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Conceptual chemistry approach towards the support effect in supported vanadium oxides: Valence bond calculations on the ionicity of vanadium catalysts

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ABSTRACT

The concept of bond ionicity, obtained via a valence bond analysis, is invoked in the interpretation of the catalytic activity of supported vanadium oxides, in analogy with previous work conducted within the framework of conceptual DFT. For a set of model clusters representing the vanadium oxide supported on SiO_2, Al_2O_3, TiO_2, ZrO_2, the ionic character of the vanadium-oxygen bond, involved in the dissociative adsorption of methanol on the catalyst, was quantified. Detailed scrutiny shows that this ionicity increases from the Al through the Zr support, in agreement with the increasing catalytic activity through this series; the case of the Si supported oxide is found to be an exception however, giving rise to the most ionic V–O bond of the different compounds studied. This finding is confirmed by calculations on smaller clusters focusing on detail in the π back bonding.

1. Introduction

Supported vanadium oxides constitute an important class of heterogeneous catalysts and consist of a vanadium oxide phase dispersed on the surface of another oxide [1–3]. Originally, it was assumed that the oxide support improved the catalytic activity due to both the increased surface area and the higher mechanical strength of the material. However, later on, it was suggested that other effects should be invoked in order to explain the increased selectivity and activity of the catalytic material [4]. This effect was "generically" termed the "support effect" and the nature of this effect remains an important topic for literature debate. In the last two decades, computational chemistry and molecular modelling has proved to be an invaluable tool for the microscopic study of many catalytic processes in heterogeneous catalysis; for examples applied to the series of systems considered in this work, see, e.g. Ref. [5–12]. Many ab initio methods, sometimes combined with molecular mechanics force field approach afford the theoretical treatment of the catalytic reactions with ever-increasing accuracy and increasing size of the system that can be computed. This enables the first principles identification of reactive species emerging during the catalytic process and the calculation of thermodynamic properties, such as reaction energies and activation barriers. Confrontation of computed quantities with experimental data then offers the possibility to emphasize the existence of certain intermediates and mechanisms. Nevertheless, it still remains important in chemistry and in catalysis to have a set of rules of thumb and concepts discussing activity and offering explanations for certain observed chemical phenomena. Concepts have a central place in chemistry but were usually put forward in an empirical way. Quantum chemistry also has provided the opportunity to formulate chemical concepts from first principles and to provide non-empirical ways to compute them. An appealing methodology in this aspect is valence bond theory, expressing the wavefunction from a chemical point of view and affording the description of chemical bonds, that are central in chemistry, as a mixture of polar and covalent terms [13,14]. Another source of chemical concepts is the so-called conceptual density functional theory [15]. In this branch of density functional theory, chemical concepts, such as electronegativity [16,17], hardness [18–21], and softness [18,19,22] are identified as response functions of the energy of a chemical system with respect to perturbations in its number of electrons and/or external (i.e. due to the nuclei) potential. These concepts have been invoked numerous times in the discussion of chemical reactivity in organic, inorganic, biochemistry and also catalysis. Cohen and co-workers also considered these concepts within the framework of materials science and surface chemistry [23].

Initially, the difference in electronegativity between the different supports have been used to explain the metal oxide support

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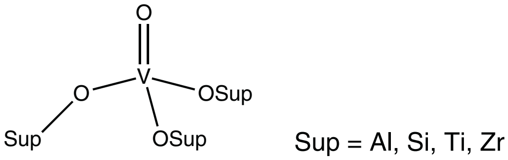
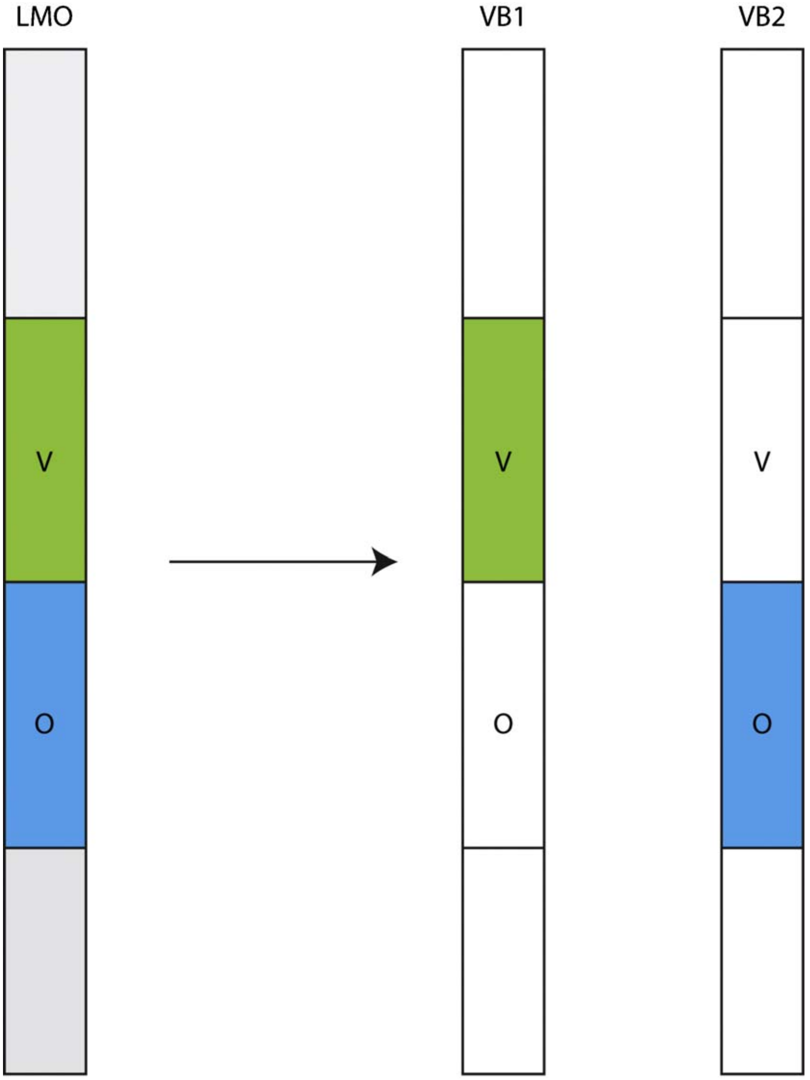
effect [24]. In the model cluster $VO(OH)_3$, the hydroxyl groups were replaced by $OSi(OH)_3$, $OTi(OH)_3$ and $OZr(OH)_3$ to model the effect of the changing support. It was shown that the resulting Sanderson electronegativity [25] of the clusters was strongly dependent on the electronegativity of the substituting metal atom. Moreover, the atomic charge of the bridging oxygen in the V–O–S linkage, obtained by the Sanderson electronegativity equalization principle [25], becomes more negative with decreasing electronegativity of the metal S, in agreement with the increase of turnover frequencies for methanol oxidation on supported vanadium oxides. The charge on V however is more positive with increasing electronegativity of S. These results clearly show that the support has an influence on the charge separation in the V–O(–S) bonds. Experimentally, atomic XAFS experiments have probed directly the changes in the electronic nature of V and reported relations between the electron charge on support oxygen atoms and the catalytic activity [26].

