On the Behavior of Brønsted-Evans-Polanyi relations for Transition Metal Oxides

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Versatile Brønsted-Evans-Polanyi (BEP) relations are found from density functional theory for a wide range of transition metal oxides including rutiles and perovskites. For oxides, the relation depends on the type of oxide, the active site and the dissociating molecule. The slope of the BEP relation is strongly coupled to the adsorbate geometry in the transition state. If it is final state-like the dissociative chemisorption energy can be considered as a descriptor for the dissociation. If it is initial state-like, on the other hand, the dissociative chemisorption energy is not suitable as descriptor for the dissociation. Dissociation of molecules with strong intramolecular bonds belong to the former and molecules with weak intramolecular bonds to the latter group. We show, for the prototype system La-perovskites, that there is a "cyclic" behavior in the transition state characteristics upon change of the active transition metal of the oxide.

INTRODUCTION

Brønsted-Evans-Polanyi (BEP) relations [1, 2] have recently been established quantitatively from density functional theory (DFT) calculations. Linear relations between activation energies and reaction energies or between transition state energies and dissociative chemisorption energies have been found for a number of surface reactions on different transition metal surfaces [3–10] and for a few transition metal compound systems [11, 12]. Several reactions on transition metals are suggested to follow a universal BEP relation, that is, they obey a reactant independent but surface structure dependent linear relation [4, 6, 9, 13].

In spite of considerable progress [14–20], theoretical understanding of the reactivity of transition metal oxides is less established than that of pure transition metals. The aim of this paper is to shed light on the reactivity of oxides. We will probe the reactivity of these materials by first investigating whether BEP relations, here taken as the relation between the transition state energies and dissociative chemisorption energies, exist for dissociation of small molecules on transition metal oxides. Secondly, we will examine whether these obey the universal BEP relation [6, 13]. When combined with scaling relations [21–23] the results of this paper will provide tools to establish activity and selectivity trends among oxide-surfaces for heterogenously catalyzed reaction as is currently established for a number of transition metal catalyzed reactions [24]. The main conclusions in this study is that BEP relations do exist for transition metal oxide surface reactions, and that they are strongly dependent on the bond properties of the dissociating molecules

and the reactivity of the surface.

In the following we will show results for a number of different oxides. The oxides we have considered here can be divided in two subgroups: binary MO_2 oxides in the rutile structure and ternary oxides ABO_3 in the perovskite structure. In this study, the rutile surface under consideration is the (110) surface (see Fig. 1), which is found to be most stable [25]. For perovskites, the (001) surface can be either AO- or BO_2- terminated. Here, the BO_2-terminated perovskite surface is considered due to its higher stability [26]. Also, results on pure metal surfaces are presented for comparison. The different metal constituents in the oxides are M = Ti, Mo, Ru, Ir, Pt, and A = Sr, La, and B = Sc, Ti, V, Cr, Mn, Fe, Ru, Co, Ni, Cu. The chosen set of adsorbates is the homonuclear diatomic molecules H_2, N_2, O_2, Cl_2, Br_2, and I_2, the heteronuclear diatomic molecules NO, CO, OH, HCl, HBr, and HI, and the triatomic molecule H_2O. Dissociation is studied not only on different oxide surfaces but also at different active sites for a given surface.

It should be noted, that while ordinary DFT calculations within the generalized gradient approximation (GGA) have proven to give reliable and reasonably accurate results for adsorption energies [27, 28] on transition metals, similar calculations for oxides are fewer and not as well tested. However, there are several studies of oxides where a good agreement between DFT calculations and experiments exists [25, 29]. Possible limitations and shortcomings of GGAs for oxides is a current research topic [20, 30–32]. We caution that there may be cases where the DFT-GGA approach employed here is not sufficiently accurate but these issues will not be considered here. The present study is focusing on the variations

in dissociation and transition state energies between different systems, and these will not be as sensitive as the absolute energies to such accuracy issues.

