





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# Trends in C–O and N–O bond scission on rutile oxides described using oxygen vacancy formation energies†

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Reactivity trends on transition metals can generally be understood through the d-band model, but no analogous theory exists for transition metal oxides. This limits the generality of analyses in oxide-based catalysis and surface chemistry and has motivated the appearance of numerous descriptors. Here we show that oxygen vacancy formation energy ( $\Delta E_{\text{vac}}$ ) is an inexpensive yet accurate and general descriptor for trends in transition-state energies, which are usually difficult to assess. For rutile-type oxides ( $\text{MO}_2$  with  $M = 3d$  metals from Ti to Ni), we show that  $\Delta E_{\text{vac}}$  captures the trends in C–O and N–O bond scission of  $\text{CO}_2$ ,  $\text{CH}_3\text{OH}$ ,  $\text{N}_2\text{O}$ , and  $\text{NH}_2\text{OH}$  at oxygen vacancies. The proportionality between  $\Delta E_{\text{vac}}$  and transition-state energies is rationalized by analyzing the oxygen–metal bonds, which change from ionic to covalent from  $\text{TiO}_2$  to  $\text{NiO}_2$ .  $\Delta E_{\text{vac}}$  may be used to design oxide catalysts, in particular those where lattice oxygen and/or oxygen vacancies participate in the catalytic cycles.

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## 1. Introduction

With the advent and increase in the use of Density Functional Theory (DFT), the theoretical description of catalytic reactions has experienced great advances.<sup>1–3</sup> The properties at the atomic scale that determine the macroscopic kinetics have been established in numerous cases and some key descriptors, such as adsorption energies of intermediates,<sup>1,4</sup> band centers,<sup>1</sup> and coordination numbers,<sup>5,6</sup> among others,<sup>7</sup> have been identified to correlate with the catalytic activity. All this has substantially facilitated the rapid screening and *in silico* design of a large number of new materials.

However, the advancements pertain mostly to metals and many fundamental properties of the surfaces of metal oxides are still poorly understood due to their inherent complexity. This is because oxide properties depend on the interplay between the geometric structure, the band structure, the local stoichiometry of the surface and the oxidation states of the components.<sup>8</sup> In this context, a great challenge is the elaboration of an atomic-scale surface chemistry theory for metal oxides<sup>3,9</sup> as comprehensive as the d-band model for transition metals.<sup>1</sup> Such a theory would undoubtedly be the groundwork for the rational design of metal oxide catalysts.

Numerous studies have been conducted to identify the key factors that affect the activity of oxide surfaces. For instance, Shao-Horn *et al.* showed that the oxygen evolution activity of perovskite oxides exhibits a volcano-shaped dependence on the occupancy of the  $e_g$  orbitals, with the peak activity achieved at an  $e_g$  occupancy close to unity.<sup>10</sup> Similarly, Rossmeisl *et al.* proposed the concept of outer electrons to capture the trends in adsorption energies of metals, rock-salt monoxides, and perovskites altogether.<sup>11</sup> Jiang *et al.* proposed an adjusted coordination number as a general descriptor for the H adsorption energy and C–H activation energies over surface facets and defects of  $\text{V}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{Co}_3\text{O}_4$ , and  $\text{NiO}$ .<sup>12</sup> Furthermore, Morgan *et al.* reported that the experimentally measured area specific resistance and oxygen surface exchange of perovskites are well correlated with the DFT-calculated oxygen p-band center and vacancy formation energy.<sup>13</sup> Similarly, Dickens *et al.* reported a correlation between the average energy of adsorbed oxygens' 2p states and their reactivity at transition metals and some oxides.<sup>14</sup> Hinuma *et al.* also reported fair correlations

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between oxygen vacancy formation energies and various adsorption energies.<sup>15</sup>

In addition, the versatile Brønsted–Evans–Polanyi (BEP) relation observed on metals is often found on rutiles and perovskites. This relation, which correlates elementary reaction thermodynamics and kinetics, seems to be universal on metals<sup>16,17</sup> but not on oxides, as it depends on the type of oxide, the active site and the dissociating molecules.<sup>18</sup>

Since the structural complexity of oxides appears to prevent the elaboration of universal descriptors, a viable strategy is to establish links between macroscopic functionality and atomic-scale properties for a given family of oxides.

