both PyH<sup>+</sup> and PyL band intensities, but the effect is more marked for Lewis acidic sites for the removal of the first Al atoms (Figure 11).

In conclusion, the results presented in Figures 9 and 10 indicate that the OH groups of the BEA sample are heterogeneous in line with the <sup>1</sup>H MAS NMR results, as well as those of FTIR of adsorbed pyridine.

**Probe of Framework Al Sites with Vanadium.** The  ${}^{51}V$  MAS NMR investigation is a very useful technique which allows to distinguish between octahedral and tetrahedral V(V) species. The signal of octahedral V(V) is generally observed



**Figure 10.** FTIR spectra recorded at room temperature of BEA(11), BEA(46), BEA(87), BEA(135), and BEA(1240) samples dehydrated in flowing oxygen (120 mL/min) at 773 K for 8 h and then outgassed for 6 h at 573 K ( $10^{-3}$  Pa) after adsorption of pyridine at room temperature and desorption at 150 °C.

with lower isotropic chemical shift  $\delta_{iso}$  (MAS) than that of the tetrahedral V(V) one. As shown earlier, <sup>39,40,57–60</sup> the signal of octahedral V(V) appears between -550 and -580 ppm, and that of tetrahedral V(V) one between -630 and -740 ppm.

The absence of a band between -550 and -580 ppm for  $V_{0.8}SiBEA$  indicates that octahedral V(V) ions are not present. In contrast, the presence of the bands in the range with  $\delta_{iso}$  higher than -700 ppm indicates that the tetrahedral V(V) species occur. Moreover, the appearance of two bands with  $\delta_{iso} = -708$  and -766 ppm (marked by an asterisk, \*, Figure 12) may be assigned to the presence of two kinds of tetrahedral V(V).

The formation of two kinds of tetrahedral V(V) species seems to be related to the presence in the initial BEA zeolite of two kinds of framework  $Al_{Td}$  sites as shown above. Thus, dealumination followed by incorporation of vanadium ion leads to two different kinds of vanadium(V) species. To the best of our knowledge, this is the first time that vanadium is used to probe the presence of different kinds of framework Al in zeolite.

As shown in Figure 13, the BEA(1500) sample obtained after full dealumination exhibits two bands at 3736 and 3708 cm<sup>-1</sup> related to isolated silanol groups, and a broadband at 3520 cm<sup>-1</sup> due to H-bonded SiOH groups, revealing the formation of vacant T-atom sites associated with silanol groups, in line with earlier work.<sup>30,39,40</sup> The incorporation of V ions leading to VSiBEA



**Figure 11.** FTIR spectra recorded at room temperature of BEA(11), BEA(46), BEA(87), BEA(135), and BEA(1240) samples dehydrated in flowing oxygen (120 mL/min) at 773 K for 8 h, then outgassed for 6 h at 573 K ( $10^{-3}$  Pa) after adsorption of pyridine for 1 h at room temperature and desorption at 150 °C for 1 h.



**Figure 12.** <sup>51</sup>V MAS NMR spectrum recorded at room temperature of  $V_{0.8}SiBEA$  ( $v_r = 14.5$  kHz, 43200 scans at 9.4 T (105.1 MHz)) in 4 mm (external diameter) zirconia rotor. The central bands are indicated by asterisks.

decreases the intensity of these bands, in particular that at 3520  $\text{cm}^{-1}$  (Figure 13) suggesting that silanol groups are consumed by reaction with the V precursor. As shown earlier by diffuse reflectance (DR) UV–vis,<sup>30–32</sup> vanadium is incorporated in



**Figure 13.** FTIR spectra recorded at room temperature of SiBEA,  $V_{0.8}$ SiBEA, and  $V_{1.8}$ SiBEA in the O–H stretching domain after calcination of the samples at 773 K for 8 h in flowing oxygen and outgassing at 573 K for 6 h ( $10^{-3}$  Pa). The intensities of the IR spectra have been normalized with respect to the intensity of the framework overtones located within the 2000 –1800 cm<sup>-1</sup> range (not shown).

SiBEA zeolite as tetrahedral V(V) species, with a V=O double bond and linked to the framework by V–OSi bonds (Scheme 1, reaction 2). DR UV–vis showed that the environment of V(V) species depends on the treatment conditions of VSiBEA. Calcinations/hydration processes allowed to distinguish different kinds of tetrahedral V(V) species with various degrees of distortion.

