



Theoretical estimation of acid–base properties of Lewis and Brønsted centres at the V-W-O catalyst surface: water molecule as the probe in DFT calculations

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Abstract

In the present work, a theoretical investigation of water interaction with cluster models for fragments of V-W-O catalysts surface was performed to study the strength of Lewis and Brønsted sites. The clusters representing two adjacent metal sites in pentacoordinated oxygen environment were chosen as working models to mimic the crystalline vanadia-like species exposing (001) V_2O_5 face. Geometry, OH stretching frequencies and water binding energy were chosen as three computed parameters to characterise the Lewis acid and basic sites and Brønsted acid sites situated in varying environment. It was shown that for Brønsted sites these parameters for both the site itself and its adduct with water molecule varied coherently and correlated well with the site acidity. For Lewis sites the problem was more complex and only water binding energy combined with characteristic adsorption geometry was a good index for the strength of both types of sites: basic and acid ones. © 2004 Elsevier B.V. All rights reserved.

Keywords: V-W-O catalyst surface; Lewis and Brønsted sites; DFT

1. Introduction

Brønsted and Lewis sites play a key role in heterogeneous catalysis. Brønsted acid centres act as proton donors, Lewis acid sites as electron pair acceptors, while Lewis basic sites serve as electron pair donors. Their presence is crucial for such catalytic processes for e.g. hydrocarbon isomerisation, cracking, alkylation and selective catalytic reduction (SCR) of NO_x . They can be also involved in the redox reactions with the $Me^{n+}O^{n-}$ acid–base couple being often considered as the centre responsible for the hydrocarbon activation in oxidation of hydrocarbons. We have chosen mixed V_2O_5 - WO_3 catalyst used in SCR process as a model system to study the properties of such sites. This catalyst presents both Brønsted and Lewis acid sites as well as Lewis basic centres [1].

The ammonia and pyridine usually serve as probe molecules in spectroscopic experiments to compare the acidity of both types of acid sites. The specific bands 1200 and 1600 cm^{-1} (for ammonia adsorbed on Lewis sites) or

1435 – 1450 and 1660 cm^{-1} (for NH_3 adsorbed on Brønsted ones), are used also to estimate the amount of different acid sites present at catalyst surface [2]. The FT-IR experiments for pyridine adsorption show characteristic bands for Lewis acid sites (1446 , 1487 , 1575 – 1608 cm^{-1}) and Brønsted ones (1534 , 1635 – 1640 cm^{-1}) [3]. The results of TPD experiments allow to estimate the adsorption energy for ammonia as about 18 – 26 kcal/mol [4,5] or 22 – 28 kcal/mol [6] without specifying the type of the site. However, ammonia's ability to act as a reducing agent even at room temperature causes some problems with its usage as a probe molecule [7]. Other reasons for shortcomings of the adsorption measurements were discussed in the review [8]. Even employing model reactions to characterise the acidity of the surface sites often cannot distinguish between Brønsted and Lewis acid centres [9]. In theoretical approaches, the calculation of the proton affinity is used for comparison of the basicity of oxygen atoms and description of the strength of Brønsted acid sites created by proton (or hydrogen atom) adsorption (for calculations for V_2O_5 see for example: Chen and Yang [10], Zhanpeisov et al. [11], Witko and co workers [12,13], Hermann and co workers [14,15] and Yin et al. [16]). The information about Lewis acid sites, however, is incomplete

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and the direct comparison with experimental data is hardly possible. On the other hand, the vibrational analysis seems to be able to predict the strength of the Brønsted acid sites but some data show that it may be taken only as a preliminary prediction, not as their final characterisation. In our calculations, we show that a water molecule seems to be a good candidate for a model probe molecule in theoretical calculations to compare the strength of acid sites of both Brønsted and Lewis type.

2. Theory

DFT methodology and small local clusters of finite size were already shown to perform reasonably well for transition metal oxides, as well diatomic molecules as models of bulk oxides, where the atoms couple via local covalent bonding with some admixture of ionic bonding [12,17,18]. The structure of V_2O_5 surface is very complicated and its full description requires a sizeable cluster model. Our earlier investigations [19,20] have shown, however, that even small two-centre cluster may be useful in describing selected properties of surface fragments. In view of the main goal of this study, which concerns the analysis of acid–base properties of Lewis and Brønsted acid sites, we have focused on small clusters representing two adjacent metal sites, bridging oxygen and vanadyl/tungstyl oxygens. This sub-unit was previously shown to be a reasonable representation of the species present on (001) plane of V_2O_5 surface since its geometry agreed well with selected crystallographic data and vibrational modes of $V=O$, as well as $V-O-V$, were reasonably reproduced (for details see [20]).