CALCULATION DETAILS

All calculations are performed using the plane wave DFT method as implemented in the DACAPO code [27, 33]. The surfaces are modeled using slabs consisting of four stoichiometric layers in a 2×2 unit cell geometry. Repeated slabs are separated by a vacuum region of at least 15 Å (18 Å) for rutiles (perovskites). During structure relaxation, the topmost two layers are relaxed while the others are kept in the optimized bulk positions. The Kohn-Sham equations are solved using a basis set of plane waves with an energy (density) cutoff of 350-400 eV (500 eV) and the Brillouin zone is sampled with a $4 \times 4 \times 1$ Monkhorst-Pack grid. To describe the core electrons, the Vanderbilt ultrasoft pseudopotentials [34] are used. The exchange correlations interactions are modeled with the RPBE functional [27] and the dipole correction is included according to the scheme in Ref. [35].

If not stated otherwise, both the dissociative chemisorption energies (ΔE_{diss}) and the transition state (TS) energies (ΔE_{TS}) are calculated relative to the gas phase diatomic molecule ($\Delta E_{diss}=E_{diss}-E_{surf}-E_{mol}$, $\Delta E_{TS}=E_{TS}-E_{surf}-E_{mol}$, where E_{diss} is the energy of the adsorbed dissociated molecule, E_{TS} is the energy of the adsorbed molecule in the transition state (TS), E_{surf} is the energy of the clean surfaces and E_{mol} is the energy of the molecule. The O_2 energy is calculated from H_2O and H_2 [36] to avoid the well-known DFT error in the O_2 energy [37]. The transition state is determined by applying a fixed-bond length method, in which the energy at various bond lengths of the molecule are calculated while the remaining degrees of freedom of the system are completely relaxed. We note that for systems where the dissociation of the reactant occurs without an energy barrier the relations between ΔE_{TS} and ΔE_{diss} become undefined. To present the data for these systems we have chosen ΔE_{TS} as the highest energy point along the reaction pathway.

The adsorbate coverage in all systems is 1/4 ML relative to the number of metal atoms in the surface layer. In addition, the influence of the adsorbate–adsorbate interaction on the BEP relations is investigated by performing calculations of N_2 and NO on RuO_2 and PtO_2 in a 2×3 unit cell geometry corresponding to a 1/6 ML coverage. The results show that the BEP relations are not significantly affected by coverage effects. The absolute ΔE_{diss} and ΔE_{TS} energies are seen to change slightly, but with the same amount, hence preserving the BEP relation.
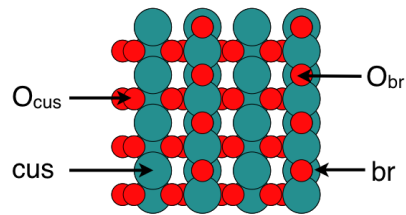

FIG. 1: Top view of the (110) rutile surface together with the different considered adsorption sites and the unit cell. Here, cus denotes the coordinately unsaturated site on top of a five-fold coordinated metal atom, the br denotes the bridge site between two fourfold coordinated metal atoms [note this corresponds to a (110) surface without O atoms], O_{br} denotes the site on top of a O in the bridge site, O_{cus} denotes the site on top of an O in the bridge site between two fivefold metal atoms.

RESULTS AND DISCUSSION

The general conclusion is that there exists a characteristic correlation between ΔE_{TS} and ΔE_{diss} for each molecule on a given dissociation site of an oxide or a metal. It is, however, not given a priori that one should be able to describe this correlation by a single linear relation given by

$$\Delta E_{TS} = \alpha \Delta E_{diss} + \beta. \qquad (1)$$

From now on we will refer to a relation of this type as the averaged BEP relation. A fine-structure analysis of the correlation shows that it, at least to a first order approximation, can be viewed as a collection of piecewise linear BEP relations.

We also find that each molecule follows its own BEP relation. This directly implies that the "universal" BEP relation only is valid as a very crude zeroth order approximation. However, for certain molecules and surfaces in a narrow energy region, the individual BEP relations are similar. It is only under such circumstances that a universal BEP relation is observed.

