Calibration of the DFT/GGA+U Method for Determination of Reduction Energies for Transition and Rare Earth Metal Oxides of Ti, V, Mo, and Ce

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ABSTRACT: GGA+U calculation were performed for oxides of Ti, V, Mo, and Ce with the objective of establishing the best value of the parameter U_{eff} to use in order to match the calculated reduction and oxidation energies of each oxide with experimental values. In each case, the reaction involved the hydrogen reduction of an oxide to its next lower oxide and the formation of water. Our calculations show that the optimal value of U_{eff} required to match calculated and experimental values of the reaction energy are significantly different from those reported in the literature based on matching lattice parameters or electronic properties and that the use of these values of U_{eff} can result in errors in the calculated redox energies of over 100 kJ/mol. We also found that, when an element exhibits more than two oxidation states, the energy of redox reactions between different pairs of these states are described by slightly different values of U_{eff}.

■ INTRODUCTION

The oxides of transition and rare earth metals, such as Ti, V, Cu, La, and Ce, are often used as catalysts for industrially important reactions.[1−6] Consequently, quantum chemical calculations for such elements are of much interest, and density functional theory (DFT) is one of the tools commonly applied to such systems. The catalytic properties of these materials are attributed to their reducibility,[7−9] where lower oxidation states correspond to occupied d and f orbitals. At the same time, d and f electrons also present difficulties for DFT calculations, because this method tends to delocalize d and f electrons excessively.[10,11] These difficulties affect a broad spectrum of oxide properties, including crystal lattice parameters, conductivity, and energies of oxide reduction and oxidation.

The difficulty in obtaining accurate property predictions for transition metal oxides from DFT calculations has been recognized for some time. Despite attempts to use hybrid functionals and dynamical mean-field theory to treat the problem, DFT with generalized gradient approximation (GGA) functionals remains an economical choice, and therefore, corrections directed at specific drawbacks of the method are introduced.

It is generally understood that the main source of error in DFT for d and f electrons is their correlated nature. A commonly used ad hoc method for improving the description of d and f electrons is the DFT+U method, in which an "on-site" potential is added to introduce intra-atomic interactions between the strongly correlated electrons. Most recent articles have used the potential proposed by Dudarev et al.,[12] which has the form

$$E = \frac{(U-J)}{2} \sum_{\sigma} (n_{m,\sigma} - n_{m,\sigma}^2) \qquad (1)$$

where U and J are the effective Coulomb and exchange parameters, respectively, and n is the occupation number of a d orbital number m with spin σ. U and J can, in principle, be computed from first principles. In reality, however, the theoretical values of U and J give poor results, and therefore, these parameters are adjusted by fitting to experimental data, such as the oxide band gap or the lattice parameters. Because eq 1 depends on only the difference, $U - J$, can be replaced with one variable $U_{eff} = U - J$ for the sake of brevity.

The value of U_{eff} is element-specific, and at least one study has suggested that it is transferable between different oxidation states of a given element.[13] U_{eff} is usually determined empirically, to fit some specific physical property, most often the crystal lattice parameters or the band gap between the occupied and unoccupied states.[7,14,15] The principal problem with this approach is that no two properties are described well by the same value of U_{eff}, and therefore, a value is picked that minimizes the average error in several properties.

Application of the on-site interaction term to transition metal oxides has been recognized as necessary because of its strong influence on the orbital energies of the occupied d and f states and, as a consequence, on the formation energy of oxygen vacancies formed during reactions that proceed through a Mars−van Krevelen mechanism. For the purposes of catalytic chemistry, we are interested in values of U_{eff} that accurately describe redox reactions. Several authors have shown that the oxygen vacancy formation energy depends strongly on the value of U_{eff}.[10,16] A notable problem with this approach is that experimental formation energies of oxygen vacancies are difficult to evaluate, and consequently, different authors have reported different values of U_{eff} for the same element.[7,8,10,13,17−20] Chemisorption energies for probe molecules can serve as a more reliable test of the value of U_{eff}. For example, CO can react with an oxide to form CO_2, which remains adsorbed as a surface carbonate. The net effect of this reaction is that the metal oxide is

Table 1. Symmetry and Magnetic Properties of the Oxides

oxide	symmetry	magnetic arrangement at STP[a]
TiO_2	$P4_2/mnm$	diamagnetic
Ti_2O_3	$R3\bar{c}$	diamagetic
V_2O_5	$Pmmn$	diamagnetic
VO_2	$P2_1/c$	diamagnetic
V_2O_3	$R3\bar{c}$	paramagnetic
MoO_3	$Pbnm$	diamagnetic
MoO_2	$P2_1/c$	paramagnetic
CeO_2	$Fm3\bar{m}$	diamagnetic
Ce_2O_3	$P3m1$	antiferromagnetic

