One Oxygen Vacancy, Two Charge States: Characterization of Reduced $\alpha$-MoO$_3$(010) through Theoretical Methods

Marcos Rellán-Piñeiro and Núria López*©

Institute of Chemical Research of Catalonia, ICIQ, and The Barcelona Institute of Science and Technology, BIST, Av. Països Catalans 16, 43007 Tarragona, Spain

Supporting Information

ABSTRACT: Molybdenum oxides are finding increasing applications that rely on their redox character. For the most common polymorph, $\alpha$-MoO$_3$, oxygen vacancy formation leaves two electrons on the surface that can be stored as small polarons. Detailed density functional theory calculations that properly account for the self-interaction term, $U_{\text{eff}}=3.5$ eV, show that the vacancy generates two different configurations: either two Mo$^{5+}$ centers (Mo$^{5+\square}$ and Mo$^{5+\equiv}$O) or a single double-reduced Mo$^{4+}$. These states are separated by 0.22 eV with a barrier for interconversion of 0.33 eV, and thus both are populated at catalytic temperatures, as shown by first-principles molecular dynamics. At higher reduction levels, vacancies can only be accumulated along a preferential direction and the energy difference between the 2xMo$^{5+}$ and Mo$^{6+}$ configurations is reduced. These results point out the need for a revision of the experimental assignments based on our characterization that includes charges, vibrational frequencies, and XPS signatures.

The properties of oxides are dominated by defects, commonly oxygen vacancies. Vacancies affect the electronic structure of materials, as the two electrons left upon O removal can be (i) a localized pair at the position of the anion (like for MgO); (ii) separated and localized at the surrounding cations like for TiO$_2$ and CeO$_2$ effectively leaving two M$^{(n-1)+}$; (iii) partially delocalized between a group of metals, like for In$_2$O$_3$. Recently, molybdenum oxides have attracted a lot of attention due to their large number of new physical and chemical applications as electro- and chromic devices, in photo-, electro-, and thermal catalysis, in solar cells, and as light-emitting diodes, photodetectors/sensors, batteries, pseudocapacitors, thermoelectric, and ferroelectric materials. All of these applications are based on the versatile geometric (with several structure forms) and electronic structure linked to the redox character that can be fine-tuned by the addition of cations or hydrogen or by oxygen removal, which leads to the formation of Magnéli phases.

In the most common polymorph, $\alpha$-MoO$_3$, Mo centers are in the oxidation state Mo$^{5+}$, and surrounded by oxygen atoms in octahedral environments with a band gap between 3.0 and 3.2 eV. $\alpha$-MoO$_3$ has an orthorhombic unit cell with $Pbnm$ symmetry, where distorted MoO$_6$ octahedra are ordered in bilayers along the $xz$ plane; see Figure 1. van der Waals interactions hold the layered structure packed. There are three nonequivalent oxygen atoms: (i) three coordinated oxygens, O$_c$, that form a symmetrical bridge along the $x$ axis between two Mo centers of the same layer and interact with a sublayer Mo; (ii) asymmetric oxygens, O$_a$, that bridge two Mo centers along the $z$ axis; and (iii) terminal oxygens, O$_t$, double bonded to only one Mo center present in the interlayer region. Oxygen depletion severely affects the electronic structure of the material, changing its very large work function (~6.9 eV) to lower values ~6.5 eV for a 10% oxygen-deficient material, introducing donor gap states. Upon reduction, the photo-emission spectra present additional features: At low vacancy concentrations, these features are assigned to the formation of Mo$^{5+}$ centers, and after a certain concentration, Mo$^{6+}$ features also appear. Electron paramagnetic resonance (EPR) studies also indicate the formation of structural point defects of Mo$^{5+}$ close to oxygen vacancies, which at higher concentrations lead to the formation of other centers associated with extended shear structures.