The averaged piecewise linear BEP relations are shown in Figs. 2, 3, and 6, while the linear fits for individual molecules are given in Table I. To simplify the discussion we divide the BEP relations in the following classes: I) a single BEP line or II) a collection of piecewise linear BEP lines (see Fig. 2). The latter can in turn be divided into two subclasses, defined by whether the BEP relation is a single- or multi-valued function of ΔE_{diss}, denoted as IIa) and IIb), respectively. In the following, the versatile nature of these correlations is discussed for different materials individually and then compared with each other.
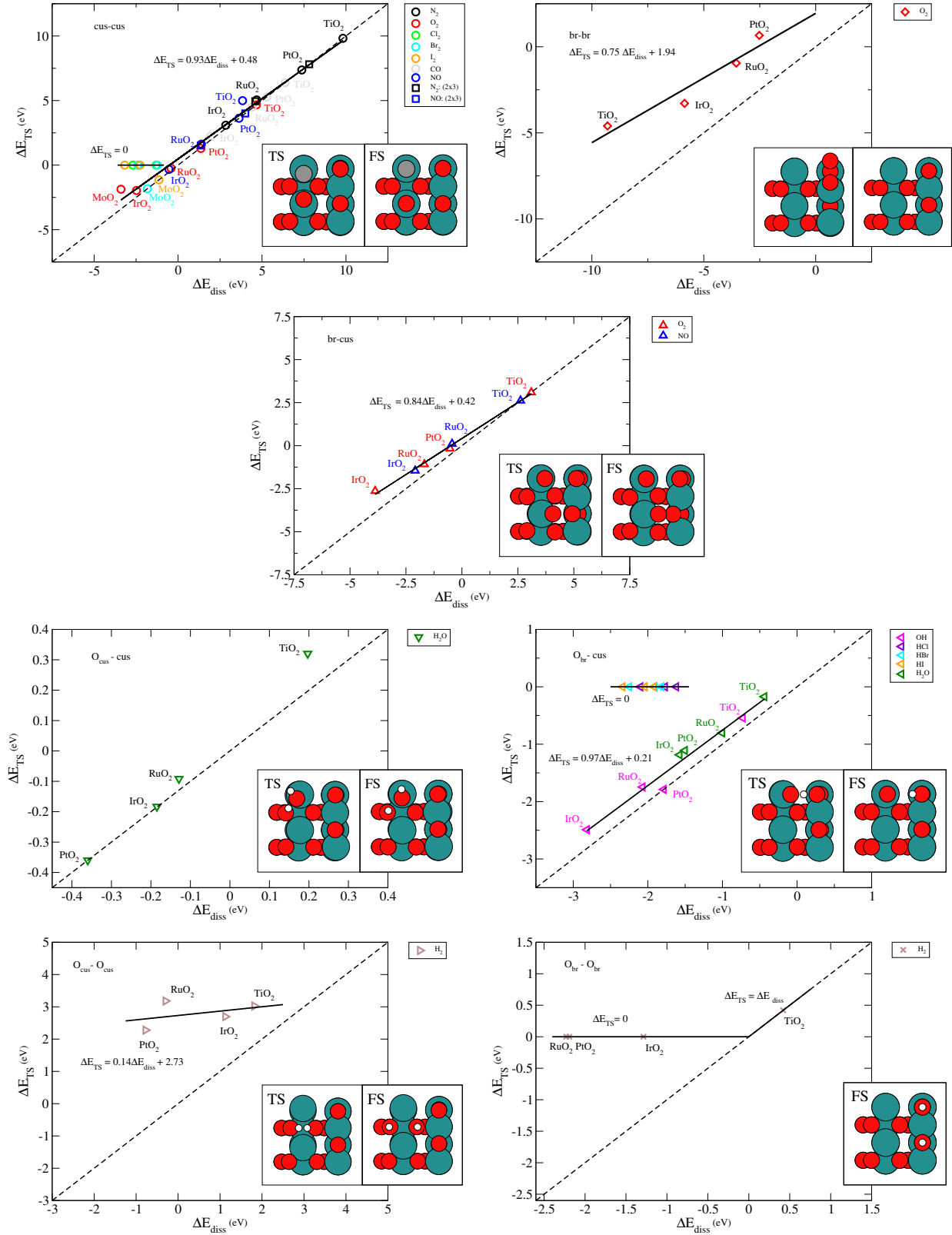
FIG. 2: Calculated transition state energy ΔE_{TS} as a function of dissociative chemisorption energy ΔE_{diss} of diatomic molecules on rutile (110) surfaces. The dissociation site is indicated in each panel. The solid black line represents the averaged BEP linear fit to the calculated data. The dashed line illustrates the dissociation line $i.e.$ $\Delta E_{TS} = \Delta E_{diss}$. Also, a top view of the structures for the transition state (TS) and the dissociated state, that is, final state (FS), are shown for a representative system. The blue, red, gray, and white spheres represent Ru, O, C, and H atoms, respectively.

