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What do vanadium framework sites look like in redox model silicate zeolites?

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ABSTRACT

Ab initio periodic DFT calculations on the structural and energy properties of different model vanadium framework sites in vanadium-substituted zeolites containing sodalite cavities are presented and related to experimental FTIR measurements on V containing SiBEA zeolite. The vanadium framework sites are characterized by their calculated geometrical parameters, vibrational frequencies and deprotonation energies. Vanadium(V) is stabilized in the zeolite framework in two different tetrahedral sites: one in the form of a very stable vanadyl group and the other possessing a hydroxyl group. Tetrahedral vanadium(IV) sites, although much less favorable, are also present with a acidic hydroxyl group. Hydration of vanadium-substituted zeolites is an athermic process. Water does not affect the coordination of vanadium and remains in the center of the cavity. These results are fully consistent with experimental data and allow to identify the molecular structure of vanadium sites in a zeolite framework.

1. Introduction

Isomorphous substitution of tetrahedral (T) sites in molecular sieve materials gives the possibility to modify their acidic and/or redox catalytic properties. Different ways to perform such a substitution are known including direct hydrothermal synthesis or post-synthesis methods. The substituted element may be strongly or weakly bound to the framework. It was discovered that the isomorphous substitution of certain transition metals such as Ti or V into the zeolite lattice creates redox catalysts with efficient activity for the partial oxidation of hydrocarbons and alcohols, the epoxidation of olefins, the hydroxylation of aromatics or the ammoxidation of ketones [1–4]. These metal-substituted zeolites have opened new ways for many applications, not only in catalysis [1,2] but also in various photochemical processes, such as the decomposition of NO, the reduction of CO_2 with H_2O or the reduction of N_2O with CO [5–8].

There has been an ongoing effort to substitute other transition metals like chromium, niobium, tungsten, molybdenum or tantalum [7,9,10] in the framework of microporous and mesoporous materials, via direct hydrothermal synthesis, to provide the latter with interesting redox properties. Tungsten(VI) complexes, for instance, lead to the best catalysts for the epoxidation of olefins using H_2O_2 as the oxidant, whereas molybdenum(VI) catalysts are superior to the latter for the epoxidation of olefins with organic alkyl hydroperoxides. However, there are only a few papers on the direct synthesis of molybdenum(VI)- or tungsten(VI)-containing catalysts [7,11,12]. The amount of transition metal is usually low and proves that isomorphous substitution by direct synthesis is generally difficult [13–15]. The same difficulty has been encountered for vanadium(V) substitution by direct hydrothermal synthesis as reported for V-loaded silicalite [16].

Recently, it has been shown [17–19] that the incorporation of vanadium in the lattice T-sites of zeolite BEA is strongly favored when the latter is previously dealuminated by treatment with nitric acid solution. The V incorporation results from the reaction between the mononuclear cationic V species of the precursor solution and the silanol groups created by dealumination. This two-step post-synthesis method allows to incorporate V and to obtain different kinds of tetrahedral vanadium(V) species as evidenced by DR UV–vis, ^{51}V MAS NMR and photoluminescence spectroscopies [19–21]. Possible models of tetrahedral V species and their probable location in the BEA structure have been proposed [21].

To confirm the models derived from spectroscopic data, quantum chemical ab initio calculations are required. Calculations on gas-phase vanadium oxide clusters have been performed in order to investigate their structural and electronic properties [22–24]. Vanadium oxide clusters supported on metal oxides [25–28] as

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well as zeolitic materials have been investigated theoretically [29–33], in line with the present research topic.

In this work, Si lattice substitution by V is investigated in a sodalite (SOD) structure, chosen to mimic the zeolite and obtain in relatively short time ab initio calculations results. Different site models are proposed after a systematic theoretical study of the substitution of a T-site by vanadium metal. The results obtained are fully consistent with experimental data reported earlier [19–21] and permit to identify the molecular structure of the vanadium sites in a zeolitic framework.

2. Methodology

2.1. Computational details

All calculations are performed using ab initio plane-wave pseudopotential calculations implemented in VASP [34,35]. The Perdew–Burke–Ernzerhof (PBE) functional [36–38] has been chosen to perform the periodic DFT calculations with accuracy on the overall convergence tested elsewhere [39–42]. The valence electrons are treated explicitly and their interactions with the ionic cores are described by the Projector Augmented-Wave method (PAW) [43,44], 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 corrections [45]. 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.

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. The frequency calculations are performed considering only the Gamma point.

