

New Bonding Model of Radical Adsorbate on Lattice Oxygen of Perovskites

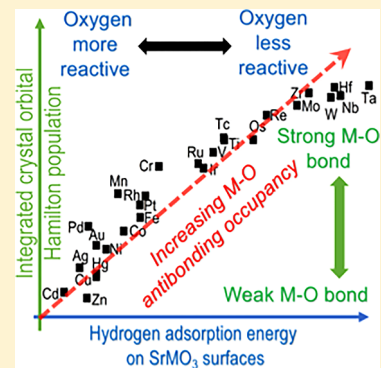
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S Supporting Information

ABSTRACT: A new model of bonding between radical adsorbates and lattice oxygens is proposed that considers both the adsorbate–oxygen bonding and the weakening of the metal–oxygen bonds. Density functional calculations of SrMO₃ perovskites for M being 3d, 4d, and 5d transition metals are used to correlate the bulk electronic structure with the surface-oxygen reactivity. Occupation of the metal–oxygen antibonding states, examined via the crystal orbital Hamilton population (COHP), is found to be a useful bulk descriptor that correlates with the vacancy formation energy of the lattice oxygen and its hydrogen adsorption energy. Analysis of density-of-states and COHP indicates that H adsorption energy is a combined result of formation of the O–H bond and the weakening of the surface metal–oxygen bond due to occupation of the metal–oxygen antibonding states by the electron from H. This insight will be useful in understanding the trends in surface reactivity of perovskites and transition-metal oxides in general.



Metal oxides are ubiquitous in the study of surface chemistry and catalysis. A better physical and chemical understanding of these materials is consequently warranted to meet the increased interest and pace of development. For transition metals, widely applicable and elegant models have been developed, such as the d-band center^{1–3} and the coordination number,^{4,5} as descriptors of adsorption and catalytic properties. However, metal oxides remain a challenge to accurately characterize due to the significantly increased complexity in electronic, magnetic, and surface structures.

Catalytic reactivity descriptors for metal oxides are frequently found to be linked to stability. From a computational standpoint, these reactivity descriptors are generally adsorption energies of relevant reactants or intermediates on the metal and O sites of the surface. For example, in electrocatalytic oxygen evolution and oxygen reduction reactions, the main descriptors involve the adsorption energies of oxygen-containing species (O, OH, OOH)^{6,7} and oxygen molecule (O₂),⁸ respectively. In the homolytic C–H activation, hydrogen adsorption energy (HAE) on the oxygen site is a very good descriptor for the first C–H activation energy.^{9–11} Meanwhile, stability descriptors are used to characterize metal oxides, including bulk formation energy^{6,12,13} and oxygen vacancy formation energy (VFE).^{10,14–19} It has been observed that HAE and VFE have a persistent correlation,^{9,10,20,21} but an electronic understanding of the underlying relation has been lacking.

In this paper, we attempt to unravel the nature of oxygen–adsorbate (O–X) bonding, whereby a radical group, as a result of dissociative adsorption or activation by surface sites, forms a strong σ -bond with a surface oxygen of a transition-metal oxide

(TMO). As the adsorption strength of these species is a prime descriptor for an oxide’s catalytic activity, establishing an energetic model for the oxygen–adsorbate interaction is a necessary step toward rational catalyst design.

Because the energetics of formation of the surface O–X bond is intrinsically linked to the electronic structure of the TMO, we begin our study first on the metal–oxygen bond in the TMO. TMOs can be characterized as having polar covalent M–O bonds from the mixing of M d states and O 2p states.^{16,22} We focus our efforts here on cubic perovskites, which prove to be computationally convenient systems with a fixed ABO₃ stoichiometry and a well-defined crystal structure. The A cation is chosen here to be Sr²⁺, which is ionically bonded to the oxygen, while the B cation varies from the transition metals in the periodic table of different orbital occupations. The varying d-electron count of cation B will allow us to explore the trends in the B–O bonding and its relation to the O–X bonding from the density functional theory (DFT) calculations of the changing electronic structure and surface energetics.

Our DFT study was based on the Perdew–Burke–Ernzerhof (PBE) functional²³ within the generalized gradient approximation (GGA). Although band gaps are usually underestimated with GGA, it has nevertheless proven to be robust in sufficiently replicating energetic quantities such as formation energy,^{13,24,25} to reveal the relative trends. HSE06,²⁶ a hybrid functional, was used to validate the PBE

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results, confirming the linear trends from PBE (Figure S1). An important concept utilized in this work is the crystal orbital Hamiltonian population (COHP),²⁷ which is a product of the density of states (DOS) and the overlap Hamiltonian element, an improvement²⁸ over the classic crystal orbital overlap population (COOP). With COHP, the chemistry of bonding–antibonding interactions can be revealed from the solid state. Further computational details can be found in the Supporting Information. Relaxed geometries were used for all computed energetics. While the basic principle for bonding on surfaces,^{22,29} particularly molecular adsorbates on metals via back-donation,^{30,31} has been proposed for many years, to date there is no explicit *ab initio* work done to study bonding trends on metal oxides from the perspective of the bonding and antibonding contributions, to our best knowledge. In this work we try to tackle the problem using COHP and the perovskite model system, and by drawing trends from screening a large number of elemental compositions.