Quantum chemical calculations were done with the use of modern electronic structure methodology based on the density functional theory (DFT). For the calculations the program package DMol of Molecular Simulations, Inc. [21] was applied. Geometry optimisation procedure was used to determine the minimum-energy structure of a system, starting from initial geometry guess. Other properties were computed after the geometry had been minimised. Electron exchange and correlation was described by the local spin density approximation based on the Vosco, Wilk and Nusair publication [22]. As the basis set, double numerical basis functions supplemented by polarisation functions (DNP) provided by the program package, was chosen equivalent to split-valence double-zeta plus polarisation basis set quality, accepted as the standard basis set in quantum chemistry. The inner core of optimised atoms was frozen. The redox conditions of the system were varied by changing total charge on the cluster. DMol software package was also used to calculate harmonic vibrational frequencies for all studied systems. For detailed energetic considerations which included determination of water binding energies on various sites, we have extended our calculational scheme by including nonlocal gradient-corrected exchange-correlation functional BPW91 with Becke exchange [23] and Perdew–Wang correlation

[24]. In this series of calculations we assumed LDA optimised geometries for each point and performed GGA energy calculations with selfconsistent potential and electron density. For further detail see [19,20].

As mentioned above the surface vanadia-like species formed in the process of oxidation-induced cation segregation in V_2O_5 - WO_3 solid solution [25] was chosen as a model system. The choice of a probe molecule was a crucial point of our investigations. We preliminary considered pyridine, ammonia, water, carbon oxide and molecular hydrogen. Wide spectrum of experimental data is based on pyridine and ammonia, which suggests these molecules as good candidates for a probe. However, the large size (pyridine) causing difficulties with distinguishing interactions of probe molecule with active sites or the ability to act as a reducing agent (ammonia) excluded these molecules from theoretical investigations. Molecular hydrogen, carbon oxide and water molecule, are small enough to properly describe their interaction with limited number of surface centres. However, the hydrogen molecule was excluded because it cannot be considered as a tool for Brønsted acid sites' characterisation. On the other hand, water is permanently present in reaction environment and our earlier investigations showed that water molecule can react with V-W-O surface, which finally led to the choice of water molecule as a probe. Moreover, water molecule can be used as a probe of both acidity and basicity of either Brønsted or Lewis sites within the same scheme. At the same time its weak interaction with all types of sites makes it more sensitive to subtle differences in the site properties, which could provide better analysis of small effects.

The calculations were performed for small clusters representing two adjacent metal sites in pentacoordinated oxygen environment, analogous to bipiramidal clusters introduced in description of the (001) surface of vanadium pentoxide [18] (Fig. 1A). This yielded the basal $V_2O_9H_8$ cluster as a working model of the vanadia-like surface species [19]. In this cluster two structurally inequivalent oxygen sites, terminal vanadyl oxygen and doubly bonded bridging oxygen were represented. These oxygen atoms are present at the (001) V_2O_5 surface. Other, originally triple-bridging peripheral oxygens were artificially saturated by hydrogen atoms, thus they could not be described by our model. Geometrical structure of the $V_2O_9H_8$ cluster was fully relaxed and optimised. In this structure tungsten might replace vanadium in V_2O_5 system forming WO_3 - V_2O_5 solid solution [20]. Substitution of W^{6+} for V^{5+} would render the cluster charge equal to +1. It is frequently assumed, however, that introducing of metal ion M^{6+} into the V_2O_5 lattice is accompanied by reduction of vanadium from V^{5+} to V^{4+} to maintain lattice neutrality [26]. This finally leads to several clusters needed to properly describe prospective vanadia-like surface species: $[V^{5+}V^{5+}O_9H_8]^0$, $[V^{5+}V^{4+}O_9H_8]^-$, $[V^{4+}V^{4+}O_9H_8]^{2-}$, $[V^{5+}W^{6+}O_9H_8]^+$, $[V^{4+}W^{6+}O_9H_8]^0$ and $[W^{6+}W^{6+}O_9H_8]^{2+}$ (for detailed description see [20]). We excluded $[V^{4+}V^{4+}O_9H_8]^{2-}$ cluster