TABLE I: Linear relations between ΔE_{TS} and ΔE_{diss} values for the considered systems. For each individual fit the α and β values (see Eq. 1) are given together with the mean absolute error. Note that there are (to a zeroth order approximation) several BEP lines for some systems, see text for more details.

	molecule	α	β (eV)	MAE (eV)
rutile				
cus–cus	N_2	0.95	0.46	0.08
	O_2	0.84	0.42	0.35
	NO	1.10	0.18	0.32
	CO	0.93	0.42	0.03
	all	0.93	0.48	0.25
	Cl_2	0	0	0
	Br_2	0	0	0
		1.0	0	0
	I_2	0	0	0
		1.0	0	0
br–br	O_2	0.75	1.94	0.53
br–cus	O_2	0.83	0.40	0.13
	NO	0.86	0.40	0.06
	all	0.84	0.42	0.10
O_{cus}–cus	H_2O	1.30	0.07	0.02
O_{br}–cus	OH	0.92	0.06	0.10
	H_2O	0.87	0.16	0.05
	all	0.97	0.21	0.09
	HCl	0	0	0
	HBr	0	0	0
	HI	0	0	0
O_{cus}–O_{cus}	H_2	0.14	2.73	0.27
O_{br}–O_{br}	H_2	0	0	0
		1.0	0	0
perovskite				
$LaBO_3$	N_2	0.86	1.44	0.46
	O_2	0.58	1.07	0.72
	NO	0.80	1.18	0.50
	CO	0.91	0.85	0.19
$SrBO_3$	N_2	0.75	1.40	0.39
	NO	0.65	0.82	0.40
	all	0.79	1.42	0.65
metal				
(211)	N_2	0.83	1.85	0.20
	O_2	0.58	0.89	0.26
	NO	0.71	1.09	0.29
	all	0.81	1.56	0.36
(111)	N_2	0.74	2.36	0.23
	O_2	0.64	1.69	0.09
	NO	0.68	1.66	0.15
	all	0.74	2.06	0.31

Rutiles

For rutiles, the calculations reveal (see Fig. 2) unique BEP lines for each of the considered dissociation sites: cus–cus, br–br, br–cus, O_{cus}–cus, O_{br}–cus, O_{cus}–O_{cus}, and O_{br}–O_{br}. The notation of the dissociation site follows the geometry of the final state, see Fig. 1. For example, O_{cus}–cus denotes that one of the two molecule fragments is adsorbed on a O_{cus} site and the other one on a cus site.

Class I: We find that the br–br site, br–cus site, and the O_{cus}–O_{cus} site (see the respective subfigures in Fig. 2) belong to class I with a simple averaged BEP relation consisting of only one line. The slopes of the BEP lines depend on the active site ($\alpha_{br-br} = 0.75$, $\alpha_{br-cus} = 0.84$, and $\alpha_{O_{cus}-O_{cus}} = 0.14$).

The adsorbate geometry in the TS differs between the active sites. For the br–cus site, the bond length between the two molecular fragments in the TS is considerably elongated, which means that the adsorbed molecule has lost its molecular identity, and the TS geometry resembles the geometry of the final state (FS). The TS geometry has more FS character the closer the point is to the dissociation line, defined by $\Delta E_{TS} = \Delta E_{diss}$.

For the O_{cus}–O_{cus} site, the bond length in the TS is close to the bond length of the free molecule. The TS geometry in the br–br site is less FS-like than the one of the br–cus site, and therefore $\alpha_{br-br} < \alpha_{br-cus}$. Hence, having a FS-like TS geometry results in a BEP line with a slope close to unity. The more initial state (IS) like the TS geometry is, the larger the deviation from the dissociation line is leading to $\alpha \ll 1$. This in turn indicates that ΔE_{TS} is very weakly dependent on ΔE_{diss}, if at all.

Class IIa: The BEP relation for dissociation of H_2 on the O_{br}–O_{br} site can be classified as IIa (see the O_{br}–O_{br} subfigure in Fig. 2). One part of the BEP relation coincides with the dissociation line while the other part coincides with the dissociation line, which corresponds to $\Delta E_{TS} = 0$. For the oxides on the dissociation (association) line the TS geometry is FS-like (IS-like). This illustrates that ΔE_{diss} is not a suitable descriptor.