![Figure 1. Structures of $\alpha$-MoO$_3$(010) pristine surface, left, and local structure of the two possible O vacancies, right. (a) O$_c$, (b) O$_a$, and (c) O$_t$. Mo: green and O: red.](image-url)
Understanding the electronic properties of α-MoO₃ from first-principles has been hampered by the presence of the layered structure, the semiconductor character of the material, and the reducibility of the cation. Hybrid methods have been applied, for instance, to evaluate the vacancy formation energy in the bulk, which is endothermic by 3.68 eV within HSE06. However, the use of these functionals remains impractical when exploring complex reaction networks on the material. Alternatively, density functional theory (DFT) generalized gradient approximations (GGAs) have been employed. In α-MoO₃ studies with pure GGA functionals, electron localization is not found, and thus isolated oxidation states cannot be assigned. The empirical U_{eff} parameter needs to be incorporated to achieve localization.

In the literature, scattered U values have been used. Bulk calculations with U_{eff} = 5.0 eV were employed to analyze the preferential oxygen eliminated. O₁ was identified as the easiest to remove, but the nature of the charge state was not described. With a value of U_{eff} = 6.3 eV, vacancy formation at O₁ position in the bulk leads to a Mo^{4+} center, while the removal of the O₂ or O₃c lattice oxygen ends up in the formation of two Mo^{5+} centers. A recent study with U_{eff} = 6.0 eV suggested the formation of two different states upon removal, but no characterization was performed, and low vacancy formation energies, ~1.50 eV, were reported.

In surface models, a value of ~6 eV was obtained by fitting to hybrids calculations on cluster structure, and it was used by Chen, Asta, and Willoc. The latter reported the formation of a Mo^{+} center. In turn, Metiu, Bell, and Willows proposed a U_{eff} value to match the experimental enthalpy of the reaction MoO₃ + H₂ → MoO₂ + H₂O, but they employed very different values, 2 and 8.6 eV, respectively. Metiu found no localization upon O₁ removal and two Mo^{5+} when the vacancy was formed at the O₂b position. Therefore, the origin of the different oxidation states observed in experiments cannot be assigned from the previous computational studies.

In this work, we reoptimized the U_{eff} value to describe the reactivity on α-MoO₃(010) accurately following a set of benchmarks that include the comparison to hybrid functionals and CCSD(T) references; see Section S1. Then, we employed PBE+U-D₂ to identify the true nature of vacancies in terms of oxidation state of the cations and the corresponding spectroscopic fingerprints.

The bulk PBE-D₂ calculated lattice parameters are a = 3.921 Å, b = 14.480 Å, and c = 3.708 Å, in agreement with the experimental values: a = 3.963 Å, b = 13.855 Å, and c = 3.696 Å. Because of the layered packing through dispersion forces along the y axis, the (010) surface is the easiest to cleave. The calculated surface energy was 0.01 eV Å⁻² within PBE-D₂. The density of states (DOS) of the pristine material shows a small band gap of 1.99 eV with the valence band formed by O(2p) and the conduction band by Mo(4d). The Bader charge analysis of the Mo centers provides a value of 2.63 e⁻, which is well below the formal charge.

Because reduced α-MoO₃ requires the use of PBE+U, the U_{eff} value was optimized with two criteria: an electronic term given by electron localization and a thermodynamic one based on reaction energies; see Section S1. Since good thermochemical data are not available, computed values for an acid-base and two redox reactions with the hybrid functional HSE06 were taken as reference. The optimized value for U_{eff} is 3.5 eV (Figure S1). This value also provides the best match in a separate test against the gold standard in molecular chemistry, the CCSD(T) method (Figure S2).

Either the terminal or the two oxygens in the plane surface could be the first ones to be removed. Vacancy (V) formation energies for the reaction MoO₃ → MoO₂ − 1/2 O₂(g) at the O₁ position are shown in Figure 2. For the O₁−O₂ pair it was found that the calculations within PBE result in similar geometries (the remaining oxygen stays at an intermediate position between that of O₁ and O₂) and similar formation energies. However, in our PBE+U calculations, the converged V_MO geometry keeps the O₂ in the surface plane, whereas all of our attempts to converge a V_MO resulted in a displacement of the O₂ to the O₁ position and the convergence in the same O₂ vacancy geometry. Therefore, no vacancies appear at O₂b positions on the (010) surface. In turn, the formation of O₂ vacancies is endothermic, between 2.61 and 2.87 eV, whereas that of O₃c requires an additional 1.80 eV; see Tables S1 and S2.