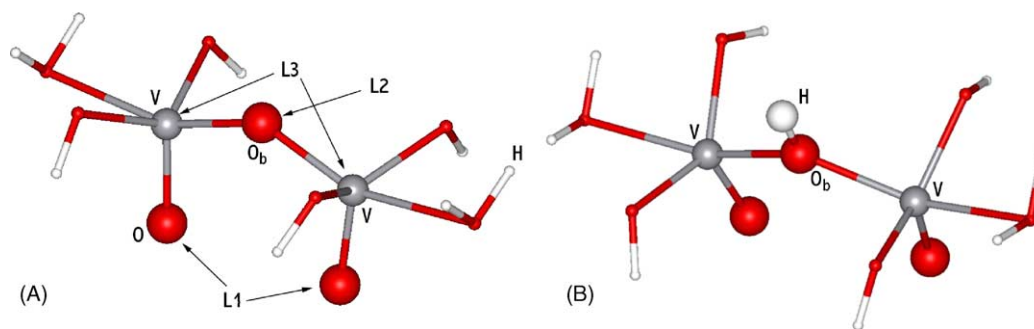


Fig. 1. Geometry of the (A) $[V^{5+}V^{5+}O_9H_8]$ cluster and the (B) $[V^{5+}V^{5+}O_9H_8H]^+$ cluster.

from our considerations because for this strongly negatively charged cluster the assumed calculational scheme could lead to less reliable results. Moreover, statistical analysis showed that such unit may appear on the surface with only very small probability.

On the ideal V_2O_5 (001) plane only the Lewis acid (V^{5+} ions) and basic (vanadyl and bridging oxygens) sites are present. Our previous calculations [20] showed, however, that on V-W-O system the dissociation of water molecule could occur on Lewis sites and lead additionally to the creation of new Brønsted acid sites associated with an OH group bonded to tungsten atom or with proton adsorption on bridging oxygen atom. Vibrational analysis shows that these two OH types can be easily separated and distinguished from the other OH's, artificially created by saturating broken bonds on the cluster boundaries. They are well resolved and decoupled from other vibrations while artificially created ones are usually strongly coupled. The additional acid sites created by water dissociation increase the number and variety of acid–base centres on the surface and probably could be responsible for wider temperature window for mixed vanadia-tungsta catalysts in SCR processes. In this work three types of Lewis sites and one type of Brønsted acid sites were chosen for further investigation. This selection stems from our assessment of the limitations of our model and its predictive reliability. Basic Lewis sites associated with vanadyl/tungstyl oxygen atoms (L1) and with doubly bonded bridging oxygen atom (L2) as well as acid Lewis ones associated with metal Me^{n+} ions (L3) are shown schematically in Fig. 1A Brønsted acid sites associated with proton situated on bridging oxygen atom (O_b) are shown in Fig. 1B.

Thus finally the DFT calculations were carried out for the following clusters: $[V^{5+}V^{4+}O_9H_8]^-$, $[V^{5+}V^{5+}O_9H_8]^0$, $[V^{5+}W^{6+}O_9H_8]^+$, $[V^{4+}W^{6+}O_9H_8]^0$ and $[W^{6+}W^{6+}O_9H_8]^{2+}$ to analyse the acidity and basicity of the Lewis sites. The Brønsted sites acidity was analysed for the following clusters: $[V^{5+}V^{4+}O_9H_8(H)]^0$, $[V^{5+}V^{5+}O_9H_8(H)]^+$, $[V^{4+}W^{6+}O_9H_8(H)]^+$, $[V^{5+}W^{6+}O_9H_8(H)]^{2+}$ and $[W^{6+}W^{6+}O_9H_8(H)]^{3+}$. One could question the choice of not neutral clusters for investigations. However, it must be taken into account that in working conditions charge equilibration of the surface refers to whole catalyst and locally uncompensated charges cannot be excluded. Moreover, such local

diversity of surface structure has already been detected experimentally by XPS and Raman spectroscopy. The strength of selected acid and basic centres was investigated by analysis of bond distances, charge displacement, calculated OH stretching frequencies and finally the energy gain caused by water interaction with the centres (BE). Water molecule was placed in the vicinity of studied sites and the geometry of the system was re-optimised. BE was estimated within nonlocal approximation from the total energy difference between the final system and the initial system composed of isolated water molecule and the cluster. Calculated BE could be compared with relevant data from experimental approaches: with the strength of bonding of probe acids and bases to the surface evaluated from the heat of their adsorption, with the desorption temperature in TPD measurements or with a shift of the IR bands of adsorbed model compounds.