Calatayud et al. computed reactivity indices, such as the electrostatic potential and Fukui function, based on periodic calculations, to explain the different chemical reactivity found for oxygen sites in V_2O_5 systems [27]. In our previous contribution, the catalytic activity of supported vanadium oxides and more specifically, the support effect, was investigated using DFT based reactivity indices [28]. Starting from a simple model for isolated vanadium oxides supported on SiO_2, Al_2O_3, TiO_2, ZrO_2 a detailed investigation of the reaction mechanism for methanol oxidation on these catalysts was conducted. These results followed the current insights into the reaction mechanism and provided a new and interesting way for rationalizing the support-effect based on the concept of bond-ionicity as probed by computed electrostatic potential based atomic charges for the vanadium and oxygen atoms. The origin of this rationalization was further investigated by visualizing the density of the determining Vanadium–Oxygen–Support structure for the different supports. On the basis of an analysis of the Electron Localization Function [29] on $OV(OH)_3$ and $OV(OTiO_2H)_3$ clusters, it was concluded that all V–O bonds can be classified as ionic [30].

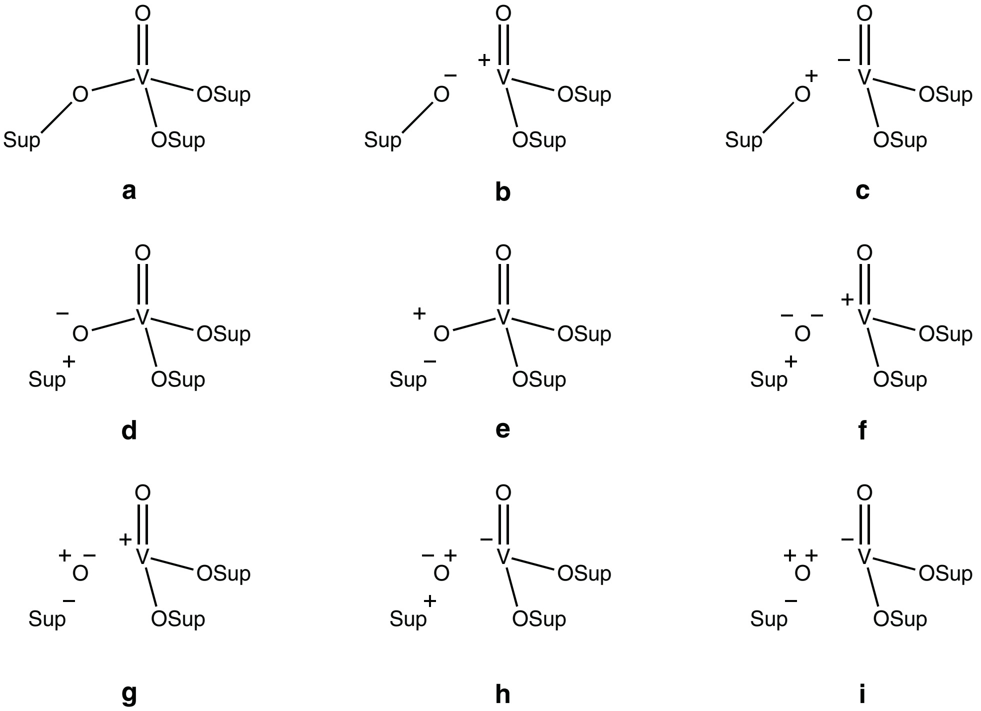
In the present contribution, these systems will be revisited using valence bond methods affording a clear-cut and unambiguous definition of ionicity.



Scheme 1. Schematic representation of the clusters under study.



Scheme 2. Schematic representation of the division of localised σ bonds in two VB orbitals that are subsequently spin-coupled to represent the bond.



Scheme 3. The nine different Valence Bond structures in the VB calculations.

2. Theory and computational details

In Valence Bond (VB) theory, the wavefunction Ψ is written in terms of structures Φ that resemble Lewis structures ($\Psi = \sum_i c_i \Phi_i$). A bond in each structure is formed by spin-coupling two orbitals φ in a singlet, $|\varphi_1\bar{\varphi}_2| - |\bar{\varphi}_1\varphi_2|$, and the final structure is the antisymmetrised product of all bonds $\Phi = \hat{A}(|\varphi_1\bar{\varphi}_2| - |\bar{\varphi}_1\varphi_2|)(|\varphi_3\bar{\varphi}_4| - |\bar{\varphi}_3\varphi_4|)(\cdots)$. The orbitals used to build the structures are expanded in basis functions, and may be optimised.

