Catalysis Today 142 (2009) 185–191

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Remarkable effect of the preparation method on the state of vanadium in BEA zeolite: Lattice and extra-lattice V species

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ARTICLE INFO

Article history:
Available online 18 November 2008

Keywords:
Vanadium
BEA zeolite
Adsorption
CO
NO
XRD
FTIR
DR UV–vis
EPR

ABSTRACT

The state of vanadium in two BEA zeolites is investigated by XRD, FTIR, DR UV–vis and EPR. One of the samples, VAlBEA (1.3 wt.% of V), is prepared by conventional ion exchange and the other, VSiBEA (2.0 wt.% of V), by a two-step postsynthesis method involving dealuminated BEA zeolite. No structural changes are observed after incorporation of vanadium into AlBEA zeolite by ion-exchange method. In contrast, the impregnation of SiBEA with V(IV) ($VOSO_4$) precursor leads to an increase of unit cell parameters of the BEA, to the consumption of silanol groups in vacant T-sites and incorporation of V in the framework of BEA zeolite as well dispersed tetrahedral V(V) species. NO and CO used as IR probe molecules, DR UV–vis and EPR allow to establish the oxidation state of vanadium in as prepared, oxidized, activated and reduced VAlBEA and VSiBEA zeolites. The IR spectra of oxidized, activated and reduced VAlBEA samples are very similar. It suggests that V introduced by ion exchange in extra-lattice position is stabilized on all samples in similar oxidation state. CO adsorption evidence the presence of vanadium in IV oxidation state via IR bands at about 2200 and 2180 cm^{-1} assigned to V(IV)–CO monocarbonyl and V(IV)–$(CO)_2$ dicarbonyl species. In contrast, the oxidation state of V in VSiBEA changes strongly in function of calcinations in oxygen, outgassing at high temperature (773 K) and reducing with hydrogen at high temperature (873 K). This shows that lattice tetrahedral V species change easily oxidation state and this property allows them to be good candidate as active site of selective redox reactions.

1. Introduction

The crystalline microporous zeolites containing transition metal ions are an important class of catalysts with remarkable catalytic properties in the selective oxidation of various organic molecules [1]. In the recent years, particular attention has been paid to V-containing zeolites, because these catalysts opened new possibilities for many applications, not only in catalysis [1–5] but also for various photochemical processes [6]. Their catalytic performance, however, depends on many factors and the most significant are the nature and local environment of V ions.

Earlier, we have shown [7] that catalytically active vanadium species may be obtained in SiBEA zeolite by impregnation with aqueous NH_4VO_3 solution, used as V(V) precursor. Vanadium was incorporated as lattice tetrahedral V(V) species. A similar postsynthesis method has been used [8] to incorporate vanadium in dealuminated BEA from an aqueous $VOSO_4$ solution, used as V(IV) precursor. However, despite the combined deployment of different techniques, it was difficult to obtain precise information concerning oxidation state and location of vanadium ions in BEA zeolite after different pre-treatments.

In this paper, we report on the effect of the preparation method on the state of vanadium ions in BEA zeolite and provide data on (1) the nature and environment of the V species formed, and (2) the reactivity of V(IV) ($VOSO_4$) precursor with vacant T-sites of SiBEA zeolite in anaerobic conditions. The combined deployment of XRD, FT-IR, DR UV–vis and EPR used for characterization of activated (outgassed at 773 K), oxidized (calcined in flowing oxygen at 773 K) and reduced (treated with hydrogen at 873 K) V-containing BEA zeolite allows to distinguish different kinds of V(V), V(IV) or V(III) species present in lattice and extra-lattice position.

2. Experimental

2.1. Materials

A tetraethylammonium BEA (TEABEA) zeolite was provided by RIPP (China). A portion of it was calcined (15 h, 823 K) to obtain

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doi:10.1016/j.cattod.2008.09.031

organic-free AlBEA (Si/Al = 12.5). A vanadium-containing sample was prepared by conventional ion exchange using a 1.1×10^{-2} mol l^{-1} aqueous solution of $VOSO_4$. The exchange procedure was repeated two times at room temperature (pH 3.2). The solid was then filtered and washed with distilled water. This sample will be hereafter refereed to as VAlBEA. According to chemical analysis, it contained 1.3 wt.% of vanadium.

Another fresh portion of TEABEA was treated, as described earlier [9–11], with a 13 mol l^{-1} HNO_3 solution (4 h, 353 K) to obtain dealuminated organic-free BEA zeolite. The resulting SiBEA zeolite (Si/Al > 1300) with vacant T-sites was recovered by centrifugation, washed with distilled water and dried overnight at 353 K. Then, in order to incorporate vanadium ions into vacant T-sites and to avoid the oxidation of V(IV), SiBEA was impregnated in an Ar atmosphere by a 3.2×10^{-2} mol l^{-1} aqueous solution of $VOSO_4$. First, 2 g of SiBEA were stirred for 24 h at 298 K in excess solvent using 200 ml of the vanadium solution. Then the suspension (pH 2.4) was stirred for 2 h in flowing Ar at 353 K until complete evaporation of water. The solid was then dried at 353 K overnight in flowing Ar. This sample will be hereafter refereed to as VSiBEA. According to chemical analysis it contained 2.0 wt.% vanadium.

VAlBEA and VSiBEA were outgassed at 773 for 2 h (or at 723 K for 1 h) to obtain activated VAlBEA and VSiBEA, calcined at 773 K for 2 h (or 1 h) under flowing oxygen, followed outgassing for 1 h at the same temperature to obtain oxidized VAlBEA and VSiBEA and treated with hydrogen at 873 K for 2 h (or 1 h) followed by 1 h evacuation at the same temperature to obtain reduced VAlBEA and VSiBEA.