[a] STP = standard temperature and pressure.

reduced. As the d band of the oxide becomes partially filled, the value of U_{eff} will have an effect on the computed adsorption energy. Huang and Fabris[21] analyzed the energetics of CO adsorption on CeO_2 as a function of U_{eff}, providing evidence that the value of this parameter presently used in the literature ($U_{eff} > 4$ eV) can lead to severe overestimation of the binding energy of CO to ceria when surface reduction is involved, whereas the values $U_{eff} = 2-3$ eV are more appropriate. Still, experimental adsorption energies tend to have a large range, depending on the condition of the surface and the experimental technique used to measure them. Therefore, the effect of the value of U_{eff} on the redox reaction energies has not been settled.

In this work, we consider the redox pairs TiO_2/Ti_2O_3, $V_2O_5/VO_2/V_2O_3$, MoO_3/MoO_2, and CeO_2/Ce_2O_3. We used bulk oxides in order to avoid the need to determine surface structures. To avoid the difficulties associated with the description of O_2 by DFT,[13] we chose H_2 as the reducing agent and gas-phase H_2O as the oxidizing agent. The reduction energy of each oxide was compared with values determined from the experimentally obtained energies of formation. We show that values of U_{eff} obtained by fitting the lattice parameters or the band gap can lead to significant errors in the reduction energy of the transition or rare earth oxides.

■ COMPUTATIONAL APPROACH

All calculations were performed using the VASP 4.6 package.[22,23] We used the revised Perdew−Burke−Ernzerhof (PBE) functional[24] and the projector-augmented wave (PAW) potentials.[25,26] The plane-wave cutoff was set to 500 eV. For integration over the Brillouin zone, Γ-centered sets of k points were tested to achieve convergence better than 1 meV/atom. The resulting sets are $17 \times 17 \times 7$ for TiO_2, $5 \times 5 \times 5$ for Ti_2O_3, $3 \times 9 \times 9$ for V_2O_5, $5 \times 5 \times 11$ for VO_2, $7 \times 7 \times 7$ for V_2O_3, $6 \times 1 \times 6$ for MoO_3, $13 \times 13 \times 13$ for MoO_2, $11 \times 11 \times 7$ for Ce_2O_3, and $7 \times 7 \times 7$ for CeO_2. Integration was performed using the tetrahedron method with Blöchl corrections.[27] The crystal symmetry and magnetic properties of each oxide are listed in Table 1. The corundum structures of Ti_2O_3 and V_2O_3 have two choices of the unit cell in use: the primitive rhombohedral unit cell with compositions V_4O_6 and Ti_4O_6 and the hexagonal unit cell with compositions $V_{12}O_{18}$ and $Ti_{12}O_{18}$. The transformation of the lattice vectors and coordinates between the rhombohedral and hexagonal unit cells was described by Cousins.[28] We used the rhombohedral cell for our calculations, but the lattice parameters discussed in the text correspond to the hexagonal lattice, as it is the one more commonly discussed. The oxide structures were fully optimized for each value of U_{eff} tested. All calculations were

Table 2. Experimental Enthalpy of Formation and Enthalpy Change between 0 and 298.15 K

	$\Delta_f H^{\circ}_{298.15}$ (kJ/mol)	$H^{\circ}_{298.15} - H^{\circ}_0$ (kJ/mol)
H_2	0	8[35]
H_2O	−242[36]	13[36]
TiO_2	−944[37]	9[37]
Ti_2O_3	−1521[38]	14[38]
V_2O_5	−1551[39]	21[39]
VO_2	−714[37]	N/A
V_2O_3	−1217[38]	17[38]
MoO_3	−745[40]	13[40]
MoO_2	−589[40]	8[40]
CeO_2	−1090[41]	10[41]
Ce_2O_3	−1800[41]	21[41]