To study the ionicity of a bond, the key concept in the present contribution, using VB theory, the bond is described as consisting from three structures, *viz.* the covalent structure $\Phi_1 = |\varphi_1\bar{\varphi}_2| - |\bar{\varphi}_1\varphi_2|$, and two ionic structures $\Phi_2 = |\varphi_1\bar{\varphi}_1|$ and $\Phi_3 = |\varphi_2\bar{\varphi}_2|$. The wavefunction then becomes $\Psi = \sum_{i=1}^{3} c_i\Phi_i$. Both the orbitals and the structure coefficients (c_i) are determined variationally. Weights (W) to the structures can be assigned following Gallup and Norbeck [31],

$$W_i = \frac{N|c_i|^2}{(\mathbf{S}^{-1})_{ii}} \qquad N^{-1} = \sum_i \frac{|c_i|^2}{(\mathbf{S}^{-1})_{ii}}$$

with $\mathbf{S}^{-1}$ the inverse of the overlap matrix of the structures, and N a normalisation constant. The importance of the ionic structures in the wavefunction is a measure of the ionicity of the bond.

The geometries of the model compounds used to represent the different supported vanadium oxides, given in Scheme 1 and used in the VB calculations, were taken from a previous study [28]. The VB calculations on the structures were performed using the 6-31G basis set, except for V and Zr for which an ECP LANL2-DZ basis was used. The TURTLE [32] package as implemented in GAMESS-UK [33] was used for all the calculations.

The start orbitals for the VB calculations were generated in the following way: first, a RHF calculation was performed, and subsequently, the canonical RHF orbitals were localised with the Pipek–Mezey scheme [34]. For one particular V–O–Support oxygen atom, the two σ bonds to vanadium and to the support were selected, together with its core and lone-pair orbitals. Each σ bond was split into two atomic centred VB orbitals (Scheme 2) and the undesired contributing atomic orbital coefficients from atomic orbitals centred on other atoms set to zero. The two atomic centred VB orbitals were spin coupled to form the bond. All other bonds were described using the localised orbitals.

The orbitals in the VB calculations on the clusters were optimised with a VB wavefunction consisting of only the covalent structure **a** (Scheme 3). The core orbitals were kept frozen. During the optimisation, the orbitals on one oxygen were constrained to remain purely atomic, and the orbitals of the other atoms were allowed to delocalise completely, except to the oxygen atom of interest. Following the VBSCF calculation with one structure, a VBCI calculation was performed with the covalent structure and eight ionic structures (Scheme 3).

As stated in the introduction, we have modelled the supported vanadium oxide catalyst by a series of cluster models, based on the model proposed by Khaliullin and Bell; [6] this model consists of a distorted tetrahedral unit with one V=O bond and three V–O bonds, connecting further to the support oxide. This oxide is mimicked by one support atom for each anchor point. All the dangling bonds on the support are then terminated by the corresponding number of hydroxyl-groups. All interactomic distances were allowed to relax. This cluster size (around 25 atoms) ensures an acceptable, although already quite considerable, computational cost for the valence bond calculations. In our previous work, it was shown that all bond distances were in reasonable agreement with experimental observations and, although the vibrational frequencies of the V=O bonds are systematically overestimated by 30–35 cm^{-1}, their trend between the different support is largely retained.

Calculations to study the π back bonding effect were performed on smaller $OV(OH)_2OMH_n$ ($MH_n = AlH_2, TiH_3, SiH_3$, and ZrH_3) clusters. The geometries of these clusters were taken from the larger clusters, and only the positions of the H-atoms were optimised. The smaller clusters allowed the use of the somewhat larger 6-31G* basis set, combined with the ECP LANL2-DZ basis set for V and Zr. To describe the π back bonding from O to V, empty d-orbitals

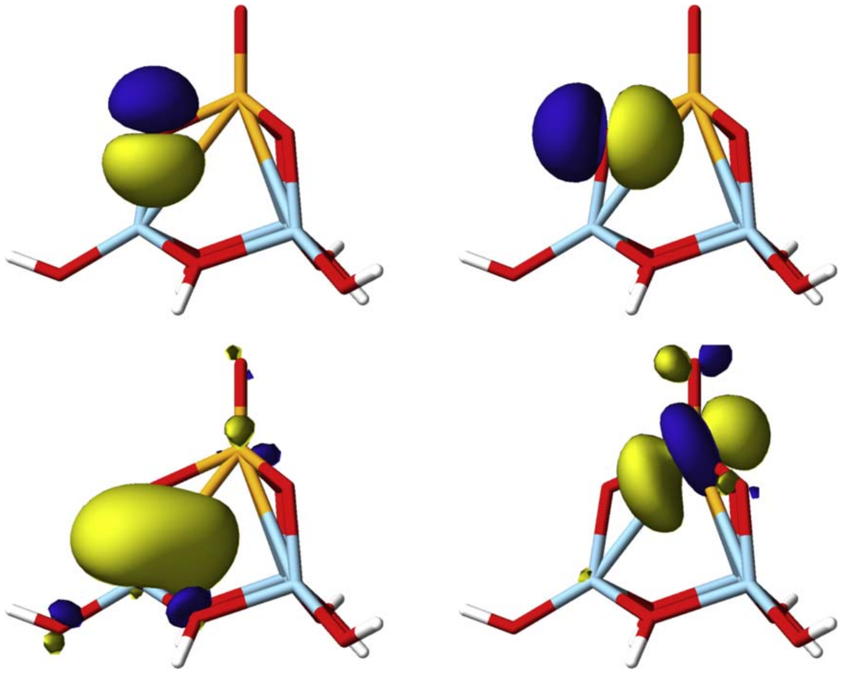


Fig. 1. The VBSCF optimised orbitals of the Al-cluster (when optimising all valence orbitals).

were added to V, and extra structures in which the formal lone-pair on oxygen forms a covalent bond with the V d-orbitals were added.

Table 1
Total energies (Hartree) of the clusters.

Support	E_{HF}	E_{VB}-1 struc	E_{VB}-9 struc
Al	−1548.93092	−1548.59875	−1548.85485
Si	−1915.94701	−1915.64973	−1915.84847
Si-4[a]	−1915.94701	−1915.49418	−1915.91106
Ti	−3594.52363	−3594.23141	−3594.42510
Ti-4[a]	−3594.52363	−3594.19040	−3594.43744
Zr-4[a]	−1187.92825	−1187.54554	−1187.84439

[a] Only the four orbitals involved in the two σ bonds are optimised.

