Journal of Catalysis **210,** 171–182 (2002)
doi:10.1006/jcat.2002.3661

Structure of Al–Lewis Site in Beta Zeolite Active in the Meerwein–Ponndorf–Verley Reduction of Ketone to Alcohol

Oleg Bortnovsky,[1] Zdeněk Sobalík, Blanka Wichterlová,[2] and Zdeněk Bastl

J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejškova 3, CZ-182 23 Prague 8, Czech Republic

Received February 7, 2002; revised April 19, 2002; accepted April 19, 2002

H-beta zeolites differing in removal of the template by calcination in an oxygen or in a stream of ammonia, and in their subsequent steam treatment at various temperatures, as well as beta zeolites exchanged with alkaline metal ions, were investigated in the MPV reduction of 4-*tert*-butyl cyclohexanone to 4-*tert*-butyl hexanol using isopropanol. FTIR of the OH groups, of the C≡N groups of adsorbed d_3-acetonitrile, and of the framework T–O–T antisymmetric mode was used to estimate the concentration of the individual Al–Lewis sites. XPS was employed to monitor the migration of the Al species into the surface layers of the zeolite crystals. The VHF band at 3780 cm^{-1} and skeletal T–O–T bands at 901, 890, and 882 cm^{-1} were found for steam-treated (ST) H-beta. Both alkali metal ion exchange and treatment of zeolite by gaseous ammonia annihilated the bands at 3780 and 882 cm^{-1}, but the bands at 901 and 890 cm^{-1} (siloxane bridges) were retained. While the bands at 3780 and 882 cm^{-1} correspond to one "partly" framework Al species bearing an OH group, we suggest that the band at 901 cm^{-1} reflects perturbation of the framework due to the presence of highly acidic extraframework AlO_x counter ions exhibiting Lewis properties inside the zeolite channels. The inability to replace these AlO_x complex ions by alkali metal ion exchange indicates their complex structure. These extraframework AlO_x species localized inside the zeolite void volume of beta zeolites represent highly active sites in the stereoselective MPV reduction of ketone to *cis*-alcohol, but their migration to the outer surface of zeolite crystals provides higher yields of *trans*-alcohol. © 2002 Elsevier Science (USA)

Key Words: **Meerwein–Ponndorf–Verley reduction; beta zeolite; IR spectroscopy; Lewis acid; 4-*tert*-butyl cyclohexanone; 4-*tert*-butyl cyclohexanol.**

INTRODUCTION

H-beta zeolites exhibit high activity in industrially important reactions such as aromatic alkylation, disproportionation and transalkylation of alkyl aromatics, catalytic cracking, and aromatic acylation (1–4). In addition to these reactions, catalyzed by Brønsted acid sites, steamed H-beta zeolites are said to exhibit high activity in the Meerwein–Ponndorf–Verley reduction via hydrogen transfer between ketones and alcohols catalyzed by Lewis sites. The size and geometry of the free void volume of beta zeolite provides optimum conditions for stereoselective MPV reduction of 4-*tert*-butyl cyclohexanone by isopropanol to *cis*-4-*tert*-butyl hexanol (5, 6).

Zeolite beta, composed of three polymorphs, A, B, and C, exhibits a three-dimensional structure with a channel size of 7.6 × 6.4 Å. Compared to, for example, ZSM-5 zeolite, the beta framework is less stable and exhibits substantial distortions, which result in an opening of the Al–O framework bonds with formation of a considerable amount of octahedrally coordinated "framework" aluminium, as well as in various extraframework aluminium species, depending on the zeolite treatment (7, 8).

The presence of a "very high frequency" VHF OH band with a characteristic vibration at 3780 cm^{-1} in H-beta zeolites was reported after their steam treatment at mild temperatures or calcination at high temperatures (above 800 K) in the presence of trace concentrations of water (6–11). Nevertheless, the structure of the species with the VHF OH band is still a matter of discussion. Recent publications describe the VHF OH band as OH groups connected to "partly" framework Al exhibiting strong Lewis properties (6, 8, 10). Vimont *et al.* (10) related the VHF band at 3780 cm^{-1} and a broad band in the transmission window region with a maximum at 880 cm^{-1}, which corresponds to an antisymmetric vibration of perturbed T–O–T bonds, to the same type of Al–Lewis site, i.e., to a partly framework Al atom coordinated to three framework oxygens, and completed its coordination sphere with an OH group. Severe steaming of beta zeolites (more than 40% water vapor at 873 K) was reported to lead to preferential formation of extraframework Al species (6). Thus, the conditions of removal of a template from the as-synthesized zeolite, as well as of zeolite further treatment, i.e., the heating rate, the time at the ceiling temperature, and the atmosphere, greatly affect the structure of the resulting catalysts, particularly of the Al-related acid sites.

We reported (12) that H-beta zeolites contain substantial concentrations of Si–OH–Al groups perturbed via hydrogen bonding, which are predominantly converted to Lewis

---

[1] On leave from the Research Institute of Inorganic Chemistry, Inc., Unipetrol group.

[2] To whom correspondence should be addressed. E-mail: wichterl@jh-inst.cas.cz.

sites under the conditions of zeolite calcination in an oxygen stream containing trace concentrations of water vapor. As these perturbed OH groups were shown to be predominantly exchanged by divalent Co ions, it has been speculated that they originate from relatively close framework Al atoms. We also reported (12) the occurrence of Al–Lewis sites bearing OH groups, reflected in the VHF band at 3780 cm^{-1} in zeolites treated in this manner. It follows that the degree of formation of Al–Lewis sites depends not only on the conditions of zeolite treatment, but also on the Al distribution in the framework. For estimation of aluminium distribution in zeolites, see Ref. (13).

Al–Lewis centers in H-beta zeolites, manifested by the broad band of the T–O–T vibration at about 880 cm^{-1} and the OH band at 3780 cm^{-1}, i.e., partly framework Al atoms coordinated to three framework oxygens with their coordination completed by OH group(s), were suggested to be the active sites in the selective MPV reduction of ketones to *cis*-alcohols and in reverse Oppenauer oxidation (5, 6). In addition to the activity of H-beta zeolites, Na-beta zeolites were also reported to be active in MPV reactions (5). However, no explanation has been given for the origin of the activity of these zeolites.

This paper attempts to contribute to the elucidation of the structure of Lewis sites active in MPV reduction. NH_4- and H-beta zeolites calcinated at different temperatures and steamed under mild or severe conditions, as well as those with subsequent exchange by Na^+ and Cs^+ ions, were investigated by recording the IR spectra of the OH groups, the C≡N groups of adsorbed d_3-acetonitrile on Brønsted and Lewis sites, and the T–O–T skeletal vibrations in the transmission window region. XPS provided estimation of changes in the Al concentration in the surface layers of the zeolites. Quantitative analysis of the characteristic IR bands of beta zeolites of various compositions and treatments was correlated with their catalytic activity in selective MPV reduction of 4-*tert*-butyl cyclohexanone by isopropanol to *cis*/*trans* 4-*tert*-butyl cyclohexanol.

EXPERIMENTAL

Parent Zeolites

H- and NH_4-BEA zeolites were used as parent materials. H-BEA (Si/Al = 12.7) with a crystal size of 0.1–0.2 μm was obtained from the PQ Corporation (BEA-1 sample). Laboratory-prepared beta zeolites were synthesized in the presence or absence of alkali cations according to procedures described elsewhere (14, 15). In the procedure, in the presence of alkali cations (BEA-2 series), the starting materials were fumed silica (Cab-o-sil), $NaAlO_2$ (Ridel-de-Haën), tetraethyl ammonium bromide (Fluka), and tetraethyl ammonium hydroxide, 35 wt% (Aldrich), as templates, and NaOH (LACHEMA, CZ). Fumed silica (Cab-o-sil), aluminium chloride (Fluka), and tetraethyl ammonium hydroxide, 35 wt% (Na, <2 ppm; K, <3 ppm), were used in alkali-free synthesis (BEA-3 series) of beta zeolite. Both types of synthesis were carried out at autogenous pressure at 413 K for 3–6 days.

To remove the organic template, the as-synthesized zeolites were calcinated using two different methods.

(i) The as-synthesized zeolites were calcinated in a stream of air at 723 K for 12 h followed by calcination in oxygen at 773 or 823 K for 12 h to obtain standard calcinated (SC) HNa-BEA-2 and H-SC-BEA-3 samples.

(ii) The as-synthesized samples were calcinated in a stream of gaseous ammonia at 723 K for 6 h to prevent framework dealumination (5). After cooling the samples, they underwent threefold ion exchange with 0.5 M NaCl to obtain Na-BEA zeolites. These zeolites were then calcinated in an oxygen stream at 773 K for 4 h to burn off the residual organics and carbon residues (denoted as ammonia calcinated (AC) samples).

