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Probing acid–base sites in vanadium redox zeolites by DFT calculation and compared with FTIR results

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ABSTRACT

Ab initio periodic DFT calculations in combination with experimental FTIR of adsorption pyridine investigations have been used to study the acid–base properties of vanadium doped zeolite materials. It is evidenced that VO-H groups of V(V) and V(IV) framework sites are more acidic than SiO-H groups present in siliceous zeolites. It is proposed for the first time that the protonation of the penta coordinated V site can lead to the formation of a stable vanadyl group containing site through proton exchange, which is expected to be the inter-conversion path between both sites. We report in this paper protonation and deprotonation energies of different vanadium sites, and a geometry of experimentally observed Lewis and Brønsted acid sites is proposed.

1. Introduction

Zeolites doped with transition metals ions are an extremely important class of catalysts with remarkable properties [1–8]. The insertion of transition metal ions into the zeolite framework can lead to modify the reactivity of zeolites, either by introduction of redox sites and modulation of acid–base properties.

In particular, introduction of vanadium ions into the zeolite allows to obtain catalysts with efficient activity in many selective oxidative processes [2,3]. The incorporation of vanadium ions into the framework was for a long time a very difficult task. Dzwigaj et al. [9–12] have reported that catalytically active vanadium (V) sites can be incorporated in the BEA framework by a two-step postsynthesis method. This method allows to incorporate V as different kinds of tetrahedral V(V) species evidenced by diffuse reflectance UV–vis, ^{51}V MAS NMR, XAS and photoluminescence spectoscopies [4,9–13]. The models of tetrahedral V(V) species and their probable location in the structure of BEA zeolite have been proposed.

To confirm these models, ab initio periodic DFT calculations have been performed [14,15]. Different vanadium framework site models were proposed after a systematic theoretical study of the substitution of a tetrahedral framework site (T-site) by vanadium atoms. The vanadium framework sites were characterized by their calculated geometrical parameters and vibrational frequencies. The results obtained were found to be fully consistent with experimental data reported earlier by Dzwigaj et al. [13,16] and allow to identify the molecular structure of the vanadium sites in the zeolite framework.

Using the acquired knowledge on the molecular structure of V sites in zeolites, their reactivity is investigated and more precisely their acid–base properties, taken into account our earlier works on the acidity and adsorption properties of zeolites [14,15,17–25].

We report in this paper protonation and deprotonation energies of different vanadium sites and a geometry of experimentally observed Lewis and Brønsted acid sites is proposed. A inter-conversion path is proposed between the vanadyl site and the penta coordinated V-OH site. These theoretical results are compared with experimental FTIR investigation of pyridine adsorption.

2. Methodology

2.1. Computational details

All calculations are performed using ab initio plane-wave pseudopotential calculations implemented in VASP [26,27]. The Perdew–Burke–Ernzerhof (PBE) functional [28–30] has been chosen to perform the periodic DFT calculations with an accuracy on the overall convergence tested elsewhere [31–34]. The valence electrons are treated explicitly and their interactions with the ionic

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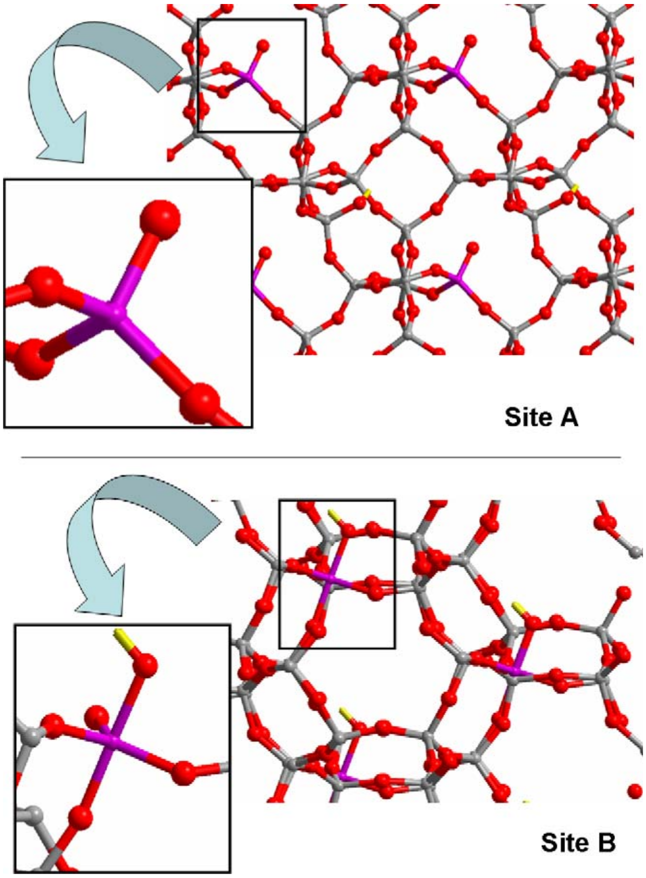

Fig. 1. Location of sites A and B in the sodalite framework.

cores are described by the Projector Augmented-Wave method (PAW) [35,36], which allows to use a low energy cut off equal to 500 eV for the plane-wave basis.