3. Results and discussion

The total energies of the larger clusters, obtained at the RHF and VB levels, are shown in Table 1; the weights of the various structures in the VBCI calculations are given in Table 2 and the energies of the structures are listed in Table 3. As expected, in all cases, the RHF level gives the lowest energy: the one-structure VB calculation is

Table 2
Weights of the different structures in the VBCI calculations.

Structure	Al	Si	Si-4[a]	Ti	Ti-4[a]	Zr-4[a]
a	0.298	0.367	0.137	0.395	0.339	0.243
b	0.138	0.059	0.336	0.058	0.183	0.212
c	0.002	0.000	0.000	0.000	0.003	0.001
d	0.475	0.537	0.325	0.511	0.396	0.437
e	0.000	0.000	0.000	0.002	0.001	0.000
f	0.048	0.020	0.176	0.013	0.043	0.057
g	0.008	0.004	0.018	0.005	0.011	0.011
h	0.031	0.012	0.008	0.016	0.025	0.039
i	0.000	0.000	0.000	0.000	0.000	0.000

[a] Only the four orbitals involved in the two σ bonds are optimised.

Table 3
Energies of the different structures in the VBCI calculations.

Struc	Al	Si	Si-4[a]	Ti	Ti-4[a]	Zr-4[a]
a	−1548.59875	−1915.64973	−1915.49418	−3594.23141	−3594.19040	−1187.54554
b	−1548.49756	−1915.51183	−1915.64096	−3594.08016	−3594.10096	−1187.51112
c	−1547.76151	−1914.84200	−1914.50698	−3593.44546	−3593.34937	−1186.68248
d	−1548.60034	−1915.61972	−1915.57109	−3594.20929	−3594.17536	−1187.61007
e	−1547.79026	−1914.79625	−1914.51605	−3593.38429	−3593.34506	−1186.73594
f	−1548.17577	−1915.18118	−1915.37037	−3593.72515	−3593.75678	−1187.19978
g	−1547.98556	−1914.93166	−1914.97754	−3593.55626	−3593.57142	−1187.06163
h	−1548.07563	−1915.10720	−1914.91177	−3593.75088	−3593.65080	−1187.11641
i	−1546.66717	−1913.71970	−1913.22994	−3592.27983	−3592.19902	−1185.51606

[a] Only the four orbitals involved in the two σ bonds are optimised.

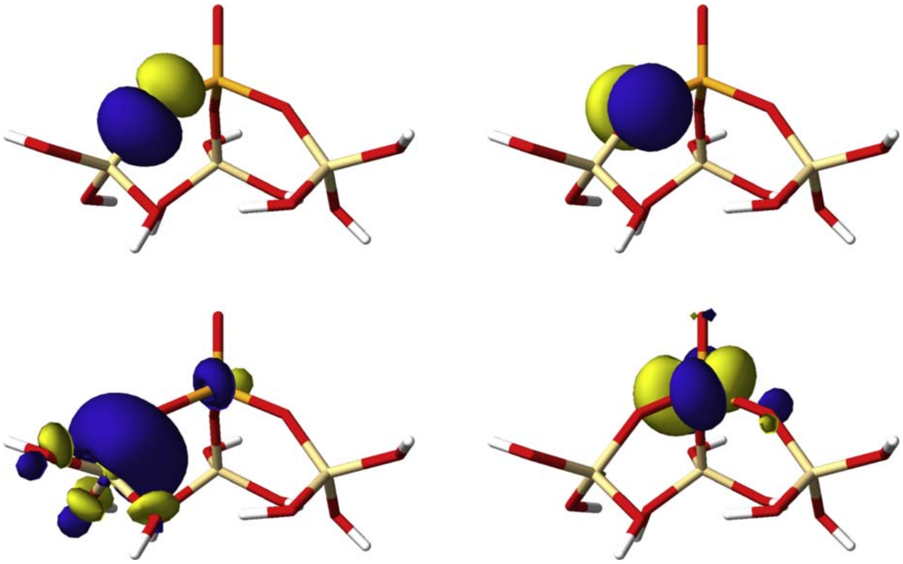


Fig. 2. The VBSCF optimised orbitals of the Si-cluster (when optimising all valence orbitals).

significantly higher, and the VB energy including ionic structures is intermediate and closer to the RHF energy.

The optimised VB orbitals for the Al-cluster are shown in Fig. 1. This Figure clearly shows on oxygen two p-orbitals that are involved in the bonding to the aluminium support atom and to the vanadium atom. The aluminium orbital that binds to oxygen has a high degree of s-character, while the vanadium orbital is more d-like.

The most important structures are structure **d**, **a**, **b**, **f**, and **h** (Scheme 3), with the highest weight for structure **d** (Table 2), which is also the structure with lowest energy (Table 3). This high weight indicates that the O-Al-support bond is rather polar, with a considerable positive charge on the Al atom of the support and a quite negative charge on the oxygen attached, in agreement with the proposal in the mechanism that this oxygen will capture the proton from the dissociative chemisorption of the methanol molecule. Unsurprisingly, structures with the negative charge on the Al-support atom do not contribute to the wavefunction. The V–O bond is also highly polar, considering the large contribution of structure **b**.

Optimisation of the valence orbitals for the Si-cluster results in the orbitals depicted in Fig. 2. It can be clearly noticed that the orbitals involved in the V–O bond resemble more a π bond than a typical σ bond. This suggests that π back bonding from the oxygen lone-pair to vanadium is important in this complex. If the V–O bond is very ionic, i.e. the (V(+)–O(−)) structure is much more important than the covalent structure V–O, then the overlap between the V and O orbitals is less important, and thus the direction of the oxygen orbital is not important. Then, mixing in π back donation, in the covalent structure with two σ bonds yields a higher energy gain then optimising the covalent σ V–O bond.