Class IIb: The cus–cus and the O_{br}–cus sites (see the respective subfigure in Fig. 2) belong to class IIb. The averaged BEP relation consists of two parts, with slopes that coincide either with the slope of the dissociation line or the slope of the association line. For a given ΔE_{diss} value, the resulting ΔE_{TS} can fall on either the association or the dissociation line. This implies that different molecules follow significantly different BEP lines. For the molecules on the averaged BEP line with $\alpha \sim 0$, ΔE_{TS} is independent of the ΔE_{diss}. This supports the finding of case IIa, that ΔE_{diss} is not a good descriptor for dissociation. From the geometrical investigation, we again find that the slope of the BEP line depends on whether the adsorbates TS geometry is FS-like, resulting in an α

value close to unity, or if it is IS-like, resulting in an α value close to zero.

From the above analysis, the molecules can be divided into two groups: molecules with quite strong or very strong intramolecular bonds, for example, N_2, and very reactive molecules, for example, the diatomic homogeneous halide based molecules or diatomic heteronuclear weakly bond molecules containing halide atoms. In conclusion, the BEP relation is strongly dependent on the dissociating molecule.

For the dissociation of H_2O into OH and H over the O_{br}–cus site (see the O_{br}–cus subfigure in Fig. 2), when fitting the points to a straight line we find a BEP slope that is larger than one. Since $\alpha > 1$ is unphysical it is likely that the barrier for H_2O dissociation is overestimated on TiO_2 and that all transition state energies exactly follow the final state behavior, note the small energy scale on the y-axis. In general, it is the OH group that determines the trend for both activation sites.

We find that many molecules prefer to dissociate over the symmetric cus–cus site. This is presumably because of the completion of the octahedral geometry of the under-coordinated metal surface atoms on the clean surface. Nevertheless, the heteronuclear diatomic molecules that contain H prefer the asymmetric O_{br}–cus site, where the H recombines with O.

Comparing sites where only surface metal atoms are involved in the dissociation, *i.e.* the cus–cus, br–br, br–cus site, one finds that for a given adsorbate the magnitude of the slopes of the BEP relations can be ordered as $\alpha_{br-br} < \alpha_{br-cus} < \alpha_{cus-cus}$. This illustrates that the BEP slope depends on the active site and that the α values can be extrapolated. On a bridge site each adsorbate atom interacts with two fourfold coordinated surface metal atoms, while on the cus site each adsorbate atom interacts only with one fivefold surface metal atom. Hence, the bridge site, which resembles a vacancy site, is highly under-coordinated and therefore substantially more reactive than the cus site. The BEP slope is smallest for br–br since the surface atoms are more reactive and the intramolecular bonds will break more easily, resulting in a TS geometry that is less FS-like.

For some molecules *e.g.* N_2 on metal surfaces it has been shown that there is a geometric effect influencing the form of the BEP relation [6, 38]. One could talk about such an effect for the br–br site, which has a significantly different geometry than the rest of the considered active sites. Another site where the BEP line experiences a rigid shift away from the dissociation line is the O_{br}–cus site. This should be compared with the cus–cus site. Dissociation over these two active sites involves the same amount of surface atoms, however, these surface atoms have different coordination and consist of different atomic species. Despite that there is no straightforward one-to-one correspondence between the geometry of the active site and the α value for the oxides.
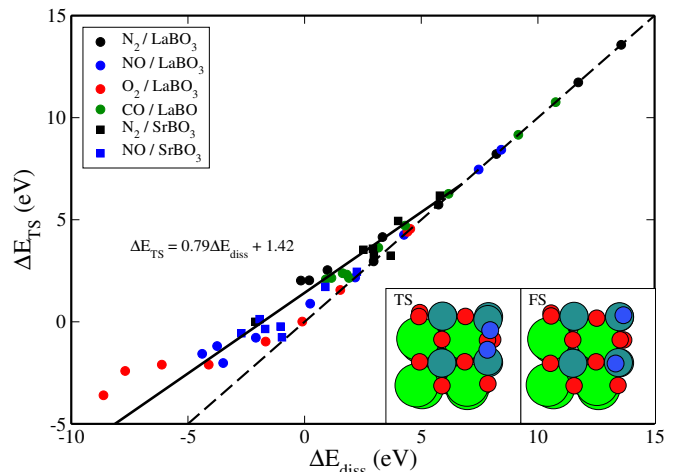

FIG. 3: Same as in Fig. 2 but for the (100) perovskite surfaces.

