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Nature of vanadium species in V substituted zeolites: A combined experimental and theoretical study

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ABSTRACT

The nature of vanadium species in V substituted zeolites is determined by combined experimental (XRD, FTIR, DR UV–vis) and theoretical (periodic DFT calculations) study. The introduction of V ions in lattice sites of SiBEA zeolite is evidenced by XRD and FTIR spectroscopy. The state of vanadium is characterized by DR UV–vis spectroscopy. The vanadium is incorporated in SiBEA zeolite as tetrahedral V(V) species, containing the V=O double bond and linked by V–OSi bounds to the zeolitic framework. DR UV–vis spectroscopy shows that environment of V(V) species depends on the treatment condition of the VSiBEA sample. The calcination/hydration processes allow us to distinguish in VSiBEA sample two different kinds of tetrahedral V(V) species, less and more distorted. Further dehydration of this sample allows detecting by FTIR two bands at 3620 and/or 3650 cm^{-1} corresponding to the presence of hydroxylated tetrahedral V(V) species, possessing the V–OH group. These O–H groups have acidic Brønsted character as shown by FTIR in the presence of adsorbed pyridine. The V(V) and V(IV) model sites are discussed using periodic DFT calculations.

1. Introduction

Isomorphous substitution of tetrahedral sites by transition metal ions in microporous zeolites, aluminophosphate and silicoaluminophosphate and mesoporous molecular sieves is a way to modify their catalytic and photocatalytic properties [1–11]. In particular, the isomorphous substitution of vanadium into the zeolite lattice allows to obtain catalysts with efficient activity in selective oxidation of different organic molecules such as hydrocarbons or alcohols [5,6,12,13].

The incorporation of vanadium into the zeolite lattice has been for a long time considered as a challenge. Most of the authors have agreed that only a minor fraction of the vanadium ions is incorporated into the zeolite framework during direct hydrothermal synthesis [14–18]. The main part of the V species is loosely bound to the zeolite walls and is easily washed out with a aqueous solution of ammonium acetate (NH_4OAc) [17,18].

For V-containing microporous materials, both V^{5+} and/or V^{4+} are incorporated in either tetrahedral or square pyramidal coordination by substituting framework Si [12,17,19–21]. Bellussi and Rigutto [12] have reviewed the synthesis of different V-containing silicates and pointed out that besides the gel composition and crystallization conditions, the vanadium source plays an important role in the incorporation of V ions. Earlier [7,9], the V-silicalites with different framework structure have been prepared by hydrothermal synthesis and their chemical properties have been reviewed. The true chemical nature and reactivity of the vanadium silicalite are related to the vanadium species incorporated into framework structure. The dispersion level of these species appears to be a key factor in controlling the photocatalytic reactivity of these catalysts. However, very often besides isolated mononuclear V species also polynuclear V species (oligomeric V species or vanadium oxide) are detected in vanadium containing zeolites [1].

The incorporation of transition metal ions into framework sites of the aluminophosphate and silicoaluminophosphate molecular sieves is also of particular interest for the design of novel catalysts. The location and structure of the reactive metal site is very important for understanding of the chemistry of such materials. In particular, the interaction of such active metal sites with reactants helps to understand catalysis on a molecular level [2,3,22].

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Information on cation location or the incorporation of transition metal ions into zeolites, aluminophosphates and silicoaluminophosphates is typically hard to obtain since the metal concentration is very low. A large number of different characterization methods have been used to collect information on the location of the transition-metal ion in the molecular sieve. Conclusive judgments can usually only be made by using complementary techniques for characterization of the same samples.

Recently, Dzwigaj et al. [23–25] showed that catalytically active vanadium (V) sites can be introduced in the zeolite lattice by reaction of V(V) (NH_4VO_3) and V(IV) ($VOSO_4$) precursors with silanol groups of vacant T-sites of SiBEA zeolite in aerobic and anaerobic conditions. The combined deployment of different techniques such as diffuse reflectance (DR) UV–vis, FTIR, ^{51}V NMR, EPR and photoluminescence have evidenced that different kinds of V(V) species are formed, which amounts depend on the V content and dehydration–hydration processes [23–25]. It is shown [23–25] that the number of V ions incorporated in lattice sites of SiBEA zeolite as tetrahedral V(V) species can increase up to 1.9 V wt.%. Above this V content, the octahedral V(V) species appears in the extra lattice position.