2.2. Techniques

Powder X-ray diffractograms (XRD) were recorded on a Siemens D5000 apparatus using Cu Kα radiation (λ = 154.05 pm).

Chemical analysis of the samples was performed with inductively coupled plasma atom emission spectroscopy at the CNRS Center of Chemical Analysis (Vernaison, France).

The FTIR spectra were recorded with Bruker Vector 22 spectrometer (at resolution of 2 cm^{-1}, accumulating 32 scans), for registering the background spectra and on Nicolet Avatar 360 spectrometer (at resolution of 2 cm^{-1}, accumulating 128 scans), for registering the spectra of adsorbed probe molecules. For the background spectra, the same amounts of AlBEA, SiBEA, VAlBEA and VSiBEA (20 mg) were pressed as self-supported wafers. After introduction of the wafers into a cell with CaF_2 windows, they were (i) outgassed at 773 K for 2 h (10^{-3} Pa) to obtain activated samples, (ii) calcined at flowing oxygen (30 ml/min, 2 h) at 773 K and then outgassed at 573 K for 1 h (10^{-3} Pa) to obtain oxidized samples. The FTIR spectra were recorded at room temperature after each step of samples treatment.

For the adsorption experiments self-supporting pellets (ca. 10 mg cm^{-2}) were prepared from the sample powders and treated directly in a purpose-made IR cell allowing measurements at ambient and low temperatures. The cell was connected to a vacuum-adsorption apparatus allowing a residual pressure below 10^{-3} Pa. Prior to adsorption of CO or NO, the VAlBEA and VSiBEA wafers were (i) activated by outgassing at 723 K for 1 h or (ii) oxidized by treatment at 773 K for 1 h under flowing oxygen, followed by outgassing for 1 h at the same temperature or (iii) reduced with hydrogen at 873 K for 1 h followed by outgassing at the same temperature for 1 h.

Carbon monoxide (>99.997 purity) was supplied by Linde AG and nitrogen monoxide (>99.0 purity) by Messer Greisheim GmbH. Before adsorption, carbon monoxide was passed through a liquid nitrogen trap while NO was additionally purified by fraction distillation.

Diffuse reflectance UV–visible (DR UV–visible) spectra of as prepared, activated, oxidized and reduced VAlBEA and VSiBEA were recorded on a Cary 5E spectrometer equipped with an integrator and a double monochromator.

EPR spectra of as prepared, activated, oxidized and reduced VAlBEA and VSiBEA were recorded on a Bruker ESP 300 computerised spectrometer at 9.3 GHz (X band) using a 100 kHz field modulation and a 10 Gauss standard modulation width. The spectra were recorded at 298 and 77 K. Computer simulation of the spectra were performed using EPRsim32 program [12].

3. Results and discussion

3.1. XRD and FT-IR evidence for incorporation of vanadium into the framework of dealuminated SiBEA

3.1.1. X-ray diffraction analysis

The introduction of vanadium ions into AlBEA by conventional ion-exchange method does not lead to detectable changes in the BEA structure, as evidenced by the same d_{302} spacing value for AlBEA and VAlBEA (d_{302} = 3.942 Å). In contrast, the introduction of vanadium ions into SiBEA by postsynthesis method using $VOSO_4$ precursor leads to increase of the d_{302} spacing from 3.912 (SiBEA) to 3.941 Å (VSiBEA) indicating some expansion of the BEA structure and suggesting that vanadium is incorporated into the lattice as tetrahedral V species (results not shown), in line with our earlier work [7–11,13–17]. The similar d_{302} spacing value for as prepared, oxidized and activated VSiBEA (d_{302} = 3.941 Å) suggests that lattice tetrahedral V species are stable in BEA structure.

The absence of any diffraction lines of extra-lattice crystalline compounds in as prepared, activated, oxidized and reduced VAlBEA and VSiBEA indicates a good dispersion of vanadium species in all these samples. It is important to note that surface area 660 and 655 m^2 g^{-1} and micropore volume 0.25 and 0.24 cm^3 g^{-1} respectively of AlBEA and SiBEA have not changed after introduction of vanadium ions into both zeolites. This means that introducing of V species does not affect of porosity of both zeolites.

3.1.2. FT-IR spectroscopy

The FT-IR spectrum of oxidized AlBEA contains five IR bands in the OH range at 3781, 3740, 3660, 3610 and 3520 cm^{-1} (Fig. 1, spectrum a) due to the OH stretching modes of AlO–H groups at 3781 and 3660 cm^{-1}, Si–O(H)–Al groups at 3610 cm^{-1}, isolated SiO–H groups at 3740 cm^{-1} and H-bonded SiO–H groups at 3520 cm^{-1} [7–11,13].

The introduction of vanadium ions into AlBEA by conventional ion-exchange method does not lead to noticeable changes in the population of hydroxyl groups, as evidenced by the similar intensities of FT-IR bands of oxidized VAlBEA (Fig. 1, spectrum b). Moreover, outgassing VAlBEA sample at 773 K for 2 h results in a similar FT-IR spectrum as that of oxidized VAlBEA one. Note that no evidence of IR bands due VO–H groups is found in both oxidized and activated VAlBEA.

A treatment of AlBEA with aqueous HNO_3 solution involves the elimination of Al atoms from the framework, as evidenced by the disappearance of IR bands at 3781, 3665 and 3609 cm^{-1} attributed to AlO–H and Si–O(H)–Al groups, respectively (Fig. 1, spectrum c), in line with earlier investigations [7–11,13,18–20]. The appearance of narrow bands at 3736 and 3710 cm^{-1} related to isolated internal silanol groups and of a broad band at 3520 cm^{-1} due to H-bonded SiOH groups in SiBEA reveals the presence of vacant T-sites associated with silanol groups (Fig. 1), as shown earlier [7–11,13].