HNa-SC-BEA-2 and Na-AC-BEA-3 zeolites were transformed by conventional fourfold ion exchange with 0.5 M NH_4NO_3 to the NH_4 form. XRD analysis and IR spectra of skeletal vibrations indicated a well-developed and highly crystalline BEA structure for all the materials. Chemical analysis of the resulting beta zeolites was carried out by X-ray fluorescence spectroscopy. The crystal sizes of the laboratory-synthesized samples, obtained from scanning electron microscopy (0.05–0.2 μm), were comparable with the commercial sample of PQ origin. The synthesis of the all-silica beta zeolite was carried out using the procedure reported by van der Waal *et al.* (16).

Catalysts Preparation

The PQ sample (H-BEA-1; the procedure for template removal is not known, but it should be noted that the parent sample contained a predominant concentration of Lewis sites) was used in the as-received H form and, after corresponding ion exchange in NH_4, in the Na form (obtained by the ion exchange procedure described above) or Cs form (ion exchange with 0.1 M CsCl). Samples of the AC-BEA-3 series were employed in their parent sodium and ammonium forms. H- and NH_4-BEA-2 and -3 series zeolites were also steamed (ST) at 773–973 K in an oxygen stream with 14–20% water vapor for 4–8 h; ST(773/20%/4 h)-BEA-2 means steam treatment of NH_4-SC-BEA-2 zeolite at 773 K in 20% water vapor for 4 h. ST(773/20%/8 h)-BEA-2 zeolite was treated with 0.1 M HCl to remove extra-framework Al (see Table 1). Details of steaming conditions and ion exchange procedures of the zeolites are given in Table 1. Note that the zeolites were investigated in dehydrated/deammoniated forms, but for clarity their abbreviation remains the same as that given for the as-prepared zeolites.

TABLE 1

Zeolite BEA Catalysts Preparation and Chemical Composition[a]

No.	Sample	Zeolite treatment	Si/Al_{bulk}	$Si/Al_{surface}$	M/Al	ν(OTO) (cm^{-1})
1	H-BEA-1	As obtained	12.7			1091
2	Na-BEA-1	NaCl ion exchange of sample 1	14.4		0.51	1089
3	Cs-BEA-1	CsCl ion exchange of sample 1	14.6		0.60	1089
4	NH_4-BEA-1	NH_4NO_3 ion exchange of sample 1	15.0			1089
5	NH_4-SC-BEA-2	SC and NH_4 ion exchange	13.7	14.5		1084
6	ST(773/20%/4 h)-BEA-2	ST treatment of sample 5	13.7	14.7		1093
7	ST(973/20%/4 h)-BEA-2	ST treatment of sample 5	13.7	12.7		1098
8	ST(773/20%/8 h)-BEA-2	ST treatment of sample 5	13.7			1093
9	HCl(8 h)-ST-BEA-2	0.1 M HCl treatment at RT of sample 8	19.2	25.1		1092
10	SC(773)-BEA-3	SC at 773 K	11.9			1088
11	SC(823)-BEA-3	SC at 823 K	11.9			1090
12	ST(873/14%/4 h)-BEA-3	ST treatment of sample 11	11.9			1094
13	Na-AC-BEA-3	AC and NaCl ion exchange	11.9	11.6	1.1	1081
14	NH_4-AC-BEA-3	NH_4NO_3 IE of sample 13	11.9			1080

[a] SC, Standard calcination at 773 K in a stream of dry air for 12 h (2 K · min^{-1}), then for 12 h in dry oxygen at 773 K (if not specified); AC, calcination in an ammonia stream at 723 K for 6 h (2 K · min^{-1}); ST, steam treatment in an oxygen stream saturated by water vapor (temperature (K)/water vapor content, vol%/period, h); ν(OTO), position of the main asymmetric O–T–O vibration.

Catalytic Measurements

4-*tert*-Butyl cyclohexanone (Aldrich) (2.5 mmol) and 1 mmol of 1,3,5-tri-*tert*-butyl benzene (Aldrich), used as an internal standard, were placed in a round-bottomed glass flask with 40 ml of isopropanol (Fluka, with molecular sieve cap), placed in a dry box. The beta zeolite sample, with a weight of 100–200 mg, was activated prior to the reaction at 623–750 K in a vacuum of 10^{-5} torr for 6 h and sealed. The sealed tube with the catalyst was opened under dry nitrogen in a dry box and the catalyst was transferred to a flask with organic reactants. The mixture was stirred and heated to 80°C under reflux with a trap for traces of water. Liquid samples (0.05 ml) of the reaction mixture were taken during the catalytic experiments, typically at 1-min intervals. The reaction mixture was analyzed using a gas chromatograph, Hewlett–Packard 6890 with FID detector and J&W DB-VRX fused-silica column (0.45-mm ID). The selectivity for alcohols was 98–99% for all catalysts. The initial rate of the reaction was calculated from the logarithmic plot of the conversion of 4-*tert*-butyl cyclohexanone vs time in 600-s intervals.

Infrared Spectroscopy

FTIR spectra of beta zeolites dehydrated/deammoniated *in situ* at 623–750 K in a vacuum of 10^{-5} torr and those followed by adsorption/desorption of base molecules were recorded on a Nicolet Magna-550 FTIR spectrometer with a low-temperature MCT-B detector. Samples in the form of self-supporting wafers with a thickness of about 5–6 mg · cm^{-2} were placed in a six-position sample holder in a heatable vacuum cell with NaCl windows and connected to a dosing system for adsorption of acetonitrile, d_3-acetonitrile, and ammonia. Acetonitrile and d_3-acetonitrile (Aldrich) were degassed by freeze–pump–thaw cycles. Adsorptions of acetonitrile and d_3-acetonitrile (10 torr) and ammonia (50 torr) were carried out at 298 K, with subsequent evacuation for 15 min at the same temperature prior to FTIR spectra measurements. Their desorption was followed by FTIR at temperatures between room temperature (RT) and 750 K. The spectra were recorded at RT with 2-cm^{-1} resolution by collecting 200 scans for a single spectrum. The spectra were normalized to a sample thickness of 5.5 mg · cm^{-2} using the integral area of the skeletal bands in the region between 1750 and 2100 cm^{-1}. The IR spectra were analyzed in the region of OH groups, in the transmission window region of T–O–T skeletal vibrations, and in the region of C≡N vibrations of adsorbed d_3-acetonitrile. The IR band of adsorbed d_3-acetonitrile at 2297 cm^{-1} corresponded to the interaction of the C≡N group with Brønsted sites and the band at 2325 cm^{-1} to that with Lewis sites. The concentrations of Brønsted and Lewis sites were calculated from the intensities of the relevant bands by using extinction coefficients $\varepsilon_B = 2.05 \pm 0.05$ and $\varepsilon_L = 3.62 \pm 0.1$ cm · μmol, taken from Ref. (17) from their determination for ZSM-5 and ferrites. The KBr technique (a pellet containing ca. 30 mg of the sample in 1 g of KBr) was used to estimate the degree of framework dealumination from the shift of the ν(OTO) main asymmetric vibration to higher wavenumbers (18, 19).

X-Ray Photoelectron Spectroscopy (XPS)

XPS was employed to monitor changes in the relative concentrations of Al to Si in the zeolite (sub)surface layers (∼50 Å), and to relate them to the bulk Si/Al composition. The spectra of Al 2p and Si 2p electron levels were monitored. The photoelectron spectra were recorded on a

VG ESCA 3 Mk II electron spectrometer using an Al $K\alpha$ ($h\nu = 1486.6$ eV) nonmonochromatized source at a power of 220 W. The spherical sector analyzer was operated at a pass energy of 20 eV. The background pressure in the analyzer chamber during spectral accumulation was in the region of 10^{-6} Pa. The samples of zeolites were spread on gold plates mounted on the sample holder by tantalum clips. The binding energies of the Al 2p and Si 2p levels did not change with the various zeolite treatments within experimental error. Quantification of the concentration of the elements was accomplished by correcting the photoelectron peak areas for the relevant photoelectron cross sections (20).

RESULTS

Catalytic Activity of Beta Zeolites in MPV Reduction of Ketone to Alcohol and Al Distribution between the Zeolite Bulk and (Sub)Surface Layers

Figure 1 depicts the conversion of 4-*tert*-butyl cyclohexanone to 4-*tert*-butyl cyclohexanol for selected H-beta samples. The initial rates of ketone reduction and *cis*/*trans* selectivity for all the tested zeolites are listed in Table 2. It was found that steamed (ST) beta zeolites are the most active catalysts, and that they exhibit high *cis*-selectivity (93–96%). The activity and *cis*-stereoselectivity of the ST zeolites was highly affected by the conditions of this treatment. The highest activity (Figure 1; initial rate, 10.56×10^{-2} mmol $\cdot$ g^{-1} $\cdot$ s^{-1}) was observed for the ST(873/14%/4 h)-BEA-3 sample treated at 873 K in an oxygen stream with 14 vol% water vapor. Prolongation of steam treatment at 773 K of NH_4-SC-BEA-2 from 4 to 8 h also led to an increase in the catalytic activity with preservation of high *cis*-selectivity. On the other hand, increasing the temperature of the steam treatment from 773 to 973 K resulted in a decrease in the catalytic activity and, moreover, to a decrease in the selectivity for *cis*-alcohol (see Table 2).