Table 3. Dependence of Lattice Parameters (in Å) on U_{eff}

	experiment	U_{eff} (eV) 0.0	2.0	5.0	8.0
TiO_2[42]					
a	4.594	4.687	4.701	4.721	4.742
c	2.959	2.981	3.011	3.055	3.096
Ti_2O_3[43]					
a	5.16	5.20	5.24	5.31	5.37
c	13.61	13.78	13.88	14.06	14.24
V_2O_5[44]					
a	11.512	11.588	11.583	11.917	11.978
b	3.564	3.597	3.624	4.526	4.549
c	4.368	5.339	5.382	3.685	3.704
VO_2[a,45]					
a	5.743	5.861	5.696	5.707	5.761
b	4.517	4.609	4.665	4.682	4.701
c	5.375	5.485	5.506	5.516	5.382
V_2O_3[46]					
a	4.95	5.03	5.13	5.16	5.29
c	14.00	14.30	14.20	14.58	14.29
MoO_3[47]					
a	3.963	4.047	4.020	3.967	3.904
b	13.855	17.184	17.180	17.140	17.203
c	3.696	3.682	3.704	3.747	3.793
MoO_2[48]					
a	5.611	5.657	5.671	5.699	5.730
b	4.856	4.896	4.908	4.933	4.959
c	5.623	5.675	5.689	5.717	5.747
CeO_2[49]					
a	5.411	5.499	5.504[b]	5.522	5.536
Ce_2O_3[50]					
a	3.891	3.88	3.92	3.96	3.97
c	6.059	6.04	6.11	6.16	6.19

[a] $\theta = 122.61°$, $122.61°$, $121.961°$, $121.808°$, and $121.841°$ for experiment and $U_{eff} = 0.0$, 2.0, 5.0, and 8.0 eV, respectively. [b] Value computed for $U_{eff} = 1.0$ eV.

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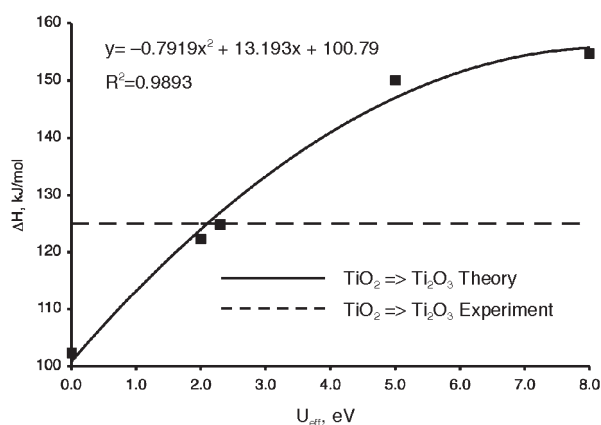
Figure 1. Enthalpy of reduction (kJ/mol) of TiO_2 to Ti_2O_3 versus on-site Coulomb repulsion, U_{eff} (eV).
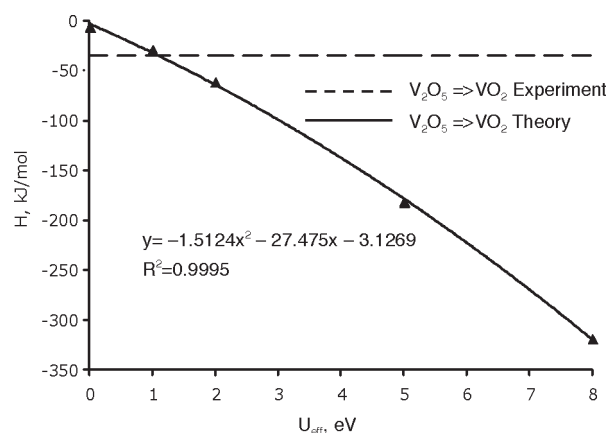

Figure 3. Enthalpy of reduction (kJ/mol) of VO_2 to V_2O_3 versus on-site Coulomb repulsion, U_{eff} (eV).
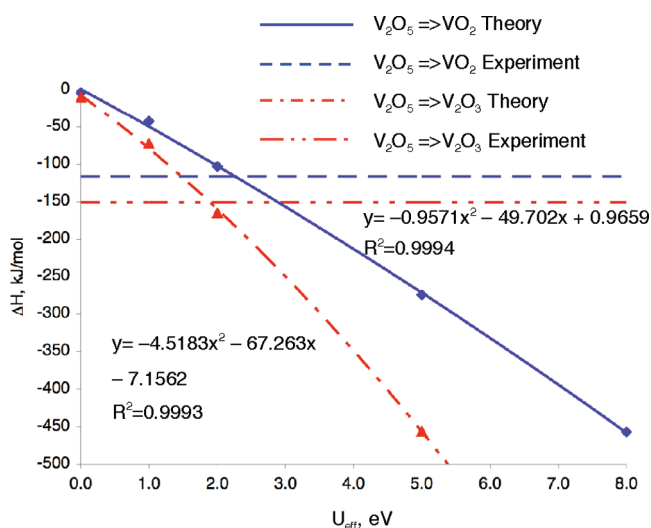

Figure 2. Enthalpy of reduction (kJ/mol) of V_2O_5 to VO_2 and V_2O_3 versus on-site Coulomb repulsion, U_{eff} (eV).

initiated with the experimentally known values of the lattice parameters (see Table 3 below). The effect of U_{eff} on the oxide lattice parameters was determined, as well as the redox energy for each of the oxide pairs of interest.