2.2. Description of the model

The sodalite structure (SOD), chosen to mimic the zeolite structure on the basis of quality/cost ratio, and usually referred to as the β-cage, contains a regular network of tetrahedral sites (T-sites) forming a truncated octahedron with a Si-atom at each vertex. The full optimized geometrical parameters of the sodalite (SOD) structure with 36 atoms ($Si_{12}O_{24}$) are in good agreement with previous experimental [46] and theoretical [47] data (Table 1).

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 and thus the modeling of the vanadium framework site. Nevertheless, it is a very suited model to perform periodic ab initio calculations and investigate the incorporation of vanadium into the zeolite framework.

In order to study the effect of the V framework site environment on the V/Si isomorphous substitution of a pure SiO_2 sodalite structure, several geometrical configurations are systematically investigated (Figs. 1 and 2). We start from the structure VSOD in which one silicon atom is isomorphously substituted by one vanadium atom. In this case, the oxidation state of vanadium is IV. To this structure, one can add H atoms, OH groups or O atoms. The structures are named following the notation: B (Bridging hydroxyl), T (Terminal OH group), V (Vanadyl group), and W (Physisorption of H_2O). The number at the end gives the oxidation state of vanadium. It is given in Arabic numbers in order not to confuse it with the symbol of vanadium.

Table 1
Geometrical parameters of sodalite SOD: comparison between experimental, earlier and present theoretical data (D: bond length, A: angle).

	Experimental data [46]	Theoretical data [47]	This work
a (Å)	8.827	8.91	8.935
D(Si–O) (Å)	1.585	1.60	1.626
A(Si–O–Si) (°)	109.5	109.5	109.5
A(O–Si–O) (°)	160.5	159.6	152.5
O Wyckoff position	0.6475	–	0.6469

Adding to VSOD one H atom gives site B3, one OH group site T5, one water molecule site W4, one dissociated water molecule site BT4, while the hydrolysis of the Si–O–V linkage gives site T4. These sites can be further oxidized, reduced, hydrated or isomerized. The interconnections between the sites are shown in Fig. 1.

In summary, we investigate 16 structures, where H, OH, H_2O, $H_2O + OH$ or $2H_2O$ are added to VSOD. It should be noted that the series presented in Figs. 1 and 2 are only a selection of the different possibilities and only the energetically most stable ones are retained.

3. Results and discussion

3.1. Geometry

The geometries are obtained after full optimization of the unit cell parameters and atom positions. The spin state is a doublet for the $3d^1$ V^{IV} and a singlet for the $3d^0$ V^V and the $3d^2$ V^{III}B3 structure. The inter-atomic distances (Table 2) of the optimized active sites are used to investigate the type of V–O bond present. The V–O bond length is a direct indicator of the oxidation state as well. Three ranges of V–O bond length are found in the models.

A short bond length (1.60 Å) is associated to a double bond, i.e., a vanadyl group. This group, stable despite the low coordination of oxygen is observed in vanadium oxide gas-phase clusters [22–24], crystals [48] and supported catalysts [26,49,50]. Such vanadyl bonds are found in BV4, V5, BV5 and BTV5.

Medium V–O bond lengths (1.70–1.80 Å) correspond to a single bond which is present in all sites.

The sites having a bridging hydroxyl show a longer D(V–O) bond length between 2.05 and 2.08 Å (see B3, BT4, BV4, BTT4). The V–OH bond lengths are around 1.9 Å. The model sites BV5 and BTV5 have one of their V–O bond lengths larger than 2.2 Å, a length associated to long range interactions, present in the bulk V_2O_5 material between successive layers [48]. Note, however, that, in our models, this indicates bond breaking to preserve tetrahedral coordination, as is the case for structure B5 formed from BV5 or V4 from BV4. Indeed, our calculated models indicate a high stability of tetrahedral vanadium (V4 regenerates BV4 without any activation barrier). Tetrahedral coordination is found for vanadium in small gas-phase clusters [22–24], while five-fold coordination is stabilized only for larger clusters [22]. Bulk V_2O_5 presents a distorted octahedral coordination with a long axial V–O distance separating layers as mentioned above. Vanadium coordination lower than four is not found to be stable.

Substituting Si by V into the SOD framework increases the volume of the unit cell by 0.2% to 2.4% depending on the vanadium site (cell parameter *a* see Table 2). The presence of $V{=}O$ and terminal V–OH groups expands the cell. The increase of the cell parameter *a* relative to the pure Si sodalite structure is 0.4% for the V^{IV} structure and 0.6% for the V^V structure. In contrast, the addition of bridging hydrogen atoms decreases the cell parameter. It is interesting to note that despite the addition of dissociated water molecule (H + OH) to V^{IV} site BT4, the volume of the cell is smaller compared to the V^V + OH site T5. This trend is observed, although less pronounced, after the addition of a second OH (site TT5) or