The rutile TiO<sub>2</sub>(110) surface is considered a prototypical system for metal oxide surfaces because of its rich surface chemistry and numerous applications in heterogeneous catalysis, photocatalysis, and gas sensors.<sup>19–22</sup> The surface reactivity of TiO<sub>2</sub>(110) has been shown to be mainly controlled by defects, particularly oxygen vacancies.<sup>23</sup> The latter can either modify the behavior of neighboring metal sites or themselves act as active sites for many surface reactions, such as water dissociation and CO oxidation.<sup>24–27</sup> Other rutile oxides such as SnO<sub>2</sub>, CeO<sub>2</sub>, IrO<sub>2</sub>, RuO<sub>2</sub> and MnO<sub>2</sub> have interesting applications in (electro)catalysis and gas sensing.<sup>28–35</sup> It has been argued that lattice oxygen may play a central role in the catalytic properties of some oxides,<sup>36–41</sup> typically *via* Mars/van Krevelen mechanisms in which oxygen vacancies are generated after lattice oxygen combines with reactants and/or intermediates.<sup>42</sup> Therefore, it is crucial to understand how oxygen vacancies affect the adsorption properties and catalytic activity of rutile oxide surfaces.

Using C–O and N–O bond scission in CO<sub>2</sub>, CH<sub>3</sub>OH, N<sub>2</sub>O and NH<sub>2</sub>OH as probe reactions, we show here that oxygen vacancy formation energy is a simple and robust descriptor for the bond-scission kinetics at oxygen vacancies of rutile-type MO<sub>2</sub>(110) (M = 3d metals from Ti to Ni) surfaces. The results are useful for catalytic reduction of greenhouse gases such as N<sub>2</sub>O<sup>43</sup> and CO<sub>2</sub>,<sup>44,45</sup> CH<sub>3</sub>OH photocatalytic oxidation,<sup>46</sup> and NH<sub>2</sub>OH electrochemistry.<sup>47</sup>

Our results allow linking the adsorption energies of stationary and saddle points, which are difficult or currently impossible to measure<sup>48</sup> and tedious to calculate, to a single, computable and experimentally available descriptor for numerous oxide materials, namely oxygen vacancy formation energies. This can potentially streamline the fundamental understanding and rational design of oxide catalysts.

## 2. Methods

Spin-unrestricted DFT calculations were performed using the VASP<sup>49</sup> with PBE.<sup>50</sup> The interaction between the ionic cores and electrons was described by the projector-augmented wave (PAW) method,<sup>51</sup> and the Kohn–Sham valence electronic wave function was expanded in a plane-wave basis set with a kinetic energy cutoff of 400 eV. (2 × 1) 4-layer (110) slabs for MO<sub>2</sub> rutile oxides were used, separated by 15 Å of vacuum. The two bottommost layers were fixed at the bulk distances, and the two topmost layers and the adsorbates were fully relaxed. The Brillouin zones were sampled with 6 × 4 × 1 Monkhorst–Pack

grids.<sup>52</sup> The calculated lattice constants of the MO<sub>2</sub> oxides fall in the regions 4.31 Å ≤ *a* ≤ 4.67 Å and 2.80 Å ≤ *c* ≤ 2.97 Å, which agree well with the experimental values, as listed in Table S1.† The adsorption energy ( $\Delta E_{\text{Ads}}$ ) was calculated using the most stable configurations ( $E_{\text{MO}_{2-v}+\text{moiety}}$ ) relative to the clean surfaces ( $E_{\text{MO}_{2-v}}$ ) and the isolated molecules or their scission moieties ( $E_{\text{moiety}}$ ):

$$\Delta E_{\text{Ads}} = E_{\text{MO}_{2-v}+\text{moiety}} - E_{\text{MO}_{2-v}} - E_{\text{moiety}} \quad (1)$$