Figure 1a shows the integrated crystal orbital Hamiltonian population (ICOHP) of the M–O bond in the bulk SrMO₃

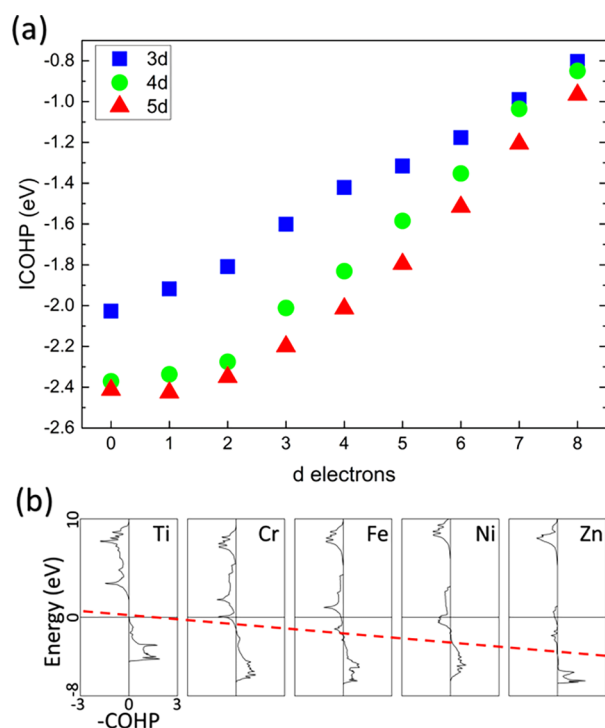


Figure 1. (a) Averaged integrated crystal orbital Hamiltonian populations (ICOHP) of the metal–oxygen (M–O) bonds as a function of the number of d-electrons in the bulk perovskite, SrMO₃, with M being 3d, 4d, and 5d transition metals. (b) Crystal-orbital Hamiltonian population (COHP) versus energy (relative to E_{Fermi}) for several 3d metals; note that $-\text{COHP}$ is used as the x -axis. The dashed line in (b) illustrates the downshift of the separation point between the antibonding (negative) and bonding (positive) states as more antibonding states are populated across a period.

perovskite that provides a useful, relative quantification of the metal–oxygen bonding. One can see a clear trend between ICOHP and the d-electron count for each of the three periods of 3d to 5d TMs: ICOHP increases with the number of d-electrons in M, consistent with the weakening of the M–O bond from group 3 to 12, implying that the M–O covalent contributions are more significant than the ionic ones. The

corresponding COHP plots are shown for several 3d perovskites (Figure 1b). For M = Ti, all states above the Fermi level are antibonding (positive COHP or negative $-\text{COHP}$). Moving to Zn, the antibonding states become progressively more occupied. The downward shift of the antibonding states relative to the Fermi level from additional d-electrons thereby leads to increasing ICOHP (Figure 1a). In conjunction with the increasing positive COHP states, the net bonding states also decrease from the overall destabilization of the M–O bond.

More interestingly, we find that ICOHP correlates well with the VFE of surface lattice oxygen for M being all the 3d–5d metal in SrMO₃ (Figure 2a). This suggests that ICOHP is a