3. Results and discussion

3.1. Brønsted acid sites

The results of vibrational and population analyses of the bare clusters with proton adsorbed on bridging oxygen were used for preliminary comparison of the Brønsted sites acidity (see columns 2 and 3 in Table 1). The calculated OH stretching frequencies correlate very well with the results of population analysis (see Fig. 2). They suggest that the oxidised vanadium–tungsten system should show the strongest acidity of such sites.

To extend the analysis of the strength of the Brønsted acid sites, we studied the interaction of H_2O probe molecule with the model system (for geometry of the composed system see Fig. 3). Water adsorption energy (BE) served as the indicator of the stability of the water binding and the main parameter characterising the Brønsted centres acidity. The distance between water molecule and adsorption site ($d_{OH...OH_2}$) and the charge on the water molecule (q_{aq}) served as the additional parameters describing acidity of the sites. All these parameters are collected in Table 1. They change coherently during oxidation of the system or tungsten substitution and correlate well with $q_{H_{ads}}$ and stretching frequencies ν_{OH} which were selected as preliminary acidity

Table 1

Parameter chosen for preliminary description of the strength of Brønsted acid sites: OH stretching frequency, charge on adsorbed proton and change of charge on bridging oxygen after proton adsorption, water binding energy, distance between adsorbed water and the Brønsted acid sites and total charge on adsorbed water

Cluster	Bare cluster			Cluster interacting with water		
	$\nu_{\text{OH}=\text{O}}$ (cm^{-1})	$q_{\text{H}_{\text{ads}}}$	q_{O_b}	BE (kcal/mol)	$d_{\text{OH}\cdots\text{OH}_2}$ (Å)	q_{aq}
$[\text{V}^{5+}\text{V}^{4+}\text{O}_9\text{H}_8\text{H}]^0$	3587.8	0.182	0.076	-2.0	1.54	0.199
$[\text{V}^{5+}\text{V}^{5+}\text{O}_9\text{H}_8\text{H}]^+$	3533.2	0.206	0.062	-14.2	1.51	0.242
$[\text{V}^{4+}\text{V}^{6+}\text{O}_9\text{H}_8\text{H}]^+$	3551.6	0.203	0.055	-9.9	1.47	0.250
$[\text{V}^{5+}\text{V}^{6+}\text{O}_9\text{H}_8\text{H}]^{2+}$	3485.7	0.229	0.053	-20.6	1.32	0.347
$[\text{W}^{6+}\text{W}^{6+}\text{O}_9\text{H}_8\text{H}]^{3+}$	3444.8	0.238	0.042	-32.7	1.10	0.530

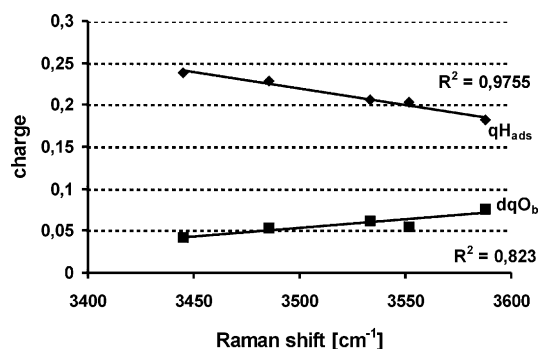


Fig. 2. Relation between population analysis and calculated vibrational frequencies for OH groups in modelled clusters. R is correlation coefficient.

indices for bare clusters (the correlation of calculated BE with other parameters is shown on Fig. 4). The analysis of the water interaction with the Brønsted acid sites shows clearly that tungsten substitution and changing redox conditions essentially influence it. The interaction of water becomes modified from the weak one for reduced vanadium cluster $[\text{V}^{5+}\text{V}^{4+}\text{O}_9\text{H}_8(\text{H})]^0$ (Fig. 3A, BE = -2.0 kcal/mol, $d_{\text{OH}\cdots\text{OH}_2} = 1.54$ Å), through the strong one for oxidised vanadium-tungsten cluster $[\text{V}^{5+}\text{W}^{6+}\text{O}_9\text{H}_8(\text{H})]^{2+}$ (Fig. 3B, BE = -20.6 kcal/mol, $d_{\text{OH}\cdots\text{OH}_2} = 1.32$ Å) up to the very strong one when water molecule adsorption on oxidised tungsten cluster $[\text{W}^{6+}\text{W}^{6+}\text{O}_9\text{H}_8(\text{H})]^{3+}$ leads to H_3O^+ ion creation (Fig. 3C, BE = -32.7 kcal/mol, $d_{\text{OH}\cdots\text{OH}_2} = 1.10$ Å).