This π back donation from O to V can be excluded from the calculation by optimising only the orbitals involved in the σ bond (thus optimising only four orbitals). Indeed, as shown in Fig. 3,

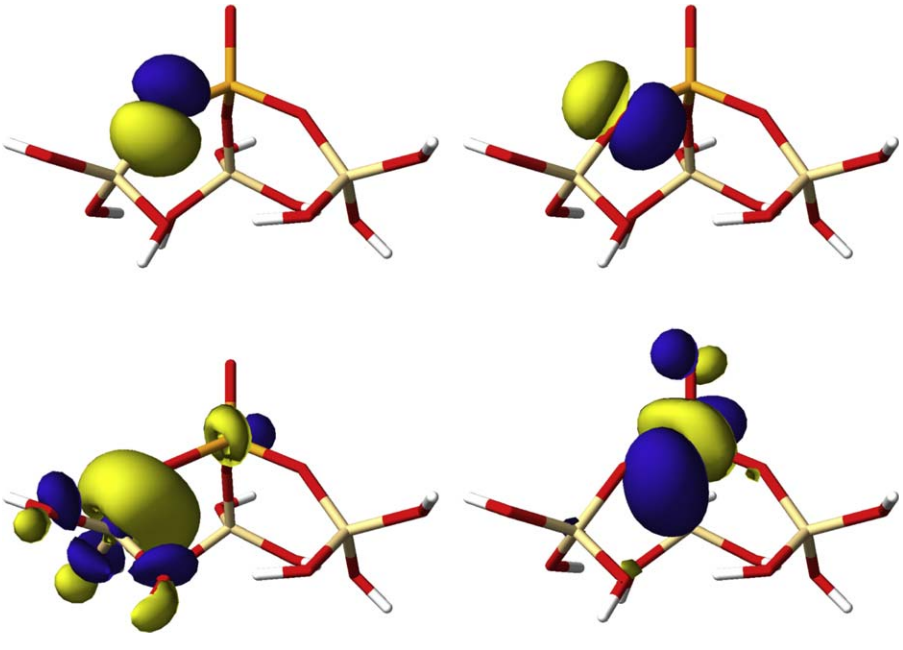


Fig. 3. The VBSCF optimised orbitals of the Si-cluster when only the four shown orbitals are optimised.

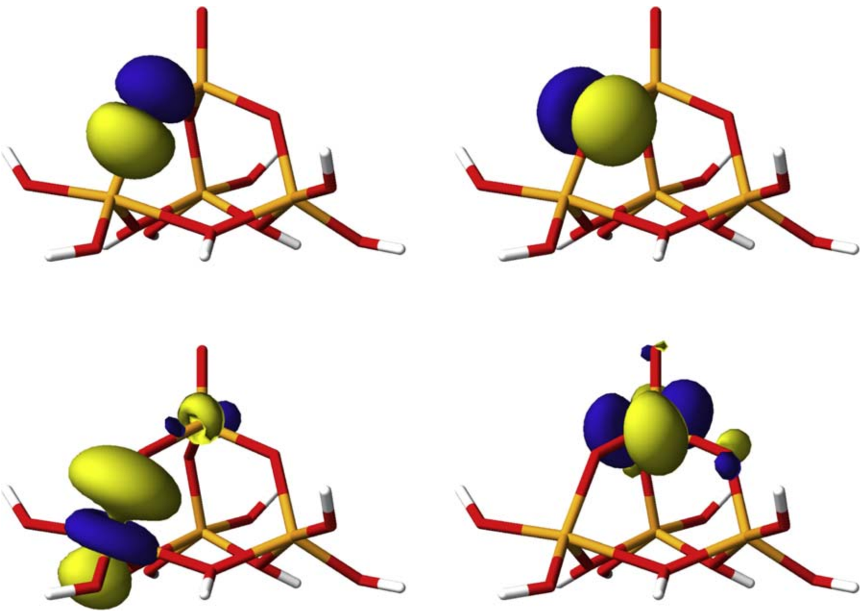


Fig. 4. The VBSCF optimised orbitals of the Ti-cluster (when optimising all valence orbitals).

the orbitals involved in the V–O bond are more σ-bond-like. This high ionicity of the V–O bond is clearly seen in the weights of the ionic structure in the calculation where only four orbitals are optimised: structure **b** has the lowest energy and the highest weight.

The O–Support bond in the silicium case is also very polar: structure **d** has a high weight, irrespective of the nature of the V–O bond (σ-bond or π-back donation bond). This holds also for the Ti and Zr clusters: structure **d** is very important. In both cases, it was also found that π back donation from O to V plays an important role (Figs. 4–6).

In order to clearly connect to and compare with the conceptual DFT results on ionicity in our previous study, [28] it is instructive to eliminate the effects of the O–Support bond in the estimation of the polarity of the V–O bond; this can be accomplished by a separate diagonalisation of the 3 × 3 **H** and **S** matrices consisting of only the structures **a**, **b**, and **c** using the matrix elements calculated in the VBCI calculations (Table 4). A significant influence exists between the calculations with all valence orbitals optimised and with only four bonds optimised. When back donation is taking into account, the weight of the covalent structure increases. If we consider only the VB calculations without π back bonding, the weight of the ionic structure **b**, indicating the degree of ionicity of the V–O–Sup bond, increases as Al < Ti < Zr < Si. This sequence

Table 4
The structure weights in 3 × 3 calculations with only the structures **a**, **b**, and **c** to probe the difference in ionicity of the O–Support bonds in the clusters.

Structure	Al	Si	Si-4[a]	Ti	Ti-4[a]	Zr-4[a]
a	0.633	0.801	0.247	0.818	0.610	0.494
b	0.362	0.198	0.753	0.180	0.384	0.502
c	0.019	0.001	0.000	0.002	0.006	0.004

[a] Only the four orbitals involved in the two σ bonds are optimised.

