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Surface oxygen in catalysts based on transition metal oxides What can we learn from cluster DFT calculations?

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Abstract

Cluster model studies by means of ab initio DFT method are performed to examine electronic properties of different surface O atoms in several V–O–X systems and to correlate them with catalytic behavior. Since chosen compounds vary in metal oxidation state and in X element, reactivity of differently coordinated surface O is studied as a function of different parameters such as coordination number, geometrical and chemical environment. In addition, the mobility of different surface oxygen species, formation of surface oxygen vacancies and the adsorption of O_2 molecule at the different vacancy is discussed on the examples of the V_2O_5 and MoO_3 systems.

Keywords: Surface oxygen centers; Adsorption of O_2 molecule; Transition metal oxides; Transition metal mixed oxides; DFT cluster model study

1. Introduction

Transition metals oxides, among them pure V–O, Mo–O oxides and mixed V–O–X (X = P, Mg), Mo–O–X (X = Co, Bi, Sb) systems represent an important class of materials due to their technological and commercial interest [1–4]. They play a crucial role in catalysis and environmental protection; their properties form a platform for totally new devices and technologies. Crystal structures of these compounds consist of metal cations coordinated by oxygen ligands in tetrahedral, square pyramidal or octahedral geometries. Different connection of M–O building units leads to structurally inequivalent oxygen sites, specially at the surfaces. Surface oxygen atoms, which are linked to one, two or three metal sites (M) and denoted, respectively, as O(1), O(2) and O(3), can be bound to the same type centers (to two or three M for O(2) or O(3), respectively) or to different metal centers (one M and one X center for O(2); two M centers and one X atom or one M center and two X atoms in case of O(3)). As a result surface oxygen species are characterized by different electronic properties and so may be expected to exhibit different reactivity in catalytic processes. In addition, various types of atomic defects, re-oxidation processes, reconstructions and rearrangements, which are so common for transition metal oxide surfaces, also impact on surface electronic structure and reactivity. Due to the richness of M–O–X (M = V, Mo) systems and structural/chemical variety of their surfaces different chemisorption and physisorption interactions exist at the surfaces. From a point of view of catalysis the most interesting are interactions connected with electron or/and oxygen transfer between surface and reacting molecule(s).

The present theoretical cluster studies, which consider a large number of M–O–X systems, are carried out to summarize detailed information concerning the electronic properties of structurally different oxygen atoms that exist at the surfaces of these compounds and to correlate them with catalytic activity of surfaces. Nowadays theoretical tools are used in parallel to experimental methods to get information on reacting systems on the atomic level (see for example [5–7]). Such knowledge is of great importance in particular for surfaces since they are responsible for the interaction and binding with the reactant(s), resulting bond changes, the reaction between the adsorbed reactant(s), and finally, for the desorption processes. In addition, the mobility of differently coordinated surface oxygen species and the adsorption of O_2 molecule at different vacancies is discussed by comparing V_2O_5 and MoO_3 systems. The possibility of electrophilic surface oxygen atoms formed as a consequence of O–O bond splitting in the adsorbed O_2 molecule is indicated.

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2. Experimental: computational and models details

All calculations are carried out by means of ab initio DFT method, using StoBe quantum chemistry program package [8]. The exchange correlation interactions are accounted for by the gradient corrected RPBE functional [9]. The Kohn–Sham molecular orbitals are expanded as a linear combination of atom-centered Gaussian-type orbitals, expressed in terms of double zeta basis sets including polarization functions. Molybdenum atoms are represented by valence basis sets with the [Ar]3d^{10} core described by a model core potential [10].

