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SCF–SW–Xα Calculations of the Removal of Oxygen from Oxide Surfaces by Vacancy Formation and Crystallographic Shear Mechanisms

It is well known that effective catalysts for selective oxidation of hydrocarbons contain Group V, VI, or VII transition metal oxides as the fundamental component of the active phase. It was shown (*1*) that in the case of, e.g., molybdate catalysts it is the Mo–O sublattice which performs the insertion of oxygen into the organic molecule. The question arises as to which properties of Group V, VI, and VII transition metal oxide lattices are responsible for this very high activity in the insertion of oxygen. One of their common features is the ability of forming shear structures, related to the facility of the rearrangement of the mode in which coordination polyhedra are linked together. Removal of oxygen ions from the lattices of these oxides results in the formation of ordered arrays of oxygen vacancies, followed by a very facile rearrangement of the layers of initially corner-linked metal–oxygen octahedra into an arrangement of edge-linked octahedra, resulting in the formation of shear plane. A hypothesis was advanced (*2–4*) that the easy release of one oxygen atom on the transformation from the corner-linked to the edge-linked arrangement of metal–oxygen octahedra may be one of the features creating the ability of these structures to insert oxygen into the organic molecule in the process of selective oxidation of hydrocarbons. In contrast to other transition metal oxides, in which the desorption of an oxygenated product must result in the generation of an oxygen vacancy (Fig. 1a) at considerable expenditure of energy, in the case of the above-mentioned systems, the desorption, accompanied by the simultaneous rearrangement of octahedra (Fig. 1b), is known to proceed readily. It seemed of interest to check this hypothesis by calculating the energy of the two possible products of the extraction of oxygen from the surface. MoO_3 was taken as an example of Group VIA oxides and ReO_3 as that of oxides of Group VIIA.

The simple octahedral clusters shown in Fig. 2 were chosen as models. The first one is the product formed after one oxygen atom has been directly removed from the MoO_3 lattice. Since the simplest model of the MoO_3 structure is that of two regular corner-linked metal–oxygen octahedra (*5*), the $[Mo_2O_{10}]^{10-}$ cluster with C_{4v} symmetry shown in Fig. 2a has been chosen in this case. The $[Mo_2O_{10}]^{10-}$ cluster of two edge-linked octahedra with D_{2h} symmetry (Fig. 2b) represents the product of removal of one oxygen atom from the MoO_3 lattice, followed by shear plane formation. The bond lengths in the first cluster were that of the MoO_3 idealized lattice, and the geometry of the second cluster was that of the model of MoO_2 derived in (*5*). The excess charge of 10 electrons is due to the formal valency of the elements, e.g., Mo^{6+} and O^{2-} plus the two extra electrons that remain after neutral oxygen removal.

The calculations have been carried out by means of the SCF–SW–Xα method in the muffin-tin approximation (*6–8*) within the spin restricted framework. Sphere radii in the muffin-tin approximation were chosen according to the "touching spheres" requirement with ratio equal to that of Slater's atomic radii. The radius of the Watson sphere (*9*) carrying an appropriate charge

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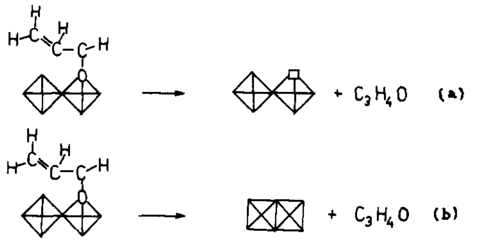
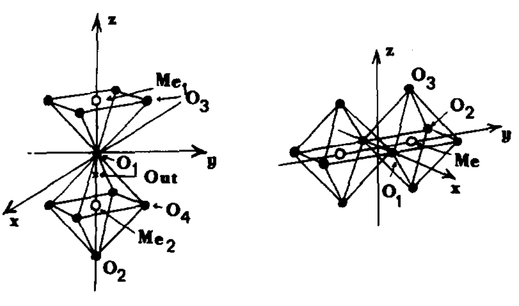


FIG. 1. Mechanism of the insertion of oxygen into a hydrocarbon molecule on oxide catalysts (*4*).

of +10 was taken to be equal to the outer sphere radius. The atomic values of the exchange parameter were equal to 0.703 for molybdenum and 0.744 for oxygen. The outer-sphere α value was the average weighted by the numbers of atoms.