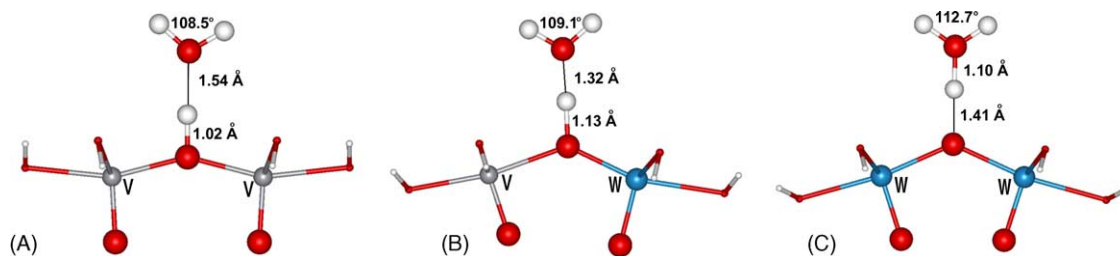


Fig. 3. Geometry of the water interacting with Brønsted acid sites on: (A) $[\text{V}^{5+}\text{V}^{4+}\text{O}_9\text{H}_8\text{H}]^0$ cluster, (B) $[\text{V}^{5+}\text{W}^{6+}\text{O}_9\text{H}_8\text{H}]^{2+}$ and (C) $[\text{W}^{6+}\text{W}^{6+}\text{O}_9\text{H}_8\text{H}]^{3+}$.

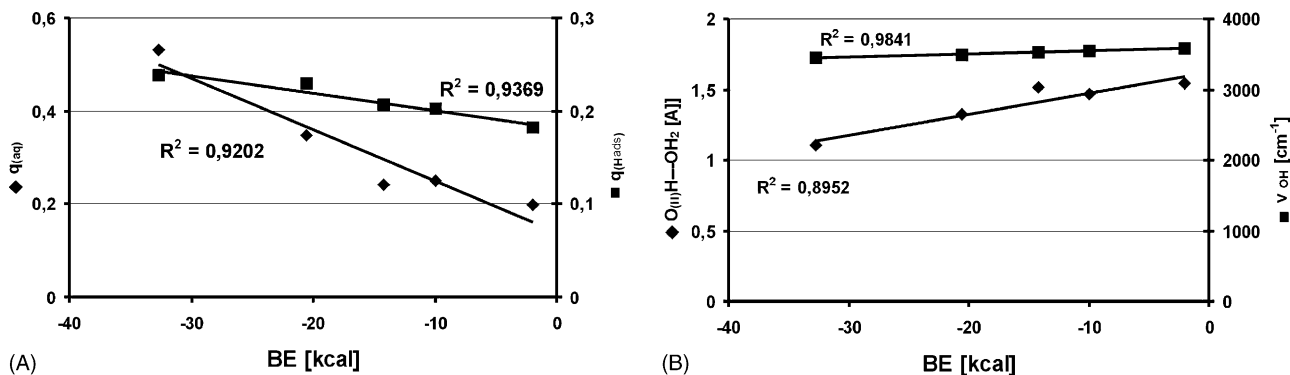


Fig. 4. Relation between water adsorption energy (BE) and charges (A) (◆) localised on water molecule and (■) localised on Brønsted proton; BE and distance (◆) between acid sites and water molecule or BE and calculated vibrational frequencies (■) (B). R is correlation coefficient.

3.2. Lewis sites

Description of the acidity or basicity of Lewis sites is more difficult due to their complex nature. Proton is not adsorbed on Lewis acid sites and thus deprotonation energy cannot be the probe for their acidity. The prediction of the strength of the Lewis basic sites (vanadyl/tungstyl oxygens and bridging oxygens) or Lewis acid sites (metal ions) from vibrational or population analysis of the clusters also seems to be ambiguous. In addition, there is a coexistence of different sites of both acid and basic character on the surface. Thus separate investigation of the interaction between each of these sites and a probe molecule used in spectroscopy (like pyridine or ammonia) is hardly possible in experiment and not diagnostic in model studies. Therefore the water molecule is postulated here again as a good probe, what was already discussed in previous sections.