The impregnation of SiBEA with aqueous $VOSO_4$ solution induces a reduction of intensity of these bands, in particular this corresponding to H-bonded SiOH groups, as shown in Fig. 1

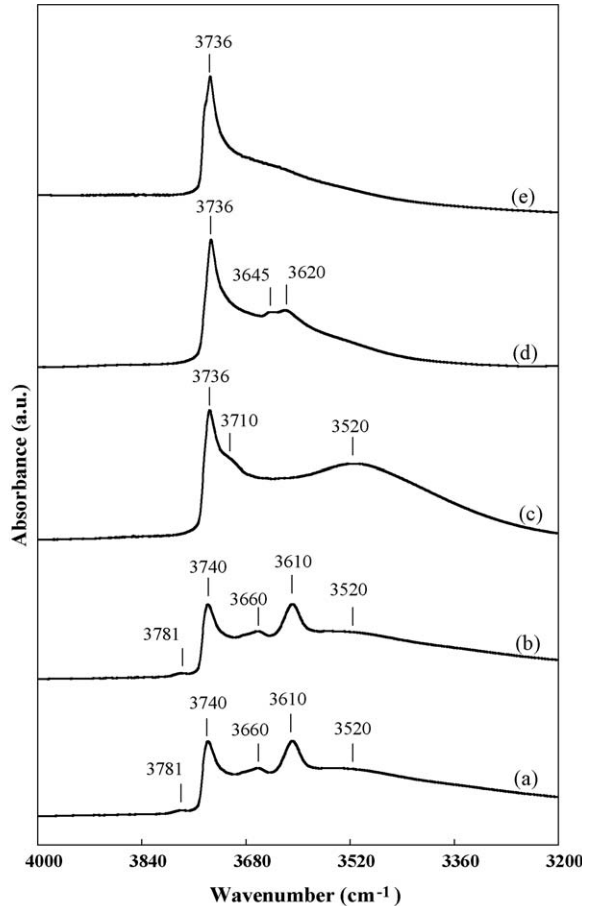

Fig. 1. FTIR spectra of (a) oxidized AlBEA, (b) oxidized VAlBEA, (c) oxidized SiBEA, (d) oxidized VSiBEA and (e) activated VSiBEA.

(spectrum d) for oxidized VSiBEA, suggesting that silanol groups are consumed in the reaction with vanadium precursor. Simultaneously, two FTIR bands at 3645 and 3620 cm^{-1} appear related to incorporation of vanadium into vacant T-sites and due to the hydroxyl vibrator of V(V)O–H groups, in line with our earlier work [13,21–23].

However, in the spectrum of activated VSiBEA these two bands are not observed (Fig. 1, spectrum e). This result indicates that outgassing of the VSiBEA at high temperature (773 K) leads to reduction of V(V) toward V(IV) species with transformation of V(V)O–H into V(IV) species according to the scheme:

$$V^{5+}\text{–OH} \rightarrow V^{4+} + {}^{\bullet}\text{OH} \qquad (1)$$

$$2{}^{\bullet}\text{OH} \rightarrow H_2O + 1/2O_2 \qquad (2)$$

3.2. Characterization of vanadium species in VAlBEA and VSiBEA zeolites

The vanadium species in VAlBEA and VSiBEA zeolites pretreated at different conditions has been characterized by FT-IR using CO and NO as probe molecules. The oxidized, activated and reduced VAlBEA and VSiBEA have been obtained from as prepared VAlBEA and VSiBEA by (i) calcination at 773 K for 1 h under oxygen, followed by outgassing at 773 K for 1 h, (ii) outgassing at 723 K for 1 h (10^{-3} Pa) and (iii) treatment with hydrogen at 873 K, for 1 h, followed by outgassing at the same temperature for 1 h, respectively.

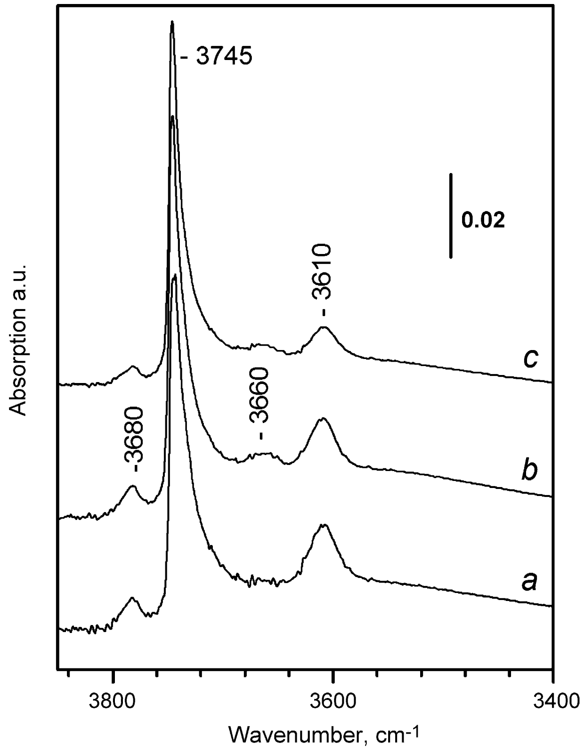

Fig. 2. FTIR spectra of (a) oxidized VAlBEA, (b) activated VAlBEA and (c) reduced VAlBEA.