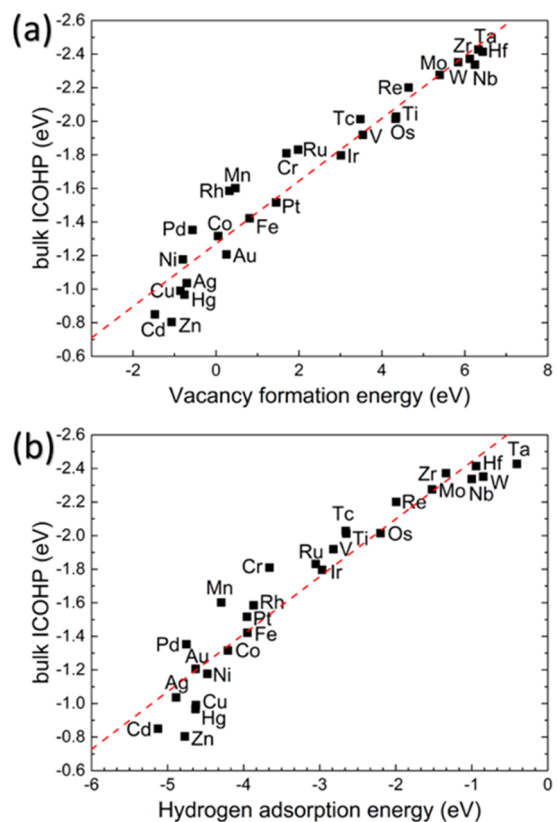


Figure 2. Correlation plots for perovskite SrMO₃(100) M-terminated surfaces with M being the transition metals denoted: (a) between bulk integrated crystal orbital Hamiltonian population (ICOHP) and vacancy formation energy of the lattice oxygen; (b) between bulk ICOHP and hydrogen adsorption energy on the lattice oxygen. The dashed red line corresponds to the linear best fit with $R^2 = 0.94$ for (a) and 0.91 for (b).

useful bulk descriptor for the surface oxygen's reactivity, since the VFE of surface lattice oxygen correlates well with the surface reactivity such as HAE and the Bader charges on the O atom (Figure 3). This correlation is further confirmed between the bulk M–O ICOHP and HAE (Figure 2b). To rule out the bond-distance effect, we plotted the M–O and O–H bond distances and found that they vary little with the number of d electrons (Figure S2). Given the destabilizing impact of increasing d-electron count on the M–O covalent bonding as manifested by the ICOHP, the correlation between ICOHP and HAE therefore suggests that adsorbate bonding can also impact the M–O covalent bonding, as we analyze next.

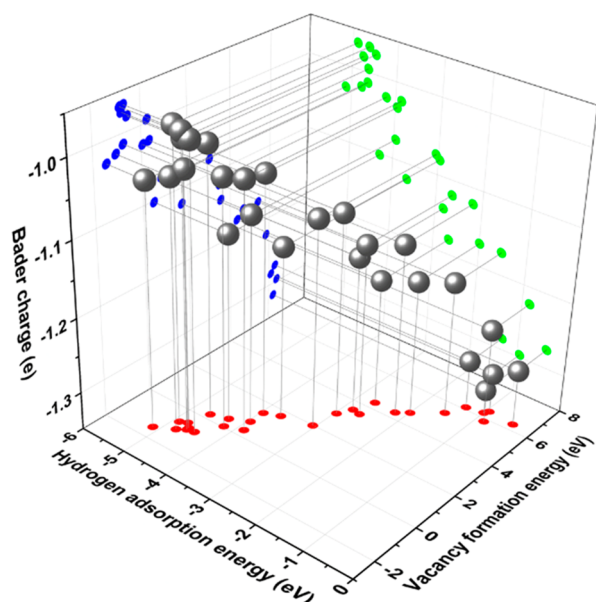


Figure 3. 3D scatterplot of hydrogen adsorption energy (HAE), vacancy formation energy (VFE), and Bader charge of the lattice oxygen on the (100) surface of the SrMO₃ perovskite with varying M. Surface relaxation was taken into account for both HAE and VFE calculations.

In an oxide surface, oxygen has a formal charge of -2 and its 2p states are situated below the Fermi level. Since the O–H antibonding state is far above the Fermi level, the electron from H will end up occupying the lower lying states in the conduction band, as schematically shown in Figure 4. For a

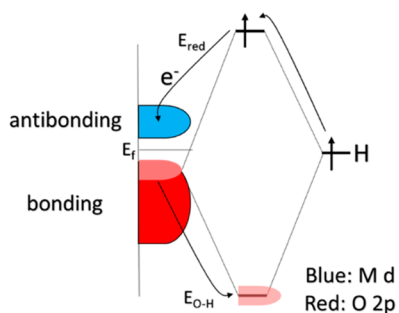


Figure 4. Diagram of the O–H bonding involving O 2p nonbonding states (pink) and one-electron reduction into the M–O antibonding states (blue).

TM oxide, as we have shown from COHP (Figure 1), the conduction band corresponds to the antibonding M–O states. Using M = Ti as a case study, the filling of the conduction band primarily onto the Ti 3d states (Figure 5a) can be seen when H is adsorbed to O. COHP plots confirm that the filling of the conduction band corresponds to an increase in occupancy in the M–O antibonding orbitals (Figure 5b). Similar reports for the phenomenon of M–O antibonding occupancy from reduction have also been observed in the case of metal clusters.³² We find a significant decrease in ICOHP for the Ti–O bond from -1.86 to -1.11 eV after H adsorption. In other words, the Ti–O bond is significantly weakened after H adsorption. Furthermore, the O–H ICOHP (Figure S3) is found to stay roughly constant with respect to the different HAEs, demonstrating that the change in HAE on