Table 2 shows collected parameters for description of Lewis sites. The table is arranged in a following way: cluster symbols are placed in the first column of the table, vanadyl group frequencies follow in the second column. In column 3, binding energies of water molecule with vanadyl/tungstyl oxygens (L1 Lewis basic sites) are placed. In columns 4 and 5, BE of water molecule with vanadium ion and distances between water oxygen and a metal site are collected. Analogous data shown in column 6 and 7 concern water molecule placed in the tungsten ion vicinity. Numbers given in columns 4–7 actually describe not only interaction of water molecule with L3 Lewis acid sites but also simultaneous interaction with L2 Lewis basic sites.

3.3. Lewis basic centres L1

In the case of pure vanadia system the strongest binding (Table 2, col. 3) occurs for the water molecule interacting by hydrogen bonding with vanadyl oxygens of the reduced cluster (for geometry see Fig. 5). This remains in agreement with the previous studies indicating the pair of vanadyl oxygens as the preferred adsorption site for water in pure vanadia system [27]. For mixed vanadia–tungsta clusters water interaction with the vanadyl/tungstyl oxygens also stabilises the neutral system but the energy gain is smaller.

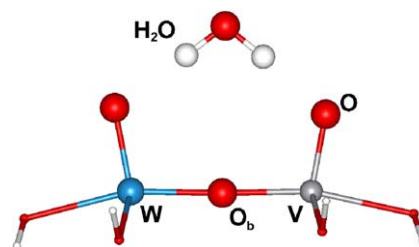


Fig. 5. Geometry of the water interacting with L1 Lewis basic sites on $[V^{4+}W^{6+}O_9H_8]^0$ cluster.

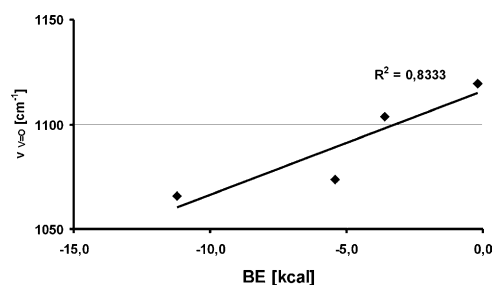


Fig. 6. Relation between water adsorption energy (BE) and calculated vibrational frequencies for V=O/W=O groups. R is correlation coefficient.

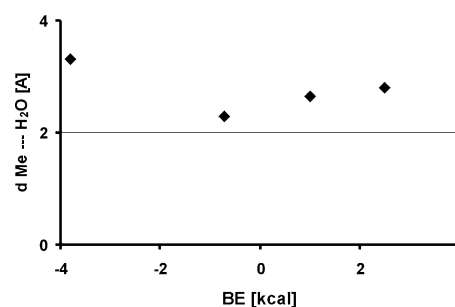


Fig. 7. Relation between water adsorption energy (BE) and distance between vanadium ion and water molecule.

3.4. Lewis centres L2 and L3

Taking together all investigated Lewis centres we can assume that neither calculated V=O/W=O frequencies nor geometry parameters of adsorbed water give satisfactory description of surface acid–base properties (see Figs. 6 and 7). Vibrational analysis gives isolated and well-resolved V=O and W=O frequencies but they are associated both

Table 2

Parameters chosen for description of Lewis sites: V=O stretching frequency, water binding energy, distance between adsorbed water and the metal sites

Cluster	$\nu_{V=O}$ (cm^{-1})	Lewis centres L1		Lewis centres L2 and L3		
		BE_{L1} (kcal/mol)	BE_V (kcal/mol)	$d_{V...OH_2}$ (Å)	BE_W (kcal/mol)	$d_{W...OH_2}$ (Å)
$[V^{5+}V^{4+}O_9H_8H]^-$	1065.7 _(sym)	−11.2	−3.8	3.31	–	–
$[V^{5+}V^{5+}O_9H_8H]^0$	1103.6 _(sym)	−3.6	1.0	2.64	–	–
$[V^{4+}V^{6+}O_9H_8H]^0$	1073.7	−5.4	2.5	2.80	0.3	2.46
$[V^{5+}V^{6+}O_9H_8H]^0$	1119.3	−11.2	−0.7	2.30	−8.8	2.38