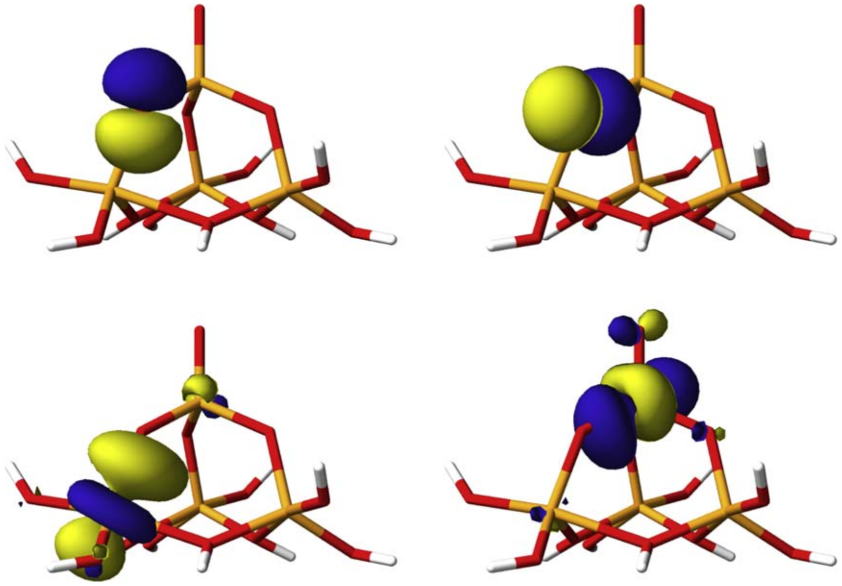


Fig. 5. The VBSCF optimised orbitals of the Ti-cluster when only the four shown orbitals are optimised.

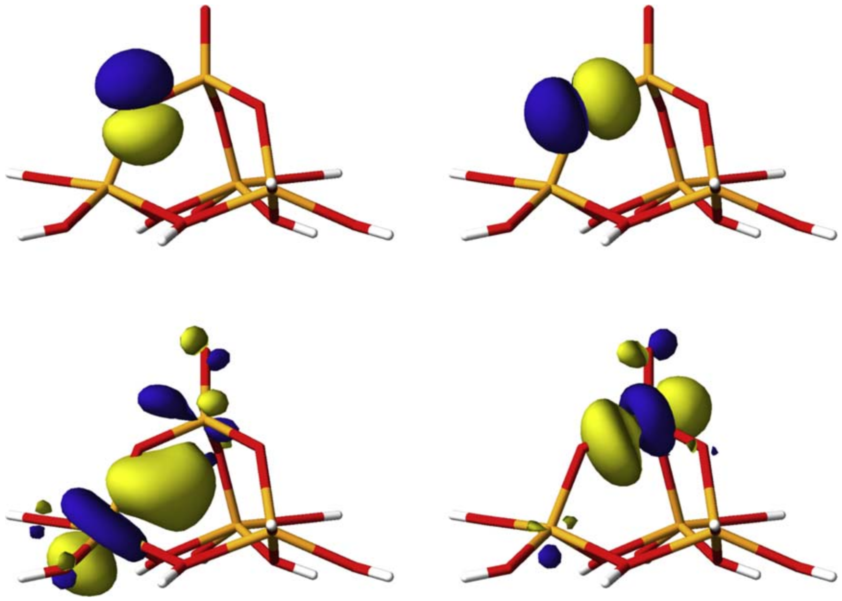


Fig. 6. The VBSCF optimised orbitals of the Zr-cluster when only the four shown orbitals are optimised.

largely parallels the sequence of the bond ionicity as estimated from electrostatic potential based atomic charges in our previous contribution [28], the only exception being the position of Si, which was previously estimated to give rise to the least ionic V–O–Sup bond. This inconsistency might point to a less optimal structural model in the case of the Si supported material. This would require however VB calculations on larger models for this compound which is not straightforward. Also, the valence bond calculations have shown that the interaction between V and O consists of the σ_{V-O} bond together with π back bonding from the oxygen lone-pair to d-orbitals on V. In the current VB calculations this latter effect has been ignored. More elaborate VB calculations are in progress to probe the effect of π back bonding on the ionicity of the V–O bond: this back bonding is expected to lower the ionicity of the V–O bond.

To study the π-back donation in more detail, VB calculations were performed on the smaller $OV(OH)_2OMH_n$ clusters. The localisation procedure revealed that in the SiH_3 and ZrH_3 clusters, the O–Support bond has such a high ionicity that the oxygen atom has two lone-pairs available for π back donation to vanadium, whereas in the AlH_2 and TiH_3 clusters the oxygen atom has only one lone-pair available for this π-back donation.

Only a few structures are important in the VB description of the V–O bonds (Table 5). The covalent V–O structure, the ionic V(+)–O(−) structure, and the neutral V(+)–O(−), Lp→V structures, where the σ bond is ionic, and one electron is back donated from an oxygen lone-pair to an empty vanadium d-orbital. The relatively high weight of the latter structure diminishes the charge separation between V and O.

The optimised VBSCF orbitals on oxygen and vanadium are shown only for $OV(OH)_2TiH_3$ in Fig. 7 and $OV(OH)_2SiH_3$ in Fig. 8 (the $OV(OH)_2AlH_2$ and $OV(OH)_2ZrH_3$ orbitals are similar to those of $OV(OH)_2TiH_3$ and $OV(OH)_2SiH_3$, respectively).

The predicted order of V–O ionicity, based on the weight of the covalent structure, of these clusters is Al < Ti < Zr < Si, which is in agreement with the previously deduced order for the larger clusters. However, the order derived from the weights of the ionic structure V(+)–O(−) is Zr < Al < Si < Ti. Note that the π back donation thwarts the classification in covalent and ionic bonding: the

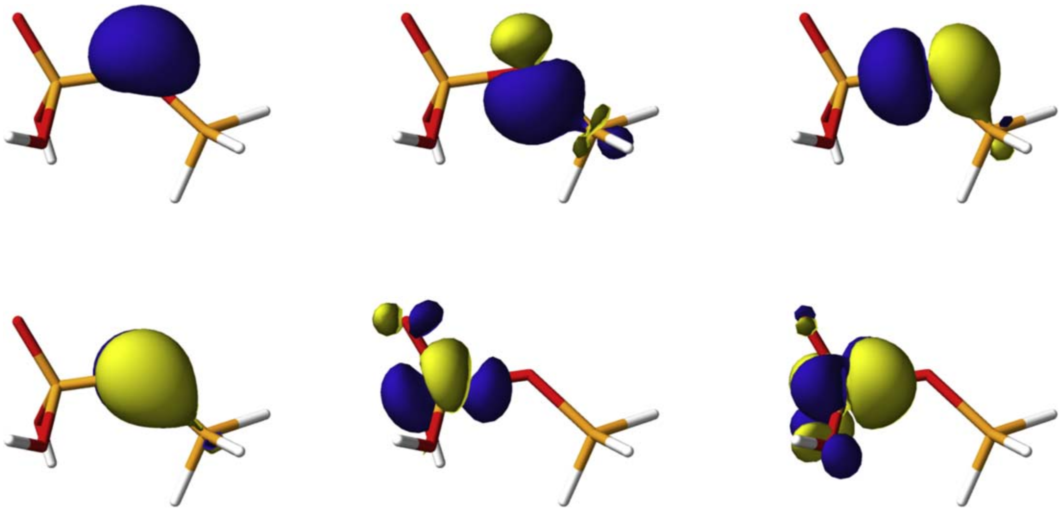


Fig. 7. The VBSCF optimised orbitals of the $OV(OH)_2OTiH_3$ cluster.