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 et al. corrections [37]. The positions of all the atoms in the super cell as well as the cell parameters are relaxed, in the potential energy determined by the full quantum mechanical electronic structure until the total energy differences between the loops decrease below 10^{-4} eV. The systems with unpaired electrons are calculated taking into account their spin state.

2.2. Description of the models

The model sites are based on the structures discussed in Refs. [14,15]. Vanadium(V) is stabilized in the zeolite framework modeled by a three dimensional sodalite framework in two different tetrahedral sites: one in the form of site A with a stable vanadyl group and the other site B possessing an hydroxyl group (Fig. 2).

Tetrahedral vanadium(IV) sites, in the form, of site B′ (Fig. 3) much less stable, are also present with an acidic hydroxyl group.

In the present work the acidity and basicity is probed by calculating deprotonation (Eq. (1)) and protonation energies (Eq. (2)) of the most stable sites. The deprotonation energy is calculated as follows:

$$\Delta E_{de\,prot.} = E(V\_Zeol^{-}) - E(V\_Zeol\_H) \tag{1}$$

and the protonation energy as follows:

$$\Delta E_{prot.} = E(V\_Zeol\_H_2{}^{+}) - E(V\_Zeol\_H) \tag{2}$$

3. Results and discussions

Site A (Figs. 1 and 2), the site containing a V(V) vanadyl group, has a protonation energy of −3.91 eV considering a proton attack

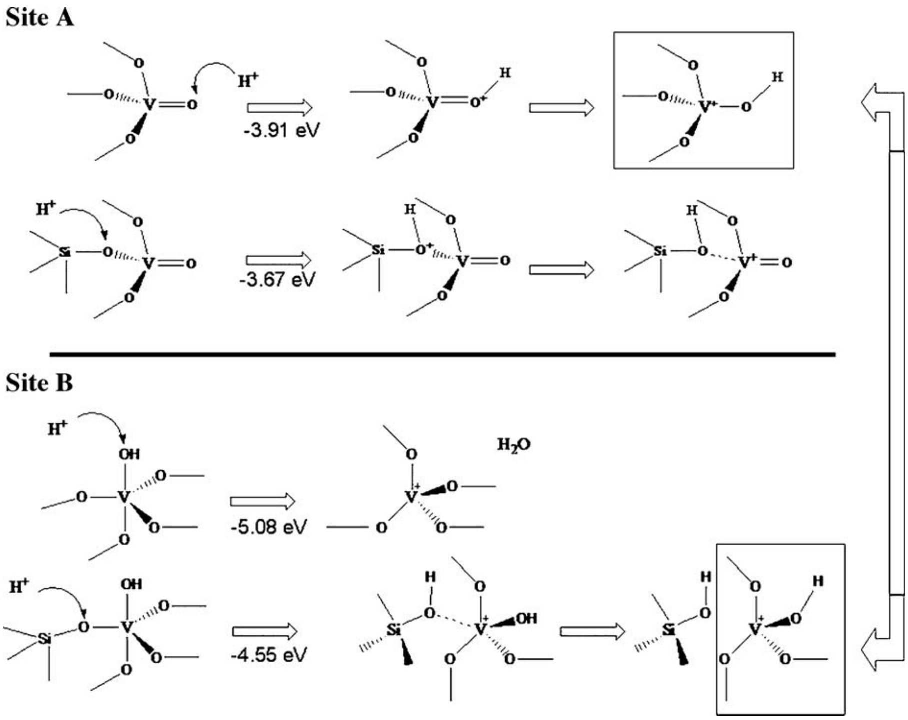

Fig. 2. Protonation of zeolite sites A and B leading to the reorganization of both sites. Both sites have a V in oxidation state +5. A possible conversion path between sites A and B is indicated with a bidirectional arrow.

on the vanadyl oxygen atom, and −3.67 eV considering an attack on the bridging oxygen atom. The bridging oxygen is, thus, found less basic, which was already predicted from the electrostatic potential and the electronic Fukui function on the same models [17,18]. It should be noted that the protonation of the vanadyl oxygen atom was found to be in competition with the protonation of silanol oxygen atom, and thus globally less basic in the zeolite than the energies show. The same result indicates that vanadium sites in zeolites have different chemical behavior than those observed for vanadium supported on reducible oxides, such as TiO_2 [38–41]. Indeed, vanadium supported on reducible oxides shows more reactive bridging oxygen atoms than vanadyl oxygen atoms.