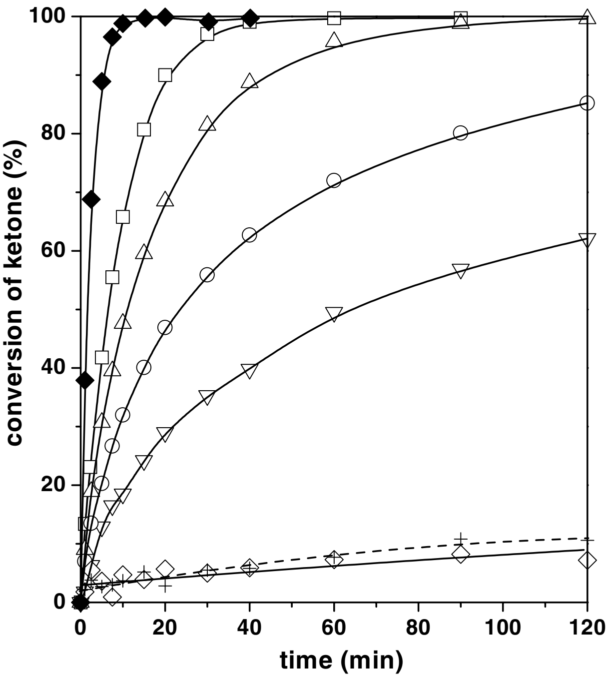

FIG. 1. Conversion of 4-*tert*-butyl cyclohexanone over beta zeolites activated at 750 K. Reaction conditions: 2.5 mmol 4-*tert*-butyl cyclohexanone, 40 ml isopropanol, 120 mg catalyst under reflux and stirring. Symbols: ◆, ST(873/14%/4 h)-BEA-3; □, H-BEA-1; △, ST(773/20%/4 h)-BEA-2; ○, ST(973/20%/4 h)-BEA-2; ▽, SC(773)-BEA-3; +, NH_4-SC-BEA-2; and ◇, NH_4-AC-BEA-3.

The measured binding energies of Si 2p and Al 2p electrons for the monitored samples (see Table 1) varied between 103.3 and 103.8 eV and 74.5 and 75.2 eV, respectively. These values fit well into the range of values obtained recently for a series of different beta zeolites of Collington *et al.* (21). Narrow Al 2p lines were found with NH4-SC-BEA-2 and Na-AC-BEA-3 samples, which exhibit the most regular coordination of aluminium in the framework. With steamed samples as well as with that treated in HCl solution a broadening of the Al 2p lines was observed, indicating a change in the coordination of a part of the aluminium present in the zeolite. It was found that the surface Si/Al ratio of the NH_4-SC-BEA-2 sample (Si/Al 14.5) was close to the value of the bulk composition (Si/Al 13.7; see Table 1) and that it did not change during zeolite steam treatment at 773 K (Si/Al_{surf} of 14.5 vs Si/Al_{bulk} of 14.7). This implies homogeneous distribution of aluminium throughout both of these zeolites. However, the surface was significantly enriched in aluminium in the zeolite steamed at 973 K (Si/Al of 12.7 for ST(973/20%/8 h)-BEA-2). This indicates that while steam treatment at 773 K did not result in substantial migration of aluminium to the surface, aluminum migrated to the outer surface during severe steaming. For the zeolite treated in this way, both the activity and the *cis*-selectivity in MPV reduction of 4-*tert*-butyl cyclohexanone to the corresponding alcohol decreased substantially.

Commercial H-BEA-1 sample (note that the calcination procedure is unknown) exhibited catalytic activity comparable to that of the other ST-BEA zeolites. BEA-3 zeolite calcinated in an oxygen stream at 823 K without addition of water vapor demonstrated almost threefold higher activity than this zeolite, calcinated at 773 K under the same conditions. It follows that the increasing temperature of calcination in the presence of traces of water substantially increased the catalytic activity. NH_4-BEA-2 and -3 zeolites (samples 5 and 14), activated only in vacuum at 750 K prior to the catalytic test, were much less active. The least active catalyst was Na-AC-BEA-3 and the NH_4-AC-BEA-3 derived from it, prepared by calcination in a gaseous ammonia stream (AC-BEA-3). These results are in agreement with Refs. (5, 6), where it is stated that only steamed beta zeolites exhibit high activity in MPV reduction.

TABLE 2

Catalytic Activity, Acid Site Concentration, and Integral Intensities of the IR Band Spectroscopic Characterization of BEA Zeolite Catalysts[a]

						Normalized relative integral intensity of IR bands		
							Deconvoluted components	
No.	Sample	Initial rate ($\times 10^{-2}$)[b]	Al$^{\mathrm{bulk}}$[c]	B[c]	L[c]	3780 cm^{-1}	882 cm^{-1}	901 cm^{-1}
1	H-BEA-1	3.29 [95 : 5]	1.22	0.13	0.52	1.00	0.76	0.31
2	Na-BEA-1	2.86 [96 : 4]	1.08	0.06	0.14	0.02	0.07	0.24
2a	Na-BEA-1	0.05 [n.d.]	1.08	—	—	—	0.03	0.06
2b	Na-BEA-1	0.08 [n.d.]	1.08	—	—	—	0.04	0.08
3	Cs-BEA-1	2.29 [96 : 4]	1.08	0.04	0.08	0.02	0.14	0.24
4	NH_4-BEA-1	1.98 [96 : 4]	1.04	0.29	0.2	0.16	0.28	0.20
5	NH_4-SC-BEA-2	0.04 [n.d.]	1.14	0.67	0.2	0.03	0.05	0.04
6	ST(773/20%/4 h)-BEA-2	1.87 [94 : 6]	1.14	0.13	0.28	0.72	0.43	0.24
7	ST(973/20%/4 h)-BEA-2	1.02 [83 : 17]	1.14	0.04	0.13	0.30	0.25	0.14
8	ST(773/20%/8 h)-BEA-2	3.78 [94 : 6]	1.14	0.13	0.18	0.69	0.72	0.43
9	HCl(8 h)-ST-BEA-2	1.47 [94 : 6]	0.82	0.16	0.22	0.47	0.25	0.17
10	SC(773)-BEA-3	0.93 [94 : 6]	1.30	0.36	0.38	0.64	0.17	0.12
11	SC(823)-BEA-3	3.05 [93 : 7]	1.30	0.19	0.24	0.76	0.27	0.25
12	ST(873/14%/4 h)-BEA-3	10.56 [93 : 7]	1.30	0.07	0.1	0.58	1.00	1.00
13	Na-AC-BEA-3	0.02 [n.d.]	1.30	0.02	0.01	0.00	0.04	0.05
14	NH_4-AC-BEA-3	0.04 [n.d.]	1.30	0.61	0.32	0.02	0.03	0.02

[a] All catalysts were activated at 750 K for 6 h in vacuum, except sample 2a, which was activated at 623 K, and sample 2b, which was activated at 673 K. B, Concentration of Brønsted sites determined from integral intensity of the band at 2297 cm^{-1} of adsorbed d_3-acetonitrile; L, concentration of Lewis sites determined from integral intensity of the band at at 2325 cm^{-1} of adsorbed d_3-acetonitrile. n.d., Not determined.

[b] In millimoles per gram per second. Results in square brackets show *cis/trans* selectivity.

[c] In millimoles per gram.

The steamed sample ST(773/20%/8 h)-BEA-2 treated with 0.1 M HCl (HCl-ST-BEA-2) exhibited 2.5 times lower activity compared with the original ST zeolite. Acid treatment of the ST-BEA-2 zeolite significantly changed the composition of the zeolites. Bulk chemical analysis indicated a substantial decrease in the aluminium content (from Si/Al 13.7 to 19.2; cf. Table 1), which was even higher in the surface layers (from Si/Al 14.5 to 25.1). These results imply that steamed zeolites of series BEA-2 exhibited a high concentration of extraframework Al species, enriched in a (sub)surface layer, which were "partly" removed by acid treatment.