3.2.1. FT-IR spectroscopy of adsorbed CO and NO on VAlBEA

The FT-IR spectrum of the oxidized VAlBEA contains five IR bands in the OH range at 3781, 3740, 3660, 3610 and 3520 cm^{-1} (Fig. 2, spectrum a) described above. Note that no evidence of VO–H species is found. The activated VAlBEA shows very similar spectra (Fig. 2, spectrum b). The spectrum of the reduced sample (Fig. 2, spectrum c) shows no substantial changes.

In order to obtain more information on the state of vanadium in VAlBEA zeolite, we have tested the samples by CO and NO as probe molecules.

Earlier, we have reported that NO appears to be a better probe for determination of the oxidation state of the supported vanadium, but CO (when adsorbed at low temperature) can give some complementary information on the coordination state of reduced vanadium sites [24]. A limitation of IR spectroscopy of molecular probes is that this techniques is blind to V(V) species (because of their coordinative saturation) and their existence can be indirectly monitored by V(V)O–H and eventually V(V)=O groups.

The spectrum of CO adsorbed at low temperature on the oxidized VAlBEA contains four intense bands at 2175, 2157, 2141 and 2135 cm^{-1} (Fig. 3a). A weak band at 2227 cm^{-1} is also discernible. The bands at 2141 and 2135 cm^{-1} are easily removed by evacuation even at 100 K (Fig. 3b and c) and are assigned to physically adsorbed CO. The next band to disappear upon outgassing is that at 2155 cm^{-1}. It is attributed to Si–OH–CO interaction and is connected with a blue shift of 90 cm^{-1} of the SiO–H stretching modes. The band at 2175 cm^{-1} is also due to OH–CO interaction but in this case the zeolite acidic hydroxyls are involved. This band is connected with a red shift of the 3610 cm^{-1} band by about 300 cm^{-1}. The band at 2127 cm^{-1} resists evacuation at 100 K and is assigned to Al^{3+}–CO species.

The disappearance of the strong carbonyl bands due to weakly adsorbed species allow to distinguish a series of low intensity

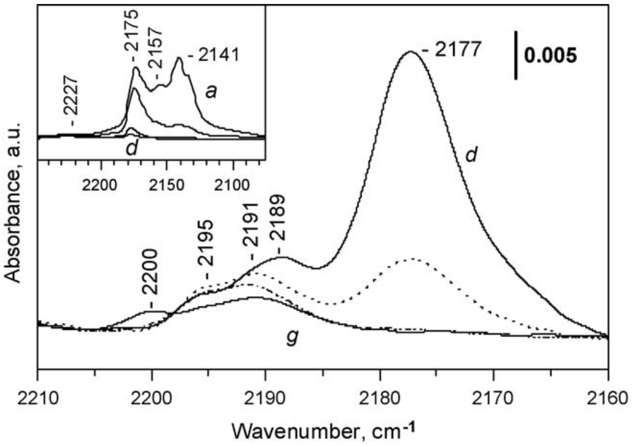

Fig. 3. FTIR spectra of CO adsorbed at 100 K on oxidized VAlBEA. Equilibrium CO pressure of 130 Pa (a) and development of the spectra during evacuation at 100 K for 1, 2 and 5 min (b–d) and at increasing temperatures (by ca. 65 K per spectrum) up to ambient temperature (e–h).

bands in the 2210–2180 cm^{-1} region: at 2200, 2195, 2191 and 2189 cm^{-1} (Fig. 3d–g). Since these bands were not recorded with the parent zeolite, they are assigned to different vanadium carbonyls. The band at 2200 cm^{-1} is the most stable towards evacuation and is registered only at very low coverages. This behavior indicates that the band characterized monocarbonyl species that are converted, at higher CO coverages, to dicarbonyls. Analysis of the spectra suggests that these dicarbonyl species are characterized by one IR band at 2195 cm^{-1}. Similar behavior has been reported for many cation-exchanged zeolites and the absence of split of the CO modes to symmetric and antisymmetric ones shows a weak interaction between the two CO ligands. Two other bands, at 2191 and 2189 cm^{-1} seem to characterize individual vanadium carbonyls.

Similar spectra were obtained with the activated VAlBEA sample (spectra not shown).

When CO is adsorbed on the reduced sample (spectra not shown) the band at 2189 cm^{-1} appeared with an enhanced intensity. In addition, a weak band at 2175 cm^{-1} is also registered at low coverages. Since it is more stable than the OH–CO band at the same frequency, the component is assigned to vanadium carbonyls. The low frequency indicates a more-reduced state of vanadium in this case.

It was suggested that NO should be used carefully in the characterization of reduced vanadium sites because of the ability of NO to participate in redox reaction [24]. NO forms with V(IV) and V(III) sites different dinitrosyls. However, no conclusions on the coordination state of vanadium can be made, since the dinitrosyls can be regarded as an adsorbed N_2O_2 molecule [28]. To suppress redox reactions with NO, it is adsorbed at low equilibrium pressure and the spectra registered immediately after adsorption.

The spectra of NO adsorbed on the oxidized and activated VAlBEA are similar (Fig. 4). A weak band at 1876 cm^{-1} is detected in both cases. This band resists evacuation at room temperature and therefore cannot be attributed to physically adsorbed NO. This band is assigned to vanadium mononitrosyl species. In addition, bands in the 1700–1600 cm^{-1} region are also produced and indicate the formation of surface nitrates. The appearance of nitrates indicates some redox processes. Therefore, one cannot conclude on the original state of vanadium in these two cases.

However, with the reduced VAlBEA no nitrates are produced. In this case, in addition to the 1876 cm^{-1} band, two more intense bands at 1785 and 1725 cm^{-1} are detected. These bands are assigned to the antisymmetric modes of two different dinitrosyl species [17,24]. The respective symmetric modes are of low intensity and are observed as shoulders of the 1876 cm^{-1} band. In particular, the band at 1785 cm^{-1} characterizes ν_{as} of $V^{4+}(NO)_2$ species (the symmetric modes appearing around 1900 cm^{-1}) while the band at 1725 cm^{-1} corresponds to ν_{as} of $V^{3+}(NO)_2$ species (symmetric modes round 1840 cm^{-1}) [17,24].