The pure and mixed transition metal oxides currently under study differ in metal oxidation state, type of M–O and X–O building units (tetrahedra, square pyramids, octahedra) and type of their connections (corner/edge). The dependence of electronic properties on these parameters is presented considering a series of vanadium-based systems whereas the mobility of differently coordinated oxygen species (surface or adsorbed) is discussed comparing V_2O_5 and MoO_3 systems. To model structurally different surface ions the following surface sections (see Fig. 1) are chosen: $V_{10}O_{31}$ (V_2O_5), $V_{17}O_{42}$ (VO_2), $V_{11}O_{33}$ (V_2O_3), $V_8P_7O_{55}$ (VPO_5), $V_{10}P_6O_{50}$ ($(VO)_2P_2O_7$), $V_8P_{12}O_{63}$ (VPO_4), $Mg_4V_4O_{28}$ ($Mg_2V_2O_7$), $Mg_8V_4O_{32}$ ($MgVO_3$), and $Mo_{15}O_{56}$ (MoO_3); dangling bonds are saturated by hydrogen atoms leading to neutral systems. For all clusters the crystallographic geometry is kept [11]. The characterization of surface O species is done by electronic (atomic charges, bond orders) and energetic parameters.

3. Results and discussion

Nature of any bond can be characterized by two contributions: ionic (measured for example by atomic charges, Q) and covalent (measured for example by bond order, BO). Table 1 summarizes geometric and electronic parameters for V–O–X systems, where X = P, V, and Mg. It lists atomic charges (Q) obtained from Mulliken populations for O(1–3) sites, Mayer bond indices (BO) and bond distances for various O(1–3)–X bonds associated with selected atoms and bonds closest to the cluster center. As can be seen all charges characterizing atoms are smaller than their formal