Experimental enthalpies of formation used in this work are listed in Table 2. Because the energy changes determined by our calculations correspond to 0 K, to compare energies of reactions, it is necessary to subtract the enthalpy difference between 0 and 298.15 K. Unfortunately, we were not able to find the change in entropy of formation for VO_2 between 0 and 298.15 K. We note, however, that, for the overall redox reactions, this correction is below 6 kJ/mol, which is comparable to the error inherent in our theoretical method. Therefore, we chose not to make the correction in the enthalpy change with temperature.

■ RESULTS AND DISCUSSION

Oxidation Energy. The effect of U_{eff} on the energy of reduction of TiO_2 to Ti_2O_3 according to the reaction

$$2TiO_2 + H_2 = Ti_2O_3 + H_2O \tag{2}$$
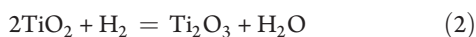
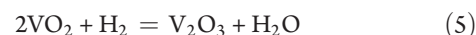is shown in Figure 1. The experimental energy, 125 kJ/mol, is matched for U_{eff} = 2.3 eV. This value is significantly smaller than that suggested by Morgan and Watson, U_{eff} = 4.2 eV, which was obtained by optimizing the position of the oxygen vacancy states in the electronic spectra of rutile.[14] Our finding is similar to the conclusion of Hu and Metiu in a recent publication.[29] They recommended using a U_{eff} value between 2 and 3 eV. The authors used this value of U_{eff} to compare the concentration of oxygen vacancies in rutile and anatase.[30] We note, however, that the value of U_{eff} determined by Morgan and Watson overestimates the enthalpy change for reaction 2 by 17 kJ/mol.

Vanadium is the only element for which we considered more than two oxides. Therefore, it is an instructive example of the limitations of the DFT+U methodology. Figures 2 and 3 summarize the dependence on U of the reactions

$$V_2O_5 + H_2 = 2VO_2 + H_2O \tag{3}$$

$$V_2O_5 + 2H_2 = V_2O_3 + 2H_2O \tag{4}$$
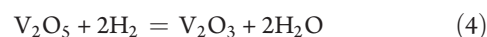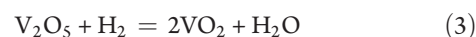
The two reactions also can be combined to obtain

$$2VO_2 + H_2 = V_2O_3 + H_2O \tag{5}$$

The experimental reaction enthalpies are −119 kJ/mol for reaction 3, −150 kJ/mol for reaction 4, and −31 kJ/mol for reaction 5. From Figures 2 and 3, one can see that, although the optimal values of the on-site repulsion term are similar for the three reactions, they are not identical. The optimal values of U_{eff} for reactions 3 and 4 are 2.3 and 1.8 eV, respectively. The difference between these two values is in line with that reported by Wang et al.[13] The optimal value for reaction 5 is U_{eff} = 1.1 eV. Therefore, although the equilibrium between V_2O_5 and V_2O_3 seems to be described reasonably well, VO_2 is artificially destabilized by the same choice of the parameter. By contrast, Scanlon et al. suggested U_{eff} = 4.0 eV based on a comparison of the computed electronic spectra with the experimental ultraviolet photoelectron spectroscopy (UPS) and X-ray photoelectron spectroscopy (XPS) data.[7] This value results in enthalpies that are lower than those observed experimentally by about 100 kJ/mol for each of the reactions. Figures 2 and 3 also show that the relative energies of the reactions diverge, rather than shifting by a
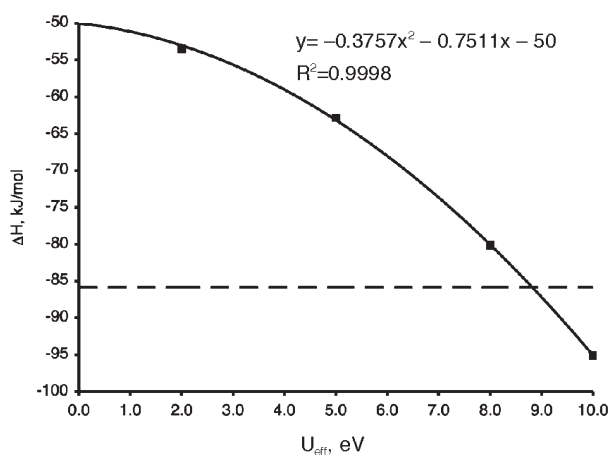
Figure 4. Enthalpy of reduction (kJ/mol) of MoO_3 to MoO_2 versus on-site Coulomb repulsion, U_{eff} (eV).