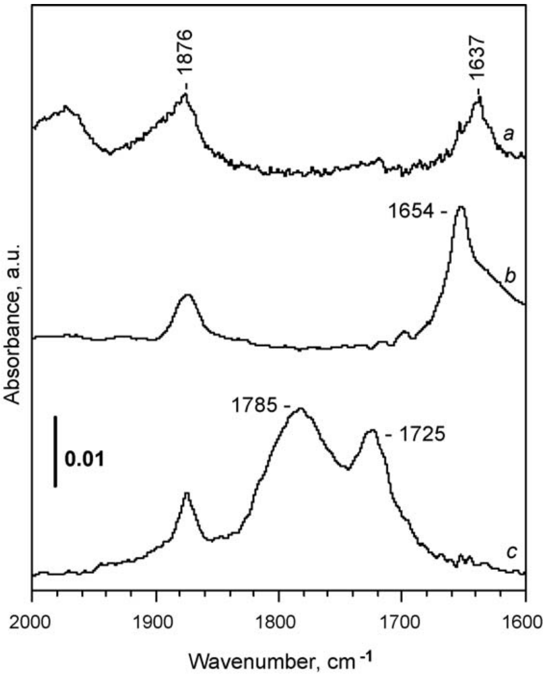

Fig. 4. FTIR spectra of NO (50 Pa equilibrium pressure) adsorbed at ambient temperature on (a) oxidized, (b) activated and (c) reduced VAlBEA.

3.2.2. FT-IR spectroscopy of adsorbed CO and NO on VSiBEA

As shown in Fig. 5 (spectrum a), in the spectrum of oxidized VSiBEA three IR bands at 3743, 3645 and 3617 cm^{-1} appear. The band at 3735 cm^{-1} is due to the hydroxyl vibrator of the isolated SiO–H groups. In contrast, the bands at 3645 and 3617 cm^{-1} are due the hydroxyl vibrators of V(V)O–H groups, as indicated above.

However, in the spectrum of activated VSiBEA sample these two bands are not observed (Fig. 5, spectrum b). This result indicate that outgassing of the VSiBEA sample at 723 K lead to reduction of V(V) toward V(IV) species with transformation of V(V)O–H into coordinatively unsaturated V(IV) ions. As expected, no V(V)–OH species are present on the reduced VSiBEA sample (Fig. 5, spectrum c).

When CO is adsorbed on the oxidized VSiBEA sample no vanadium carbonyls are detected, suggesting that all vanadium ions are in V(V) oxidation state (spectra nor shown).

Adsorption of CO at 100 K on the activated VSiBEA sample results in the appearance of four intense bands at 2200, 2156, 2141 and 2135 cm^{-1} (Fig. 6, inset, spectrum a). In addition, a shoulder at 2191 cm^{-1} is discernible. The bands at 2141 and 2135 cm^{-1} were already assigned to physically adsorbed CO and that at 2156 cm^{-1}, to attributed to Si–OH–CO interaction. At low coverages two bands, at 2200 and 2191 cm^{-1} are well seen (Fig. 6, spectrum d). Additional evacuation leads to a decrease of both bands in intensity and, appearance, at their place, of a new band located at 2196 cm^{-1}. The latter is still visible after evacuation at room temperature (Fig. 6). The band at 2196 cm^{-1} is assigned to V^{n+}–CO species [25,26]. The split of the CO modes at higher coverages indicates formation of polycarbonyl species. Usually, dicarbonyls are characterized by low-intense symmetric modes at higher

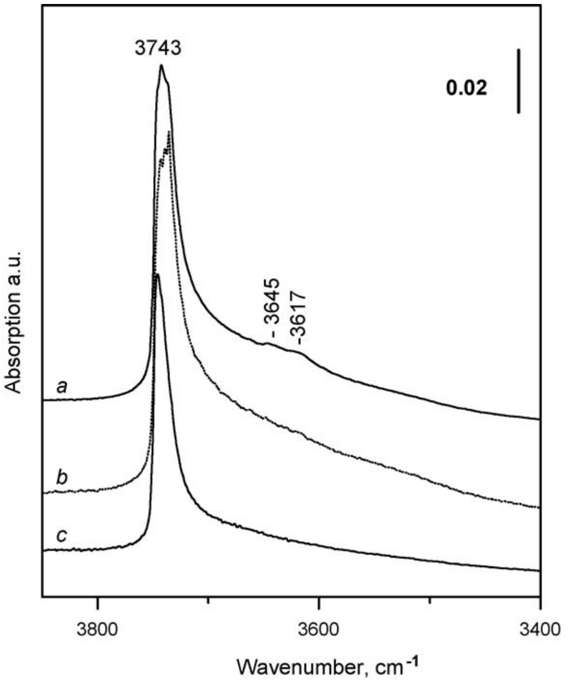

Fig. 5. FTIR spectra of (a) oxidized VSiBEA, (b) activated VSiBEA and (c) reduced VSiBEA.

frequencies [25], which is just opposite to the observed in our case phenomena. Therefore, the most probable assignment of the bands at 2200 and 2191 cm^{-1} is to tricarbonyl species. However, dicarbonyls with more intense symmetric mode have been recently well evidenced [27]. The determination of the exact number of the CO ligands requires ^{12}CO–^{13}CO co-adsorption experiments. Nevertheless, the results evidence the existence of reduced vanadium sites that are highly coordinatively unsaturated. Note that in this case a split of the CO modes occurs, which indicates a strong ligand–ligand interaction. This behavior is different from the behavior of the dicarbonyls observed with the ion-exchanged sample. At present we cannot give a definite answer to this question, but suggest that this is due to steric reasons.