In conclusion, the BEP relations for rutiles show a delicate interplay between the type of molecule and the electronic structure of the active site in the conformation of the TS.

Perovskites

Figure 3 shows the results for the (100) surfaces of La- and Sr-perovskites. Also for this group of oxides BEP relations exist with an averaged relation given by $\Delta E_{TS} = 0.79\Delta E_{diss} + 1.42$ eV on a zoomed out level. However, the individual relations for each adsorbate and perovskite group (see Table I) show that different adsorbates obey their own BEP relations. In other words, the universal relation for perovskites is insufficient to describe the fine-structure behavior of the dissociation barriers.

The considered adsorption site on perovskites is atop of the surface B atoms, which leads to a locally fully coordinated structure around the surface B atom (see inset in Fig. 3). For the perovskites adopting or being very close to the ideal cubic symmetry, the relaxed adsorbate geometry is where the two atoms in the adsorbed molecule are positioned symmetrically atop of the B surface atoms. Otherwise the adsorbate geometry gets skewed due to tilting of the octahedral framework.

When it comes to the transition state geometries, the perovskites on or in the close proximity of the dissociation line have FS-like geometries. In the next section, the character of the TS will be discussed in more detail.

Transition state character: La-perovskites

To study the variations in character of the TS, we here consider dissociation of N_2, NO, and O_2 on $LaBO_3$ per-
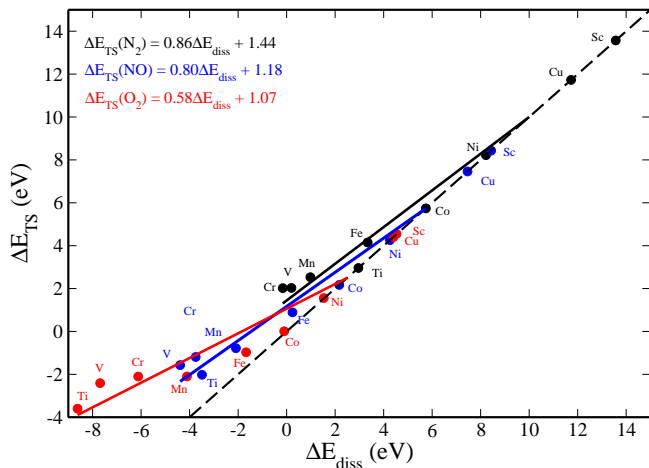
FIG. 4: Individual averaged BEP relations for N_2, NO and O_2 on $LaBO_3$. The labels indicate the B metal of $LaBO_3$.

ovskites with different B metal atoms belonging to the $3d$ metals. First of all for each molecule the BEP relation (see Fig. 4) approaches the dissociation line for high ΔE_{diss} values and deviates from the dissociation line as the ΔE_{diss} becomes more negative. The α-values change as 0.86, 0.80, to 0.58 for N_2, NO, and O_2, respectively.

Secondly, if the reactivity of an oxide would depend solely on the position of the B metal atom constituent in the Periodic Table, the reactivity trend should be monotonous along a period. The situation is, however, more complicated, for example, the reactivity of the $LaBO_3$ perovskites for N_2 dissociation is $LaScO_3 < LaCuO_3 < LaNiO_3 < LaCoO_3 < LaFeO_3 < LaTiO_3 < LaMnO_3 < LaVO_3 < LaCrO_3$.

In Fig. 5, the calculated potential energy along the dissociation path is given for each adsorbate. For N_2, the TS is FS-like for $LaCuO_3$, it becomes less FS-like as the group number of the B metal decreases. It is maximally IS-like for $LaCrO_3$. Then it becomes less IS-like and reaches FS-like character for $LaCrO_3$. Similar results are found for NO and O_2, with the difference that the turning points are found for different B metals in the perovskites.

