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Study of MoO_3 (0 1 0) surface clusters by ab initio HF approaches

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Abstract

The clusters $Mo_2O_{11}H_{10}$, $Mo_3O_{16}H_{14}$ and $Mo_7O_{32}H_{22}$ of MoO_3 (0 1 0) surface were studied by using ab initio HF approaches. The geometry of each cluster was fully optimized at RHF or UHF/MINI/ECP-SBK level of theory. The bonding properties, electronic structures and orbital populations of structurally different oxygens were obtained. It was shown that there exist some differences in the bonding properties between Mo atoms and the different oxygens. The symmetrically bridging oxygens exhibit more ionic feature while the terminal oxygens are more covalent. Moreover, information on explaining the active sites for the insertion of oxygen into allylic species in the second step of the oxidation processes of propylene to acrolein could be inferred from the frontier orbital populations of MoO_3 surface cluster.

Keywords: MoO_3; Ab initio HF approaches; Bonding properties; Orbital populations

1. Introduction

Molybdenum trioxide, MoO_3, is an important catalyst for the selective oxidation of hydrocarbons such as propylene to acrolein, due to its structural and electronic properties. It is well established that selective oxidation proceeds in a series of consecutive elementary steps of hydrogen abstraction and nucleophilic oxygen insertion [1]. However, the nature of the active sites and the mechanistic details of the selective oxidation of propylene over MoO_3 catalysts have not been well understood, leaving continuous debate on the genesis of active sites on MoO_3 surface in the literature. Volta et al. [2–4] proposed that selective oxidation of propylene to acrolein proceeds mainly on the side face (1 0 0), whereas the total oxidation to CO_2 occurs only on the basal face (0 1 0). Bruckman et al. [5] assumed that activation of propylene takes place at the (1 0 0), (0 0 1) and/or (1 0 1) faces of MoO_3, the basal (0 1 0) face is responsible for the insertion of oxygen into the activated hydrocarbon molecule and that total oxidation occurs at all faces. This assumption was supported by further experiments [6]. Recently, theoretical approaches based on the adequate description of the bonding and electronic structures of MoO_3 surface clusters have increasingly been used to explore the nature of MoO_3 catalyst [7–12], throwing a light on a better understanding of all the aspects of catalytic nature of oxidation processes over MoO_3 catalyst. The calculations [7,11–12] indicated that the interatomic binding at the surface of MoO_3 is determined by both ionic and covalent contributions with a clear distinction between terminal oxygens and different bridging surface oxygens. The adsorption of H on MoO_3 (0 1 0) surface was also studied [9,11]. Hermann et al. [9] found that the bonding of H with terminal oxygen is strongest although H adsorbed at all oxygen sites, and the surface OH formed by H

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adsorption on the terminal oxygens bond strongly to the surface whereas those involving bridging oxygens are mobile. Studies by Chen et al. [11] showed that hydrogen is most strongly adsorbed over the terminal oxygen, followed by the asymmetrically bridging oxygens, and then the symmetrically bridging oxygens.

In most papers mentioned above [7–9,12], the geometry of the clusters was cut from the ideal crystal of the MoO_3 and all bond lengths in their clusters were fixed to experimental values. Considering that the surface structure of the crystal may exhibit reconstruction compared to the bulk, the structures of all the clusters are first optimized in this study. The bonding and electronic properties as well as the frontier orbital populations of the (0 1 0) surface of MoO_3, which contains the surface sites being essential for the selective oxidation, are analyzed from the optimized geometry.

2. Computational details

The crystal lattice of MoO_3 monocrystal has orthorhombic symmetry with the space group P_{bnm}, and the cell parameters defined as a=3.963 Å, b=13.855 Å, c=3.696 Å [13]. Bulk MoO_3 is a layered material with bilayers paralleling to the (0 1 0) plane. The bilayers consist of periodic units of MoO_6-distorted octahedron. They are linked together by sharing oxygen atoms by two or three molybdenum atoms. There are only weak interactions between the double layers, which account for the easy cleavage along (0 1 0) face. The (0 1 0) plane modeled in the following studies contains three kinds of structurally different oxygen centers O_T, O_A and O_S (O_{S1} and O_{S2}; see Fig. 1). First, terminal oxygen atom (O_T) coordinates to only one Mo center at a distance of 1.67 Å. Then asymmetrically bridging oxygen atom (O_A) coordinates to one Mo center with $d_{Mo–O}$=1.73 Å and weakly couples to another Mo atom at a distance of 2.25 Å. And the last symmetrically bridging oxygen atom (O_S) bonds to two Mo centers symmetrically at distance of 1.95 Å and weakly couples to a Mo center of the underlying sublayer with $d_{Mo–O}$=2.33 Å [14].

