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Stable Surfaces That Bind Too Tightly: Can Range-Separated Hybrids or DFT+U Improve Paradoxical Descriptions of Surface Chemistry?

Qing Zhao and Heather J. Kulik

ABSTRACT: Approximate, semilocal density functional theory (DFT) suffers from delocalization error that can lead to a paradoxical model of catalytic surfaces that both overbind adsorbates yet are also too stable. We investigate the effect of two widely applied approaches for delocalization error correction, (i) affordable DFT+U (i.e., semilocal DFT augmented with a Hubbard U) and (ii) hybrid functionals with an admixture of Hartree–Fock (HF) exchange, on surface and adsorbate energies across a range of rutile transition metal oxides widely studied for their promise as water-splitting catalysts. We observe strongly row- and period-dependent trends with DFT+U, which increases surface formation energies only in early transition metals (e.g., Ti and V) and decreases adsorbate energies only in later transition metals (e.g., Ir and Pt). Both global and local hybrids destabilize surfaces and reduce adsorbate binding across the periodic table, in agreement with higher-level reference calculations. Density analysis reveals why hybrid functionals correct both quantities, whereas DFT+U does not. We recommend local, range-separated hybrids for the accurate modeling of catalysis in transition metal oxides at only a modest increase in computational cost over semilocal DFT.
(i.e., piecewise linearity or the derivative discontinuity\textsuperscript{88,90,91}), albeit at the cost of worsening static correlation error (SCEx\textsuperscript{89,92–96}) but typically improving densities.\textsuperscript{86,87} We have selected hybrids and DFT+U rather than approaches that can eliminate DE and SCE simultaneously\textsuperscript{89,96} because of the former methods’ widespread use in the catalysis community.

We study the catalytic MoO\textsubscript{2}(110) surface\textsuperscript{51,97,98} of seven representative\textsuperscript{50} rutile transition metal dioxides (M = Ti, V, Mo, Ru, Rh, Ir, and Pt) spanning the d-block of the periodic table, chosen for the availability of their experimental crystal structures\textsuperscript{99} (Figure 1 and Supporting Information Tables S1 and S2). Throughout this work, we focus on tuning the PBE\textsuperscript{100} semilocal functional through incorporation of global hybrid exchange (i.e., $a_{HF} = 0–50\%$) with a localized basis set (LBS) or through addition of a +U correction ($U = 0–10$ eV) in a plane wave basis set (PWBS) (see Computational Details). Despite this difference, both PBE/PWBS and PBE/LBS lattice parameters are in good agreement with each other and with experiment (ca. 0–3% error, Tables S1 and S2). Both hybrid and DFT+U minimally affect lattice parameters (average, 0.1 Å; maximum, 0.2 Å), although HF exchange decreases the lattice parameters whereas DFT+U generally increases them (Tables S1 and S2).

For each of these rutile transition metal oxides, we computed the PBE\textsuperscript{100} MoO\textsubscript{2}(110) surface formation energies, $E_f$, as

$$E_f = \frac{E_{slab} - NE_{bulk}}{2A} \quad (1)$$

where $N$ is the ratio of the number of atoms in the slab to the number in the bulk unit cell and $A$ is the material-dependent surface area. Absolute $E_f$ values are higher for PBE/LBS than for PBE/PWBS, but trends are consistent between the two implementations: within a row, later transition metals form more stable surfaces, and within a period, increasing principal quantum number (i.e., 3d to 5d) increases $E_f$ values (Figure 2).

Incorporating HF exchange or a +U correction destabilizes all surfaces, albeit to varying degrees (Figure S1). To quantify these differences, we approximated the sensitivity, $S_f(E_f)$ to variation of parameter $p$ (i.e., $a_{HF}$ or $U$), following prior work\textsuperscript{26,81,86,87,101} as $\Delta E_f / \Delta p \approx \Delta E_f / \Delta p$, which holds well across all materials studied, especially at moderate $a_{HF}$ and $U$ values (Figures 2 and S1). No correlation is observed between the sensitivities and the $E_f$ values themselves, in contrast with observations on spin-state ordering sensitivities\textsuperscript{18} (Figure S2). Disproportionately high hybrid sensitivities, $S_{HF}(E_f)$, for RuO\textsubscript{2} and PtO\textsubscript{2} lead to these two surfaces being the least stable above 30% HF exchange, reversing the d-filling trends observed with PBE GGA (Figures 2 and S1). For DFT+U, $S_f(E_f)$ values are significantly smaller than with hybrid tuning excluding only the early transition metal TiO\textsubscript{2} and VO\textsubscript{2} cases (Figures 2 and S1). Only the large, positive $S_f(E_f)$ for TiO\textsubscript{2} leads to the reversal of its relative stability with respect to PtO\textsubscript{2} for moderate (6 eV or higher) $U$ values (Figure S1). Thus, the two delocalization-correcting approaches diverge for most rutile transition metal oxides studied, with DFT+U PtO\textsubscript{2}(110) being a relatively stable surface, whereas hybrid PtO\textsubscript{2}(110) is among the least stable.