The conclusion is that when moving in the $3d$ series from Cu to Sc, the TS goes through a "cycle" from being FS-like (like B = Cu), where the points fall on the dissociation line, to IS-like (like B = Fe), and becoming FS-like (like B = Sc), falling back on the dissociation line. Compounds with the most IS-like character are located to the left of the BEP lines and, therefore, deviate the most from the dissociation line. There is no reason not to believe that this "cyclic" behavior should be valid for substrates with B metals with other group numbers outside the studied range. It is also this cyclic behavior that is responsible for non monotonous reactivity order of the
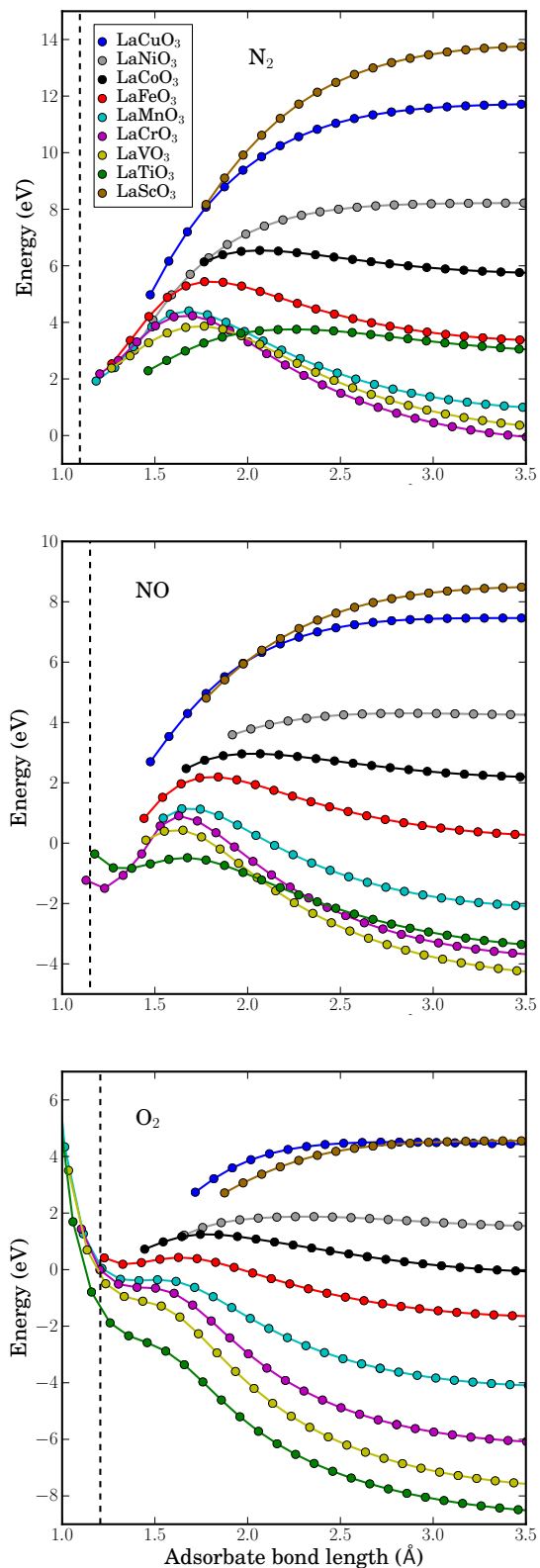

FIG. 5: Calculated adsorption energy of the molecule as a function of the molecular bond length for N_2, NO and O_2 on La-perovskite (100) surfaces. The vertical dashed line indicates the bond length of the molecule in the gas phase.
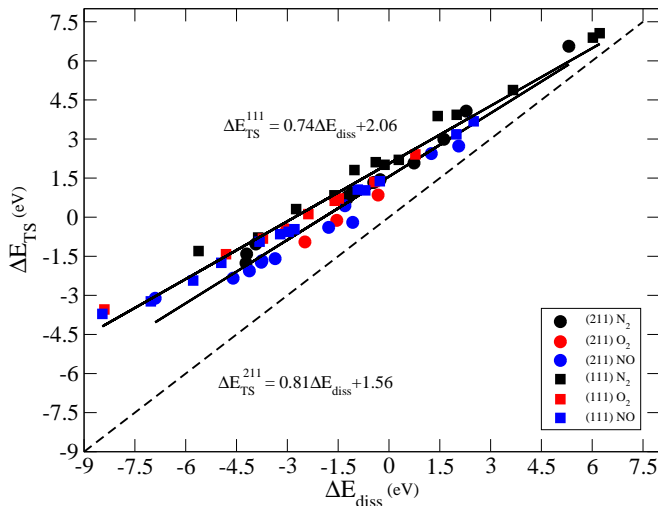
FIG. 6: Same as in Fig. 2 but for the (211) and the (111) transition metal surfaces.