Since it was shown that for high V content, the distorted tetrahedral V(V) species are highly sensitive to calcination/rehydration treatments and can easily change their coordination upon these processes [23–25], we have tried to clarify the vanadium environment in VSiBEA zeolite containing 1.9 V wt.% (maximum amount of V atoms possible to introduce in the lattice position of SiBEA zeolite upon postsynthesis preparation condition) by means of different experimental techniques combined with a computational study. The introduction of vanadium ions in vacant T-sites and their reaction with silanol groups are evidenced by XRD and FTIR, respectively. Generation of acidic Brønsted and Lewis sites is shown by FTIR of pyridine adsorption. The oxidation state and environment of vanadium in VSiBEA zeolite is characterized by DR UV–vis.

To better describe the V sites in the zeolite's framework a detailed theoretical ab initio study is indispensable. In this work, in line with our former studies on zeolite reactivity [26–30], the Si lattice substitution by V is investigated in a sodalite (SOD) structure by means of the modeling of V(V) and V(IV) sites.

2. Experimental

2.1. Material preparation

VSiBEA zeolite (with 1.9 V wt.%) are prepared by the two-step postsynthesis method reported earlier [26,27,29]. To obtain a sample with 1.9 V wt.%, 2 g of siliceous BEA zeolite (Si/Al > 1300), obtained by treatment of a tetraethyl ammonium BEA zeolite (Si/Al = 11) in a 13 mol L^{-1} HNO_3 solution (4 h, 353 K), is contacted at room temperature with 20 ml of aqueous solution of ammonium metavanadate (7.2×10^{-2} mol L^{-1}, pH 2.5) for 3 days without any stirring. Then, the solid recovered by centrifugation and dried at 353 K overnight contains 1.9 wt.% of V and is labeled VSiBEA. It is further calcined at 773 K for 3 h in flowing air and denoted C-VSiBEA. This sample is then hydrated at room temperature in moist air and labeled Hyd-C-VSiBEA, where C stands for calcined and Hyd for hydrated. The color of VSiBEA and C-VSiBEA is white and that of Hyd-C-VSiBEA yellow.

2.2. Methods of characterization

Powder X-ray diffractograms are recorded on a Siemens D5000 using the CuKα radiation (λ = 154.05 pm).

Transmission FT-IR spectra of self-supported wafers are recorded at 298 K on a Bruker IFS 66 V spectrometer, with a resolution of 2 cm^{-1}. Before measurements, the wafers are dehydrated in flowing oxygen (120 ml/min, 8 h) to 773 K (heating rate of 100 K/h) then outgassing for 6 h at 573 K (10^{-3} Pa). Gaseous pyridine is introduced on dehydrated wafers at room temperature and the physisorbed part eliminated by evacuation at the same temperature for 1 h.

DR UV–visible spectra were recorded on a Cary 5E spectrometer equipped with an integrator and a double monochromator. The parent V-free materials were used as references.

2.3. Computational details

2.3.1. Methods

All calculations are performed using ab initio plane-wave pseudopotential periodic DFT as implemented in VASP [31,32]. The Perdew–Burke–Ernzerhof (PBE) functional [33–35], has been chosen to perform the periodic DFT calculations. The accuracy of the method has been tested elsewhere [36–38]. The valence electrons are treated explicitly and their interactions with the ionic cores are described by the Projector Augmented-Wave method (PAW) [39–41] which allows the use of a low energy cut off for the plane-wave basis. The cut off used in the calculations is set equal to 500 eV. A ($3 \times 3 \times 3$) k-point grid is used in the Brillouin-zone sums, and the partial occupancies are set for each wave function using the tetrahedron method with Blöchl corrections [40]. The k-point choice emerges from a quality/cost ratio. The convergence is