Table 5
Energies and weights of the most important structures of the $OV(OH)_2MH_n$ clusters.

	$OV(OH)_2AlH_2$	$OV(OH)_2TiH_3$	$OV(OH)_2SiH_3$	$OV(OH)_2ZrH_3$
E_{RHF}	−614.39140	−1221.33304	−661.91780	−419.07168
E_{VB}	−614.40699	−1221.33988	−661.94861	−419.10503
$W_{V–O}$	0.334	0.297	0.225	0.276
$W_{V(+)O(-)}$	0.265	0.387	0.295	0.242
$W_{V(+)O(-)Lp1\rightarrow d}$	0.376	0.301	0.233	0.292
$W_{V(+)O(-)Lp2\rightarrow d}$	–	–	0.222	0.156
$E_{V–O}$	−614.19245	−1221.07960	−661.63640	−418.83445
$E_{V(+)O(-)}$	−614.13853	−1221.12120	−661.68762	−418.81731
$E_{V(+)O(-)Lp1\rightarrow d}$	−614.26555	−1221.18110	−661.75437	−418.92704
$E_{V(+)O(-)Lp2\rightarrow d}$	–	–	−661.74585	−418.85949

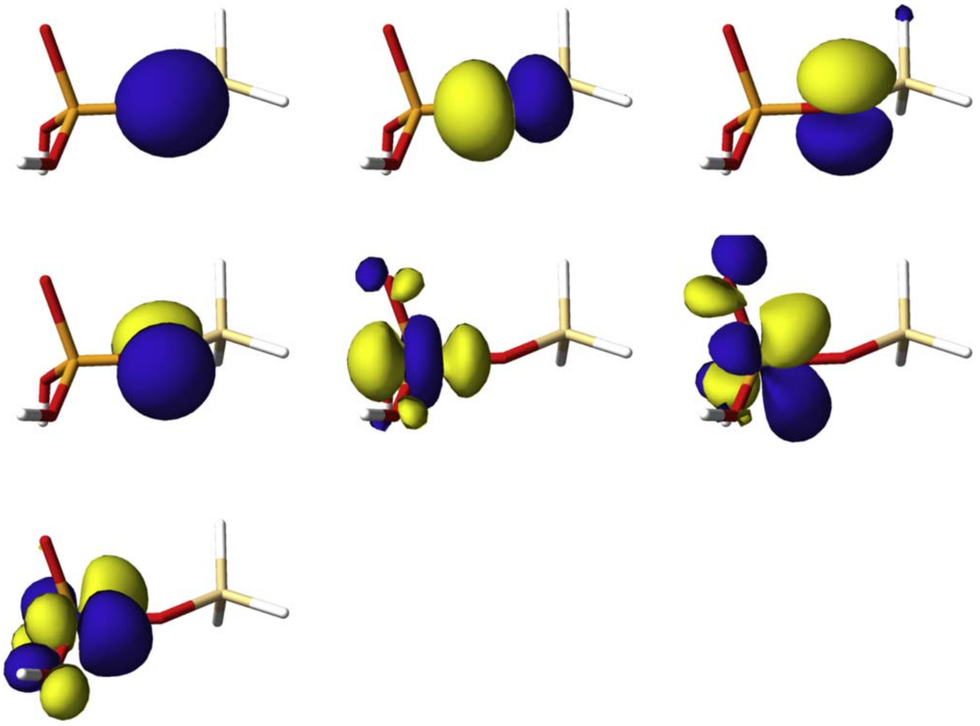


Fig. 8. The VBSCF optimised orbitals of the $OV(OH)_2OSiH_3$ cluster.

important structures in which back occurs would lead to a neutral V and O atoms. In such complex situations, where multiple bonding exists, charge distributions or ionicities are better reflected in atomic charges, as used for the present systems [28]. As such VB calculations on these systems offer a complementary insight in the nature of the chemical bonds in these systems.

4. Conclusions

In this contribution, we have investigated the catalytic activity of 4 vanadium oxides, supported on SiO_2, Al_2O_3, TiO_2, ZrO_2. These materials were represented as small clusters and valence bond calculations were performed on these clusters to investigate the ionicity of the vanadium-oxide bond, where the oxide atom is the atom connecting to the support atoms. In our previous work, conducted within the framework of conceptual DFT, the ionicity of this bond was found to explain the trend in catalytic activity along the series of four supported vanadium oxides. From our VB analysis, it is clear that the ionic structure V(+)–O(−) has an important weight in the wavefunction and that, consequently, this is a highly polar bond, enabling the dissociative adsorption of methanol on this bond. In order to connect to our previous work, the effects of the oxygen–support bonds were eliminated in the estimation of the V–O bond ionicity. This yielded a bond ionicity order $Al < Ti < Zr$, in agreement with the observed trends in the catalytic activity along these supports. An exception to this trend is the silicon supported vanadium oxide, for which our analysis points to a highly ionic V–O bond, whereas this material exhibits the lowest catalytic activity along the series. Back donation influences the charge separation between V and O, but does not influence the order of the V–O σ bond ionicity in these clusters.