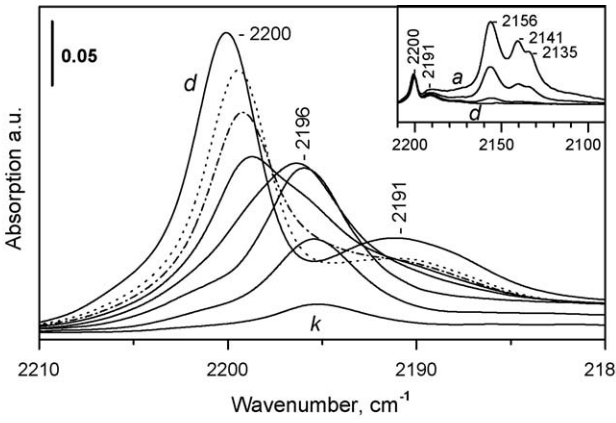

Fig. 6. FTIR spectra of CO adsorbed at 100 K on activated VSiBEA. Equilibrium CO pressure of 130 Pa (a) and development of the spectra during evacuation at 100 K for 1, 3 and 5 min (b–d) and at increasing temperatures (by ca. 30 K per spectrum) up to ambient temperature (e–k).

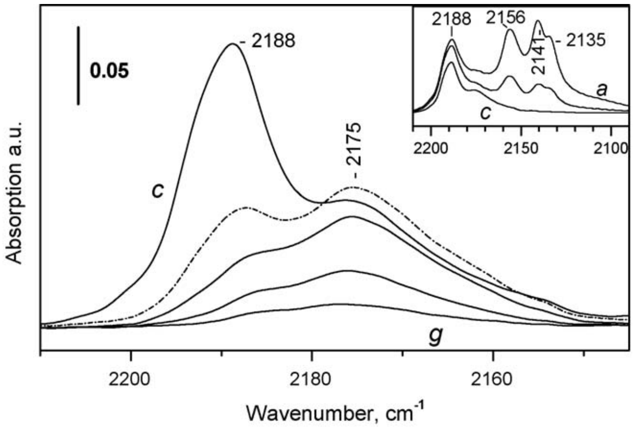

Fig. 7. FTIR spectra of CO adsorbed at 100 K on reduced VSiBEA. Equilibrium CO pressure of 130 Pa (a) and development of the spectra during evacuation at 100 K for 1 and 10 min, respectively (b and c) and at increasing temperatures (by 30 K per spectrum) up to ambient temperature (d–j).

Low temperature CO adsorption on reduced VSiBEA sample results, in addition to the bands arising from physically adsorbed CO (2143 and 2135 cm^{-1}) and SiOH–CO species (2156 cm^{-1}), to the appearance of an intense band at 2188 cm^{-1} with shoulders at 2200, 2191 and 2175 cm^{-1} (Fig. 7, spectrum a). Most probably the bands at 2200 and 2191 cm^{-1} are the same as those observed with the activated sample, but detailed analysis is hindered because of the superimposition with the other intense carbonyl bands. Evacuation leads to decrease in intensity of the band at 2188 cm^{-1} without change in position at the initial evacuation stages. Then the band is shifted to 2186 cm^{-1} and the shoulder at 2175 cm^{-1} gains some intensity. Both bands decease in concert and finally disappear from the spectra. The lower frequency of the carbonyls observed in this case (as compared to the activated sample) are indicative of a lower oxidation state of the respective vanadium sites. Here again, the spectra suggest formation of different polycarbonyl species. We assign the most intense band at 2188 cm^{-1} to V^{4+}–CO species [13]. The set of bands at 2186 and 2175 cm^{-1} are most probably due to dicarbonyls, while most probably a component of the band around 2188 cm^{-1} together with a band around 2176 cm^{-1}, to tricarbonyls.

The results on NO testing of the sample after different pretreatments are presented in Fig. 8. It is seen that NO is not adsorbed on the oxidized sample which is consistent with the results on CO adsorption experiments, i.e. the absence of reduced vanadium sites (Fig. 8, spectrum a).

The spectra of NO adsorbed on the activated VSiBEA sample are characterized by lower intensity bands (Fig. 8, spectrum b). In this case the band around 1837 cm^{-1} appears with a strongly enhanced intensity, showing a component around 1850 cm^{-1}, suggesting that V^{4+}–NO mononitrosyl species could adsorb at this wavenumber, which is in line with earlier report [24]. However, in this case again, bands due to $V^{3+}(NO)_2$ adducts are detected. These results seem to contradict the results on the CO adsorption experiments which suggested the existence of one kind (most probably V^{4+}) of reduced vanadium sites. However, bands around 1640 cm^{-1}, assigned to surface nitrates are produced in this case. This could indicate that some particular V^{4+} sites are reduced by NO to V^{3+} and, simultaneously, nitrates are formed.