We next computed the oxygen adsorbate (O*) binding energy to a metal site on the MoO\textsubscript{2}(110) surface of each rutile transition metal oxide, $\Delta E_O$, as (Figure 1)

$$\Delta E_O = E(O^*) - E(*) - (E(H\textsubscript{2}O) - E(H\textsubscript{2})) \quad (2)$$

where $E(*)$ is the energy of the pristine surface and $E(O^*)$ is the energy of the relaxed surface with an O atom adsorbate. The last term is the gas-phase O atom energy reference following literature recommendations\textsuperscript{102} for its insensitivity to functional choice, but we note it can yield positive $\Delta E_O$ values for favorably (i.e., geometrically) bound O adsorbates (Tables S3 and S4). Absolute $\Delta E_O$ values are slightly higher for PBE/PWBS than for PBE/LBS, but trends are consistent: binding energies are most favorable for early- to midrow VO\textsubscript{2} and MoO\textsubscript{2}, increase in favorability with increasing principal quantum number (i.e., 3d to 5d), and are least favorable for the earliest (e.g., TiO\textsubscript{2}) and latest (e.g., PtO\textsubscript{2}) transition metal oxides (Figure 3).

Incorporating HF exchange or a +U correction uniformly disfavors O atom adsorption but with system- and method-dependent differences (Figure S3). The sensitivity to HF exchange of O atom binding, $S_{HF}(\Delta E_O)$, is highest for TiO\textsubscript{2}...
transition metal oxides are primarily unchanged by either adsorption energies, but the relative adsorption energies of the adsorption energies and surface formation energies provide parameters: $a$ DFT+U and hybrids are again divergent in their $e$ values for the remaining materials (Figures 3 and S3). Thus, transition metal oxides (TiO$_2$ and VO$_2$) and uniformly positive energies, with zero $d$-filling for the remaining rutile metal oxides (Figures 3 and S3). Unlike in the case of surface energies, $S_{HF}(\Delta E_O)$ is correlated to the absolute $\Delta E_O$ value, with the highest sensitivities for the most weakly bound species (Figure S2). The $+U$ correction has the opposite trend with $d$-filling for $\Delta E_O$ values that it had on surface formation energies, with zero $S_U(\Delta E_O)$ magnitudes for the earliest rutile transition metal oxides (TiO$_2$ and VO$_2$) and uniformly positive values for the remaining materials (Figures 3 and S3). Thus, DFT+U and hybrids are again divergent in their effect on adsorption energies, but the relative adsorption energies of the transition metal oxides are primarily unchanged by either tuning approach (Figures S2 and S3).

Analyzing the simultaneous effects of functional tuning on adsorption energies and surface formation energies provide insight into how surface science properties can be altered (Figures S4 and S5). Across early, midrow, and late transition metal oxides, hybrid tuning uniformly makes surfaces more reactive while also binding adsorbates less favorably (Figure S4). In contrast, DFT+U has a significant effect on only one quantity at a time, producing a qualitatively distinct trend in descriptions of DFT+U surface properties in comparison to hybrids (Figure S5). We confirmed that our observations on period dependence are not sensitive to changes in principal quantum number: for 3$d$ FeO$_2$ and NiO$_2$, DFT+U tunes only $\Delta E_O$ values and has no effect on $E_\sigma$, whereas hybrid functionals tune both properties (Figure S6 and Table S5). These observations are also not a consequence of the change in lattice parameter, as trends in $\Delta E_O$ and $E_\sigma$ with HF exchange or $U$ are qualitatively the same on PBE lattice parameter structures (Figure S7).