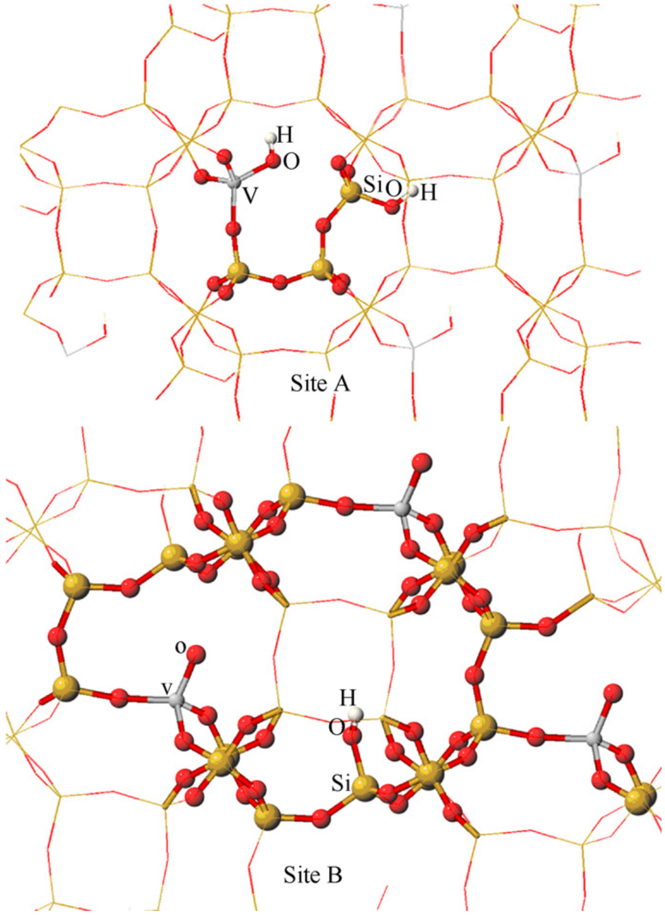

Fig. 1. Site A showing the tetracoordinated V(IV) with an hydroxyl group and site B showing its V=O vanadyl site and its silanol. Both sites are represented in their optimized geometry.

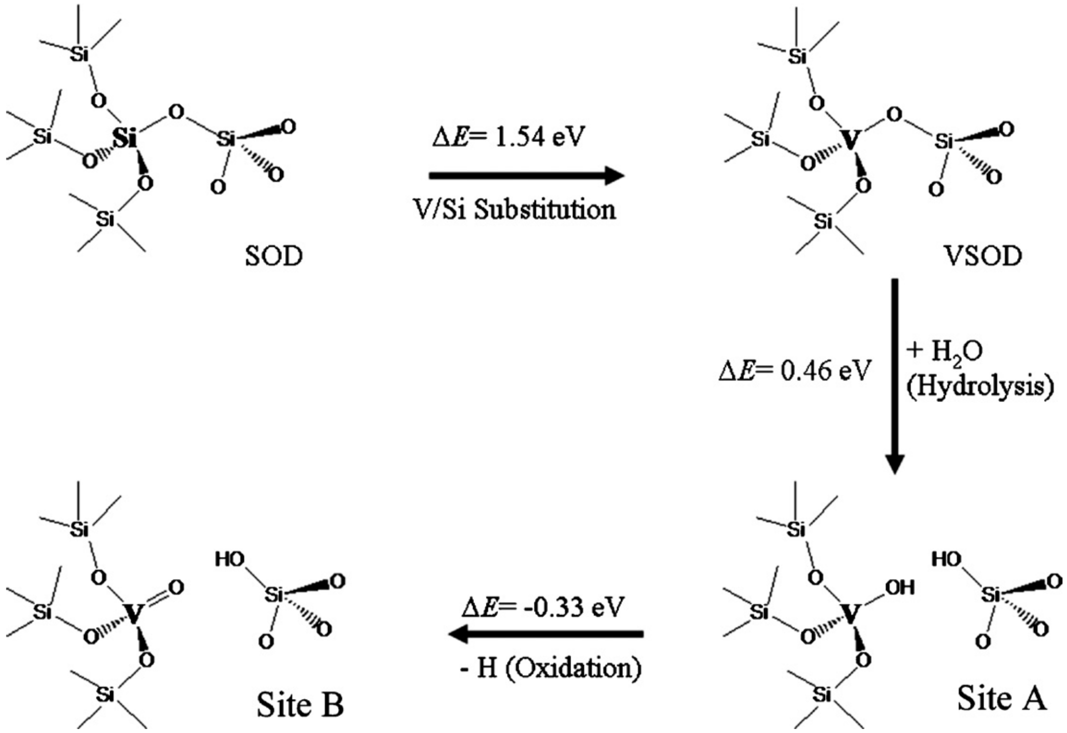

Fig. 2. Schematic representation showing the relative energies for the "theoretical" framework site A containing a V(IV) and model site B containing a V(V).

checked with the number of *k*-points for the pure SiO_2 sodalite. The positions of all the atoms in the supercell are relaxed, in the potential energy determined by the full quantum mechanical electronic structure until the total energy differences between the loops is less than 10^{-4} eV.