where moiety = CO<sub>2</sub>, CO, N<sub>2</sub>, N<sub>2</sub>O, CH<sub>3</sub>OH, CH<sub>3</sub>, OH, NH<sub>2</sub>OH, NH<sub>2</sub>, and  $\frac{1}{2}$ O<sub>2</sub>. We calculated the adsorption energies of oxygen at the bridge oxygen vacancy on the MO<sub>2</sub>(110) surfaces using DFT + U and found that the use of U does not alter the trends for oxygen adsorption, see Fig. S1a.† We also performed single-point DFT + U calculations for the activation energies and reaction energies of CO<sub>2</sub> and N<sub>2</sub>O decomposition. Fig. S2† shows that the relationship between thermodynamics and kinetics also remains linear. Since we mainly focus on the trends in the present work, U was not included in the analysis.

We have also considered the effect of dispersion corrections for the particular case of  $\Delta E_{\text{Ads}}(\text{CO}_2)$ .<sup>53</sup> It can be seen from Table S2 and Fig. S1b† that the corrections only shift the adsorption energies downwards by 0.19 eV on average, without altering the overall trend.

Enthalpy changes ( $\Delta H$ ) are usually approximated as:  $\Delta H \approx \Delta E + \Delta \text{ZPE}$  (ZPE: zero-point energy). For adsorbate \*AB, one has:  $\text{ZPE}_{\text{AB}} \approx \text{ZPE}_{\text{A}} + \text{ZPE}_{\text{B}}$ , so that for dissociation reactions  $\Delta \text{ZPE} \approx 0$  and  $\Delta H_{\text{Diss}} \approx \Delta E_{\text{Diss}}$ . For \*CH<sub>3</sub>OH at NiO<sub>2</sub>(110),  $\text{ZPE}_{\text{CH}_3\text{OH}}$ ,  $\text{ZPE}_{\text{OH}}$  and  $\text{ZPE}_{\text{CH}_3}$  are 1.42, 0.38 and 0.97 eV. Thus,  $\Delta \text{ZPE} = 0.07$  eV, which is negligible considering the accuracy of DFT and BEP relations. Besides, the ZPEs do not appreciably change among rutile oxides:  $\text{ZPE}_{\text{CH}_3\text{OH}}$  is 1.42 eV on both NiO<sub>2</sub>(110) and TiO<sub>2</sub>(110). Thus, including ZPEs will not sizably affect the BEP relations reported here. In this order of ideas, the reaction energy ( $\Delta H_{\text{Diss}}$ ) of elementary reactions was approximated as:

$$\Delta H_{\text{Diss}} \approx \Delta E_{\text{Diss}} = E_{\text{FS}} - E_{\text{IS}} \quad (2)$$

where  $E_{\text{FS}}$  and  $E_{\text{IS}}$  are the energy of the most stable configurations for the adsorption of the intermediates in the final state ( $E_{\text{FS}}$ ) and initial state ( $E_{\text{IS}}$ ). For example, for CH<sub>3</sub>OH scission the initial state is adsorbed \*CH<sub>3</sub>OH, and the final state is \*CH<sub>3</sub> + \*OH.

All transition states (TSs) were located by the force reversed method<sup>54</sup> and the climbing-image nudged elastic band method (CI-NEB)<sup>55</sup> and confirmed by vibrational frequency analysis. The relaxations stopped when the residual forces on each atom were smaller than 0.03 eV Å<sup>-1</sup>. The elementary activation barrier ( $\Delta E_{\text{Act}}$ ) was calculated using the TS ( $E_{\text{TS}}$ ) with respect to the most stable configurations for the adsorption of species at the IS ( $E_{\text{IS}}$ ):

$$\Delta E_{\text{Act}} = E_{\text{TS}} - E_{\text{IS}} \quad (3)$$

The formation energy of a surface oxygen vacancy ( $\Delta E_{\text{Vac}}$ ) is:

$$\Delta E_{\text{Vac}} = \frac{1}{2}E_{\text{O}_2} + E_{\text{MO}_{2-v}} - E_{\text{MO}_2} \quad (4)$$



where  $\frac{1}{2}E_{O_2}$ ,  $E_{MO_2-v}$  and  $E_{MO_2}$  are half the energy of molecular oxygen and the energies of the defective and pristine rutile slabs, respectively. We calculated  $\frac{1}{2}E_{O_2}$  using the DFT-assessed free energies of  $H_2$  and  $H_2O$  and the experimental free energy change of the reaction  $H_2O \rightarrow \frac{1}{2}O_2 + H_2$ , which is 2.46 eV. This is done to avoid the direct calculation of the total energy of  $O_2$ ,<sup>56,57</sup> which is generally problematic within the DFT formalism.<sup>58</sup> All the adsorption, reaction, activation, and vacancy formation energies are found in Tables S3–S5.†