Figure 5. Enthalpy of reduction (kJ/mol) of CeO_3 to Ce_2O_3 versus on-site Coulomb repulsion, U_{eff} (eV).

constant value, which makes calculations for metals with multiple oxidation states particularly sensitive to the choice of U_{eff}.

The energy of reduction for the reaction

$$MoO_3 + H_2 = MoO_2 + H_2O \qquad (6)$$
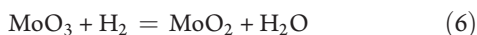
is 86 kJ/mol and can be matched using a value of $U_{eff} = 8.6$ eV, as can be seen from Figure 4. Once again, this value differs from those previously reported. Coquet and Willock[8] used the DFT+U method with the PBE functional to study the formation of oxygen defects on the (010) surface of α-MoO_3. From comparison of periodic plane-wave and cluster calculations, they arrived at the value of $U_{eff} = 6.3$ eV. On the other hand, in a study of magnetism in MoO_2, Wang et al.[17] used a range of values for U_{eff} between 1 and −1 eV, citing weak correlation in Mo.

Cerium dioxide (CeO_2) is used as an oxygen-storage material for the three-way control of automotive emissions. Consequently, a number of authors have examined the issue of parametrization of the DFT+U method. Fabris et al.[10] suggested that the optimal value of U_{eff} required to match the energy for the reaction

$$2CeO_2 = Ce_2O_3 + \frac{1}{2} O_2 \qquad (7)$$
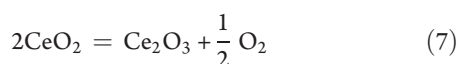
is around 1 eV for GGA+U with atomic-like orbital projectors. Jiang et al.[18] used GGA+U to compute the effects of oxygen partial pressure on the CeO_2 surfaces. They calibrated U_{eff} to the electronic spectra and arrived at a value of 6.3 eV. Skorodumova et al.[16] have published several articles on cerium oxides, and in a recent publication, they dealt with the choice of the Coulomb repulsion parameter for reaction 7. The raw data suggested an optimal value of U_{eff} for the GGA functional of about 2 eV; however, the authors noted that the binding energy of O_2 used in their calculations was overestimated, and hence, they recommended the value of $U_{eff} = 5$ eV. Nolan et al.[19] obtained a value of U_{eff} in their study of ceria surfaces based on the degree of delocalization of the f electrons. They observed that, for $U_{eff} < 5$, the electrons were partly delocalized, but at $U_{eff} = 5$ eV, localization became complete, leading them to conclude that the appropriate value was $U_{eff} = 5$ eV. This value of U_{eff} was later used for a study of NO_2 adsorption on ceria.[31] Castleton et al. optimized the value of U_{eff} for electronic spectra and structure and recommended $U_{eff} = 5.5$ eV for GGA+U, conceding it as a compromise between several properties. Da Silva et al.[32] compared the performances

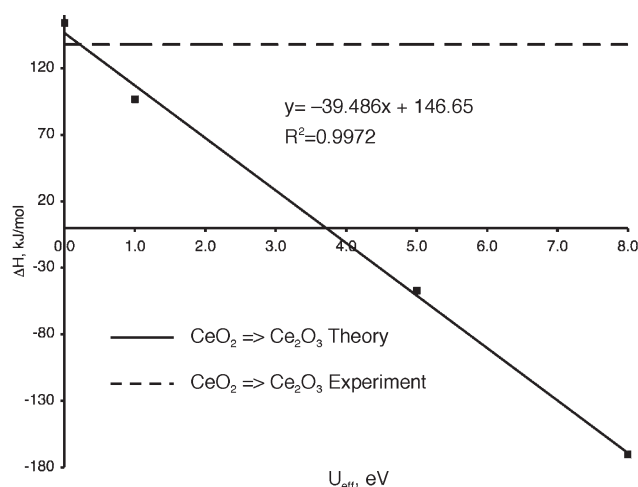of the hybrid and GGA functionals, including GGA+U. They noted the large deviation of the oxidation energy with a typical estimation of $U_{eff} = 4.5$ eV from the experimental values and suggested that the value of 2 eV be used instead. This conclusion coincides with the results of Loschen et al.[33] Huang and Fabris[21] also suggested a value for U_{eff} of 2−3 eV based on their calculations of the energy for CO adsorption.