The cluster models for point oxygen vacancy and shear plane formation mechanism in rhenium oxides were exactly the same as in the case of molybdenum. The detailed description of the structural and atomic parameters, i.e. atomic coordinates, sphere radii, and α parameters can be found in Ref. (*10*). The "thawed-core" approximation was used, namely, the molybdenum, rhenium, and oxygen core orbitals were allowed to adjust their energies to the molecular potential but only inside the atomic spheres and with only one angular component.

The values of the total energies of the $[Me_2O_{10}]^{10-}_{D_{2h}}$ and $[Me_2O_{10}]^{10-}_{C_{4v}}$ clusters are shown in Fig. 3 with the value of the total energy of the $[Me_2O_{11}]^{10-}$ cluster representing the solid taken as the reference level. The total energy calculated in the SCF-SW-Xα method within the muffin-tin scheme is only a rough approximation to the exact value because of the non-muffin-tin correction. In our case, however, the two $[Me_2O_{10}]^{10-}$ clusters, the D_{2h} and C_{4v} ones, are composed of the same atoms with a similar pattern. All the corresponding muffin-tin radii are similar and fortunately the radii of the outer spheres and the percentage of space occupied by the atomic spheres are very close. Thus we believe that non-muffin-tin corrections have similar values in both cases and that the results of the calculations correctly reflect the true order of stability of the two clusters. Conversely, the $[Me_2O_{11}]^{10-}$ total energy can be considered only as a reference state for semiquantitative comparison because the outer-sphere radius in this case was much larger (8.158 Å as compared with 6.760 Å). Thus, although the total energy differences between the initial cluster and the two clusters representing the two possible models of the deoxygenation process have no



(a) (b)

FIG. 2. Geometrical structure of $[Me_2O_{10}]^{10-}_{D_{2h}}$ and $[Me_2O_{10}]^{10-}_{C_{4v}}$ clusters.

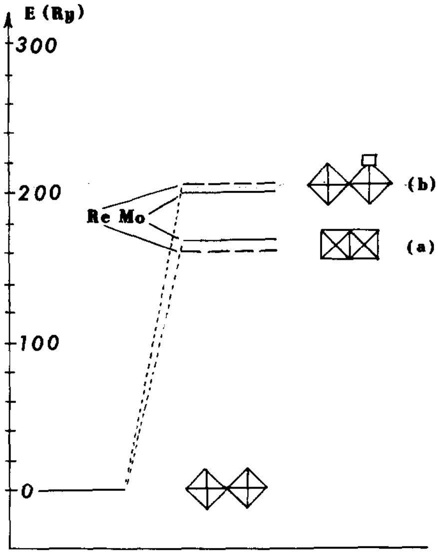


FIG. 3. Total energies (ry) of the two products of the deoxygenation process $[Me_2O_{10}]^{10-}_{C_{4v}}$ (a), and $[Me_2O_{10}]^{10-}_{D_{2h}}$ (b), with the total energy of $[Me_2O_{11}]^{10-}$ taken as the reference level.

quantitative physical meaning they correctly indicate the preferential pathway of the reaction.

Arguments may be raised that the calculations have been carried out for isolated clusters, whereas in the case of a real surface considerable strain energy might be involved in the shearing of octahedra, rendering this process less favourable. It should be remembered, however, that many irregularities such as steps, edges, kinks, etc. exist at the surface, where the situation may be well approximated by isolated clusters. Moreover, crystallographic shear is a cooperative phenomenon in which the strain is released by the movement of the whole lattice plane. Our calculations indicate that the amount of energy required to remove one oxygen atom is 25% smaller when this is accompanied by shearing. It seems that this energy difference is large enough to make this pathway more favourable despite all the above-mentioned factors.

