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Probing the Incorporation of Ti(IV) into the BEA Zeolite Framework by XRD, FTIR, NMR, and DR UV–jp810722bis

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The method (Dzwigaj, S., et al. *Chem. Commun.* **1998**, 87) proposed earlier to incorporate V(V) ions into the BEA zeolite framework at the solid–liquid interface from V precursors in aqueous solution has been successfully extended to the solid–gas interface and titanium, with TiCl₄ vapor as the precursor. The use of TiCl₄ vapor has the advantage to restrict the speciation of titanium to this single species and to lead to a significant amount of Ti (~5 Ti wt %) determined by chemical analysis. The incorporation of Ti into the SiBEA zeolite framework is evidenced by XRD. The reaction of TiCl₄ vapor with H-bonded and terminal SiO–H groups of vacant T-atom sites is monitored by FTIR, ²⁹Si MAS NMR, ¹H–²⁹Si CP MAS NMR and ¹H MAS NMR. The presence of tetrahedral Ti(IV) as the main titanium species is evidenced by diffuse reflectance UV–vis. A possible pathway for the formation of framework tetrahedral Ti(IV) in TiSiBEA is proposed.

Introduction

Since its hydrothermal synthesis by Taramasso et al.,¹ TS-1 has been much investigated^{1–10} and found to be an effective catalyst for the selective oxidation of a large family of organic compounds under mild conditions by hydrogen peroxide.^{2–6} The use of TS-1 is interesting because it is active in several reactions, including epoxidation, ammoxidation, and hydroxylation, whereas aqueous hydrogen peroxide can be used as a green oxidant due to the fact that its byproduct is water. The success of TS-1 as catalyst has prompted many investigations on Ti-containing microporous and mesoporous materials prepared by either hydrothermal synthesis^{11–13} or postsynthesis methods.^{14–18} Because the use of TS-1 is restricted to oxidation of relatively small organic molecules, large-pore TiBEA was synthesized to avoid diffusion limitations for the oxidation of bulkier substrates.^{19,20} TiBEA appears to be more active than TS-1 for the oxidation of cyclic and long, linear alkenes, as well as cyclic and branched alkanes.^{19–21}

Because tetrahedral Ti atoms at framework sites are considered to be catalytically active in selective oxidation,^{17,22,23} the incorporation of Ti into the zeolite framework appears to be the key objective. Because direct synthesis generally leads to a rather low content (≤2 wt %) of transition metal introduced by

isomorphous substitution,^{24–26} other methods are thus necessary, if higher contents are needed.

The goal of the present work is to extend the method proposed earlier for vanadium^{27–30} to the solid–gas interface and to titanium, with TiCl₄ vapor as the precursor. The use of TiCl₄ vapor has the advantage to restrict the speciation of titanium to this single species and to lead to a significant amount of Ti incorporated. This incorporation is evidenced by chemical analysis, XRD, FTIR, ²⁹Si cross-polarization (CP) magic angle spinning (MAS) NMR, ¹H–²⁹Si CP MAS NMR, ¹H MAS NMR, and diffuse reflectance UV–visible (DR UV–vis).

Experimental Section

Materials. A tetraethylammonium BEA (TEABEA) zeolite (RIPP, China) was separated into two fractions. The first one was calcined (air, 15 h, 823 K) to obtain an organic-free AlBEA (Si/Al = 11), which was used as reference. The second fraction was treated in a 13 mol L^{−1} HNO₃ solution (4 h, 353 K) to obtain a dealuminated organic-free BEA, as described earlier.^{27–34} The resulting SiBEA (Si/Al > 1300) with vacant T-atom sites was recovered by centrifugation, washed with distilled water, and dried overnight at 353 K in air.