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References

[1] M.A. Banares, I.E. Wachs, J. Raman Spectrosc. 33 (2002) 359.
[2] B.M. Weckhuysen, D.E. Keller, Catal. Today 78 (2003) 25.
[3] G. Deo, I.E. Wachs, J. Haber, Crit. Rev. Surf. Chem. 4 (1994) 141.
[4] G. Deo, I.E. Wachs, J. Catal. 146 (1994) 323.
[5] P. Boulet, A. Baiker, H. Chermette, F. Gilardoni, J.C. Volta, J. Weber, J. Phys. Chem. B 106 (2002) 9659.
[6] R.Z. Khaliullin, A.T. Bell, J. Phys. Chem. B 106 (2002) 7832.
[7] J. Döbler, M. Pritzsche, J.J. Sauer, Am. Chem. Soc. 127 (2005) 10861.
[8] L.J. Burcham, M. Baldani, I.E. Wachs, J. Catal. 203 (2001) 104.
[9] A. Goodrow, A.T. Bell, J. Phys. Chem. C 111 (2007) 14753.
[10] A. Goodrow, A.T. Bell, J. Phys. Chem. C 112 (2008) 13204.
[11] M.V. Ganduglia-Pirovano, C. Popa, J. Sauer, H. Abbott, A. Uhl, M. Baron, D. Stacchiola, O. Bondarchuk, S. Shaikhutdinov, H.J. Freund, J. Am. Chem. Soc. 132 (2010) 2345.
[12] P. Gonzalez-Navarrete, L. Gracia, M. Calatayud, J.J. Andres, Phys. Chem. C 114 (2010) 6039.
[13] S.S. Shaik, P.C. Hilberty, A Chemist's Guide to Valence Bond Theory, Wiley, New York, 2007.
[14] R.W.A. Havenith, J.H. Van Lenthe, J.J. Engelberts, Faraday Discuss. 135 (2007) 299.
[15] (a) R.G. Parr, W. Yang, Density-Functional Theory of Atoms and Molecules, Oxford University Press, UK, 1989;
(b) R.G. Parr, W. Yang, Annu. Rev. Phys. Chem. 46 (1995) 701;
(c) W. Kohn, A.D. Becke, R.G. Parr, J. Phys. Chem. 100 (1996) 12974;
(d) H. Chermette, J. Comput. Chem. 20 (1999) 129;
(e) P. Geerlings, F. De Proft, W. Langenaeker, Chem. Rev. 103 (2003) 1793;
(f) P.W. Ayers, J.S.M. Anderson, L.J. Bartolotti, Int. J. Quantum Chem. 101 (2005) 520;
(g) J.L. Gázquez, J. Mex. Chem. Soc. 52 (2008) 3;
(h) P. Geerlings, F. De Proft, Phys. Chem. Chem. Phys. 10 (2008) 3028;
(i) S.B. Liu, Acta Phys. Chem. China 25 (2009) 590.
[16] For a detailed account on different scales of electronegativity, see e.g. J. Mullay, in: K.D. Sen, C.K. Jørgenson (Eds.), Electronegativity (Structure and Bonding, vol. 66), Springer-Verlag, Berlin/Heidelberg, 1987, p.1.
[17] R.G. Parr, R.A. Donnelly, M. M. Levy, W.E. Palke, J. Chem. Phys. 69 (1987) 3801.
[18] R.G. Pearson, Hard and Soft Acids and Bases, Dowen, Hutchinson and Ross, Stroudsberg, 1973.
[19] R.G. Pearson, Chemical Hardness, Wiley-VCH, NewYork, 1997.
[20] R.G. Parr, R.G. Pearson, J. Am. Chem. Soc. 105 (1983) 1503.
[21] P.W. Ayers, Faraday Discuss. 135 (2007) 161.
[22] W. Yang, R.G. Parr, Proc. Natl. Acad. Sci. U. S. A. 82 (1985) 6723.
[23] (a) M.H. Cohen, M.V. Ganduglia-Pirovano, J. Chem. Phys. 101 (1994) 8988;
(b) M.H. Cohen, M.V. Ganduglia-Pirovano, J. Kudrnovsky, Phys. Rev. Lett. 72 (1994) 3222;
(c) M.H. Cohen, M.V. Ganduglia-Pirovano, J. Kudrnovsky, J. Chem. Phys. 103 (1995) 3543;
(d) M.H. Cohen, M.V. Ganduglia-Pirovano, V. Natoli, Kudrnovsky, in: J.R. Chelikowski, S.G. Louie (Eds.), Quantum Theory of Real Materials, Kluwer Academic Publishers, 1996, p. 315.
[24] X. Gao, I.E. Wachs, Top. Catal. 18 (2002) 243–250.
[25] R.T. Sanderson, Polar Covalence, Academic Press, New York, 1983.
[26] D.E. Keller, S.M.K. Airaksinen, A.O.I. Krause, B.M. Weckhuysen, D.C. Koningsberger, J. Am. Chem. Soc. 129 (2007) 3189.
[27] M. Calatayud, F. Tielens, F. De Proft, Chem. Phys. Lett. 456 (2008) 59.
[28] T. Fievez, B.M. Weckhuysen, P. Geerlings, F. De Proft, J. Phys. Chem. C 113 (2009) 19905.
[29] (a) A.D. Becke, K.E. Edgecombe, J. Chem. Phys. 92 (1990) 5397;
(b) B. Silvi, A. Savin, Nature 371 (1994) 683.
[30] L. Gracia, P. González-Navarrete, M. Calatayud, J. Andrés, Catal. Today 139 (2008) 214.
[31] G.A. Gallup, J.M. Norbeck, Chem. Phys. Lett. 21 (1973) 495.
[32] J. Verbeek, J.H. Langenberg, C.P. Byrman, F. Dijkstra, J.J. Engelberts, M. Zielinski, J.H. van Lenthe, TURTLE, an ab initio VB/VBSCF program, Utrecht, The Netherlands, 1988–2010.
[33] M.F. Guest, I.J. Bush, H.J.J. van Dam, P. Sherwood, J.M.H. Thomas, J.H. van Lenthe, R.W.A. Havenith, J. Kendrick, Mol. Phys. 103 (2005) 719.
[34] J. Pipek, P.G. Mezey, J. Chem. Phys. 90 (1989) 4916.