Figure 2 (a) V_MO vacancy formation energy according to the reaction MoO₃ → MoO₂ + 1/2 O₂(g) calculated on the (2 × 2) and (3 × 3) supercells at PBE+U and HSE06 levels. (b) V_MO vacancy formation energy as a function of oxygen depletion for 2×Mo^{4+} and Mo^{5+} states at PBE+U. U_{eff} = 3.5 eV.

The Journal of Physical Chemistry Letters
the same spin, in two different d orbitals of the Mo$^{4+}$ center, according to the calculated magnetization of 1.70 $\mu_B$. Therefore, this structure is assigned to the formation of a single double-reduced Mo$^{4+}$ ($\square$) center.

The formation of two different electronic states can be understood as follows. The ground-state 2$\times$Mo$^{5+}$ can disproportionate to Mo$^{6+}$ and Mo$^{4+}$ centers because the relative energies to increase the oxidation state of Mo$^{5+}$ (toward Mo$^{6+}$) and reduce it (toward Mo$^{4+}$) cancel each other out. The higher electrostatic interaction between the Mo centers and the surrounding oxygens in the 2$\times$Mo$^{5+}$ is responsible for its larger stability; see Section S3.

Benchmarks performed with the hybrid functional at this concentration (1/9) and the PBE+U geometries lead to a slightly higher vacancy formation energy range: 2.82 and 3.18 eV. The reoptimized PBE+U ($U_{\text{eff}} = 6.3$ eV) energies are much lower, 1.72 and 1.88 eV, but even at these geometries the HSE06 values are 2.93 and 3.30 eV, thus highlighting the critical choice of the $U_{\text{eff}}$ when reproducing the formation energies. In summary, the ground state can be identified as a bipolaron, where two electrons are localized on two neighboring Mo centers (Mo$^{5+}$), whereas the metastable state corresponds to a single dipolaron at the same center (see Figure 4a) and the energy difference is well-represented by PBE+U, $U_{\text{eff}} = 3.5$ eV.

We have inspected how concentration affects the V$_{Ot}$ vacancy formation energies (Figure 2b). 2$\times$Mo$^{5+}$-like defects are increasingly more costly (with a linear dependence on concentration), whereas Mo$^{4+}$ ones are independent of the concentration until coverage reaches 0.5. Moreover, vacancies cannot be accumulated through the [100] direction for both configurations; see Table S1. The origin of this vacancy alignment is at the core of the relaxations observed when the vacancy is formed. When two neighboring vacancies are aligned along [100], the shared O$_3c$ sinks toward the subsurface Mo atom (reduces its bond length by 0.1 Å). This ends up increasing the vacancy formation energy. Vacancies would then accumulate on the perpendicular direction, generating crystal shears that induce the formation of Magnéli phases.

Next, we analyzed the interconversion between the two vacancy configurations. α-MoO$_3$ is known to generate small polarons upon electron addition, which are highly mobile, with reported barriers of 0.35 eV in the plane and 0.50 eV between bilayers. The CI-NEB results in a barrier for the interconversion of the two different states corresponding to the V$_{Ot}$. Magnetization, $\mu$, in $\mu_B$; Bader charges, $q$, in $|e|$; XPS displacement in eV; and frequencies, $\nu$ in cm$^{-1}$.

Figure 3. (a) Projected density of states, (b) local geometry with Mo$\cdots$O bond distances, in angstroms, and (c) fingerprints for the clean surface and the two different states corresponding to the V$_{Ot}$. Magnetization, $\mu$, in $\mu_B$; Bader charges, $q$, in $|e|$; XPS displacement in eV; and frequencies, $\nu$ in cm$^{-1}$.