To calculate the Hessian matrix, finite differences are used, *i.e.* each ion is displaced in the direction of each Cartesian coordinate, and the Hessian matrix is determined from the forces. All atoms are displaced in all three Cartesian directions. The frequency calculations are performed considering one *k*-point. All calculations are performed on an IBM regatta power 4 of the supercomputing center IDRIS.

2.3.2. Description of the model

The sodalite (SOD) structure is chosen as a model zeolitic environment on the basis of prize/quality ratio. The sodalite cage is a building block of several zeolites such as faujasite or zeolite A. The cage is rather small, which might restrict the framework flexibility during the isomorphous substitution of vanadium ions. Nevertheless, it is a very suited model to perform periodic ab initio calculations and investigate the isomorphous substitution of vanadium into a zeolite framework. The SOD structure has been calculated and discussed by Richardson et al. [42].

The sodalite cage, commonly referred as the β-cage, contains a regular network of tetrahedral sites (T-sites) and resembles a truncated octahedron with each vertex corresponding to a Si-atom; in total it counts 36 atoms ($Si_{12}O_{24}$).

Two models for the active sites are proposed. The models are partially based on previous studies of Dzwigaj [43] and Dzwigaj et al. [44] on the V loaded SiBEA zeolite. For modeling the V sites in zeolites one silicon atom is substituted by one vanadium atom and the so-formed Si–O–V linkage is broken by adsorption of water (hydrolysis). The obtained site is called site A (see Figs. 1 and 2) and has a tetracoordinated vanadium in oxidation state +4. The second site (site B) is considered to be formed by oxidation of the former one (Fig. 2). Site B has a V=O bond and its vanadium in oxidation state +5.

3. Results and discussion

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

As reported earlier [23–25], unit-cell parameters of BEA zeolite are difficult to determine from powder diffractograms because of the coexistence of monoclinic and tetragonal polytypes. A narrow diffraction peak, near 22.60, can however be used to detect lattice contraction/expansion, in line with earlier report [23,24]. The decrease of $d_{3\,0\,2}$ spacing related to this peak from 3.942 Å (AlBEA) (with 2θ of 22.55°) to 3.912 Å (with 2θ of 22.71°) (SiBEA) upon dealumination indicates contraction of the matrix (Fig. 3, diffractograms a and b). In contrast, the significant increase to 3.940 Å (with 2θ of 22.60°) upon introduction of vanadium into SiBEA (Fig. 3, diffractogram c) indicates expansion of the matrix and incorporation of V ions into the lattice. The incorporation of V into zeolite structure does not affect its crystallinity, as evidenced by similar X-ray diffractograms of the AlBEA, SiBEA and VSiBEA samples (Fig. 3, diffractograms a, b and c).

As shown earlier [23,24], after dealumination of HAlBEA zeolite by treatment with nitric acid and obtention of SiBEA zeolite, IR bands at 3736 and 3706 cm^{-1} related to isolated 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. The incorporation of V ions leading to VSiBEA induces a reduction of intensity of these bands, in particular the band at 3520 cm^{-1} suggesting that silanol groups are consumed in the reaction with V precursor. Simultaneously, new OH bands at 3620 and 3645 cm^{-1} appear in the IR spectrum of VSiBEA sample. It is important to mention here that on silica-supported vanadium oxide catalysts only one V(V)–OH band is observed at 3660 cm^{-1} as shown by Keller et al. [45]. Both OH groups are related to acidic V(V)–OH as deduced from their disappearance upon adsorption of pyridine (spectrum not shown), in line with our earlier results [24]. Brønsted acidic character of these groups is confirmed by