The H-BEA-1 zeolite and those exchanged by Na^+ and Cs^+ ions exhibited very high, nearly comparable MPV activities (see Table 2). Part of the Al was removed from the zeolite during ion exchange and the maximum ratio of M/Al ($M = Na^+$ or Cs^+) attained was only 0.5 and 0.6, respectively. Accordingly, a considerable amount of extraframework Al species in H-BEA-1 zeolite, balancing the negative framework charge, could not be removed by alkaline cation exchange. It should be noted that complete Na ion exchange was found with AC-BEA-3, indicating that all the aluminium atoms were situated in the framework. In addition, the surface Si/Al value for this zeolite was close to that for the bulk composition (Si/Al 11.6 vs 11.9, respectively; see Table 1). The MPV activity of the Na-AC-BEA-3 zeolite was negligible.

FTIR Spectra of Beta Zeolites

Although the shift in the symmetric ν(OTO) vibration (see Table 1) cannot provide information on the state of aluminium, it reflects changes in the concentration of aluminium in the framework and thus the degree of framework dealumination (18, 19). The lowest ν(OTO) value (1080 cm^{-1}) for samples of the BEA-3 series indicates that the most aluminium is present in the "regular" tetrahedral sites. More-severe steaming increased the shift of the ν(OTO) vibration; the highest shift with the band at 1098 cm^{-1} was found with the zeolite of the BEA-2 series steamed at 973 K (see Table 1).

Figures 2A–2C depict the IR spectra of H-beta zeolites in the region of the OH groups, the T–O–T vibrations, and the C≡N groups of adsorbed d_3-acetonitrile, respectively. In addition to the silanol terminal OH group at 3745 cm^{-1} and bridging OH groups at 3610 cm^{-1}, the VHF OH band at 3780 cm^{-1} and the OH band at 3660 cm^{-1} were detected in the spectra of the SC-BEA-3, H-BEA-1, and ST-BEA-2 and -3 zeolites (spectra b–e in Figure 2A), but not in NH_4-AC-BEA-3 (spectrum a in Figure 2A) and in NH_4-SC-BEA-2

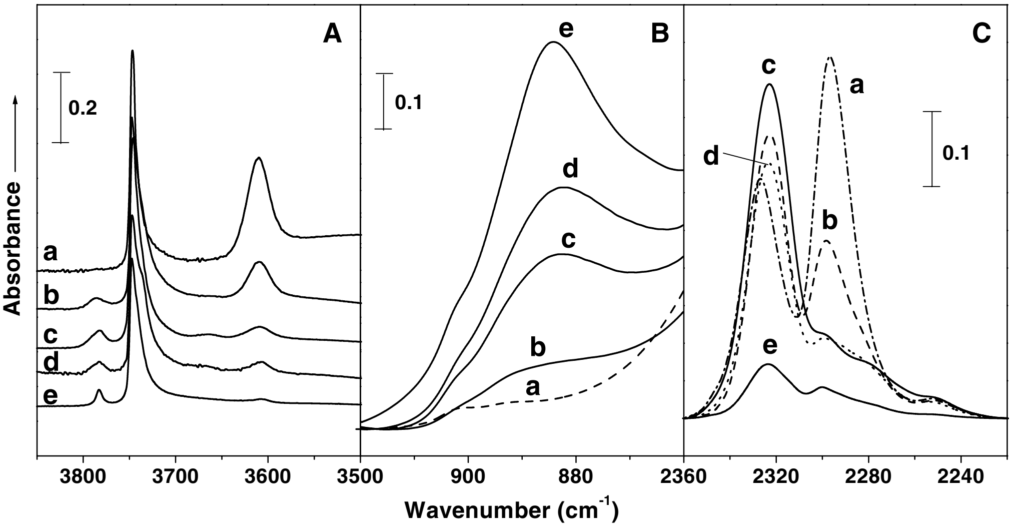

FIG. 2. (A) FTIR spectra of H-beta zeolites after evacuation at 750 K in the region of OH groups. (a) NH_4-AC-BEA-3; (b) SC(773)-BEA-3; (c) H-BEA-1; (d) ST(773/20%/4 h)-BEA-2; (e) ST(873/14%/4 h)-BEA-3. (B) FTIR spectra of H-beta zeolites after evacuation at 750 K in the T–O–T region. (a) NH_4-AC-BEA-3; (b) SC(773)-BEA-3; (c) H-BEA-1; (d) ST(773/20%/4 h)-BEA-2; and (e) ST(873/14%/4 h)-BEA-3. (C) FTIR spectra of H-beta zeolites after d_3-acetonitrile adsorption followed by evacuation at RT in the region of the C≡N group vibration. (a) NH_4-AC-BEA-3; (b) SC(773)-BEA-3; (c) H-BEA-1; (d) ST(773/20%/4 h)-BEA-2; and (e) ST(873/14%/4 h)-BEA-3.

(not shown in the figure). It should be noted that the band at 3780 cm^{-1} became narrower with higher temperature of steaming (compare spectra b and e in Fig. 2A). This indicates that this band might consist of several components corresponding to various Al structures bearing OH groups, which probably dehydroxylate at different temperatures.

Most of the H-beta samples exhibited a low-intensity band of OH groups at 3660 cm^{-1} (see Fig. 2A). This band is generally attributed to hydroxyls connected to extraframework Al (8), but its intensity was not found to correlate with the concentration of the extraframework Al species, as not all Al extraframework sites can be expected to bear such OH groups. Alkali metal ion exchange (see also Fig. 3A) did not eliminate this band but led to a shift in the position of this band from 3665 to 3680 cm^{-1}. The nature of this new band is not clear (see Ref. (22) and references therein). Because of the low intensity of the band ascribed to OH groups bound to extraframework Al and variability of the structure of these species, their structure is not discussed in connection with the activity of beta zeolites in MPV reactions.

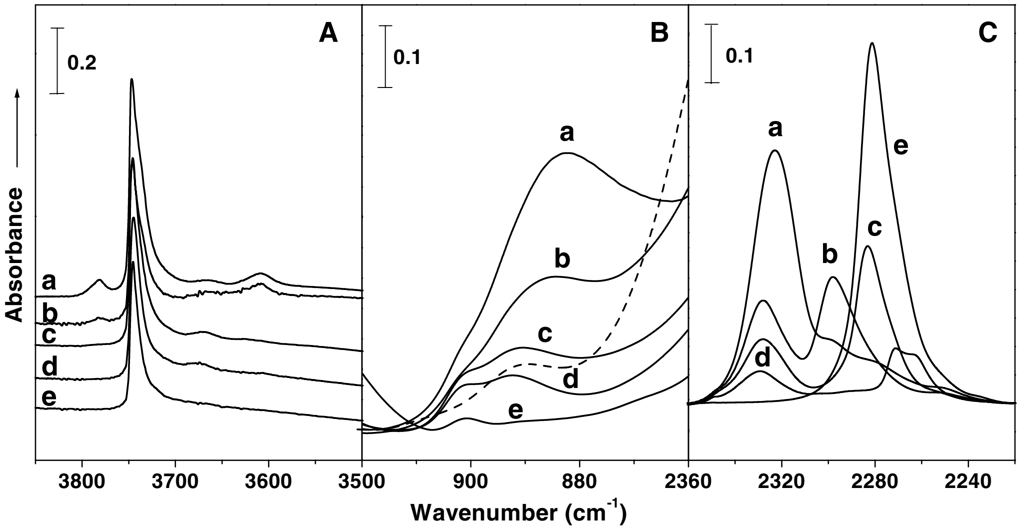

FIG. 3. FTIR spectra of beta zeolites after evacuation at 750 K: (A) in the region of OH groups; (B) in the T–O–T region; and (C) after d_3-acetonitrile adsorption and followed evacuation at RT in the region of the C≡N group vibration. (a) H-BEA-1; (b) NH_4-BEA-1; (c) Na-BEA-1; (d) Cs-BEA-1; and (e) Na-AC-BEA-3. Dashed line in Fig. 3B represents all-silica beta zeolite.

Divalent (23, 24) or trivalent cations (24) in a zeolite cationic position cause perturbation of framework T–O–T bonds caused by cations bonding to the zeolite framework. However, in the presence of divalent and trivalent cations, the T–O–T bands appear in the region of 940–880 cm^{-1}, depending on the nature and valence of the cations, due to the redshift of the main asymmetric T–O–T vibration at around 1080–1100 cm^{-1}. The region of the transmission window is shown for the same samples in Fig. 2B. An intense broad band with a maximum at 882 cm^{-1} with clear shoulders on the high-frequency side increased in intensity with the severity of steam treatment. The intensity generally followed the intensity of the VHF band at 3780 cm^{-1} shown in Fig. 2A.