To introduce Ti(IV) ions in vacant T-atom sites (*T* = Al, Si), 2 g of SiBEA was treated in a fixed-bed reactor at 423 K for 3 days in flowing oxygen. The temperature was increased to 573 K, and the sample was subjected for 22.5 h to a nitrogen flow (100 cm³ min^{−1}) through a saturator containing liquid TiCl₄ (Aldrich, purity 99.9%) at 266 K, as described earlier for the preparation of mesoporous TiSiMCM-41.³⁵ The TiCl₄ vapor pressure in the saturator was 200 Pa, and the volume-to-volume (v/v) ratio of TiCl₄ and N₂ was equal 0.2%. The solid was treated under TiCl₄-containing nitrogen flow at 573 K for 2 h; cooled to room temperature; and exposed to moist air for 12 h; dried

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in air at 353 K for 12 h; and finally, calcined in flowing dry air at 723 K for 4 h.

Techniques. Chemical analysis of titanium was performed by inductively coupled plasma spectrometry at the Service Central d'Analyse, CNRS, Vernaison.

Powder X-ray diffractograms were recorded at room temperature and ambient atmosphere on a Siemens D5000 using Cu K α radiation ($\lambda = 154.05$ pm).

Transmission FT-IR spectra of self-supported wafers were recorded at room temperature on a Perkin-Elmer Spectrum One spectrometer with a resolution of 2 cm $^{-1}$ after calcination at 773 K for 3 h in flowing dry air and then outgassing to 10 $^{-3}$ Pa at 573 K. Dehydrated wafers were contacted with gaseous pyridine via a separate cell containing liquid pyridine. Physisorbed pyridine was outgassed (10 $^{-3}$ Pa) for 2 h at 423, 473, 523, and 573 K.

^{29}Si NMR spectra of as-prepared samples, transferred at ambient atmosphere into 7 mm zirconia rotors, were recorded with a Bruker Avance spectrometer at 79.5 MHz, some in CP mode (^{29}Si CP-MAS NMR). Chemical shifts of silicon were measured by reference to tetramethylsilane (TMS). ^{29}Si MAS NMR spectra were obtained with 4 kHz spinning speed, 2.5 ms excitation pulse, and 10 s recycle delay. Polydimethylsilane was used for setting the Hartmann–Hahn condition. The proton $\pi/2$ pulse duration, the contact time, and recycle delay were 6.8 ms, 5 ms, and 5 s, respectively.

^1H MAS NMR spectra were recorded at 400 MHz with a 90° pulse duration of 3 ms 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 free induction decay.

DR UV–vis spectra were recorded at room temperature and ambient atmosphere on a Cary 5E spectrometer equipped with a double integrator with BaSO $_4$ as reference.

Results and Discussion

Evidence for the Incorporation of Titanium into the Framework of Dealuminated BEA. *Chemical Analysis.* The sample prepared by the postsynthesis method, hereafter referred to as TiSiBEA, is white and contains 5.3 Ti wt %.

X-ray Diffraction. As reported earlier,^{27,28,36} dealumination of zeolite BEA by nitric acid does not affect its crystallinity, as evidenced by similar X-ray diffractograms of AlBEA and SiBEA samples (Figure 1). The narrow diffraction peak, near 22.6°, can be used to detect lattice contraction/expansion (Figure 1).³⁷ The decrease of d_{302} spacing related to this peak from 3.942 (AlBEA; $2\theta = 22.55^\circ$) to 3.912 Å (SiBEA; $2\theta = 22.71^\circ$) upon dealumination indicates contraction of the matrix. The significant increase of d_{302} spacing to 3.939 Å (TiSiBEA; $2\theta = 22.64^\circ$) upon incorporation of Ti(IV) into SiBEA indicates expansion of the matrix due to the longer Ti–O bond distance (1.79 Å, for tetracoordinated Ti species),³⁷ as compared to that of Si–O (typically 1.60–1.65 Å in zeolites).³⁸

FTIR Spectroscopy. The FT-IR spectrum of AlBEA exhibits five bands at 3781, 3740, 3665, 3609 and 3520 cm $^{-1}$ (Figure 2) assigned to the OH stretching modes of AlO–H groups (3781 and 3665 cm $^{-1}$), Si–O(H)–Al groups (3609 cm $^{-1}$), isolated SiO–H groups (3740 cm $^{-1}$) and H-bonded SiO–H groups (3520 cm $^{-1}$).^{27–31,39} After treatment of AlBEA by HNO $_3$ solution, the bands at 3781, 3665, and 3609 cm $^{-1}$ are no longer observed, evidencing the removal of Al atoms from the structure (Scheme 1, reaction 1) leading to a fully dealuminated SiBEA. The appearance of narrow bands at 3736 and 3710 cm $^{-1}$ related to isolated SiO–H groups and of a broadband at 3520 cm $^{-1}$ due