Considering observations made previously for metal surfaces,10 we expected that the ability of a correction method to tune both properties would be critical for improving descriptions of transition metal oxide surface chemistry. To test this hypothesis, we focus on one example, TiO$_2$, and compare DFT results to correlated wave function theory (WFT)-corrected references (Figure 4 and see Computational Details and Method S1, Figure S8, and Table S6 in the Supporting Information). Indeed, the reference-WFT-corrected TiO$_2$ adsorption energy is less favorable and the surface is less stable than the PBE GGA results (Figure 4). Consistent with observations on bulk metals,20 revisions to the PBE$^{100}$ GGA either improve only $E_\sigma$ (e.g., PBEsol$^{105}$) or $\Delta E_O$ (e.g., revPBE$^{103}$), while the BLYP$^{104,105}$ GGA somewhat worsens treatment of both (Figures 4 and S9). Although DFT+U at moderate $U$ values improves $E_\sigma$, it does not at the same time properly weaken oxygen atom adsorption (Figure S6). Global hybrids with around 15%–20% exchange provide good agreement with the reference, consistent with values suggested based on the nonempirical, dielectric tuning76,106 approach in titania86 (Figure 4). These observations hold for other metals (e.g., PrO$_2$) as well (Figure S10). Incorporating semiempirical dispersion corrections that are likely important$^{107,108}$ for obtaining quantitative correspondence to experiment (e.g., for physisorption energies) shifts quantitative values slightly but does not alter conclusions for DFT+U or hybrids (Figures S11 and S12).

Figure 3. (top) MO$_x$(110) $\Delta E_O$ in eV for plane wave (PW, red circles) or localized basis set (LBS, blue circles) GGA references. (bottom) Sensitivity of GGA $\Delta E_O$ to tuning $U$ ($\Delta E_O/10$ eV $U$, as indicated in legend, red bars) and HF exchange ($\Delta E_O$/HFX, where 1 HFX is the range from 0% to 100% exchange, blue bars).

Figure 4. TiO$_x$(110) $E_\sigma$ in eV/(110) unit area (u.a.) versus $\Delta E_O$ in eV for (left) HF tuning the PBE0 global hybrid (GH) functional, (middle) $\alpha$-tuning (i.e., global exchange), or (right) $\omega$-tuning the HSE06 range-separated hybrid (RSH) functional. Symbols are colored according to tuning parameters: $a_{\sigma}$ tuning (circles) from 0% (white) to 50% (blue), $\omega$ tuning (squares) from 0.00 bohr$^{-1}$ (white) to 0.40 bohr$^{-1}$ (red). The BLYP (empty green triangle) or PBEsol (empty orange triangle) result is added for comparison, and the DLPNO–CCSD(T) reference is shown with a gray diamond annotated "REF".
Given the high computational cost of global hybrids within a plane wave formalism, we also considered whether the local, range-separated hybrid HSE06\textsuperscript{109,110} could be tuned to reproduce the WFT-corrected result (Figure 4). Agreement is improved over the global hybrids, likely fortuitously, when HSE06 is tuned either to have slightly less (i.e., 20%) local exchange or a slightly longer than default range-separation decay ($\omega = 0.2$ bohr\textsuperscript{−1}), providing the best agreement with the WFT-corrected reference (Figure 4). Unlike in bulk metals,\textsuperscript{20} both local hybrids and global hybrids correct semilocal DFT descriptions of adsorption and surface energies in transition metal oxides. We therefore recommend the use of local hybrids for efficient and accurate modeling of transition metal oxide catalysis. Across a wider range of oxides (i.e., MO$_2$, where M = Ti, Mo, Ru, or Pt), neither of the more affordable (i.e., semilocal cost) DFT+$U$ or revPBE\textsuperscript{105} functionals consistently improve surface and adsorption energy agreement with hybrid or reference results (Figures S4, S5, and S9).

Considering the widespread use\textsuperscript{49,111–115} of DFT+$U$\textsuperscript{55–59} in catalysis, it is important to understand what physical characteristics of the rutile transition metal oxides result in the method tuning only either adsorption or surface energies. Here, we apply the most commonly employed\textsuperscript{55–57} functional form of the +$U$ correction:

$$E^U = \frac{1}{2} \sum_{i,\sigma} U [\text{Tr}(n^{i,\sigma}_{\text{ff}}(1 - n^{i,\sigma}))]$$ (3)

where $I$ is the Hubbard atom (here, each metal) with a relevant valence subshell (here, 3d, 4d, or 5d), $\sigma$ a spin index, and $n$ the occupation matrix of the subshell obtained by projecting all extended states onto the atomic states obtained during the all-electron calculation of each atom used in pseudopotential generation.\textsuperscript{55,57} In a first-order approximation, the sensitivity of a property to the +$U$ correction can be estimated from the difference in PBE fractionality\textsuperscript{77,88,89,114} (i.e., $\Delta \text{Tr}[n(1 - n)]$) of the structures being compared. For $E_{\text{ad}}$, this difference in fractionality is between the surface and bulk metal sites, whereas for $\Delta E_{\text{ads}}$, this difference is between the pristine surface and the adsorbed surface metal sites (Figure 5).