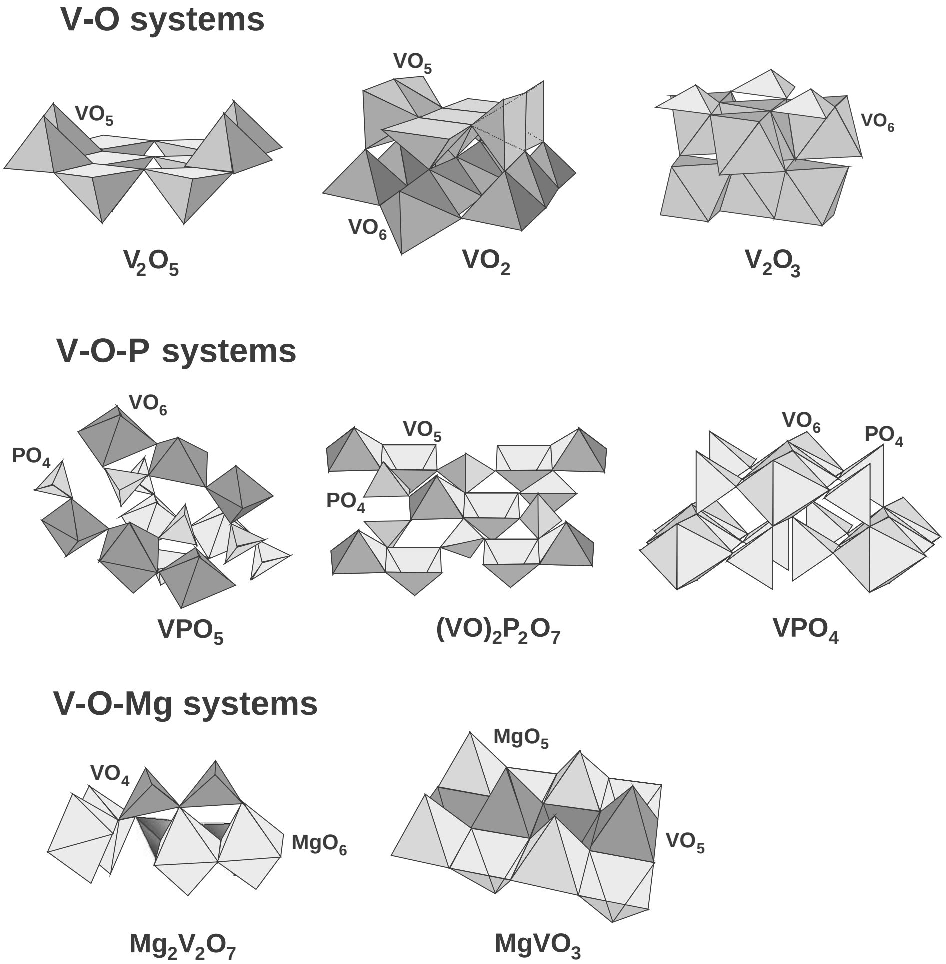

Fig. 1. Surface sections used to model surfaces of the different V–O, V–O–P and V–O–Mg systems. In addition building units M–O and X–O are shown.

Table 1
Atomic charges (*Q*) obtained from Mulliken population analysis for O(1–3) sites, Mayer bond order indices (BO) and bond lengths (*R*) in (Å) describing the X–O bonds (X = V, P, Mg) of the $V_{10}O_{31}H_{12}$ (V_2O_5), $V_{17}O_{42}H_{16}$ (VO_2), $V_{11}O_{33}H_{33}$ (V_2O_3), $V_8P_7O_{55}H_{37}$ (VPO_5), $V_{10}P_6O_{50}H_{30}$ ($(VO)_2P_2O_7$), $V_8P_{12}O_{63}H_{42}$ (VPO_4), $Mg_4V_4O_{28}H_{28}$ ($Mg_2V_2O_7$), $Mg_8V_4O_{32}H_{32}$ ($MgVO_3$), and $Mo_{15}O_{56}H_{22}$ (MoO_3) clusters.

	V–O–P system			V–O system			V–O–Mg system		
O(1)		QO(1)	BO/R (P=O)		QO(1)	BO/R (V=O)		QO(1)	BO/R (Mg=O)
	VPO_5 (V^{5+})	−0.49	1.46/1.53Å	V_2O_5 (V^{5+})	−0.33	2.06/1.58Å	$Mg_2V_2O_7$ (V^{5+})	–	–
	$(VO)_2P_2O_7$ (V^{4+})	−0.66	1.65/1.56Å	VO_2 (V^{4+})	–		$MgVO_3$ (V^{4+})	−0.56	0.66/1.89Å
	VPO_4 (V^{+3})	−0.61	1.58/1.57Å	V_2O_3 (V^{3+})	–		–	–	–
O(2)		QO(2)	BO/R (V–O), BO/R (P–O)		QO(2)	BO/R (V–O), BO/R (V–O)		QO(2)	BO/R (V–O), BO/R (Mg–O)
	VPO_5 (V^{5+})	−0.71	0.38/1.90Å, 1.13/1.52Å	V_2O_5 (V^{5+})	−0.69	0.83/1.78Å, 0.83/1.78Å	$Mg_2V_2O_7$ (V^{5+})	−0.59	1.50/1.68Å, 0.32/2.06Å
	$(VO)_2P_2O_7$ (V^{4+})	−0.65	0.50/1.92Å, 1.29/1.48Å	VO_2 (V^{4+})	−0.55	0.95/1.86Å, 0.95/1.87Å	$MgVO_3$ (V^{4+})	–	–
	VPO_4 (V^{3+})	−0.64	0.72/1.93Å, 1.10/1.50Å	V_2O_3 (V^{3+})	−0.45	1.08/1.96Å, 0.99/2.06Å	–	–	–
O(3)		QO(3)	BO/R (V–O), BO/R (V–O), BO/R (P–O)		QO(3)	BO/R (V–O), BO/R (V–O), BO/R (V–O)		QO(3)	BO/R (V–O), BO/R (V–O), BO/R (Mg–O)
	VPO_5 (V^{5+})	–	–	V_2O_5 (V^{5+})	−0.87	0.49/1.88Å, 0.54/1.88Å, 0.39/2.02Å	$Mg_2V_2O_7$ (V^{5+})	−0.59	0.54/1.93Å, 0.55/1.82Å, 0.31/2.15Å
	$(VO)_2P_2O_7$ (V^{4+})	−0.84	0.36/2.09Å, 0.39/2.05Å, 0.87/1.56Å	VO_2 (V^{4+})	−0.81	0.59/1.76Å, 0.48/2.01Å, 0.62/2.03Å	$MgVO_3$ (V^{4+})	–	
	VPO_4 (V^{3+})	−0.82	0.20/2.08Å, 0.31/2.08Å, 1.12/1.57Å	V_2O_3 (V^{3+})	−0.82	0.90/1.96Å, 0.37/1.96Å, 0.55/2.06Å	–	–	