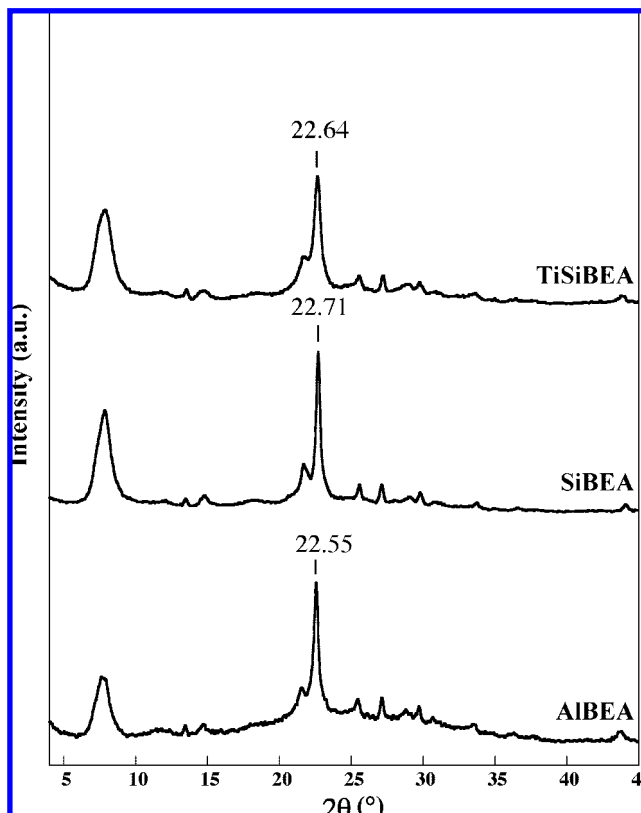


Figure 1. X-ray diffractograms of AlBEA, SiBEA, and TiSiBEA as prepared recorded at room temperature at ambient atmosphere.

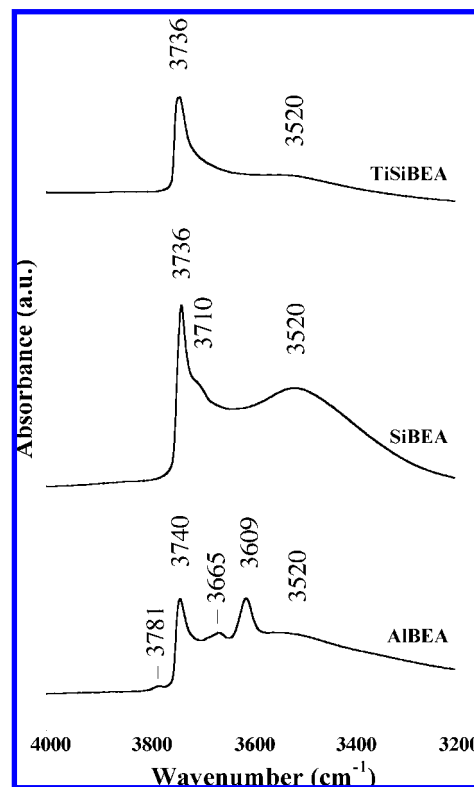
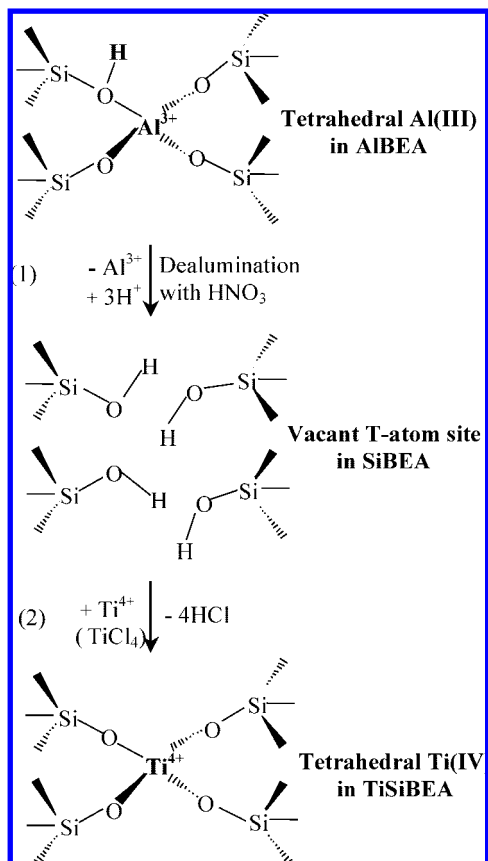