The C≡N vibration region of adsorbed d_3-acetonitrile is shown in Fig. 2C. Already moderate steaming led to a substantial decrease in the intensity of the band at 2297 cm^{-1}, corresponding to adsorption of d_3-acetonitrile on Brønsted sites, whereas the intensity of the band at approximately 2325 cm^{-1}, corresponding to that at Lewis sites, passed through the maximum reached with the zeolite steamed at mild conditions (compare the samples in the ST-BEA-2 series treated at 773 and 973 K, Fig. 2C and Table 2).

A summary of the IR bands for beta zeolites in the region of OH vibrations, framework T–O–T vibrations, and C≡N vibrations of adsorbed acetonitrile is given in Table 3.

In NH_4-AC-BEA-3 and NH_4-SC-BEA-2 zeolites, the OH bands at 3780 and 3660 cm^{-1} and the T–O–T skeletal broad band with a maximum at 882 cm^{-1} were absent (see Figs. 2A and 2B and Table 2). These zeolites exhibited much higher concentrations of Brønsted sites compared with the steamed zeolites (e.g., 0.61 mmol/g for NH_4-AC-BEA-3 and 0.07 mmol/g for ST(873/14%/4 h)-BEA-3; see Table 2).

Figure 3 depicts regions of IR spectra similar to those in Fig. 2 for zeolites ion exchanged by alkali metal ions, which originally exhibited bands at 3780 and 882 cm^{-1}, i.e., bands ascribed to the presence of partly framework Al species but not regularly tetrahedrally coordinated. It can be seen that, compared to H- and NH_4-BEA-1 zeolites, Na- and Cs-BEA-1 (spectra c and d, respectively, in Figs. 3A and 3B) did not exhibit, respectively, the band at 3780 and broad absorption with maximum at 882 cm^{-1}. Only two absorption bands of low intensity, at 901 and 890 cm^{-1}, were observed. The all-silica beta zeolite activated at 750 K exhibited absorption at 890 cm^{-1} in the skeletal window (see the dashed line in Fig. 3B). The component at 890 cm^{-1} was also reported in silicallite-1 activated at 750 K and was attributed to siloxane bridges formed by dehydration of two vicinal silanols (26). The IR spectrum of the Na-AC-BEA-3 zeolite exhibited practically no bands in the region between 900 and 880 cm^{-1}.

In addition to Brønsted (2297 cm^{-1}) and Lewis sites (2325 cm^{-1}), the bands at 2282 and 2271 cm^{-1} in the spectra of Na- and Cs-BEA zeolites were observed due to interaction of the C≡N group with Na^+ and Cs^+ cations (see Fig. 3C). Ion exchange of H-BEA-1 zeolite with NH_4^+, Na^+, and Cs^+ cations caused a dramatic decrease in the concentration of Lewis sites (see Fig. 3C and Table 2); however, some Lewis sites were still present. On the other hand, the IR spectrum of the Na-AC-BEA-3 zeolite prepared in the presence of ammonia did not manifest the presence of Lewis sites.

As the Na^+ and Cs^+ ion exchange of H-BEA-1 zeolite caused a substantial decrease in the intensity of the intense band at 882 cm^{-1}, the other bands between 900 and 880 cm^{-1} became clearly visible (see Fig. 3B). The changes in the spectral intensities and spectral deconvolution indicates that the broad band with a maximum at 882 cm^{-1} consists of at least three components, at 901, 890, and 882 cm^{-1} (see Fig. 4). The positions and FWHM of the IR bands and

TABLE 3

Position and FWHM of IR Bands in the Regions of OH groups, T–O–T Vibrations, and C≡N Vibrations of Adsorbed d_3-Acetonitrile

Region	Position (cm^{-1})	FWHM^{a} (cm^{-1})	Description	Ref.
OH region	3780		$(SiO)_2$–Al$^{\square}$–OH and SiO–Al$^{\square}$–$(OH)_2$	8
	3745		Terminal Si–OH groups	8
	3660		OH group on EFAL	8
	3605–3610		Bridging ≡Si–OH–Al≡ groups	8
	3700–3300		Perturbed close bridging OH groups	12
T–O–T region deconvoluted components	882		≡Si–O–Al (SiO)OH	10
	901	8–12	Extra-framework AlO_x counter cation	This work
	892	12–15	Siloxane bridge	22
	882	23–25	≡Si–O–Al(SiO)OH	10
C≡N region deconvoluted components	2325–2330	20–23	Strong Al-Lewis sites (Al$^{\square}$. . . N≡C)	17
	2310–2315	9–12	Weak Al-Lewis sites (Al$^{\square}$. . . N≡C)	17
	2296–2299	14–17	Brønsted sites (H^+. . . N≡C)	17
	2277–2284	20–24	Terminal hydroxyls (SiOH. . . N≡C)	17
	2283–2285	10–12	Sodium cation (Na^+. . . N≡C)	12

[a] This work.

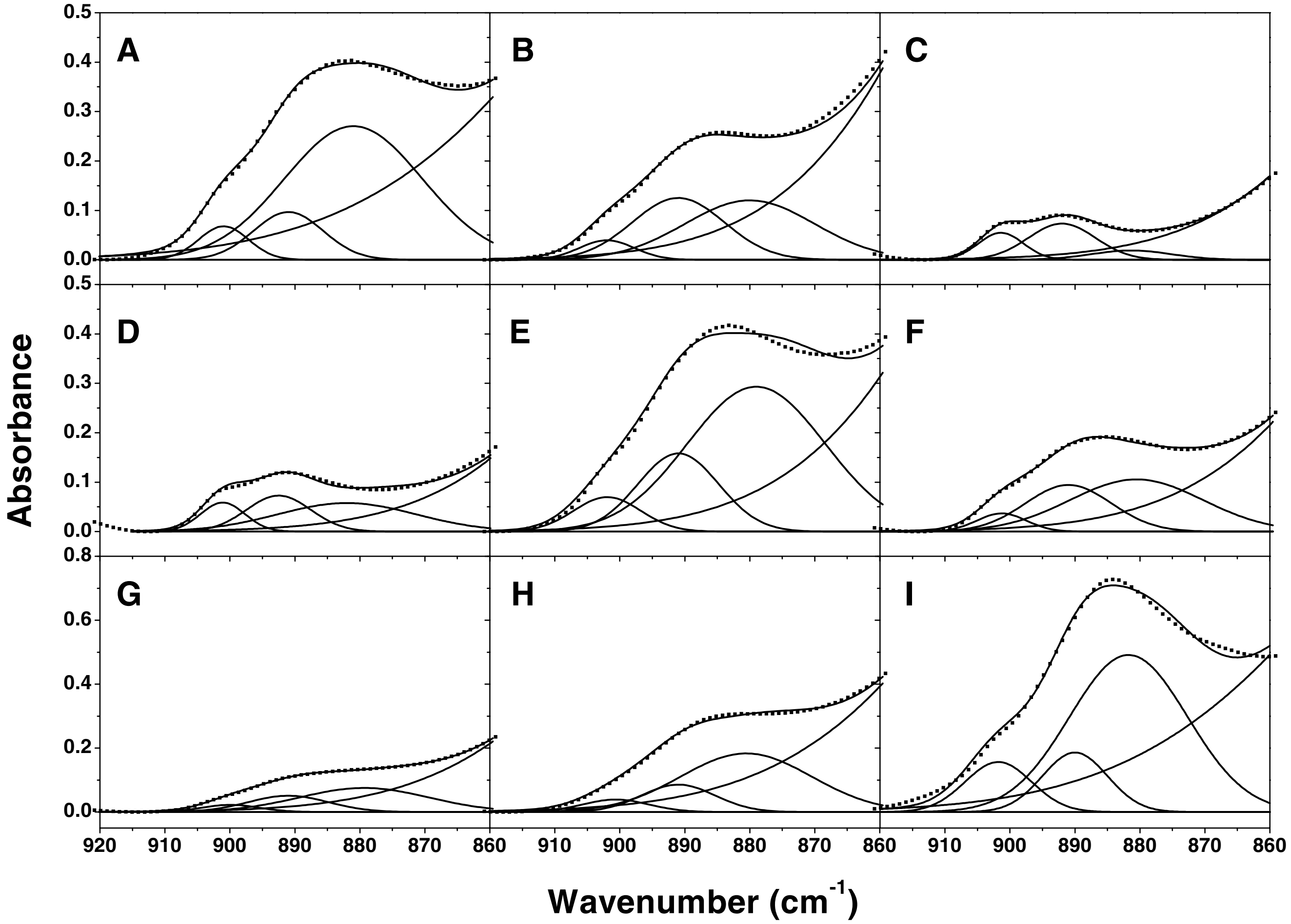

FIG. 4. Illustration of deconvolution of a broad adsorption centered at 882 cm^{-1} for three components, at 901, 890, and 882 cm^{-1}, using Gaussian profiles overlapping symmetric vibration at 795 cm^{-1}: (A) H-BEA-1; (B) NH$_4$-BEA-1; (C) Na-BEA-1; (D) Cs-BEA-1; (E) ST(773/20%/8 h)-BEA-2; (F) HCl-ST-BEA-2; (G) SC(773)-BEA-3; (H) SC(823)-BEA-3; and (I) ST(873/14%/4 h)-BEA-3.