Analysis of the electronic structure of the clusters, i.e., the orbital energies and the character of the one-electron wavefunctions, provides more information about the mechanism of the investigated process. The highest occupied molecular orbitals are the most important from the point of view of the bond formation. The appropriate data for molybdenum and rhenium oxides are given in Table 1. In columns 1, 2, and 3 the symmetry, occupancy and the orbital energies for the highest occupied and the lowest unoccupied molecular orbitals are given. The last column shows the orbital character estimated from the charge on the appropriate atom and the coefficient in the partial wave expansion of a given molecular orbital. Each of the presented orbitals has 35 to 50% metal d character which makes them crucial for the description of metal–metal interaction. In the $[Me_2O_{11}]^{10-}$ cluster all these energies are nearly degenerate and it appears that the binding interaction is very weak in this case (in MoO_3 all these levels are empty). In $[Me_2O_{10}]^{10-}_{C_{4v}}$ clusters all

TABLE 1

Ground State Upper Valence and Lower Virtual Levels for Model Oxide Clusters

Metal	$[Me_2O_{11}]^{10-}$				$[Me_2O_{10}]^{10-}_{C_{4v}}$				$[Me_2O_{10}]^{10-}_{D_{4h}}$			
	Sym.	Occup.	E(ry)	Char.	Sym.	Occup.	E(ry)	Char.	Sym.	Occup.	E(ry)	Char.
Mo	E_g	0.0	−0.307	$d_{xz} + d_{xz}$	E	2.0	−0.174	$d^{(1)}_{xz}$	A_{1g}	2.0	−0.293	$d_{x^2-y^2} + d_{x^2-y^2}$
Re		1.0	−0.364			2.0	−0.213			2.0	−0.304	
Mo	B_{2g}	0.0	−0.298	$d_{xy} + d_{xy}$	B_2	0.0	−0.166	$d^{(1)}_{xy}$	B_{1u}	0.0	−0.225	$d_{yz} - d_{yz}$
Re		1.0	−0.362			2.0	−0.206			2.0	−0.235	
Mo	B_{1u}	0.0	−0.297	$d_{xy} - d_{xy}$	B_2	0.0	−0.142	$d^{(2)}_{xy}$	A_{1u}	0.0	−0.202	$d_{xz} - d_{xz}$
Re		0.0	−0.352			0.0	−0.181			0.0	−0.211	
Mo	E_u	0.0	−0.295	$d_{xz} - d_{xz}$	E	0.0	−0.141	$d^{(2)}_{xz}$	B_{2g}	0.0	−0.194	$d_{xz} + d_{xz}$
Re		0.0	−0.352			0.0	−0.180			0.0	−0.205	

these orbitals are shifted to higher energy values (destabilization process). The bonding–antibonding difference is larger, the orbitals composed mostly of d functions of the metal atom connected with the oxygen vacancy are more stable and they are occupied additionally by the electrons left in the lattice after removal of the neutral oxygen atom. In the $[Me_2O_{10}]^{10-}_{D_{2h}}$ clusters of edge-linked octahedra, metal–metal interaction is strong and there is a quite clear differentiation between bonding σ $(d_{x^2-y^2} + d_{x^2-y^2})$ and π $(d_{yz} - d_{yz})$ orbitals, nonbonding $(d_{xz} - d_{xz})$ orbitals, and finally the antibonding ones. The orbital energies are lowered with respect to the C_{4v} cluster, and this phenomenon may be interpreted in terms of the stabilization of this particular structure by direct metal–metal bond formation.

Analysis of the results of the calculations therefore enables two general conclusions to be formulated. Firstly, release of oxygen by the surface of the oxide is more facile when accompanied by the structural rearrangement resulting in crystallographic shear. This may create a more favourable pathway for the insertion of lattice oxygen into the organic molecule in the process of selective oxidation. Secondly, one of the important factors contributing to the stabilization of shear structures is the formation of direct metal–metal bonds.

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