Figure 4. (a) Energy profile for the electron hopping for the conversion 2$\times$Mo$^{5+} \rightarrow$ Mo$^{4+}$ on the (2$\times$2) and (3$\times$3) supercells and calculated spin density for the two surface states at 0.01e Å$^{-3}$. (b) Surface Mo local magnetization as a function of time for the molecular dynamics run at 300 °C and $\theta_{\text{Vo}} = 0.25$ ML (atom labels shown in the scheme). (c) Calculated XPS at different vacancy coverages, $\theta_{\text{Vo}}$, at 350 °C. Green Mo$^{6+}$, red Mo$^{5+}$, and blue Mo$^{4+}$.
conversion between oxidation states $2\text{Mo}^{5+} \leftrightarrow \text{Mo}^{6+}$ of $\sim 0.3$ eV, higher within HSE06, 0.40–0.60 eV, but still easy to surmount at reaction temperatures. The barrier is low enough to ensure that the two states are in equilibrium even at room temperature. Therefore, we performed first-principles molecular dynamics (MD) simulations to illustrate the dynamic nature of the electronic states in $V_{\text{Mo}}$. The local magnetization of the surface centers is shown in Figure 4b along the 10 ps trajectory at 300 °C. The main features are that the Mo$_{\text{ox}}$ is preferentially Mo$^{5+}$ but also samples Mo$^{6+}$ states and the second polaron is localized either preferentially along the [001] direction or in zigzag but not in the nearest neighbor along the [100] direction. At the temperatures at which α-MoO$_3$-catalyzed reactions take place ($\sim 300$ °C), the relative Boltzmann population at low reduction levels ($\theta_{\text{ox}} = 0.25$ ML) is $\sim$93% of Mo$^{5+}$ and $\sim$7% of the Mo$^{6+}$ configuration; from our MD trajectory, these values are 95 and 5%. This is remarkable because experiments have shown that materials reduced at 350 °C and quantified by the XPS fingerprints provide 93:7 Mo$^{5+}$:Mo$^{6+}$.

The experimental fingerprints of oxygen-deficient α-MoO$_3$ can then be reanalyzed considering the dual nature of the vacancies. For instance, the Raman fingerprint of α-MoO$_3$ has three characteristic bands: Mo=O, Mo−O$_2$, and Mo−O$_{\text{ox}}$ stretchings at 996, 823, and 667 cm$^{-1}$, respectively. We have calculated the vibrational modes of the different coordination spheres of Mo centers. The reference Mo=O is 974 cm$^{-1}$, which increases by 15 cm$^{-1}$ for the hexacoordinated Mo$^{5+}$ in the Mo$^{5+}$–O$_{\text{ox}}$ bond, and is reduced by 5–40 cm$^{-1}$ for Mo−O$_2$ and Mo−O$_{\text{ox}}$ stretching vibrations. The frequency for the Mo−O$_{\text{ox}}$ stretching increases for the undercordinated cations: 10 and 36 cm$^{-1}$ for Mo$^{6+}$ and Mo$^{5+}$, respectively. Thus, the frequency in the Mo−O$_{\text{ox}}$ stretching increases for the undercordinated cations: 10 and 36 cm$^{-1}$ for Mo$^{6+}$ and Mo$^{5+}$, respectively. Thus, this mode can be used to discriminate different states. Complementary, experimental XPS on the exposed redox Mo$^{5+}$, Mo$^{6+}$, and Mo$^{5+}$ surface centers. For Mo$^{5+}$ the peaks are displaced around $-1.80$ eV, and for Mo$^{6+}$ $-3.00$ eV. We calculated the theoretical XPS displacement and obtained values of $-0.84$ and $-1.29$ eV for Mo$^{5+}$ and Mo$^{6+}$, respectively. As shown in Figure 4c, increasing vacancy concentrations would have a dramatic effect on the shape of the XPS spectra.