All values are associated with selected atoms and bonds closest to the cluster center.

valence charges, which clearly indicates mixed ionic and covalent character of oxygen–metal bonds in studied systems. Charges on surface O atoms scale with their coordination number, bridging oxygen atoms are always characterized by larger negative charge i.e. are more nucleophilic than terminal ones (see V–O–P, V–O, and V–O–Mg series). Larger accumulations of negative charge at oxygen centers of higher coordination suggest larger ionic contributions to the M–O(3) bond compared to M–O(2) or M–O(1) bonding. Reduction of vanadium (compare oxygen of the same coordination number in $V_2O_5 \rightarrow VO_2 \rightarrow V_2O_3$ or $VPO_5 \rightarrow (VO)_2P_2O_7 \rightarrow VPO_4$ series) causes oxidation of neighboring O sites, which become less nucleophilic independently of the coordination number (see for example O(2), with charges changing in order −0.71, −0.65, −0.64 for V–O–P or −0.69, −0.55, −0.45 for V–O systems when going from V^{5+} to V^{4+} and then V^{3+}). The changes are more visible for pure V–O system than for mixed V–O–X systems. Replacement of one V in V–O–V with Mg or P (see V–O–Mg or V–O–P series) also influences the charge on oxygen atoms; magnesium decreases nucleophilicity of each oxygen site whereas P causes increase in nucleophilic character of each O site independently of its coordination. For example, charge on O(2) varies like −0.71, −0.69, −0.59 when going from VPO_5, to V_2O_5 and to $Mg_2V_2O_7$ system (row associated with V^{5+}).

Terminal oxygen atom, which is coordinated to one vanadium, binds by a strong, double bond (BO = 2.06). The O atom singly coordinated to phosphorus forms a bond intermediate in character between double and single (BO about 1.6 for different V–O–P systems). In the case of the V–O–Mg system, O(1) atom binds to magnesium at relatively large (1.89 Å) distance compared to V–O and V–O–P systems (V=O and P=O bond lengths close to 1.6 Å), which leads to weak Mg–O interaction (BO = 0.66). Bridging oxygen atoms, O(2) and O(3), are coordinated to metal atoms by bonds, in which the covalent contribution (measured by BO) depends on the chemical character of metal neighbors. The Mg–O bonds are the most ionic whereas the P–O bonds are characterized by the largest covalent contribution, which is in accordance with metal electonegativities (Mg = 1.2, V = 1.5, P = 2.1). For example, covalent contribution of X–O bond for doubly coordinated oxygen atom changes in the order BO = 0.32, 0.83. 1.13 for X = Mg, V, P (see Table 1, V–O–P, V–O and V–O–Mg systems row describing systems with V^{5+}). The same is true for triply coordinated oxygen atom where different bonds are of different strengths depending on metal electronegativity (weak Mg–O, stronger V–O and the strongest P–O bonds).

Catalytic properties of all oxide-based catalysts depend strongly on their ability to provide surface oxygen as a reactant. Therefore, theoretical study on mobility of surface oxygen atoms as well as on energies needed to create each respective oxygen vacancy can elucidate details of the elementary reaction steps. The mobility of differently coordinated surface oxygen may be defined by many parameters; one of them being sum of the bond orders to the neighboring metal atoms. Among V–O systems vanadium pentoxide surface posses surface oxygen atoms (in particular bridging O(3)) that are more easily to be removed from the surface than in case of VO_2 and V_2O_3. The mobility of the particular type of oxygen decreases with decreasing vanadium oxidation state (for example a sum of BO changes in order $1.66 < 1.90 < 2.07$ for O(2), whereas in case of O(3) as $1.42 < 1.69 < 1.82$ when going from V^{5+} to V^{4+} and V^{3+} oxides).