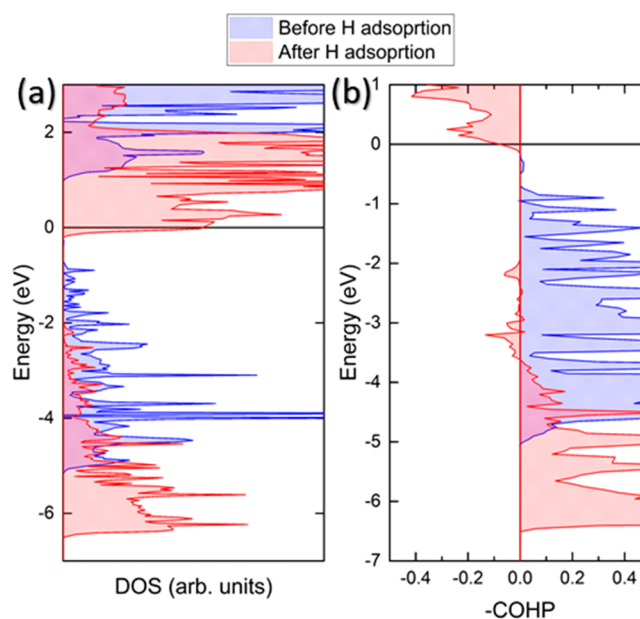


Figure 5. (a) Ti 3d partial density of states before and after hydrogen adsorption on the lattice oxygen of SrTiO₃. (b) –COHP plot of the local Ti–O bond before and after hydrogen adsorption.

different perovskites must be linked to the extent of weakening of the M–O bond from reduction.

Traditionally, as a radical adsorbate (X) approaches a surface, a bond is drawn between O and X, and the neighboring metal center is reduced by one electron (Figure 6a). Our present findings suggest that such a picture may be

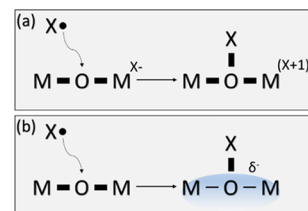


Figure 6. Two different models for O–X bonding on an oxide: (a) conventional picture involving the one-electron reduction of a neighboring metal center; (b) new model proposed in this work showing delocalization of reducing electron into nearby surface states centered on O and partially on M, as well as weakening of M–O bonds.

oversimplified. Indeed, Bader charge analysis shows that the electron transfer from hydrogen to the neighboring metal sites is significantly lower than expected from the traditional bonding scheme (Table S1). Instead, we propose a revised model (Figure 6b) where the reduction by the electron takes place mainly at the M–O bonds. Hence the oxygen charge, the M–O bonding states, and the M site reducibility all contribute to the surface reactivity of the oxide. The qualitative cross-correlation between properties such as VFE and O Bader charge with HAE (Figure 3) can thereby be explained. The stronger the M–O bonds, the more positive the VFE and the more negative the O charge; consequently, the extent of destabilization from the occupation of the M–O antibonding states is greater, which leads to a less negative HAE or weaker adsorption for H. Conversely, the weaker the M–O bonds, the smaller the VFE and the less negative the O charge; in this

case, the already weakened M–O bond leaves the O atom with more free valence to react with H, leading to more negative HAE or stronger adsorption.

The proposed O–X bonding model can be generalized beyond hydrogen adsorption to other radical species such as CH₃, NH₂, and SH, which can also covalently bond with oxygen and reduce the surface. We found that the adsorption energies of these adsorbates on the lattice oxygen have close linear relationships with HAE (R^2 values close to one; Figure S4), indicating that they will follow the same ICOHP trends and surface reduction mechanisms. Deviations from the linear correlations can be attributed to the different spin states, especially for the 3d transition metals. Further and full analysis on the spin distributions is warranted in the future.

In conclusion, analysis of crystal orbital Hamilton population (COHP) from density functional theory calculations of SrMO₃ perovskites (M being all 3d, 4d, and 5d transition metals) shows that reductive adsorption on oxygen sites of perovskite surfaces is best described as a compromise between the energetic stabilization of forming a strong O–X bonding and the destabilizing effect of electron transfer into the surface M–O antibonding states. On the same oxygen site, metals with strong M–O bonds become destabilized to a greater extent from electron transfer, and consequently, the formation of O–X bonds becomes more energetically disfavored compared to those with weak M–O bonds. Hence one can understand why hydrogen adsorption energy is a universal descriptor for any radical adsorption on perovskite surfaces and transition metal oxides in general. With our model, the deliberate tuning of oxygen charge, M–O bond strength, and M sites can be rationalized in understanding adsorption properties on lattice oxygen of metal oxide catalysts.^{33,34}

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcllett.8b02749.

Computational details; validation with the HSE06 hybrid function; variation of M–O and O–H distances with the number of d electrons; variation of O–H ICOHP with hydrogen adsorption energy; linear correlation between radical adsorbates; Bader charges after hydrogen adsorption (PDF)

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Notes

The authors declare no competing financial interest.

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