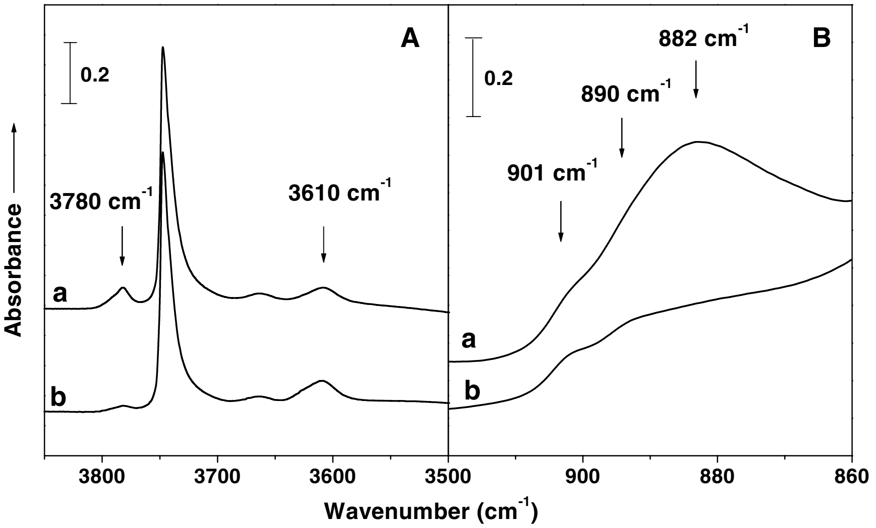

FIG. 5. Adsorption and desorption of ammonia on H-BEA-1 zeolite. (A) OH groups region; (B) T–O–T region. (a) Activated at 750 K; (b) after adsorption of ammonia and its desorption at 750 K.

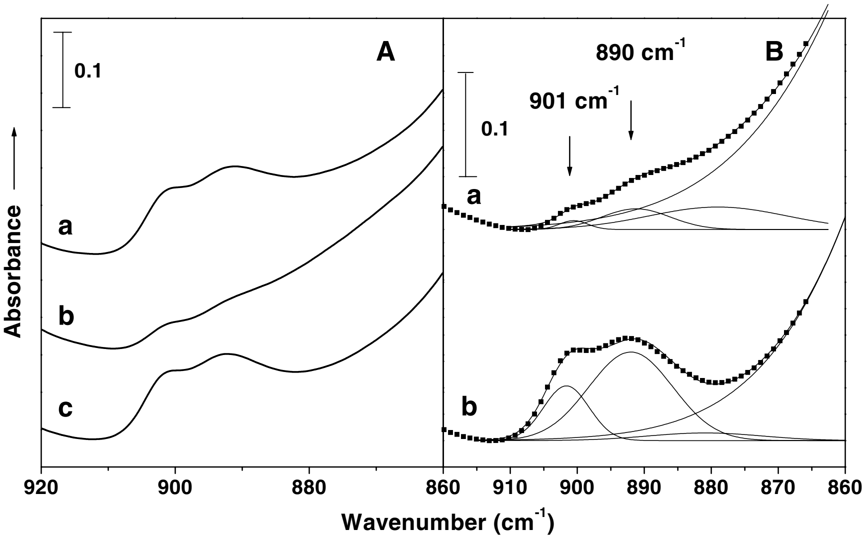

FIG. 6. (A) Adsorption and desorption of acetonitrile on Na-BEA-1 zeolite. (a) Activated at 750 K. Adsorption of acetonitrile followed by desorption at (b) 673 K and (c) 750 K. (B) Dehydration of Na-BEA-1 zeolite at (a) 673 K and (b) 750 K.

deconvoluted components in the regions of the OH groups, the T–O–T vibrations, and the C≡N vibrations of adsorbed d_3-acetonitrile are summarized in Table 3.

Compared to ST(773/20%/4 h)-BEA-2, ST(973/20%/4 h)-BEA-2 exhibited a lower band intensity at 901 cm^{-1}, and a shift of the main asymmetric T–O–T vibration to higher wavenumbers (1098 vs 1093 cm^{-1}; Tables 1 and 2). Treatment of ST (773/20%/8 h)-BEA2 with 0.1 M HCl led to a decrease in the intensity of the T–O–T band at 901 cm^{-1} (see Table 2).

To investigate the acidity strength and possible transformation of different Al species, adsorption of ammonia and acetonitrile and their desorption at different temperatures were monitored in the region of the T–O–T skeletal and OH group vibrations. Nondeuterated acetonitrile was used to avoid deuteration of acidic OH groups, which might lead to formation of a band at 897 cm^{-1} overlapping the bands in the region 900–880 cm^{-1}. The IR spectra of H-BEA-1 zeolite activated at 750 K and after adsorption of ammonia and its desorption at 750 K are depicted in Figs. 5A and 5B. The IR spectrum of dehydrated H-BEA-1 exhibited an intense band at 3780 cm^{-1} of OH groups and a broad intense band of T–O–T vibration centered at 882 cm^{-1}. Whereas the bands at 901 and 890 cm^{-1} retained their original intensity after ammonia adsorption and desorption at 750 K, the bands at 3780 and 882 cm^{-1} were highly perturbed, and at the same time the intensity of the bands of the bridging OH groups at 3610 cm^{-1} increased.

Figure 6A depicts the spectra of Na-BEA-1 zeolite dehydrated at 750 K (spectrum a) and after adsorption and subsequent desorption of acetonitrile at temperatures of 673 and 750 K (spectra b and c, respectively). The intensity of the T–O–T bands at 901 and 890 cm^{-1} was restored only after acetonitrile desorption at a temperature of 750 K. Quantitative analysis of the IR spectra of adsorbed d_3-acetonitrile shows that 0.02 mmol/g of Lewis sites is still covered with acetonitrile molecules after acetonitrile desorption at 673 K. It should be pointed out that this concentration of Lewis sites is approximately 10% of the total concentration of Lewis sites in the Na-BEA-1 zeolite

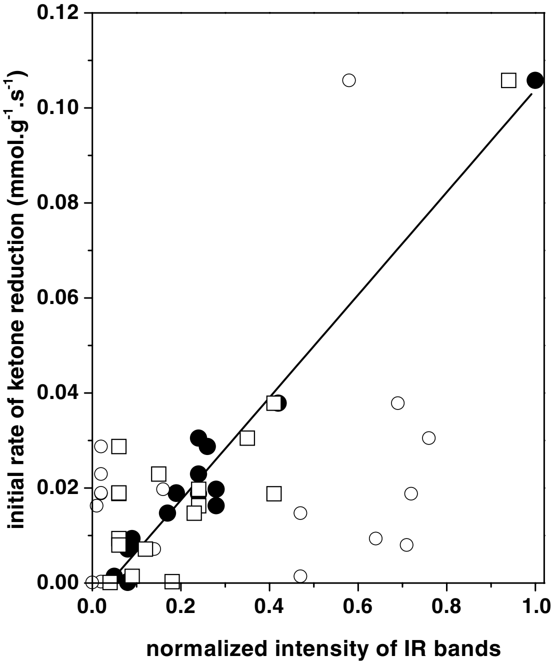

FIG. 7. Dependence of initial rate of ketone reduction on normalized intensity of IR bands. Symbols: ●, band at 901 cm^{-1}; ○, band at 3780 cm^{-1}; and □, band at 882 cm^{-1}.

measured after evacuation of adsorbed d$_3$-acetonitrile at RT (see Table 2). Similar behavior of the T–O–T bands was observed during stepwise dehydration of the Na-BEA-1 zeolite (see Fig. 6B). Upon zeolite dehydration at 673 K, Na-BEA-1 exhibited a low intensity of the T–O–T bands at 901 and 890 cm^{-1} as well as very low MPV activity (see Table 2 and Fig. 6B). Only zeolite dehydration at 750 K restored both the original intensity of the bands at 901 and 890 cm^{-1} and the high activity in the MPV reduction.

Figure 7 depicts the dependence of the initial rate of ketone reduction to alcohol on the intensities of the IR bands at 901, 882, and 3780 cm^{-1}. It is clearly seen that for all the investigated beta catalysts, the integral intensity of the T–O–T band at 901 cm^{-1} is satisfactorily correlated with the rate of MPV reduction of ketone, in contrast to the integral intensities of the bands at 882 and 3780 cm^{-1}. It should be pointed that the estimated TOF value of 5150 h^{-1} for the Al species reflected in the T–O–T band at 901 cm^{-1} is very high.