With the reduced VSiBEA sample (Fig. 8, spectrum c) a strong band at 1723 cm^{-1} with a shoulder at 1760 cm^{-1} are detected. Two weak bands at 1900 and 1837 cm^{-1} are also seen. The appearance of the bands at 1837 and 1723 cm^{-1} is related to the presence of $V^{3+}(NO)_2$ dinitrosyls. With time and in the presence of 200 Pa NO equilibrium pressure the bands at 1837 and 1723 cm^{-1} decrease in intensity while the bands at 1900 and 1760 cm^{-1} develop (Fig. 8, spectrum d). These results suggest that $V^{3+}(NO)_2$ species (1837 and

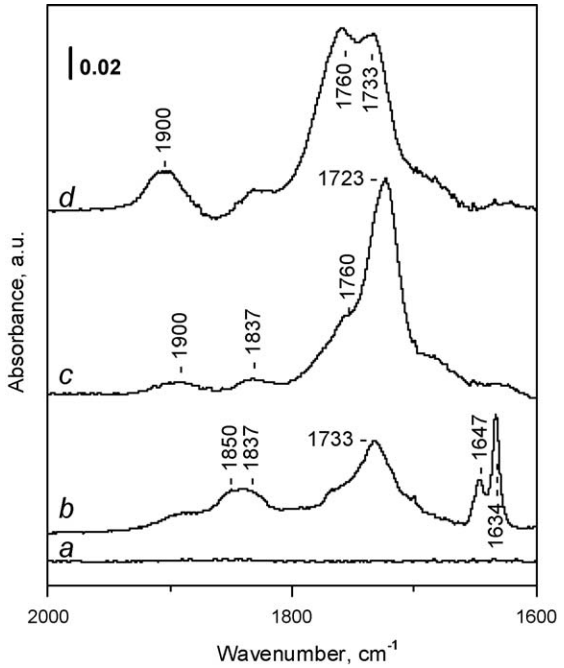

Fig. 8. FTIR spectra of NO (50 Pa equilibrium pressure) adsorbed at ambient temperature on (a) oxidized, (b) activated and (c) reduced VSiBEA. (d) Spectrum taken 10 min after introduction of 200 Pa NO to the reduced VSiBEA.

1723 cm^{-1}) are oxidized to $V^{4+}(NO)_2$ dinitrosyls (1900 and 1760 cm^{-1}).

3.3. Environment and oxidation state of vanadium species in VSiBEA zeolites

In order to obtain more information about the environment and oxidation state of vanadium species present in the VSiBEA zeolite that strongly change upon different pre-treatment as shown above, we investigate further as prepared, activated and reduced VSiBEA by DR UV–vis and EPR.

The DR UV–vis and EPR spectra of as prepared, activated and reduced VSiBEA are shown in Figs. 9 and 10, respectively.

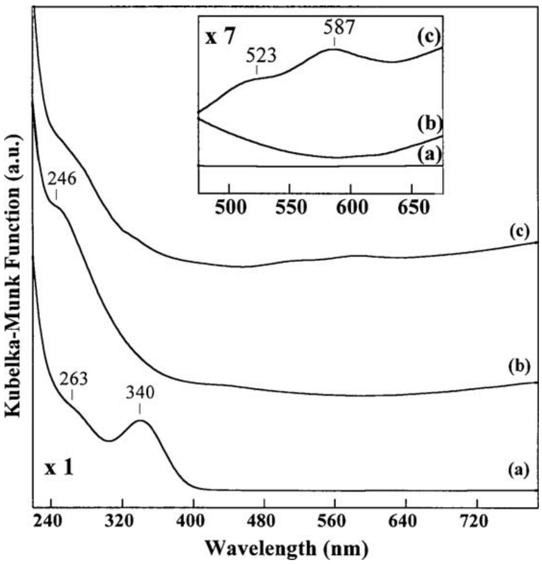

Fig. 9. DR UV–vis spectra recorded at ambient temperature of (a) as prepared, (b) activated and (c) reduced VSiBEA.

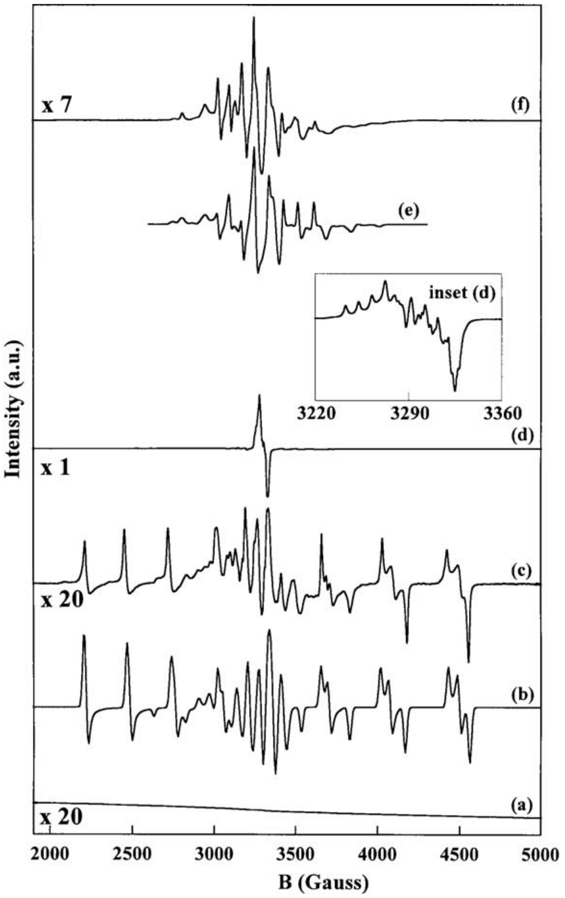

Fig. 10. EPR spectra recorded at 77 K of (a) as prepared, (c) activated, (d) and (c) + addition of 266 Pa of O_2 and (f) reduced VSiBEA. (b) and (e) Simulation of spectra (c) and (f), respectively.