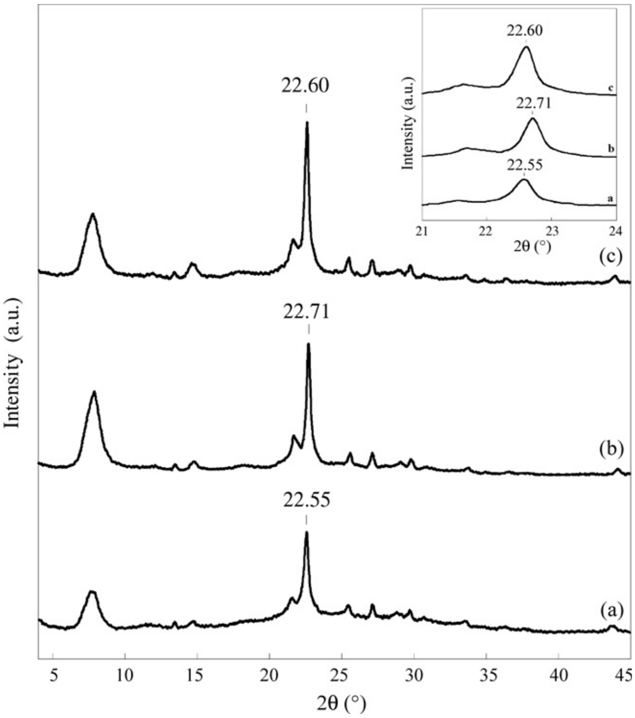

Fig. 3. X-ray diffractograms recorded at room temperature of as-prepared (a) AlBEA, (b) SiBEA and (c) VSiBEA samples.

appearance of bands due to pyridinium cations [24] at 1542 and 1638 cm^{-1} (Fig. 4, spectrum b). These pyridinium cations IR bands are not observed for dehydrated SiBEA sample. Indeed, only the bands at 1608 (shoulder), 1596, 1580, 1490, 1485, 1446 and 1439 cm^{-1} are observed (Fig. 4, spectrum a) corresponding to pyridine interacting with Lewis acidic sites and/or physisorbed, in line with earlier report [24]. The latter bands also appear for VSiBEA sample but with higher intensity suggesting much higher amounts of Lewis acidic sites than in SiBEA sample.

3.2. Probing of two kinds of tetrahedral vanadium species in VSiBEA by DR UV–vis

The nature and environment of the V species in VSiBEA have been studied by DR UV–vis spectroscopy. This technique allows distinguishing both tetrahedral and octahedral V species.

DR UV–vis spectra of as-prepared VSiBEA sample exhibit two main bands at 270 and 340 nm (Fig. 5, spectrum a). Due to the absence of (*d*–*d*) transition in the range 600–800 nm and of any V(IV) ESR signal, these bands can only involve diamagnetic vanadium(V) ions and are assigned to $\pi(t_2) \rightarrow \mathrm{d(e)}$ and to $\pi(t_1) \rightarrow \mathrm{d(e)}$ oxygen–tetrahedral V(V) charge transfer (CT) transitions, involving bridging (V–O–Si) and terminal (V=O) oxygen, respectively, in agreement with earlier data [20,24].

After calcination of this sample at 773 K, DR UV–vis spectrum of the C-VSiBEA is composed of a large band in the range 230–340 nm, with a maximum at 235 nm and shoulder at about 270 nm (Fig. 5, spectrum b). The white color of this sample is likely due to the presence of isolated tetrahedral V(V) species. The shift of the UV–vis charge transfer bands to lower wavelengths upon calcination and the simultaneous decrease of their intensity (see Fig. 5, spectra a and b) suggest a greater distortion of tetrahedral V(V) in calcined C-VSiBEA than in as-prepared VSiBEA, in line with the conclusions reported earlier for $KVOF_4$ and the VO_4^{3-} complex [46,47]. Increase of the distortion of tetrahedral V(V) species after calcination has been confirmed by Dzwigaj et al. [48] in earlier work. Indeed, as reported by photoluminescence spectroscopy the calcination of VSiBEA zeolite provokes an increase of the amount of strongly distorted tetrahedral V species (with a vibrational energy