We note that some oxides such as  $CoO_2$  and  $NiO_2$  may not exhibit the rutile phase under catalytic conditions. However, this does not affect the main purpose of this work, which is the identification and description of general reactivity trends for an important family of oxides.

### 3. Results and discussion

As shown in Fig. 1a, there is a linear Brønsted–Evans–Polanyi (BEP)-type relationship<sup>59</sup> between activation energies ( $\Delta E_{Act}$ ) and reaction energies ( $\Delta E_{Diss}$ ) for  $CO_2$ ,  $CH_3OH$ ,  $N_2O$  and  $NH_2OH$  dissociation (see the reactions in Fig. 1a) at the bridge oxygen vacancy on the rutile (110) surfaces. This suggests that scission kinetics and thermodynamics are proportional and well correlated in this case.

Compared to  $CO_2$  and  $CH_3OH$  decomposition ( $-0.51 \text{ eV} \leq \Delta E_{Diss} \leq 3.19 \text{ eV}$ ;  $0.62 \text{ eV} \leq \Delta E_{Act} \leq 3.23 \text{ eV}$ ),  $N_2O$  and  $NH_2OH$  decomposition is generally more exothermic ( $-3.80 \text{ eV} \leq \Delta E_{Diss} \leq 0.23 \text{ eV}$ ), and the corresponding  $\Delta E_{Act}$  values are lower, falling in the range of 0.13–1.25 eV (see Table S3† for the specific values). A good relationship is also observed for  $CO_2$ ,  $N_2O$  and  $NH_2OH$  dissociation barriers and the transition-state geometries, represented by N–O or C–O bond lengths ( $d$  in Fig. 1b and Table S3†). Briefly, the shorter the N–O or C–O bond length at the TS, the lower the barrier, which agrees well with previous DFT study results for CO oxidation on metals and metal oxides.<sup>18,60</sup>

Identifying a BEP relationship enables relatively fast assessment of catalytic activities by using the reaction energy  $\Delta E_{Diss}$  as a descriptor for trends in transition-state (TS) barriers. Nevertheless, we note that calculating  $\Delta E_{Diss}$ , which involves both initial (IS) and final (FS) states (eqn (2)), is still a demanding task when dealing with a great number of systems and/or large unit cells. In the following, we will show that more affordable and experimentally available descriptors exist.

In Fig. 2 we plot the adsorption energies  $\Delta E_{Ads}$  of  $CO_2$ ,  $CH_3OH$ ,  $N_2O$  and  $NH_2OH$  and their cleaved moieties against  $\Delta E_{Diss}$ . Fig. 2 and Table S4† show that the ISs for  $CO_2$ ,  $CH_3OH$ ,  $N_2O$  and  $NH_2OH$  decomposition are almost independent of the chemical nature of the element M in  $MO_2$ . To illustrate this, consider the case of  $CO_2$ : the adsorption energies ( $\Delta E_{Ads}$ ) vary only by  $\sim 0.25 \text{ eV}$  on the bridge oxygen vacancy of the analyzed rutile surfaces, but  $\Delta E_{Diss}$  changes by  $\sim 3.7 \text{ eV}$  (see the values in Tables S3 and S4† and the structures in Fig. S3†).

The results in Fig. 2 suggest that, as the adsorption energies of initial states (ISs) are nearly constant, the trends in  $\Delta E_{Diss}$  (eqn (2)) are mainly determined by the final states (FSs).