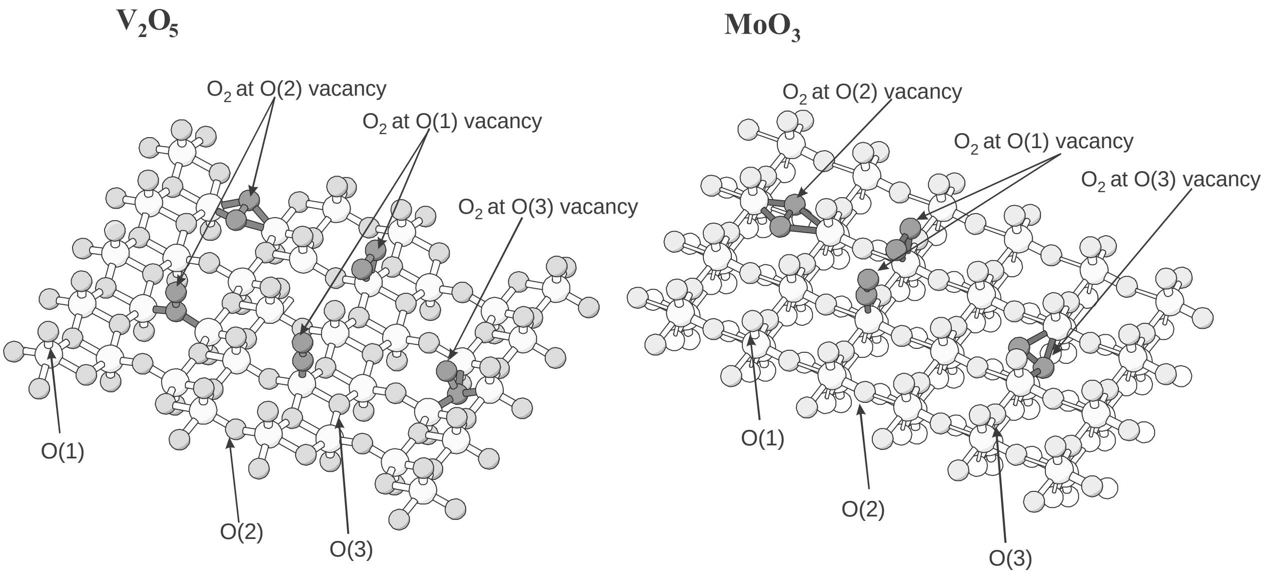

Fig. 2. Sketch of computed equilibrium geometries of an adsorbed O_2 molecule at different vacancy sites of the V_2O_5(0 1 0) and MoO_3(0 1 0) surfaces. The results are obtained by optimizing the O_2 position and geometry in the $V_{10}O_{30}H_{12}$ and $Mo_{15}O_{55}H_{22}$ vacancy cluster models. The O_2 adsorbate species is shown by shaded balls while the surface lattice is sketched.

Table 2

Energies of vacancy formation E_D, molecular oxygen adsorption at a vacancy $E_B(O_2)$, and atomic oxygen adsorption at the surface $E_B(O)$ for surface sites O(1), O(2), O(3) at the $MoO_3(0\,1\,0)$ and $V_2O_5(0\,1\,0)$ surfaces using $Mo_{15}O_{56}H_{22}$ and $V_{10}O_{31}H_{12}$ clusters, respectively.