Figure 2. FT-IR spectra of AlBEA, SiBEA, and TiSiBEA calcined at 773 K for 3 h in flowing air, followed by outgassing at 573 K (10 $^{-3}$ Pa) for 2 h recorded at room temperature.

to H-bonded SiO–H groups in SiBEA reveals the presence of vacant T-atom sites associated with silanol groups, as reported earlier.⁴⁰ The incorporation of Ti into SiBEA induces a reduction

SCHEME 1: Possible Pathway of Formation of Tetrahedral Ti(IV) in TiSiBEA Zeolite


of intensity of these bands, in particular, the one at 3520 cm^{-1} (Figure 2), suggesting that SiO–H groups have reacted with TiCl_4 vapor.

^{29}Si MAS NMR and ^1H – ^{29}Si CP MAS NMR. The ^{29}Si MAS NMR spectrum of AlBEA (Figure 3a) shows three resonances at -103.7 , -111.0 , and -114.7 ppm. The peaks at -111.0 and -114.7 ppm are due to framework Si atoms in a $\text{Si}(\text{OSi})_4$ environment, located at different crystallographic sites, in line with an earlier report.⁴¹

The broad peak at -103.7 ppm is assigned to Si atoms in a $\text{Si}(\text{OAl})(\text{OSi})_3$ environment, in line with earlier work.³⁶ The small contribution from Si atoms associated with OH groups in a $\text{Si}(\text{OH})(\text{OSi})_3$ environment is revealed by a small increase in intensity of the peak at -103.2 ppm when CP is applied (Figure 3b), a technique which preferentially enhances the signal of ^{29}Si nuclei close to protons, as in the case of the $\text{Si}(\text{OH})(\text{OSi})_3$ site. In addition, in the CP spectrum of AlBEA, a small proportion of Si atoms in a $\text{Si}(\text{OH})_2(\text{OSi})_2$ environment is also evidenced by the weak peak at -92.5 ppm (Figure 3b).

In the spectrum of SiBEA, the peak at -101.7 ppm (Figure 3a) can correspond only to Si atoms in the $\text{Si}(\text{OH})(\text{OSi})_3$ environment because of the removal of all Al atoms from BEA zeolite upon nitric acid treatment ($\text{Si}/\text{Al} > 1300$). This is confirmed by the strong increase in the intensity of the peak at -101.8 ppm in the CP spectrum (Figure 3b). Furthermore, a small proportion of Si atoms in a $\text{Si}(\text{OH})_2(\text{OSi})_2$ environment is also evidenced by the weak peak at -92.3 ppm (Figure 3b). The peak at -111.3 with a shoulder at 114.0 ppm appears to be due to framework Si atoms in a $\text{Si}(\text{OSi})_4$ environment, located at different crystallographic sites.