In TiO$_2$, fractionality increases for the slab surface over the bulk because of a slight increase in overall occupations on the metal sites, producing a positive $S_0(E_{\text{ad}})$ value (Figures 5 and S13 and Tables S7–S10). Analyzing PtO$_2$ reveals more varied, site-specific increases and decreases that cancel, leading to a near-zero $S_0(E_{\text{ad}})$ (Figure 5 and Tables S11–S14). The opposite trend is apparent in $\Delta E_{\text{ads}}$ fractionalities: depletion of density on the adsorption site of PtO$_2$ increases that site’s fractionality and produces high $S_0(\Delta E_{\text{ads}})$ values, whereas subtler shifts in fractionality for TiO$_2$ yield a more modest sensitivity (Figures 5 and S6 and Tables S11–S14). Thus, the ability of DFT+$U$ to correct $E_{\text{ad}}$ or $\Delta E_{\text{ads}}$ should be evident from PBE calculations. For large-scale catalysis modeling, modifications to the projections\textsuperscript{57} or choice of model Hamiltonian functional form\textsuperscript{89,96} could improve DFT+$U$ performance further.

We next examined whether the ability of hybrid tuning to increase surface energies while weakening adsorbate binding could both be rationalized by a single effect\textsuperscript{86,87} of exchange tuning (Figures S14 and S15). Between PBE bulk and surface models, electron density is higher on the metal sites of the latter in TiO$_2$. In both configurations HF exchange localizes density away from the metal and onto the lattice oxygen, but it has a greater effect on the bulk structure (Figures 6, S14, and S15). Greater delocalization is also observed for the PBE TiO$_2$ adsorbate case than the pristine surface, and incorporating exchange depletes density in the bond, localizing it onto the oxygen adsorbate (Figures 6 and S15). Thus, hybrids penalize the more delocalized densities in both surfaces and adsorbate configurations, destabilizing the energetics of both.

To simplify the extension of this analysis to the other rutile transition metal oxides, we computed the shift in metal partial charge

$$\Delta q(M) = q(M)_{\text{surf}} - q(M)_{\text{bulk}}$$ (4)

from values in the bulk and in those surfaces (see Computational Details). For all materials considered, the negative $\Delta q(M)$ PBE value grows with increasing HF exchange (Table S15). DFT+$U$ is consistent with HF exchange tuning...
on Δq(M) only for the few materials (i.e., TiO2 and VO2) where energetic corrections were also consistent (Table S16). To analyze the role of density localization on ΔE0, we also computed the density at the bond critical point (BCP) and O atom partial charge (see Computational Details and Tables S17–S20). Incorporating HF exchange uniformly decreases the density at the BCP, localizing density onto an increasingly neutral oxygen atom, a trend replicated by DFT+U only for the systems for which S_0(ΔE_0) was significant (e.g., IrO2 and PtO2; see Tables S17–S20). Overall, this density analysis points to surface destabilization and the weakening of adsorbate binding originating from a single effect of HF exchange on delocalization error. Hybrid tuning has a greater effect on properties of the surface density, which is more delocalized with PBE than the corresponding bulk density, destabilizing the surface with respect to the bulk and increasing surface formation energies. Incorporating an adsorbate leads to even more delocalization in PBE that is penalized further upon incorporation of HF exchange. When DFT+U corrects either quantity, it has a similar effect on the density as a hybrid, but the lack of detection of delocalization error in the occupations on which the +U correction acts leads to the failure of DFT+U in most cases.