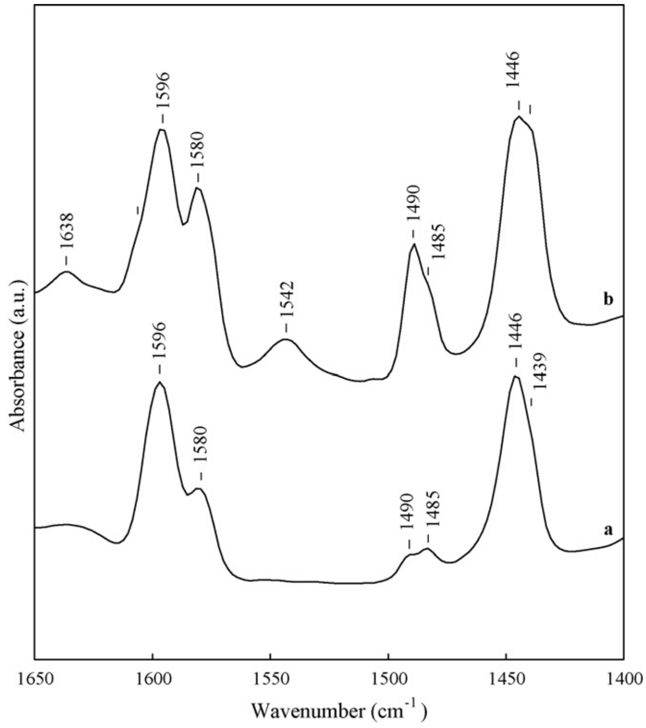

Fig. 4. FTIR spectra recorded at room temperature of (a) SiBEA and (b) VSiBEA samples after adsorption of pyridine (room temperature, 1 h) and evacuation (room temperature, 1 h, 10^{-3} Pa).

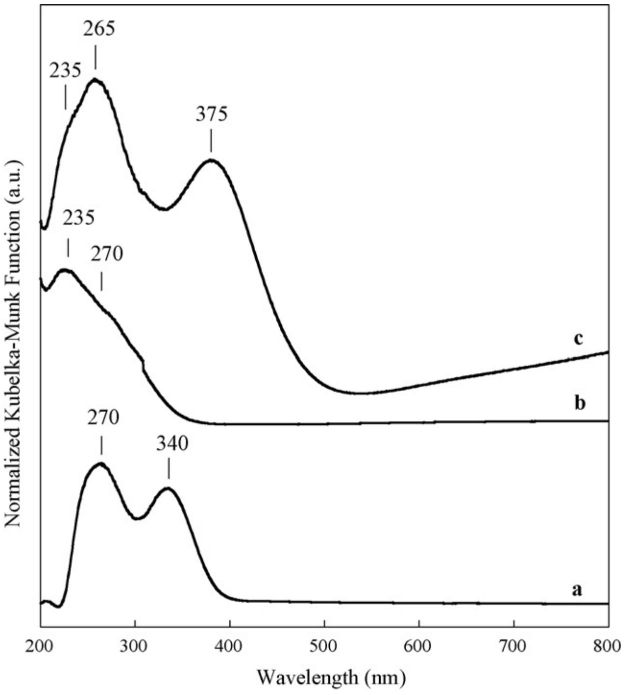

Fig. 5. Diffuse reflectance UV–vis spectra recorded at room temperature of (a) VSiBEA, (b) C-VSiBEA and (c) Hyd-C-VSiBEA samples. Spectra were measured with SiBEA as reference.

of 1036 cm^{-1}) and a decrease of the amount of less distorted ones (with a lower vibrational energy of 1018 cm^{-1}).

After hydration of C-VSiBEA at room temperature, two broad bands at around 265–270 and 370–375 nm with a shoulder at 235 nm appear in Hyd-C-VSiBEA sample (Fig. 5, spectrum c). As reported earlier [20,25], the band at around 235–270 nm can be attributed to $\pi(t_2) \rightarrow d(e)$ oxygen-to-tetrahedral V(V) charge transfer transition with oxygen in bridging position (V–O–Si) and the band at around 370–375 nm to an oxygen-to-octahedral V(V) charge transfer transition with oxygen in terminal position (V=O). The shoulder at 235 nm and the band at 265 nm suggest the presence of two different kinds of tetrahedral V(V), strongly and less distorted, respectively, in line with the results reported on for $KVOF_4$ compound and the VO_4^{3-} complex [20,25,46,47]. It may be mentioned here that the spectrum of the VSiBEA sample after calcination/hydration treatments do not show the band at 340 nm. This band may be covered by the broad band at 370–375 nm. Moreover, the light yellow color of the Hyd-C-VSiBEA sample suggests that in addition to tetrahedral V(V) species also some amount of octahedral V(V) species is present. A weak EPR signal of paramagnetic V(IV) ions (not shown) observed for Hyd-C-VSiBEA sample, very similar to that reported earlier by Dzwigaj et al. [25], clearly indicates that upon calcination and hydration of VSiBEA sample a small amount of V(IV) species is formed. A quantitative EPR measurements performed earlier by Dzwigaj et al. [25] and Dzwigaj and Che [49] on the calcined and hydrated VSiBEA samples prepared by postsynthesis method using both NH_4VO_3 and $VOSO_4$ vanadium precursors reveal that V(IV)/V(IV+V) molar ratio is lower than 0.01. It confirms that the majority of vanadium ions are present in Hyd-C-VSiBEA as V(V) species.