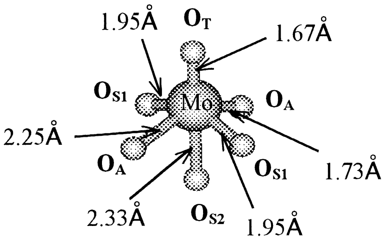


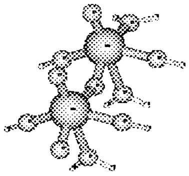
Fig. 1. The different kinds of oxygen atoms in MoO_3 (0 1 0) surface (bond length is in Å).

The clusters chosen to represent MoO_3 (0 1 0) face are in the form of $Mo_mO_nH_x$ (m=2, 3, 7; see Fig. 2), where Mo_mO_n fragments are cut from the (0 1 0) surface with hydrogen atoms electronically saturating the peripheral oxygens (if needed). The saturation scheme was proved to be reasonable [7,9,12]. The largest cluster $Mo_7O_{32}H_{22}$ contains at least one of each structurally different oxygens and their entire neighbors. The two smaller ones, $Mo_2O_{11}H_{10}$ and $Mo_3O_{16}H_{14}$ as subunits of the largest cluster are studied to examine the dependence of the calculation results on the cluster size. The bond lengths within the clusters are initially set according to the experimental values taken from the literature as mentioned above [14], and then optimized by ab initio MO approaches.

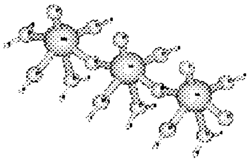
All calculations in this work are performed by using the software GAMESS [15], a general atomic and molecular electronic structure system, on P(II) computers or SGI workstations. The geometry of each cluster is fully optimized by using ab initio HF methods at RHF or UHF/MINI/ECP-SBK level of theory with C_S symmetry. The cutoff of SCF energy, density convergence and energy gradient are 1.0×10^{-8}, 1.0×10^{-5} and 1.0×10^{-4}, respectively.

3. Results and discussion

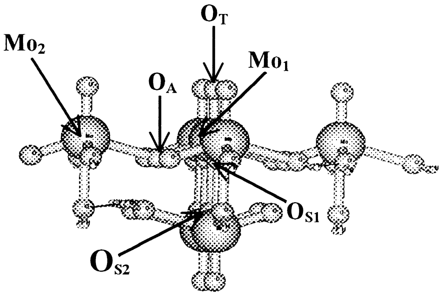
Table 1 summarizes the results of Mulliken population and charge distribution analysis for the calculated clusters. The molybdenum atom is always positive with atomic charge 1.86–2.05 a.u. All oxygen atoms form negatively charged sites. Bridging oxygen atoms, including symmetrically bridging oxygen (0.68–0.85 for O_{S1} and 0.61–0.85 for O_{S2}) and asymmetrically bridging oxygen (0.67–0.68) carry more negative charges than the terminal oxygen atom (0.46–0.50). The present data confirm the ionic nature of the MoO_3 compound as suggested by basic chemical intuition. The increased charge at the bridging oxygen sites hints at their increased local reactivity



$Mo_2O_{11}H_{10}$



$Mo_3O_{16}H_{14}$



$Mo_7O_{32}H_{22}$

Fig. 2. The cluster models of MoO_3 (0 1 0) surface (with the molybdenum and oxygen atoms listed in the tables pointed out in the largest clusters).