DISCUSSION

Conditions of template removal from the as-synthesized beta zeolite strongly affect Al bonding in its framework. It has been reported by Creyghton *et al.* (5) and Kunkeler *et al.* (6) that calcination in an ammonia stream, in contrast to standard calcination in oxygen, leads to replacement of the tetraethyl ammonium counterion by an ammonium cation, and most of the template is desorbed. According to Ref. (6), octahedrally coordinated Al was absent in the samples obtained under template removal in the presence of ammonia. Generally, it has been clearly demonstrated that ammonium and also metal cations balancing negative-framework charge prevent formation of octahedrally coordinated Al in beta zeolites (7).

We also observed only a small shift in the asymmetric main ν(OTO) vibration mode to higher wavenumbers, indicating the preservation of "regular" tetrahedrally coordinated Al in the framework with negligible dealumination for beta zeolites, where the template was removed in the presence of ammonia (Tables 1 and 2, AC samples 13 and 14). The H-beta zeolites prepared in this way exhibited high intensity of the band at 3610 cm^{-1} of the bridging OH groups and intense broad absorption at 3700–3300 cm^{-1}, corresponding to perturbed close acidic OH groups (12). The concentration of Brønsted sites (sum of the unperturbed and perturbed OH groups) for these zeolites was much higher compared to the concentration of Lewis sites (see Fig. 2C and Table 2). The values of the concentrations of Brønsted and Lewis sites for sample 14, compared to the Al content in the zeolite, indicate that one Lewis site is formed from two Brønsted sites. This finding implies that the Lewis sites are represented by Al atoms which are still bound in the framework, but their environment is highly distorted. Also activation of NH$_4$-beta zeolite (sample 4) led to a catalyst with a relatively high concentration of Brønsted sites, and the Lewis sites were also represented by distorted framework Al atoms. These catalysts were practically inactive in MPV reduction. Thus, the Brønsted sites as well as the above-described "framework-distorted" Lewis sites cannot be expected to be the active sites for this reaction.

In contrast, the samples calcinated under standard conditions in the presence of oxygen with traces of water vapor (SC) exhibited a shift of the ν(OTO) mode to higher wavenumbers, a broad intense T–O–T band with a maximum at 882 cm^{-1}, and the OH bands at 3780 and 3660 cm^{-1} ascribed to hydroxyls bound to partly framework and to extraframework Al centers, respectively (see Figs. 2A and 2B and Table 2). The standard calcination procedure led to a lower concentration of Brønsted sites and higher concentration of Lewis sites compared to samples calcinated in the presence of ammonia (AC). This decrease in the concentration of Brønsted sites and the increase in the concentration of Lewis sites originated mostly from dehydroxylation of perturbed bridging OH groups. The easy dehydroxylation of perturbed OH groups indicates that the relatively close Al atoms exhibit a higher tendency toward perturbation of their environment and formation of Lewis sites compared to the unperturbed Si–OH–Al groups, which are represented by distant framework Al atoms (Fig. 2C and Table 2). A recent study by van Bokhoven *et al.* (27) employing ^{27}Al MQMAS NMR indicated two different aluminium framework T sites in beta zeolites in relation to their stability under steam treatment. The OH band at 3780 cm^{-1} and skeletal band with a maximum at approximately 882 cm^{-1}, both occurring in beta zeolites that were mildly steamed or calcinated at high temperatures, were unambiguously ascribed to the same center, i.e., to the partly framework Al atoms exhibiting Lewis properties. It was suggested (10) that this corresponds to the following structures formed by stepwise framework perturbation (for the relevant characteristic IR bands, see Table 3):

$$2{\equiv}\text{Al–OH–Si}{\equiv} \rightarrow {\equiv}\text{Al}^{\square} + \text{AlO}_4^- \rightarrow 2{=}\text{Al}^{\square}\text{–OH} \rightarrow 2\text{Al}^{\square}\text{O}^+ \rightarrow \text{alumina clusters;}$$

$$\begin{array}{llll} \text{Brønsted sites} & \rightarrow \text{framework} & \rightarrow \text{partly framework} & \rightarrow \text{extraframework} \\ & \text{Lewis sites} & \text{Lewis sites} & \text{Lewis sites.} \end{array}$$

It is shown here that the beta zeolites possessing partly framework Al–Lewis sites (with characteristic bands at 3780 and 882 cm^{-1}) exhibited slightly higher activity in MPV reduction of ketone to alcohol, particularly in samples treated at higher temperatures (cf. samples 10 and 11) or those steamed under mild conditions, i.e., 773 K (samples 6 and 8). The highest MPV activity was achieved with the zeolite steamed at 873 K (sample 12). These samples contained, in addition to partly framework Al atoms, extraframework

Al species (with Lewis properties) as indicated by (i) a lower concentration of Lewis sites compared to that expected to be formed by dehydroxylation of Brønsted sites, and (ii) an increase in the concentration of Al in the surface layers of zeolites. It is generally known that extraframework Al species exhibit a tendency to migrate to the zeolite surface layers (see, e.g., Ref. (27)), and that not all these aluminium atoms possess Lewis properties. It should be stressed that the most active steamed zeolite (sample 12) also exhibited the highest intensity of the band at 901 cm^{-1} and a relatively low total concentration of Lewis sites. Figure 7 strongly supports our suggestion, by showing a good correlation between the rate of the MPV reaction and the integral intensity of the band at 901 cm^{-1} ascribed to framework perturbation due to extra-framework exchanged AlO_x at the cationic site.

As the extraframework Al species on the outer zeolite surface mediates in ketone reduction to *trans*-alcohol, this indicates that extraframework Al–Lewis sites inside the zeolite channel, but not those partly framework Lewis sites still bound to the framework, are the active sites. To bring further insight into the nature of the active sites for the MPV reaction, the effect of the calcination procedure and ion exchange with monovalent cations on the OH vibration and T–O–T skeletal regions was investigated (see Figs. 3A and 3B and Tables 1 and 2). After ion exchange of sodium, cesium, or ammonium ions in H-BEA-1, not only the band at 3780 cm^{-1} (see Fig. 3A) but also a large part of the broad band centered at 882 cm^{-1} vanished; however, the bands at 901 and 890 cm^{-1} were still present (see Fig. 3B). This observation is in agreement with the statement of Bourgeat-Lami *et al.* (7) that partly framework Al species bearing OH groups can be reinserted into the framework when the hydrogen counterion is replaced by an alkali or ammonium cation. We found almost the same activity with H-BEA-1 and with the related Na-BEA-1 zeolite (samples 1 and 2, respectively). No VHF hydroxyls at 3780 cm^{-1} were observed in Na- and Cs-BEA-1 and the T–O–T band at 882 cm^{-1} dramatically decreased in intensity. In spite of the chemical analysis data that only 53–60% of Al was balanced by alkali cations, no hydroxyls at 3610 cm^{-1} were observed in the spectra of Na- and Cs-BEA-1 samples and the concentration of Brønsted sites was also very low (see Table 2). Nonetheless, the Lewis sites were still present and their concentration corresponded to 14–20% of the original value in H-BEA-1 (see Fig. 3C and Table 2). This finding, together with the correlation given in Fig. 7, is decisive for attribution of the MPV activity of beta zeolite to Lewis sites reflected in the band at 901 cm^{-1}.

Also adsorption and subsequent desorption of ammonia led to the same conclusion as that implied from the ion exchange with monovalent cations (see Figs. 5A and 5B). The results are in agreement with those of Creyghton *et al.* (5) and Kuehl and Timken (29) that ammonia treatment of H-beta zeolite leads to transformation of octahedrally coordinated Al into the regular tetrahedral framework sites. These findings indicate that the partly framework octahedrally coordinated Al atoms are not extraframework species, but that they are part of the framework.

As extraframework Al species were not removed from the zeolite during cation exchange, this indicates the complexity of their AlO_x structure. Stepwise dehydration of zeolites (see Fig. 6B) and desorption of adsorbed acetonitrile (see Fig. 6A) indicated that these sites strongly adsorbed water and acetonitrile up to 673 K, and thus they exhibit strong acidity. This finding is in agreement with the observation that the activity of Na-BEA-1 zeolite activated at 673 K was only 5% of that of zeolite activated at 750 K. This is also in agreement with the observed negative effect of a small amount of adsorbed water or other bases on the activity of Lewis sites active in the MPV reduction, which was also reported in Ref. (6).