Moreover, O–H groups at 3620 and 3645 cm<sup>-1</sup> (Figure 13) suggest that VSiBEA also contain V(V) sites with V(V)O–H groups. The intensity of these two bands increases with the vanadium content in VSiBEA (Figure 13). Note that for V<sub>1.8</sub>SiBEA), the band at 3620 cm<sup>-1</sup> increases more strongly than that at 3645 cm<sup>-1</sup>. This confirms the heterogeneity of the T-atom sites in BEA zeolite. Both types of V(V)O–H groups have Brønsted acidic character, as shown by FTIR with their simultaneous disappearance upon pyridine adsorption and appearance of the bands due to pyridinium cations at 1545 and 1638 cm<sup>-1</sup> (Figure 14). The intensities increase with increasing of the intensities of the IR bands of Brønsted acidic V(V)O–H groups at 3620 and 3645 cm<sup>-1</sup> (Figure 13).

Moreover, a reduction of both  $V_{0.8}SiBEA$  and  $V_{1.8}SiBEA$ samples with  $H_2$  at 873 K leads to an Electron Paramagnetic Resonance (EPR) signal with two hyperfine structures (hf) characterized by small A<sub>II</sub> hf constants (both close to 150 G at 77 K), very similar to that published earlier,<sup>40</sup> evidencing two kinds of tetrahedral V(IV) sites. These V(IV) sites could be formed as a results of reduction of V(V) sites present in initial  $V_{0.8}SiBEA$  and  $V_{1.8}SiBEA$ . It confirms that in these samples two kinds of tetrahedral V(V) are present in different environments.

#### Conclusions

The objective of this work was to investigate framework Al atoms in BEA zeolite by XRD, FTIR, NMR techniques and V probe.

The dealumination of BEA zeolite upon treatment by nitric acid is shown by XRD and FTIR. 2D <sup>27</sup>Al 3Q and 5Q MAS



**Figure 14.** FTIR spectra recorded at room temperature of  $V_{0.8}SiBEA$  and  $V_{1.8}SiBEA$  dehydrated in flowing oxygen (120 mL/min) at 773 K for 8 h, then outgassed for 6 h at 573 K (10<sup>-3</sup> Pa) after adsorption of pyridine for 1 h at room temperature and then its desorption at the same temperature for 1 h.

NMR spectra of dealuminated BEA zeolite evidence two kinds of tetrahedral Al framework atoms  $(Al_{Td})$  whose relative amounts depend on the Si/Al ratio.

<sup>29</sup>Si and <sup>1</sup>H MAS NMR spectra of dealuminated BEA samples, which confirm the above results, exhibit two resonances at around -114 and -111 ppm ascribed to Si sites in the Si(OSi)<sub>4</sub> environment of two different crystallographic sites. Moreover, Si atoms associated with hydroxyl groups are evidenced by the increase of intensity of the resonance at -102 ppm upon <sup>1</sup>H $-^{29}$ Si cross-polarization.

FTIR and <sup>1</sup>H MAS NMR spectra of BEA samples evidence two kinds of Al–O(H)–Si Brønsted sites with different acid strength, related to the presence of the two kinds of  $Al_{Td}$  sites. The first type of Brønsted site, more acidic, is characterized by a signal at 4.9 ppm while the second type, less acidic, is characterized by a signal at 3.8 ppm.

The Brønsted and Lewis acidic sites in dealuminated BEA zeolites are characterized by IR measurements of adsorbed pyridine, allowing one to determine two kinds of bridging hydroxyl groups (Si-O(H)-Al) with different acid strength. The introduction of vanadium atoms into vacant T-atom sites of fully dealuminated SiBEA zeolite gives rise to two kinds of tetrahedral V(V) sites, as evidenced by <sup>51</sup>V MAS NMR at  $\delta_{iso} = -708$  and -766 ppm, confirming the presence of two kinds of Al sites in the initial BEA zeolite.

Moreover, the FTIR bands at 3620 and 3645 cm<sup>-1</sup> indicate that VSiBEA also contains V(V) sites with V(V)O–H groups. The appearance of these two IR bands confirms the presence of two kinds of framework V(V) sites in VSiBEA zeolite. Both V(V)O–H groups have acidic Brønsted character, as shown by FTIR spectra of adsorbed pyridine.

The present results evidence that two kinds of framework V(V) sites exist in the initial VSiBEA sample. They also show

that vanadium, used as probe, can help investigate framework Al sites in zeolite.

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