After incorporation of Ti ions in the SiBEA, the intensity of the peak at around -101 ppm is significantly reduced (Figure

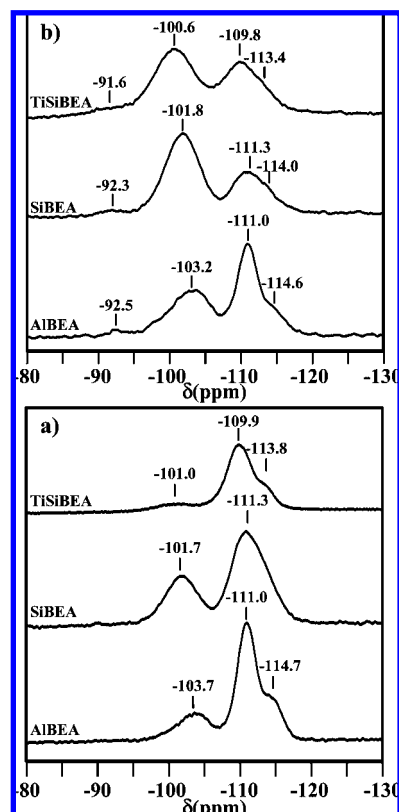


Figure 3. (a) ^{29}Si MAS NMR spectra of AlBEA, SiBEA, and TiSiBEA as prepared recorded at room temperature in 7 mm (external diameter) zirconia rotor. (b) ^1H – ^{29}Si CP MAS NMR spectra of AlBEA, SiBEA, and TiSiBEA as prepared recorded at room temperature in 7 mm (external diameter) zirconia rotor.

3a), confirming the reaction between TiCl_4 vapor and silanol groups. It is important to note that up to four H-bonded SiO–H groups may be consumed for each Ti ion incorporated into the vacant T-atom site (Scheme 1, reaction 2). This is confirmed by the CP spectrum of TiSiBEA (Figure 3b), which shows that the peak at -100.6 ppm corresponding to Si atoms in the $\text{Si}(\text{OH})(\text{OSi})_3$ environment is significantly smaller than that observed at -101.8 ppm for SiBEA.

^1H MAS NMR. In the ^1H MAS NMR spectrum of AlBEA zeolite (Figure 4), two main peaks are observed at 1.32 and 5.92 ppm due to isolated silanol protons and protons of bridged Si–O(H)–Al Brønsted groups or H-bonded silanol groups at defect sites, respectively, in line with earlier data.^{42–46}

The ^1H MAS NMR spectrum of SiBEA ($\text{Si}/\text{Al} > 1300$) (Figure 4) exhibits a very intense peak at about 5.27 ppm due to protons of H-bonded SiO–H groups formed by removal of Al atoms upon nitric acid treatment of AlBEA (Scheme 1, reaction 1) and a peak at 1.32 ppm (Figure 4) due to protons of isolated or terminal SiO–H groups. These peaks, more intense than the corresponding ones of AlBEA, confirm that they originate from the removal of Al atoms and formation of vacant T-atom sites associated with SiO–H groups. In addition, the small peak at 3.25 ppm is probably due to protons of H-bonded SiO–H groups located in a second type of crystallographic site. This chemical shift is comparable with those observed for silicalite and silica gel.^{47,48} In silicalite, two peaks were observed: at 1.8 ppm due to terminal SiO–H groups and at 3.2 ppm due to H-bonded SiO–H groups.

The disappearance of the peaks at 5.27, 3.25, and 1.32 ppm upon incorporation of Ti atoms in SiBEA (Figure 4) evidences the reaction of TiCl_4 vapor with H-bonded and terminal SiO–H

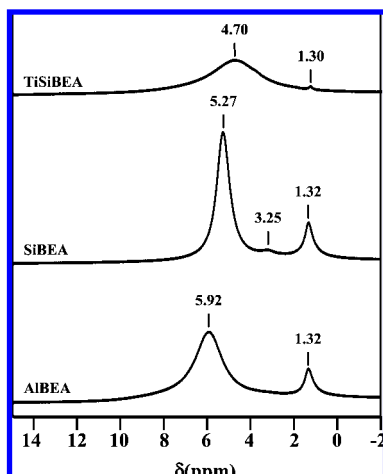


Figure 4. ^1H MAS NMR spectra of AlBEA, SiBEA, and TiSiBEA as prepared recorded at room temperature in 4 mm (external diameter) zirconia rotor.