Generally, it is difficult to determine the concentration of active extraframework Al sites (reflected in the IR band at 901 cm^{-1}) by any spectral techniques because of their low concentration in the predominant amounts of the other Al sites. The total concentration of Al–Lewis sites in highly active Na-BEA-1 and Cs-BEA-1 corresponds to approximately 14–20% of the values in H-BEA-1, although the activity of H-BEA-1 is only slightly higher compared to the Na– and Cs–zeolites. The concentration of Lewis sites (with adsorbed acetonitrile) after acetonitrile desorption at 673 K is approximately 10% of its original value. At the same time, only 15% of the original intensity of the band at 901 cm^{-1} was restored after acetonitrile desorption at 673 K. Thus, we suggest that the T–O–T band at 901 cm^{-1} corresponds to the most acidic Lewis sites, which still adsorbed acetonitrile at 673 K. The concentration of these Lewis sites is only approximately 0.02 mmol/g, representing only ca. 2–3% of the total Al in the zeolite. Accordingly, quantitative analysis of these species is very difficult; however, there is clear evidence that the band at 901 cm^{-1} reflects the Al species with strong Lewis acidity responsible for the MPV reduction of 4-*tert*-butyl cyclohexanone to *cis*-4-*tert*-butyl hexanol.

All this implies that the activity of steamed H-beta zeolite in the stereoselective Meerwein–Ponndorf–Verley reduction of 4-*tert*-butyl cyclohexanone to 4-*cis*-*tert*-butyl cyclohexanol can be related to the characteristic T–O–T band at 901 cm^{-1}, which reflects the presence of the most acidic extraframework cationic Al sites of complex structure located inside the zeolite channels.

CONCLUSIONS

Analysis of the structure of various Al-related acid sites in H-beta zeolites by means of the IR spectra in the region of the OH groups, the C≡N groups of adsorbed acetonitrile, and the T–O–T framework vibrations, and the distribution of Al between the zeolite bulk and surface layers obtained from XPS, together with the catalytic activity of calcinated, ammonium or steamed, NH_4-, H-, Na-, and Cs-beta zeolites in the selective MPV reduction of 4-*tert*-butyl cyclohexanon to 4-*tert*-butyl cyclohexanol revealed the following:

1. The highest activity in *cis*-stereoselective MPV reduction of 4-*tert*-butyl cyclohexanone to 4-*cis*-*tert*-butyl cyclohexanol can be achieved on H-beta zeolite steamed under defined conditions at 873 K. The template removal procedure from beta zeolites already greatly affects the formation of active sites.
2. There is a range of different Al–Lewis sites in H-beta zeolites. Three types of characteristic Al-related Lewis sites were identified in H-beta zeolites. It has been shown that (i) the majority of Al–Lewis sites consists of framework Al with a distorted environment, (ii) the VHF OH band at 3780 cm^{-1} and T–O–T vibration at 882 cm^{-1} belong to one species, i.e., the partly skeletal Al cation bearing an OH group, and (iii) the T–O–T band at 901 cm^{-1} reflects perturbation of the framework as a result of the presence of extraframework AlO_x complex counterions coordinated at the cationic site.
3. The MPV activity (with high *cis*-selectivity) has been found to correlate with the intensity of the band of the T–O–T vibration mode at 901 cm^{-1}, and not with either the total concentration of Al–Lewis sites or the intensity of the band of the OH groups at 3780 cm^{-1}. Thus, the MPV activity is attributed to the extraframework AlO_x counter cations inside the pores of the cationic sites of beta zeolites, and not to partly framework Al atoms. As Na^+, and Cs^+ ion exchange does not remove this activity, it is suggested that the charged AlO_x species exhibits a complex structure.
4. This conclusion on the structure of active site for MPV reduction is supported by the observation that in severely steamed beta zeolites containing surface layers enriched by aluminium, i.e., by extraframework AlO_x species, the Lewis sites possessed MPV activity but lost their *cis*-stereoselectivity.
5. The highly active extraframework AlO_x counterions exhibit Lewis acidity with very high acid strength. Due to such high acidity, their activity is also very high, reaching TOF values of 5150 h^{-1} per AlO_x–Lewis site. The high acidic strength and high activity of these sites means, however, that they are easily poisoned by trace concentrations of water adsorbed on the zeolite.

ACKNOWLEDGEMENTS

The authors thank Dr. B. Knob for chemical analysis by XRF spectroscopy. The work was supported the Grant Agency of the Academy of Sciences of the Czech Republic under project S4040015. Additional financial support by Unipetrol, Inc. is gratefully acknowledged.

REFERENCES

1. Reddy, K. S. N., Rao, B. S., and Shiralkar, V. P., *Appl. Catal. A* **95**, 53 (1993).
2. Tsai, T. C., Ay, C. L., and Wang, I., *Appl. Catal.* **77**, 199 (1991).
3. Boretto, L., Camblor, M. A., Corma, A., and Perez-Pariente, J., *Appl. Catal. A* **82**, 37 (1991).
4. Hoefnagel, A. J., and van Bekkum, H., *Appl. Catal. A* **97**, 87 (1993).
5. Creyghton, E. J., Ganeshie, S. D., Downing, R. S., and van Bekkum, H., *J. Mol. Catal. A* **115**, 457 (1997).
6. Kunkeler, P. J., Zuurgeed, B. J., van der Waal, J. C., van Bokhoven, J. A., Koningsberger, D. C., and van Bekkum, H., *J. Catal.* **180**, 234 (1998).
7. Bourgeat-Lami, E., Massiani, P., Di Renzo, F., Espiau, P., and Fajula, F., *Appl. Catal.* **72**, 139 (1991).
8. Kiricsi, I., Flego, C., Pazzuconi, G., Parker, W. O., Jr., Millini, R., Perego, C., and Bellussi, G., *J. Phys. Chem.* **98**, 4627 (1994).
9. Jia, C., Massiani, P., and Barthomeuf, D., *J. Chem. Soc. Faraday Trans.* **89**, 3659 (1993).
10. Vimont, A., Thibault-Starzyk, F., and Lavalley, J. C., *J. Phys. Chem. B* **104**, 286 (2000).
11. Lohse, U., Altrichter, B., Donath, R., Fricke, R., Jancke, K., Parlitz, K., and Schreir, E., *J. Chem . Soc. Faraday Trans.* **92**, 159 (1996).
12. Bortnovsky, O., Sobalík, Z., and Wichterlová, B., *Microporous Mesoporous Mater.* **46**, 265 (2001).
13. Dědeček, J., Kaucký, D., and Wichterlová, B., *Chem. Commun.* 970 (2001).
14. Eapen, M. J., Reddy, K. S. N., and Shiralkar, V. P., *Zeolites* **14**, 295 (1994).
15. Camblor, M. A., Corma, A., Mifsud, A., Pérez-Pariente, J., and Valencia, S., *Stud. Surf. Sci. Catal.* **105**, 341 (1997).
16. van der Waal, J. C., Rigutto, M. S., and van Bekkum, H., *Chem. Commun.* 1241 (1994).
17. Wichterlová, B., Tvarůžková, Z., Sobalík, Z., and Sarv, P., *Microporous Mesoporous Mater.* **24**, 223 (1998).
18. Flanigen, E. M., *in* "Zeolite Chemistry and Catalysis," ACS Monograph, Vol. 171, p. 80. Am. Chem. Soc., Washington, DC, 1976.
19. Maache, M., Janin, A., Lavalley, J. C., Joly, J. F., and Benazzi, E., *Zeolites* **13**, 419 (1993).
20. Band, I. M., Kharitonov, Yu. I., and Trzhaskovskaja, M. B., *Atom. Data Nucl. Data Tables* **23**, 443 (1979).
21. Collington, F., Jacobs, P. A., Grobet, P., and Poncelet, G., *J. Phys. Chem.* **B105**, 6812 (2001).
22. Yang, C., and Xu, Q. H., *J. Chem. Soc. Faraday Trans.* **93**, 1675 (1997).
23. Sárkány, J., and Sachtler, W. M. H., *Zeolites* **14**, 7 (1994).
24. Sobalík, Z., Tvarůžková, Z., and Wichterlová, B., *J. Phys. Chem. B* **102**, 1077 (1998).
25. Sobalík, Z., Šponer, J. E., and Wichterlová, B., *Stud. Surf. Sci. Catal.* **130B**, 1463 (2000).
26. Zecchina, A., Bordiga, S., Spoto, G., Marchese, L., Petrini, G., Leofanti, G., and Padovan, M., *J. Phys. Chem.* **96**, 11979 (1993).
27. van Bokhoven, J. A., Koningsberger, D. C., Kunkeler, P., van Bekkum, H., and Kentgens, A. P. M., *J. Am. Chem. Soc.* **122**, 12842 (2000).
28. Wichterlová, B., Nováková, J., Kubelková, L., and Jírů, P., *in* "Proc. Vth Int. Symp. on Zeolites" (L. V. C. Rees, Ed.), p. 373. Leyden, London, 1980.
29. Kuehl, G. H., and Timken, H. K. C., *Microporous Mesoporous Mater.* **35–36**, 521 (2000).