In conclusion, we have investigated the effect of two widely applied approaches for delocalization error correction, (i) affordable DFT+U (i.e., semilocal DFT augmented with a Hubbard U) and (ii) hybrid functionals with an admixture of HF exchange, on surface and adsorbate energies for seven rutile transition metal oxides. Delocalization errors for semilocal DFT descriptions of the transition metal oxides were expected to underestimate surface energies (i.e., underestimate reactivity) but paradoxically overestimate adsorbate binding energies (i.e., overestimate reactivity). We confirmed this expectation with respect to accurate reference calculations in TiO2 and determined that only hybrid functionals could simultaneously correct both quantities. For DFT+U, we instead observed strongly row- and period-dependent trends: surface formation energies were tuned only for early transition metals (e.g., Ti, V), and adsorbate energies were decreased only in late transition metals (e.g., Ir, Pt). Both global and local hybrids instead destabilized surfaces and reduced adsorbate binding across the transition metal oxide systems studied. Analysis of density properties and occupations confirmed that these two energetic errors in surface science were related to delocalization error imbalances that could be suitably addressed with hybrid functionals but not with DFT+U. We recommend local, range-separated hybrids for the accurate modeling of catalysis in transition metal oxides at only a modest increase in computational cost over semilocal DFT. Further improvements to DFT+U-like projections and functional forms should be expected to improve overall performance, especially through benchmarking against hybrids, an approach we are currently investigating.

### COMPUTATIONAL DETAILS

Lattice parameters and atomic positions of nonmagnetic bulk MO2 crystals were optimized with DFT functionals using 12 × 12 × 12 Monkhorst–Pack k-point grids (Tables S1 and S2). Using bulk lattice parameters and 4 × 4 × 1 Monkhorst–Pack k-point grids, atomic positions in the outermost of four trilayers in 2 × 1 unit cell models were relaxed for Ea calculations, and atoms in the two topmost trilayers and a single adsorbate were relaxed for ΔE0 calculations. Slab spacing included at least 15 Å of vacuum. Hybrid calculations with a LBS were performed using CRYSTAL115 with default and tuned56,86,87 PBE0116,117 global hybrid (default, 25% HF; tuned, 0–50% HF in 5% increments) or HSE06109,110 range-separated local hybrid (default, 25% HF, ω = 0.11 bohr−1; tuned, HF % as in the GH and ω from 0 to 0.4 in 0.1 bohr−1 increments), in addition to the pure BLYP104,105 or PBEsol33 GGA functionals. At least a double-ζ split-valence basis set was used for all atoms, and triple-ζ split-valence basis sets were used for Pt and Ir, with all basis sets obtained from the CRYSTAL115 Web site (Table S21). These basis sets were chosen from those available to ensure comparison across materials compared, but the effect of incorporating polarization was also considered and found to have a limited effect on trends (Table S21 and Figure S16). Hubbard U-corrected56 global hybrid (i.e., with PBE100) was carried out with U from 0 to 10 eV in 1 eV increments using Quantum-ESPRESSO.118 The revPBE103 functional was also employed using Quantum-ESPRESSO because of its lack of availability in CRYSTAL, and then values were shifted by comparison to differences in PWBS and LBS PBE properties for a subset of oxides (Figure S9). These calculations employed a PWBS (cutoffs: 35 Ry for wave function, 350 Ry for charge density) with ultrasoft pseudopotentials119 obtained from the Quantum-ESPRESSO website (Table S22). In order to aid self-consistent field (SCF) convergence, an electronic temperature of 0.005 hartree was applied in all spin-polarized calculations. Real-space Bader atomic partial charges120 were obtained from the ‘TOPOND package’21 or the BADER program,122 and built-in post-processing codes were used to obtain electron density cube files. Domain-based local pair natural orbital DLPNO–CCSD(T)123 calculations with a localized basis set, aug-cc-pVTZ, on transition metal complexes were carried out using ORCA124 (Method S1 in the Supporting Information).

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.9b01650.

Lattice parameters of rutile metal oxides with HF exchange or +U correction; surface formation energy and adsorbate energy dependence with HF or +U correction; O atom adsorbate geometries; surface formation energy or adsorbate energy versus sensitivity values; adsorbate energy versus surface energy for early, midrow, and late transition metals with HF or +U; effect of lattice parameter choice and basis set choice on trends; additional revPBE results; comparison of PtO2 tuning trends to WFT reference; diagram of unique metal sites on the pristine and O-adsorbed surface; occupation matrix analysis of Ti and Pt rutile metal oxides; electron density difference of TiO2 surfaces; charge in charges across metal oxides with HF or U; analysis of BCP density with HF or U; O atom partial charge with HF or U; Fe and Ni rutile metal oxide analysis with HF and U; revPBE surface energy and adsorbate energy analysis; description of DLPNO–CCSD(T) reference calculations; basis sets and pseudopotentials for all calculations (PDF).
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Notes
The authors declare no competing financial interest.

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