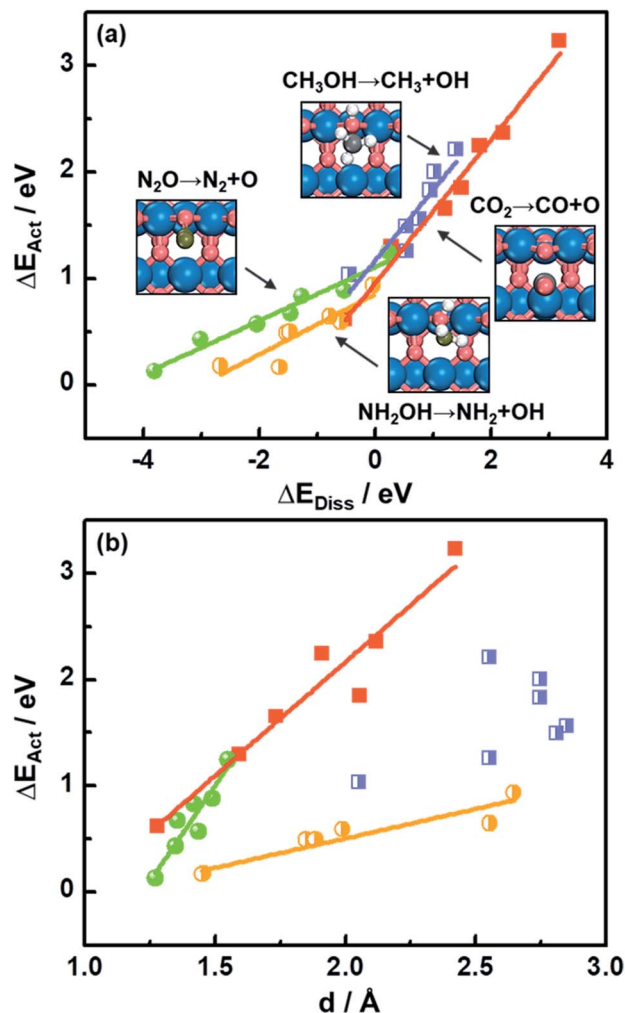


Fig. 1 Activation energies ( $\Delta E_{Act}$ ) for C–O and N–O bond scissions as a function of (a) reaction energies ( $\Delta E_{Diss}$ ) and (b) the C–O or N–O distances ( $d$ ) at the transition states on rutile  $MO_2(110)$  surfaces. Insets: transition-state structures for C–O and N–O bond scission. Blue, vermilion, grey, ochre and white balls represent 3d metals (Ti–Ni) and O, C, N and H atoms, respectively.

The downward shift of the FS curve can lead to more negative  $\Delta E_{Diss}$  and to the shift of the reaction coordinate of the transition state closer to the ISs.<sup>59</sup> This explains the relationship between  $\Delta E_{Act}$  and N–O or C–O bond distance  $d$  at the TSs in Fig. 1b well. The deviation from the linear trend of  $\Delta E_{Act}$  vs.  $d$  in the case of  $CH_3OH$  dissociation is justified by the surface reconstruction of  $CoO_2(110)$  and  $NiO_2(110)$ .

Compared to the trivial molecular adsorption at the ISs shown in Fig. 2 and Table S4,† the trends in dissociative adsorption, *i.e.* the FSs, are slightly more elaborate. We have identified two groups in the trends: (1) intermediates such as  $*CO$ ,  $*N_2$  and  $*CH_3$  adsorbed at the coordinatively unsaturated 3d metals on the FSs do not exhibit strong dependence on the chemical nature of M (Fig. S3b, e and g†). (2)  $*O$ ,  $*OH$  and  $*NH_2$  adsorption at the bridge oxygen vacancy and coordinatively unsaturated 3d metals on the FSs are oxide-dependent (Fig. S3c, h and j†), with the largest differences in  $\Delta E_{Ads}$  being 4.10, 1.98 and 1.25 eV, respectively (see Table S4†).