The reaction considered in the present study is

$$2CeO_2 + H_2 = Ce_2O_3 + H_2O \qquad (8)$$
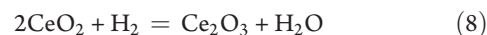
As seen in Figure 5, varying the value of U_{eff} from 0 to 6 eV changes the enthalpy of reaction 8 by more than 200 kJ/mol, as well as its sign. The experimental value of 138 kJ/mol is matched with $U_{eff} = 0.2$ eV. However, if one uses the commonly recommended value of 4.5 eV, the reaction enthalpy becomes −31 kJ/mol, which is almost 170 kJ/mol lower than the experimental value.

Lattice Parameters. The GGA in general produces inaccurate lattice constants, and we would not suggest using these parameters to fit the value of U_{eff}. However, we include a discussion of lattice parameters for two reasons. First, the data are already available from the present calculations. Second, because lattice parameters are sometimes used as one of several parameters to justify the selection of the value of U_{eff},[16,33] it is important to discuss what sort of errors should be expected from a given choice of U_{eff}.

The effect of U_{eff} on the lattice parameters of the oxides investigated in this study is shown in Table 3. In all cases, the lattice parameters are overestimated using the GGA functional, and the extent of overestimation increases as the Coulomb repulsion term grows. Therefore, GGA+U worsens the description of the crystal lattice compared to that obtained with GGA. By contrast, the local density approximation (LDA) functional typically underestimates lattice constants, so the use of LDA+U is a viable means for determining values of U_{eff} required to match calculated and observed lattice parameters.

The single exception to the trend in lattice parameters with U_{eff} is MoO_3, for which the lattice parameters a and b generally decrease with increasing values of U_{eff} and the parameter c increases. This structure is characterized by well-defined layers perpendicular to the b axis. The interactions between the layers are weak and presumably largely of van der Waals in character. Studies by

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Coquet and Willock[8] and Scanlon et al.[34] indicated that the effect of such weak binding was the absence of a minimum in the plot of energy versus the length of the b lattice parameter. These two studies worked around the problem by freezing the b vector at its experimental value and then relaxing the a and c parameters so as to minimize the total energy. In our study, we were able to locate such a minimum, by frequent updates to the plane wave basis set. The optimized b vector was overestimated by a much larger amount than is typical of GGA. Nevertheless, we decided against manually freezing the lattice parameters. We consider that full optimization is more appropriate because, during calculations of reaction or adsorption energies, as a rule, the oxide atoms are fully relaxed. This relaxation releases some of the energy that would be stored in the atomic bonds that would be strained because of the frozen lattice parameters. However, it is not clear how to separate the adsorption or reaction energy from the contribution due to relaxation of the lattice. We believe that, for consistent treatment of MoO_3, all atoms should be allowed to fully relax, even though the lattice constants turn out to be different from those observed experimentally.

■ CONCLUSIONS

It has been shown that variations in U_{eff} result in significant deviations of the reaction enthalpies from the experimental values. We tried to put this interdependence into the context of a catalytically relevant energy scale. The magnitude of the variation differs from about 5 kJ/mol of enthalpy per 1 eV of U_{eff} for the MoO_3/MoO_2 pair, to about 100 kJ/mol of enthalpy per 1 eV of U_{eff} for the V_2O_5/V_2O_3 pair. The optimal values of U_{eff} corresponding to different pairs of the oxidation states for the same element are close to one another, but not exactly the same. Therefore, to use the DFT+U method, the value of U_{eff} must be adjusted for each reaction. For calculations of the energy of oxygen-atom transfer carried out using the GGA functional, we recommend the following values: U_{eff} = 2.3 eV for Ti, 2.0 eV for V, 8.6 eV for Mo, and 0.2 eV for Ce. Application of the same value of U_{eff} for calculations of different physical properties is questionable. We conclude that values of U_{eff} determined by matching the band gaps or lattice parameters cannot be used to obtain energies for oxide reduction and oxidation that match experimentally observed values.

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■ ACKNOWLEDGMENT

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