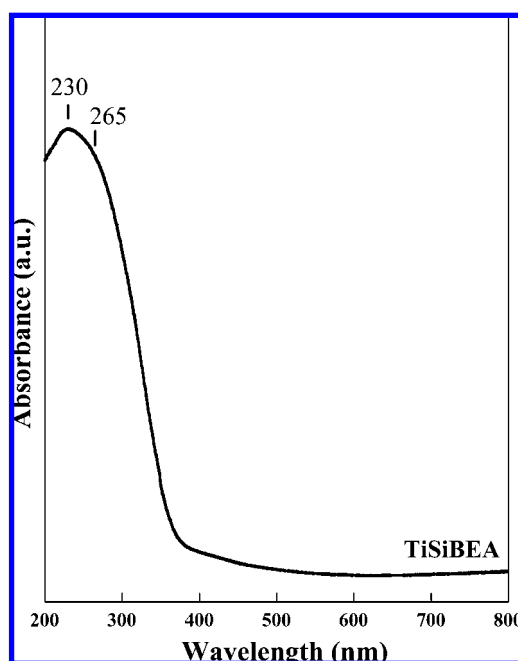


Figure 5. DR UV-vis spectrum of TiSiBEA as prepared recorded at ambient atmosphere.

groups (Scheme 1, reaction 2). The spectrum of TiSiBEA exhibits a broad peak at 4.70 ppm assigned to H-bonded SiO-H groups still present in TiSiBEA and not consumed by reaction 2 (Scheme 1). Those groups give the band at 3520 cm^{-1} (Figure 2) and the peak at -100.6 ppm (Figure 4). The very small peak at 1.30 ppm (Figure 4) is probably due to protons of isolated or terminal SiO-H present in TiSiBEA in very low content, in line with earlier data.^{42–46}

Diffuse Reflectance UV-vis. The DR UV-vis spectrum of TiSiBEA (Figure 5) essentially exhibits an intense and asymmetric band at around 230 nm, which can be assigned to an oxygen-tetrahedral Ti(IV) ligand-to-metal charge transfer transition, as reported earlier,^{49–51} confirming the incorporation of Ti atoms into the SiBEA zeolite framework. The shoulder at about 265 nm could be attributed to octahedral Ti(IV) in framework and extra-framework position, originating from the high titanium content (5.3 Ti wt %). A similar shoulder has been observed by Carati et al.⁵² for TiBEA and Lin et al.⁵³ and Marchese et al.⁵¹ for TiMCM-41 materials.

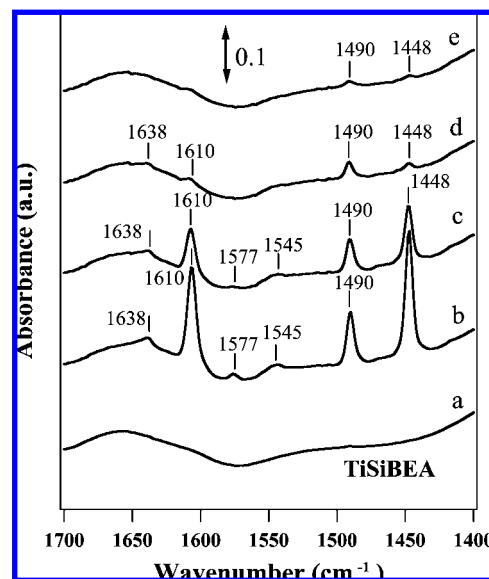


Figure 6. FTIR spectra of (a) TiSiBEA after calcination at 773 K for 3 h in flowing air followed by outgassing at 573 K (10^{-3} Pa) for 2 h, (b) adsorption of pyridine at room temperature followed by desorption for 2 h at 423 K, (c) 473 K, (d) 523 K, and (e) 573 K recorded at room temperature.

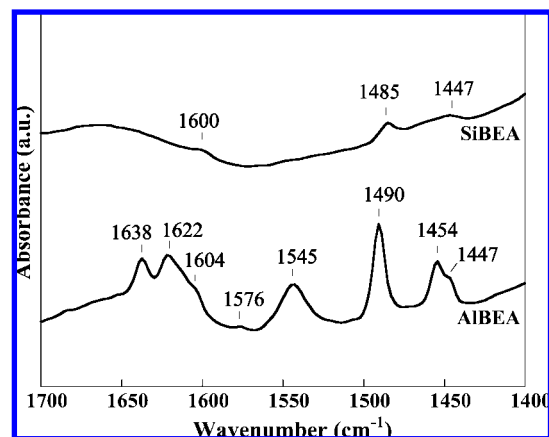


Figure 7. FTIR spectra of AlBEA and SiBEA after calcination at 773 K for 3 h in flowing air followed by outgassing at 573 K (10^{-3} Pa) for 2 h and adsorption of pyridine at room temperature and then desorption at 423 K for 2 h recorded at room temperature.