Table 1
The Mulliken populations and charges on molybdenum and different oxygen atoms in the clusters of MoO_3 (0 1 0) surface[a]

Atoms	$Mo_2O_{11}H_{10}$		$Mo_3O_{16}H_{14}$		$Mo_7O_{32}H_{22}$	
	Populations	Charges	Populations	Charges	Populations	Charges
Mo	39.9863	2.0137	39.9474	2.0526	40.1441	1.8559
O_T	−8.4893	−0.4893	8.4984	−0.4984	8.4601	−0.4601
O_A	−8.6671	−0.6671	8.6793	−0.6793	8.6808	−0.6808
O_{S1}	−8.6833	−0.6833	8.6906	−0.6906	8.8544	−0.8544
O_{S2}	−8.6113	−0.6113	8.6288	−0.6288	8.8532	−0.8532

[a] The Mo (Mo, Mo_1 and Mo_2) in Tables 1–3 refer to the central molybdenum atoms in the clusters, the O_T, O_A, O_{S1} and O_{S2} refer to the different type of oxygen atoms coordinated to the central molybdenum atom.

with respect to nucleophilic attacks and indicates that the strongest ionic contributions to the Mo–O bonds is from molybdenum atoms and symmetric bridging oxygens. At the same time, the actual ionic charge is found to be smaller than suggested by the formal oxidation states of the atoms, which identifies covalent contributions to the Mo–O interatomic binding. The covalent character of Mo–O bonds is also reflected in bond order indices (Table 2). The bond order indices between terminal oxygen and molybdenum center are nearly 2 (1.91–1.92) which suggests a strong Mo=O double bond. This is consistent with the single coordination of O_T to the molybdenum center below it. The bond order indices between asymmetrically bridging oxygen and one molybdenum center are also larger than 1 (1.46–1.52), indicating a nearly double bond, but the bond order between another adjacent molybdenum center is much smaller than 1 (0.21–0.25)

Table 2
The bond lengths and bond orders between Mo and different oxygen atoms

Bond	$Mo_2O_{11}H_{10}$		$Mo_3O_{16}H_{14}$		$Mo_7O_{32}H_{22}$		Values from [16]	
	Lengths	Orders	Lengths	Orders	Lengths	Orders	Lengths	Orders (v.u.)
Mo–O_T	1.689	1.914	1.688	1.916	1.688	1.913	1.671	2.064
Mo_1–O_A	1.730	1.520	1.741	1.461	1.735	1.458	1.734	1.500
Mo_2–O_A	2.204	0.212	2.165	0.247	2.141	0.244	2.251	0.464
Mo–O_{S1}	1.887	0.737	1.896	0.720	1.916	0.720	1.948	0.779
Mo–O_{S2}	2.334	0.122	2.379	0.112	2.291	0.212	2.332	0.418

which suggests a weak coupling. This indicates that O_A has a similar bonding scheme as O_T, i.e. O_A is coordinated mainly to one molybdenum center. The symmetrically bridging oxygen atom bonds to two adjacent molybdenum atoms symmetrically with bond order 0.72–0.74, which indicates a single bond, and weakly couples with a molybdenum center of the underlying sublayer with bond order of 0.11–0.21. Taking the bond order indices as a measure of the covalent properties of Mo–O bonds, one can conclude that the bonds between molybdenum centers and terminal oxygens exhibit strongest covalent bonding characters, whereas the symmetrically bridging oxygens are the weakest ones. This conclusion is in agreement with the bonding features derived from the previous charge analysis.

By comparing the data in Table 1 it can be found that only a little difference exists in charge distributions on molybdenum atom (ΔC=0.20), O_T (ΔC=0.04) and O_A atom (ΔC=0.01) between the three clusters, while a little larger difference (ΔC=0.17 and 0.24) can be found on O_{S1} and O_{S2}. That may be caused by the fact that in the smaller clusters the nearest molybdenum atoms bonded to O_S are substituted by hydrogen atoms. From Table 2 one can find that the bond lengths and bond orders calculated from the three clusters are in agreement with each other. Also, the values calculated from $Mo_7O_{32}H_{22}$ are well consistent with the bond strength values (in valence units) which could be served as bond orders taken from literature [16]. This indicates that the surface does not exhibit major reconstruction as suggested from the experiment [14]. It also demonstrates that the current cluster models are efficient for the present studies, and the cluster size has some effect on the calculation results of the electronic structures while it has little effect on the bonding features. At the same time, $Mo_7O_{32}H_{22}$ is the best cluster to simulate the MoO_3 (0 1 0) surface.