The absence of the d–d band expected in the range 500–800 nm for V(IV) ($3d^1$) ions [13,14,29] in the spectrum of as prepared VSiBEA (Fig. 9a) suggests that this sample contains no significant amount of V(IV) ions. This is confirmed by no EPR signal neither at 298 nor at 77 K (Fig. 10, spectrum a) indicating the absence of paramagnetic V(IV) ions. In contrast, the presence of two broad bands at 263 and 340 nm (Fig. 9a) attributed to oxygen-tetrahedral V(V) charge-transfer (CT) transitions indicates that vanadium is present as diamagnetic V(V) species (d^0) in tetrahedral coordination, in line with earlier results [14,23]. Moreover, the absence of the bands near 400–450 nm indicates that octahedral V(V) species are not present in this sample.

Outgassing of as prepared VSiBEA at 773 K (10^{-3} Pa) for 2 h, induces a strong shift of the DR UV–vis bands to lower wavelengths. This is illustrated with a large band in the 240–340 nm range, with a maximum at 246 nm (Fig. 9, spectrum b). The shift of the DR UV–vis charge-transfer bands to lower wavelengths upon outgassing of VSiBEA (Fig. 9, spectrum b) and the simultaneous decrease of their intensity, suggest a greater distortion of tetrahedral V(V) species in activated VSiBEA than in as prepared VSiBEA, in line with earlier work [13,14,30,31].

Moreover, this pre-treatment leads to the reduction of V(V) species to V(IV) one (d^1), as shown by the corresponding EPR spectrum (Fig. 10, spectrum c). In the EPR spectrum of outgassed VSiBEA, two signals are distinguished. A dominant one, with orthorhombic symmetry, exhibits a large hyperfine constant ($A_i \sim 300$ G). This signal has been reported recently for the first time by Pietrzyk et al. [32]. A second unknown signal is also identified. The computer simulation of the dominant V(IV) signal

(Fig. 10, spectrum b) gives the following values: $g_x = 1.814$, $g_y = 1.947$, $g_z = 1.970$, $A_x = 280$, $A_y = 330$ and $A_z = 320$ G, which dramatically differ from those known for monooxo V(IV)O^{2+} species [8,33–36]. On the basis of earlier DFT calculations [32] and other literature data [37], this signal may be assigned to V(IV)O_2 radicals stabilized inside BEA zeolite. The dioxovanadium(IV) radical is very active and its interaction with dioxygen results in immediate formation of a new orthorhombic EPR signal with following Hamiltonian parameters: $g_x = 2.0076$, $g_y = 2.0026$, $g_z = 2.0020$, $A_x = 5.8$, $A_y = 4.8$ and $A_z = 10.0$ G (Fig. 10, spectrum d). This signal is consistent with the superoxide radical attached to vanadium species forming a bent $(V^VO_2)–O_2^-$ complex [38,39] of potential relevance for mimicking turnovers of haloperoxidases activity of enzymes.

However, the absence of d–d transitions in the DR UV–vis range (500–800 nm) (Fig. 9, spectrum b) indicates that the amount of V(IV)O_2 species is not important.

In contrast, after reduction of VSiBEA with hydrogen at 873 K a much more important amount of V(IV) species is formed as shown by appearance of the DR UV–vis bands at 523 and 587 nm. They correspond to d–d transitions in V(IV) species. Simultaneous decreasing of the intensity of the broad band in the 240–340 nm range, with a maximum at 246 nm (Fig. 9, spectrum c) assigned to tetrahedral V(V) species confirm that an important part of V(V) species is reduced to V(IV) one.

Moreover, after reduction of VSiBEA with H_2, the EPR spectra exhibit at 298 and 77 K (Fig. 10, spectrum f) a signal with a well resolved hyperfine (hf) structure indicating the absence of dipolar interaction between V(IV) ions and thus the high dispersion of the latter [23,34]. The computer simulation of this EPR signal (Fig. 10, spectrum e) with orthorhombic symmetry give the following Hamiltonian parameters values: $g_x = 1.992$, $g_y = 1.962$, $g_z = 1.999$, $A_x = 84$, $A_y = 81$ and $A_z = 149$ G. The A_z value suggests that this signal arise from isolated tetrahedral V(IV) species as already suggested for reduced V-silicalite [23]. Note that in order to better simulate the EPR signal, a second minor V(IV) signal has been considered exhibiting larger couplings ($A_x = 143$ G, $A_y = 49$ G and $A_z = 180$) and slightly different g values ($g_x = 1.950$, $g_y = 2.0144$, $g_z = 1.959$) related to the presence of a small amount of isolated octahedral V(IV) species.

4. Conclusions

This work shows the remarkable effect of the preparation method on the oxidation state and environment of V introduced in BEA zeolite.

No structural changes are observed after incorporation of vanadium into AlBEA zeolite by ion-exchange method. In contrast, the incorporation of V into SiBEA leads to (i) an increase of unit cell parameters of the BEA, (ii) the consumption of silanol groups in vacant T-sites and (iii) incorporation of V in the framework of BEA zeolite as well dispersed tetrahedral V(V) species using V(IV) ($VOSO_4$) precursor.

NO and CO used as IR probe molecules, DR UV–vis and EPR allow to establish the oxidation state of vanadium in as prepared, oxidized, activated and reduced VAlBEA and VSiBEA zeolites.

The IR spectra of as prepared, oxidized, activated and reduced VAlBEA are very similar. It suggests that V introduced by ion exchange in extra-lattice position is stabilized on all VAlBEA samples in similar oxidation state. CO adsorption evidence the presence of vanadium in IV oxidation state via IR bands at about 2200 and 2180 cm^{-1} assigned to V(IV)–CO monocarbonyl and V(IV)–$(CO)_2$ dicarbonyl species.

In contrast, the oxidation state of V in VSiBEA changes strongly in function of calcinations in oxygen, outgassing at high temperature (773 K) and reducing with hydrogen at high temperature (873 K). This shows that lattice tetrahedral V species change easily oxidation state and this property allows them to be good candidate as active site of selective redox reactions.

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