The ability of the Mo centers to reach different oxidation states can have implications in the chemistry of the oxide. To analyze this we have calculated the adsorption for the two key species in the Formox (methanol to formaldehyde) process. While methanol adsorbs through the hydroxyl to the Mo$_{\text{ox}}$ by $-1.55$ eV in both Mo$^{5+}$ and 2xMo$^{3+}$; formaldehyde bonds to both Mo$_{\text{ox}}$ and an O$_{\text{ox}}$ by $-1.60$ and $-1.83$ eV for the Mo$^{5+}$ and the Mo$^{6+}$ centers, respectively (see Figure 5a). The single-site adsorption by lone-pair donation of methanol is rather independent of the oxidation state of the metal atom. In contrast, the covalent bifunctional coordination of formaldehyde perturbs the structure (for 2xMo$^{5+}$ the Mo$_{\text{ox}}$:O$_{\text{ox}}$: Mo angle changes from 160 to 155° upon adsorption but does not affect Mo$^{5+}$), and thus the adsorption energies for the electronic configurations are different.

In summary, a reaction-thermodynamics-adapted PBE+U scheme has been employed to describe the nature of vacancies in $\alpha$-MoO$_3$(010). The removal of terminal oxygens generates two different configurations. The ground-state configuration is constituted by two Mo$^{5+}$ polarons that is separated from the metastable configuration with a single Mo$^{5+}$ by 0.2 eV. The interconversion is possible through polaron hopping, and at relevant catalytic temperatures the relative populations are 93:7. Therefore, the complex spectroscopic patterns observed for this material might be due to the different population of ground and metastable states that correspond to a unique type of atom deficiency. This might have implications in the electronic and transport properties, Magnéli phase formation, and chemical properties because the adsorption from the different states can be different. This phenomenon will appear for oxides in which the cations can adopt multiple low oxidation states.

## COMPUTATIONAL METHODS

The Vienna Ab Initio Simulation Package (VASP), version 5.3.3, was used to perform the DFT calculations on slabs models. PBE$^{48,49}$ with Grimme’s semiempiric D2$^{50}$ and U approximation$^{51}$ (PBE+U-D2) and BEEF-vdW$^{52}$ that contains vdW-DF2$^{53}$ nonlocal correlation energy were used in the benchmark. In addition, single points with the hybrid HSE06 functional were performed at PBE+U geometries with $U_w = 0$, 3.5, and 7.0 eV.$^{54,55}$ The core electrons were described by the projector-augmented wave (PAW) pseudopotentials$^{56}$ (with 14 valence electrons for Mo atoms), and valence ones were expanded in plane waves with a kinetic cutoff energy of 450 eV. Spin polarization was taken into account in all cases.

The bulk was optimized for the PBE functional with a 11 × 3 × 11 k-point mesh and a cutoff energy of 600 eV and employed in all calculations. The (010) surface containing two bilayers was cleaved, and benchmark calculations were performed on a (2 × 2) supercell with a 5 × 5 × 1 k-point sampling. Vacancy formation was studied on a (2 × 2), (3 × 3), (2 × 3), and (3 × 2) supercell with a 3 × 3 × 1, 5 × 5 × 1, 5 × 3 × 1, and 3 × 3 × 1 k-point sampling, respectively. HSE06 single-point calculations were performed with 3 × 3 × 1 k-point mesh for the (2 × 2) supercell and Γ-point sampling for (3 × 3) supercell. During the optimizations, the upper bilayer and adsorbates were relaxed, except where stated otherwise. A vacuum gap of 15 Å was added to prevent the interaction between slabs together with the dipole correction.$^{57}$ Complementary, the first-principles MD run was performed in the Born–Oppenheimer approximation on a (2 × 2) supercell with one vacancy defect at 300 °C during 10 ps with 2 ps of equilibration. The most relevant structures have been added to the ioChem-BD database$^{58}$ and can be consulted in the following link.$^{59}$

## ASSOCIATED CONTENT

Supporting Information

$U_w$ fitting, detailed vacancy formation energies, electrostatic model, adsorption study (PDF)

## AUTHOR INFORMATION

**Corresponding Author**

E-mail: nlopez@iciq.es.

**ORCID**

Núria López: 0000-0001-9150-5941

**Notes**

The authors declare no competing financial interest.
REFERENCES