System	Energy	O(1) parallel	O(2) parallel	O(3) parallel
V_2O_5	E_D	7.16 (4.67) (1.17)	7.95 (5.33) (0.92)	7.01 (4.06) (0.08)
	$E_B(O_2)$	−2.53	−3.27	−1.03
	$E_B(O)$	−1.50	−1.38	0.05
MoO_3	E_D	6.80 (4.51) (1.47)	6.75 (4.11) (−0.20)	6.50 (3.12) (–)
	$E_B(O_2)$	−2.98	−1.11	−0.08
	$E_B(O)$	−1.77	−0.02	0.82

All energies are given in eV.

Another measure of the mobility of surface oxygen atom is energy (E_D) required to form surface oxygen vacancy (see Fig. 2). The large values of energies, which are given in Table 2, demonstrate that the lattice oxygen is always very strongly bound at the surfaces of both oxides, stronger at V_2O_5 than MoO_3. These energies can be decreased (see numbers in parentheses) by adsorption of hydrogen atom(s) and formation of surface hydroxyl or water species, which may be easily desorbed, as shown previously (see [5] and references therein). Formation of oxygen vacancies at the surfaces leads to the changes in surface geometries that strongly depend on the vacancy type (number of coordination of the missing oxygen atoms). Generally, the rearrangement at the $V_2O_5(0\,1\,0)$ surface is negligible, whereas at the $MoO_3(0\,1\,0)$ changes are larger (specially connected with the removal of O(1) and O(2) oxygen atoms). All created surface vacancies may become re-oxidized either through exchange with gaseous oxygen or via diffusion of bulk oxygen atoms. More detailed information on this reaction proceeding due to molecular adsorption is given in [12]. The adsorption of O_2 molecule at different surface vacancies leads to geometries that are shown in Fig. 2. In addition, Table 2 lists the energies ($E_B(O_2)$) connected with the adsorption of molecular oxygen at different vacancy sites, the process that leads to filling of the respective vacancy. In all cases the O_2 adsorption is an exothermic process and the ordering of adsorption energies goes parallel with the energies of vacancy formation; the most difficult vacancy to create—is the first to be filled. This means that adsorbed molecular oxygen can replace the surface oxygen occupying a specific lattice site. Moreover, the oxide surface is able to incorporate a large amount of (weakly bound) oxygen species. From Table 2 it is also evident that prior H adsorption, which results in formation of hydrogen containing surface species, plays a very important role in energetics connected with creation of local surface defects. Energies gain in oxygen adsorption may influence formation of local surface vacancy in vicinity.

In order to restore the initial state one oxygen atom has to be removed after the O_2 molecule is adsorbed at the vacancy. The energies corresponding to the removal of oxygen ($E_B(O)$) which are equal to the energies of the adsorption of atomic oxygen, are listed also in Table 2. For both oxides, the removal of O atom from O_2 molecule adsorbed at the O(3) vacancy is spontaneous. Small, negative values of $E_B(O)$ for all other cases indicate the presence of easily released active oxygen atom. Thus, this atom can be proposed as the electrophilic surface oxygen species responsible for total oxidation of hydrocarbons.

4. Conclusions

The performed calculations clearly show the existence of different surface oxygen as well as different local vacancies and point out their possible different sources. The richness of variety of surface oxygen sites originates from different structural (in the sense of electronic and geometrical) factors. Structurally inequivalent surface oxygen sites are characterized by different electronic states and, as a result, exhibit different catalytic properties. Lattice oxygen are strongly bound to the surface therefore formation of oxygen vacancies is highly endothermic process. Prior H adsorption, which results in formation of hydrogen containing surface species decreases energy needed for vacancy creation. All created surface vacancies may become re-oxidized either through exchange with gaseous oxygen or via diffusion of bulk oxygen atoms, where the O_2 adsorption is an exothermic process. Adsorbed molecular oxygen can replace the surface oxygen occupying a specific lattice site, which means that the oxide surface is able to incorporate a large amount of oxygen species that are weakly bound and may impact catalytic behavior of the V–O/Mo–O systems.

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