The atomic overlap populations shown in Table 3 also confirm the mixed ionic and covalent character of binding in MoO_3. Overlap populations are not appropriate indices of reactivity, since low values correspond to ionic bonds and not necessarily to weak bonds [17]. The fact that the overlap between the symmetrically bridging oxygen and Mo center is smaller than the terminal oxygen and asymmetrically bridging oxygen indicates that the strongest ionic contribution to the Mo–O bonds comes from Mo atoms and symmetric bridging oxygens.

The catalytic reactivity of different oxygen sites could be inferred from the frontier orbital populations. Table 4 shows HOMO and LUMO distributions on AOs of different oxygens in $Mo_7O_{32}H_{22}$ cluster. It needs to be emphasized that the HOMO of the MoO_3 surface is predominately contributed by oxygen atoms, and Mo sites have a little contribution to it. According to the literatures [5,14] the second step of propylene selective oxidation, namely the allyl to acrolein conversion occurs on MoO_3 (0 1 0) surfaces. It is indicated that the C–O σ-bond is formed through the interaction of the LUMO of allylic species and HOMO of

Table 3
Mulliken atomic overlap populations between molybdenum and different oxygen atoms

Atom-pair	$Mo_2O_{11}H_{10}$	$Mo_3O_{16}H_{14}$	$Mo_7O_{32}H_{22}$
Mo–O_T	0.3050	0.3076	0.2993
Mo_1–O_A	0.2565	0.2449	0.2471
Mo_2–O_A	0.0517	0.0582	0.0466
Mo–O_{S1}	0.1432	0.1384	0.1424
Mo–O_{S2}	0.0273	0.0251	0.0577

Table 4
HOMO–LUMO distributions on AOs of different oxygens in $Mo_7O_{32}H_{22}$ cluster

Orbital	O_T	O_S	O_A
HOMO (E=−0.3386)	2p$_z$ (−0.2151)	2p$_y$ (0.0886) 2p$_z$ (0.2160)	2p$_z$ (−0.1121)
LUMO (E=0.0753)	2p$_z$ (−0.0859)	2p$_y$ (0.0204) 2p$_z$ (0.0770)	2p$_z$ (0.2833)

O^{2-}. From Table 4, we can find that among the three kinds of oxygens the largest contribution is from the 2p$_z$ orbital of symmetrically bridging oxygens, and the contribution from the 2p$_z$ orbital of terminal oxygens is very close to it. It is obvious that the nucleophilic attack of oxygen on the allylic species is facilitated when negative charge is concentrated on the oxygen sites, and we know that the symmetrically bridging oxygens are more negatively charged than the terminal oxygens from the previous Mulliken charge analysis. So it can be concluded that the symmetrically bridging oxygen site is the most probable active site in the process of oxygen insertion into the allylic species to form acrolein which is in agreement with the results inferred from the experiment. ESR studies by Bruckman et al. [5] showed that surface oxygen bridging two adjacent octahedrons in the double strings of edge linked MoO_6 octahedron, namely the symmetrically bridging oxygen, is removed from the (0 1 0) face of MoO_3 on interaction with a reducing agent. TPR studies [18] showed that the Mo–O–Mo sites are more easily reduced than the Mo=O sites. Additionally, ^{18}O-exchange experiment [19] showed that the bridging Mo–O–Mo sites are more easily regenerated by gas-phase oxygen. All these experimental results indicated that the bridging oxygens are more easily removed from the MoO_3 (0 1 0) surface and also are more active in oxygen insertion reactions than the terminal oxygens.

4. Conclusions

The results from the present work confirm the mixed ionic and covalent character of binding in MoO_3, and the symmetrically bridging oxygens exhibit more ionic feature while the terminal oxygens are more covalent. Moreover, the frontier orbital populations of the MoO_3 (0 1 0) cluster indicates that the symmetrically bridging oxygen sites are probably the active sites for the insertion of oxygen into allylic species in the second step of the oxidation processes of propylene to acrolein.

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