Acidity of TiSiBEA Zeolite. To check the acidity of TiSiBEA, pyridine was adsorbed at room temperature on the sample calcined at 773 K for 3 h in flowing air and then outgassed at 573 K (10^{-3} Pa) for 2 h. The FTIR spectra recorded after desorption of pyridine at different temperatures are given in Figure 6, spectra b–e. A small band typical of pyridinium cations is observed at 1545 cm^{-1} for dehydrated TiSiBEA, indicating the presence of a small amount of Brønsted acidic sites. The bands at 1638, 1610, 1577, 1490, and 1448 cm^{-1} (Figure 6, spectrum b) correspond to pyridine interacting with Lewis acidic sites or pyridine physisorbed, in line with earlier data.^{54–56} The intensities of these bands rapidly decrease with increasing desorption temperature (Figure 6, spectra c–e).

The number of Brønsted acidic sites in TiSiBEA is much lower than in the initial AlBEA zeolite (compare spectrum b in Figure 6 with that of AlBEA in Figure 7, both recorded after adsorption of pyridine at room temperature, followed by desorption at 423 K). The band of pyridinium cations at 1545 cm^{-1} less intense for TiSiBEA than for AlBEA zeolite indicates a lower number of Brønsted acidic sites in the former. It suggests

that in TiSiBEA, the Ti atoms are present mainly as tetrahedral Ti(IV) with $\text{Ti}(\text{OSi})_4$ structure (Scheme 1, reaction 2).

The absence of the band due to pyridinium cations at 1545 cm^{-1} for SiBEA (Figure 7) suggests that Brønsted acidic sites are not present and indicates that upon treatment of AlBEA with nitric acid, all Al atoms are removed. For SiBEA, only the bands at 1600 , 1485 , and 1447 cm^{-1} are observed (Figure 7) due to pyridine's interacting with weak Lewis acidic sites or pyridine physisorbed, in line with earlier reports.^{54–56}

Conclusions

The goal of the present work was to extend the method proposed earlier for vanadium to the solid–gas interface and to titanium, with TiCl_4 vapor as the precursor. The use of TiCl_4 vapor has the advantage to restrict the speciation of titanium to this single species and to lead to a significant amount of Ti incorporated. Chemical analysis shows that a significant amount of Ti can be incorporated into the BEA zeolite framework (5.3 Ti wt %).

The specific reaction between TiCl_4 vapor and SiO-H groups of vacant T-atom sites created by dealumination of BEA zeolite allows incorporation of Ti(IV) ions into the BEA zeolite framework, as shown by XRD. The reaction of TiCl_4 vapor with H-bonded and terminal SiO-H groups of vacant T-atom sites is evidenced by FTIR, ^{29}Si MAS NMR, ^1H – ^{29}Si CP MAS NMR, and ^1H MAS NMR. The presence of framework tetrahedral Ti(IV) as the main titanium species is shown by diffuse reflectance UV–vis. Some amount of octahedral Ti(IV) is also evidenced, which can be present in framework and extra-framework position, originating from the high titanium content (5.3 Ti wt %).

As shown by pyridine adsorption, the number of Brønsted acidic sites in TiSiBEA is much lower than in the initial AlBEA zeolite. It suggests that, in TiSiBEA, the Ti atoms are present mainly as tetrahedral Ti(IV) with $\text{Ti}(\text{OSi})_4$ structure (Scheme 1).

Further studies of TiSiBEA zeolites by XPS, XANES, EXAFS, and EPR are underway to better characterize the nature of titanium species as a function of Ti content. The catalytic activity of TiSiBEA zeolites will be investigated in the selective oxidation of alkenes by hydrogen peroxide.

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