La-perovskites.

Metals

In Fig. 6, we present some data for dissociation on the (211) and (111) metal surfaces for comparison. The BEP relations for the lowest TS barriers can be characterized as class I, with the averaged relations given by $\Delta E_{TS} = 0.81\Delta E_{diss} + 1.56$ eV and $\Delta E_{TS} = 0.75\Delta E_{diss} + 2.06$ eV for the (211) and (111) surfaces, respectively. They are in agreement with the relations from Ref. [6], $\Delta E_{TS} = 0.87\Delta E_{diss} + 1.34$ eV and $\Delta E_{TS} = 0.90\Delta E_{diss} + 2.07$ eV, for the (211) and (111) surfaces, respectively. The difference in the relations found in the current study and the one in Ref. [6] is assigned to the somewhat different composition of the calculated data points on which the linear regressions are made. In the current study, metal surfaces in a broader reactivity range are included. Including more reactive metals, that is more negative ΔE_{diss}, results in a larger deviation from the dissociation line. The individual fits for each adsorbate on these surfaces are given in Table I. It is found that O_2 has an α-value that is substantially different from the averaged BEP α-value. This implies that there is a significant fine structure in the BEP relation for both transition metals as well as for oxides.

Oxides vs metals

When comparing the BEP relations associated with the lowest TS for metals and oxides, we find (considering the N_2, O_2 and NO molecules) that both groups of oxides obey relations that are closer to the dissociation line than the (111) and (211) metal surfaces. The ru-

tiles have very low (if any) barriers with respect to the gas phase, while the perovskites exhibit more pronounced barriers. The averaged α-value for the perovskites is in-between the α-value of the (111) and the (211) surfaces, whereas the averaged β-value is closer to the β-value of the (211) surfaces. Hence, there is a major difference between the two types of oxides. The fact that molecules with strong or moderate intramolecular bonds dissociate without any substantial barriers on rutiles, make these oxides extremely interesting as catalysts for dissociation of diatomic molecules compared to the metals. In the energy region most relevant for catalysis i.e. where $\Delta E_{diss} \sim 0$ eV, we find rutiles as RuO_2 and IrO_2.

SUMMARY AND OUTLOOK

In summary, density functional theory calculations show that BEP relations also exist for oxides and that they have a richly detailed structure. Among the molecules and oxides investigated in this study, one finds the whole spectrum of BEP relations with slopes from one to almost zero. A slope equal to zero corresponds to a system with no activation barrier and hence the ΔE_{TS} by definition is not a well defined quantity. Surprisingly, we have found that the BEP relations for molecules with strong intramolecular bonds on the most stable site on rutiles follow a relation that almost coincides with the dissociation line. This suggests that these oxides are interesting as alternative catalysts for reactions involving the dissociation of diatomic molecules compared to transition metals. The perovskites could also be interesting for some reactions, since with respect to their dissociative abilities they intrinsically resemble the steps on transition metals.

Our results show that if the underlying nature of bonding in the TS and the dissociated state are similar, that is the TS is FS-like, these are correlated via a BEP relation with a slope close to unity. This is the case for molecules with strong intramolecular bonds. On the other hand, if the TS is more IS-like the BEP relations become FS-independent and the dissociative chemisorption energy becomes an invalid descriptor for the dissociation barrier. This is the case for very reactive surfaces or molecules with weak intramolecular bonds. We have identified a "cyclic" behavior in the TS character, that is it can change from being FS to IS and back to FS as the metal constituent of the oxide is varied through a period in the Periodic Table. This implies that on a detailed level the concept of universal BEP relation is an insufficient model unable to take into account the fine-structure observed in this study.

It is also found that, for a given molecule and active site, the BEP relation is a continuous function that depends on the strength of the bond formed between the surface and the molecule. At the moment we do not have

a completely predictive approach of what the form of the BEP relation should look like, but we know that it to a god approximation can be viewed as a piecewise linear relation. This will be the subject of future studies.

The combined knowledge of BEP relations and scaling relations opens up the possibility to evaluate the activity of oxides in terms of simplified descriptors. Hence, extending the fundamental knowledge of the reaction chemistry at the atomic level may widen our perspectives of oxides as future heterogeneous catalysts.

Acknowledgments

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