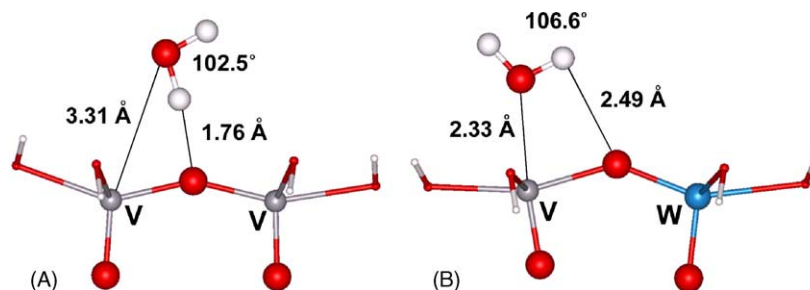


Fig. 8. Geometries of the water interacting with L2 Lewis acid and basic sites on (A) $[V^{5+}V^{4+}O_9H_8]^-$ cluster and (B) $[V^{5+}W^{6+}O_9H_8]^+$ cluster.

with basic vanadyl/tungstyl oxygens and acidic metal ions thus they cannot distinguish these two sites. The possible simultaneous interaction of water with metal ions and the bridging oxygen also makes analysis of the acid–base properties from geometrical parameters difficult. The adsorption energy of water (probe molecule) seems to be the most reliable parameter to analyse the Lewis acidity and basicity.

Non-negligible water binding energy (Table 2, col. 4) emerged for the vanadium centres of reduced cluster. In this system water molecule interacts not only by lone pair from the water oxygen with acid Lewis sites (V^{4+}) but additionally by hydrogen bonds with basic bridging oxygen (Fig. 8A). Quite different results show up for neutral vanadium cluster $[V^{5+}V^{5+}O_9H_8]^0$ and mixed vanadia-tungsta clusters $[V^{5+}W^{6+}O_9H_8]^+$, $[V^{4+}W^{6+}O_9H_8]^0$ where weak water adsorption takes place only by lone pair from the water oxygen with acid sites—the vanadium or tungsten centres (Table 2, col. 4 and 6, Fig. 8B). However, only after substitution of vanadium by tungsten in oxidising conditions the stability of the water bound to the metal ion is substantial. For the neutral mixed cluster the bonding of water on metal-acid sites strongly diminishes. In summary, inspection of the BE values described in Table 2 leads to the following conclusions. Stable water binding may occur on the metal site either in the case of reduced vanadia, where co-operation of both acid and basic Lewis centres (L3 and L2) occurs, or in the case of oxidised vanadia–tungsta system, where tungsten substitution and cluster oxidation makes the metal ion more electrophilic.

Detailed analysis of the water interaction with studied clusters shows that the modelled V–W–O surface contains different acid and basic Lewis sites, which can either compete or co-operate. Vanadium and tungsten Lewis acid sites and basic oxygen atoms may compete for a water molecule or the water may co-operatively interact with both bridging oxygen and a metal centre. This shows how complex situations may occur on mixed oxide surfaces.

4. Conclusions

Presented results show that for Brønsted sites, all chosen parameters were coherent and could be useful for description of the strength of the Brønsted acid site. All parameters

(calculated OH stretching frequencies ν_{OH} , proton charge q_{Hads} , charge on the interacting water molecule q_{aq} , the distance between water molecule and adsorption site $d_{OH...OH_2}$, water adsorption energy—BE) for both the site itself and its adduct with water molecule varied coherently and correlated well with the site acidity. For Lewis sites the problem was much more complex. The geometry parameters and vibrational analysis could not satisfactorily describe Lewis acid and basic centres. Only water binding energy together with characteristic adsorption geometry was a good index for the strength of both basic and acid sites.

By the use of water as the model probe molecule, one could analyse the process of competition and co-operation of different acidic and basic centres even when situated close to each other. Moreover, it was possible to compare the strength of acid Lewis and Brønsted sites within the same scheme.

All the results obtained for (001) V–W–O catalysts surface showed that the strength of the Brønsted acid sites as well as Lewis acid sites increased during tungsten substitution and oxidation of the surface. Opposite behaviour was observed for the strength of Lewis basic sites. The biggest energy gain caused by water interaction with the centres was observed for the reduced system $[V^{5+}V^{4+}O_9H_8]^-$.

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