When the Hyd-C-VSiBEA is recalcined at 773 K for 2 h in flowing oxygen, the sample change the color from yellow to white and the spectra characteristic of C-VSiBEA (Fig. 5, spectrum b) are restored, with the large band in the range of 230–340 nm. The subsequent exposure of the latter samples to room atmosphere resulted in a UV–visible spectrum similar to that observed for Hyd-C-VSiBEA (Fig. 5, spectrum c), indicating that the dehydration (during calcination) and hydration (upon exposure to room atmosphere) processes are reversible. The dehydration/hydration processes allow to evidence that at least two different kinds of tetrahedral V(V) species are present in VSiBEA zeolite.

The DRX, DR UV–vis and FTIR techniques used in combination reveal that V ions are incorporated in SiBEA zeolite with formation of tetrahedral (V(V)) site containing the V=O double bond and linked by V–OSi bounds to the zeolitic walls. Moreover, two O–H vibrators at 3620 and 3645 cm^{-1} evidenced in the VSiBEA sample by FTIR measurements [24] indicate that also V(V) site containing V(V)–OH group is present. Both V(V)–OH groups have acidic Brønsted character as shown via FTIR by their simultaneous disappearance after adsorption of pyridine. Recently, Dzwigaj et al. [25] have evidenced by EPR measurements that two kinds of tetrahedral V(IV) could be formed when VSiBEA zeolite with tetrahedral V(V) species is reduced with hydrogen at 873 K. An EPR signal with two hf structures and with small $A_{\|}$ hf values (both close to 151 G) determined at 77 K have evidenced the presence of two paramagnetic V(IV) species. It may suggest that in initial (no reduced) VSiBEA sample two different kinds of tetrahedral V(V) sites exist.

3.3. Two kinds of tetrahedral vanadium sites modeled by DFT study

In order to interpret and compare our experimental spectroscopic data of the vanadium sites in zeolites, quantum chemical calculations on two different vanadium model sites were performed.

The energy difference between site B with vanadium in +5 oxidation state and site A with vanadium in +4 oxidation state (Fig. 2) is found to be 0.33 eV in favor of site B. This energy is obtained calculating the energy of reaction (1):

$$\text{SiteA} \rightarrow \text{SiteB} + (1/2)\text{H}_2 \qquad (1)$$

Using the Boltzmann relation the ratio A/B sites is predicted to be 0.01 at 700 K, which is in agreement with the experimental results obtained for V loaded SiBEA [23–25,48,50], SiMCM-41 and SiSBA-15 [51–53] materials.

The interatomic distances obtained from our optimized models give a clear view on the type of V–O bond that are present in the reactive site. The V–OH distance is found to be 1.87 Å and the vanadyl V=O one is found to be 1.60 Å. These results are very similar to that obtained by experimental studies for the V–OH bonds in mono nuclear VO_4 clusters (1.72–1.80 Å) [54] and for the vanadyl bond measured in BEA zeolite (1.58 Å) [48]. The calculated bond lengths are also in agreement with former theoretical results obtained for gas phase clusters [55,56].

The vibrational frequencies of the fully geometrically optimized structures of site A and site B have been calculated. The theoretical vibrational frequency of the SiO–H bond of site B is 3812 cm^{-1}. For site A the SiO–H vibrational frequency is 3863 cm^{-1} and the V(IV)O–H is 3694 cm^{-1}. Due to the anharmonicity of O–H vibrator, the vibrational frequencies were scaled with a factor 0.98 [57]. After this scaling we obtain for the SiO–H bond in site B a vibrational frequency value of 3736 cm^{-1}, for the Si–OH bond in site A of 3786 cm^{-1}, and for the V(IV)O–H bond in site A a value of 3620 cm^{-1}. These scaled vibrational frequencies are in very good agreement with the experimental ones [45]. Indeed, in the IR spectrum of calcined and dehydrated VSiBEA the bands at 3736 and 3620 cm^{-1} are present, and might thus be attributed to SiO–H and VO–H vibrations, respectively.