If the oxygen of VO-H group is protonated (site B, Fig. 2), a hydrated tetrahedral $(VO_4)^+H_2O$ site is formed with protonation energy of −5.08 eV, while the protonation of the bridging oxygen, with energy of −4.55 eV, leads to the formation of tetrahedral hydroxylated $(VO_4OH)^+$ site by hydrolysis of the Si–O–V linkage and a reorganization of this site (Fig. 1). The latter site might lead to the formation of site A (see Fig. 2).

These results indicate that also for site B the bridging oxygen is less basic than the hydroxyl oxygen. Protonation of this site leads after reorganization (without energy barrier) to a tetrahedral V^+ Lewis acid site, which is observed experimentally [10]. Interesting, is that the protonation of the bridging oxygen atom of site B can lead to the formation of site A (see Fig. 2), with a calculated reaction energy gain for this process equal to (−4.55 − (−3.91) eV) −0.64 eV in favor of site A. Protonation of site B can thus lead to the site A, without taking into account kinetic and structural effects.

The terminal oxygen atoms, from vanadyl or V-OH groups, are in both sites the most reactive atom towards protonation. It was found that site A is the most stable site [14], and, protonation of its vanadyl oxygen is energetically less favorable than protonation of site B.

Site B (with V(V)) (Fig. 3) and site B′ (with V(IV)) (Fig. 3) have a deprotonation energy of 4.68 and 4.86 eV, respectively, which suggests that the VO-H groups of both sites are more acidic than the SiO-H groups (5.92 eV).

These theoretical results are in line with experimental FTIR data of adsorption pyridine, used as probe molecule for measuring acidity of O-H groups in SiBEA and VSiBEA zeolites [14,15]. Brønsted acidic character of O-H groups in the case of VSiBEA zeolites is confirmed by appearance of bands of pyridinium cations at 1542 cm^{-1} after adsorption of pyridine at room temperature. In contrast, this pyridinium cations IR band is not observed for SiBEA sample. In contrast, for both zeolite samples, the bands at 1638, 1596, 1580, 1490, 1485, 1446 and 1439 cm^{-1} are observed (results not shown) corresponding to pyridine interacting with Lewis acidic sites and/or physisorbed in line with earlier work [10]. The latter bands appear also for VSiBEA zeolite but with much higher intensity suggesting higher amounts of Lewis acidic sites than for SiBEA zeolite. These experimental results are in agreements with theoretical ones discussed above and confirm the formation of the tetrahedral V^+ Lewis acid site upon incorporation of vanadium ions into the framework of zeolite.

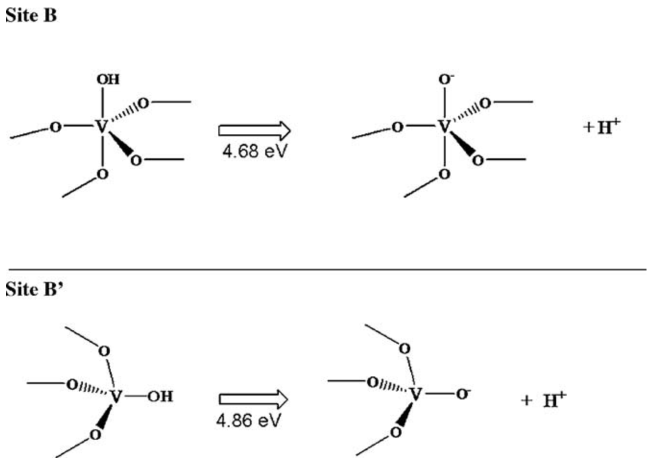

Fig. 3. Deprotonation of zeolite sites B and B′. The site B has the V and site B′ IV oxidation state.

Our theoretical results suggest in good relation with ab initio periodic DFT calculation data and first approximation that energetically, the model of tetrahedral V^+ Lewis acid site is created in the framework of V-loaded zeolite upon protonation (Fig. 2, site B).

Moreover, these results show that energetically, more favorable process is protonation, indicating that vanadium loaded zeolites are more basic than acidic. This result is in agreement with former theoretical results of Tielens et al. [17,18] using the theoretical reactivity descriptors, such as the electrostatic potential and Fukui functions, in group 5 loaded zeolite structures.

4. Conclusions

Periodic DFT calculations used in combination with FTIR investigations have evidenced that VO-H groups of V(V) and V(IV) framework sites are more acidic than SiO-H groups present in siliceous zeolites. It is important to mention that experimental FTIR measurements with adsorption of pyridine, used as probe molecule, allow distinguishing in VSiBEA zeolite both Lewis and Brønsted acidic sites. The geometry of Lewis acid site is found to be a tetrahedral V^+ site, and the Brønsted acid site a penta coordinated V sites having an OH group.

The theoretical calculations suggest that V sites present in V-loaded zeolite are more basic than acidic. It is found that the protonation of the least stable B site can lead to the formation of stable A site containing vanadyl group through proton exchange, which can be expected as the inter-conversion path between both sites.

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