It is important to mention that the appearance of two IR bands in the experimental spectrum at 3620 and 3645 cm^{-1} seems to be related to the presence in BEA zeolites of two kinds of non-equivalent crystallographic T-sites, in line with earlier report [58]. However, for SOD only one V(IV)O–H band is evidenced by DFT calculation since in this zeolite structure only one kind of non-equivalent crystallographic T-sites is present. Another point is that the VO–H vibration observed experimentally cannot be that of a V(IV)O–H site since from the EPR results it is concluded that there are only 1% of the V sites as V(IV). Such a low concentration cannot be detected in IR spectra. This leads us to state that there should be another kind of V site present having a V(V)O–H group.

The acidity of the OH groups present in the zeolite is usually measured experimentally by adsorption of probe molecules such as pyridine, NH_3 or CO. In theoretical studies, the acidity of the OH groups present in the different models can be calculated as a difference of energy of base (SOD–O$^-$) and conjugated acid (SOD–OH). This energy difference corresponds to the deprotonation energy $\Delta E_{\text{deprot.}}$:

$$\Delta E_{\text{deprot.}} = E(\text{SOD}-\text{O}^-) - E(\text{SOD}-\text{OH}) \qquad (2)$$

Negative energy corresponds to an exothermic process. It is well known that when the deprotonation energy increases the acidity decreases [27]. The $\Delta E_{\text{deprot.}}$ of the V(IV)O–H group in site A is calculated to be 4.86 eV. The $\Delta E_{\text{deprot.}}$ of the SiO–H group in the same site A could not be obtained due to the low stability of the anion (conjugated base), which indicates the low acidity of this type of silanol. The $\Delta E_{\text{deprot.}}$ of SiO–H group in site B is calculated to be 5.92 eV. These results show that the silanol groups are much less acid than the V(IV)O–H group.

It should be noted that for the higher oxidation states (+5) in site B there is vanadyl V═O group, which do not show Brønsted acid properties but Lewis base properties, which is not studied in this work. However just as a matter of completeness we can mention that the calculated ν(V═O) frequency in site B is 1076 cm^{-1} (1054 cm^{-1} scaled).

4. Conclusions

The presence of tetrahedral vanadium sites introduced into zeolite frameworks (siliceous BEA and SOD) is evidenced by experimental XRD and FT-IR measurements as well as periodic DFT calculations. The state of vanadium ions in VSiBEA zeolite is characterized by DR UV–vis. It is shown that environment of V(V) species depends on the treatment condition of the VSiBEA sample. In the as-prepared VSiBEA sample vanadium is present as tetrahedral V(V) species. In calcined VSiBEA sample more distorted tetrahedral V(V) species are present. After rehydration of calcined VSiBEA at room temperature at least two kinds of tetrahedral V(V) species are evidenced, less and more distorted.

The formation of two kinds of hydroxylated V species, possessing the V(V)–OH groups, in the VSiBEA sample is evidenced by FTIR measurements (O–H vibrations at 3620 and 3645 cm^{-1}). Both V(V)–OH groups have acidic Brønsted character as shown using FTIR by their simultaneous disappearance after adsorption of pyridine. It may suggests that in VSiBEA sample two different kinds of tetrahedral V(V) sites exist, one for each crystallographic tetrahedral site.

The DRX, DR UV–vis and FTIR techniques used in combination reveal that V ions are incorporated in SiBEA zeolite as tetrahedral V(V) species, containing the V═O double bond and linked by V–OSi bounds to the zeolitic walls. From DFT calculations it is shown that the V(V) sites contain the vanadyl group and are much more stable than V(IV) having the hydroxyl group. Both sites are modeled and discussed using periodic DFT calculations. Finally, it is concluded that another kind of V(V) site should be present in the zeolite framework, having a V(V)–OH group. This is related with the fact that the amount of V(IV) species in calcined and hydrated VSiBEA zeolite is almost lower than 1% of total V content [25,49]. Such a low concentration cannot be detected in IR spectra. This leads us to state that there should be another kind of V site present having a V(V)O–H group. In the next step of our DFT investigation we will look for this kind of V site containing V(V)–OH groups.

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