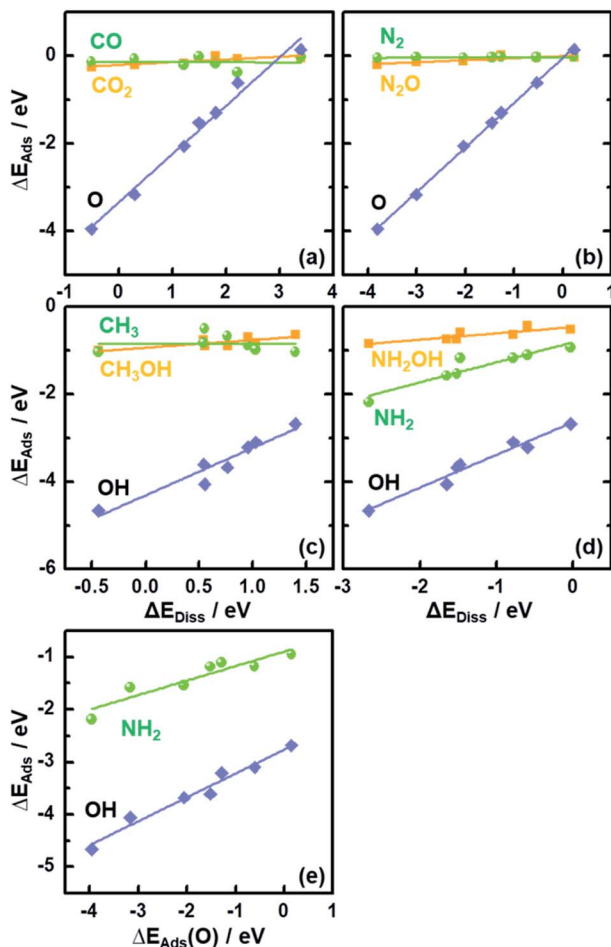


Fig. 2 Adsorption energies ( $\Delta E_{\text{Ads}}$ ) of reactants and products of C–O bond scission for (a) CO<sub>2</sub> and (c) CH<sub>3</sub>OH and N–O bond scission for (b) N<sub>2</sub>O and (d) NH<sub>2</sub>OH plotted as a function of the reaction energies ( $\Delta E_{\text{Diss}}$ ) on MO<sub>2</sub>(110). (e)  $\Delta E_{\text{Ads}}$  of NH<sub>2</sub> and OH plotted against that of O.

Since  $\Delta E_{\text{Ads}}(\text{OH})$  and  $\Delta E_{\text{Ads}}(\text{NH}_2)$  scale linearly with  $\Delta E_{\text{Ads}}(\text{O})$ , as shown in Fig. 2e, the trends in  $\Delta E_{\text{Diss}}$  for the C–O and N–O bond scission reactions are modulated by a single metal-dependent parameter, namely  $\Delta E_{\text{Ads}}(\text{O})$ . Since creating an oxygen vacancy is the reverse process of oxygen adsorption at such a vacancy, we have:  $\Delta E_{\text{Ads}}(\text{O}) = -\Delta E_{\text{Vac}}$ , see eqn (1) and (4). This is important, as  $\Delta E_{\text{Vac}}$  is a common parameter for oxide systems.

Recapitulating, transition-state energies and reaction energies are connected through a linear BEP relation ( $\Delta E_{\text{Act}} = \gamma + \phi \Delta E_{\text{Diss}}$ , see Fig. 1a), and reaction energies and the O adsorption energies are in turn connected ( $\Delta E_{\text{Diss}} = \varepsilon + \delta \Delta E_{\text{Ads}}(\text{O})$ , see Fig. 2). Since  $\Delta E_{\text{Ads}}(\text{O})$  is the additive inverse of  $\Delta E_{\text{Vac}}$ , one can expect the following, where  $\alpha$  and  $\beta$  depend on the specific dissociation reaction:

$$\Delta E_{\text{Act}} = \alpha - \beta \Delta E_{\text{Vac}} \quad (5)$$

This is exactly what we observe in Fig. 3, where  $\Delta E_{\text{Act}}$  correlates well with  $\Delta E_{\text{Vac}}$  for all oxides and reactions considered in this study, in all cases with a negative slope. The linear relationships between  $\Delta E_{\text{Act}}$  and  $\Delta E_{\text{Vac}}$  found for all the C–O and N–O bond

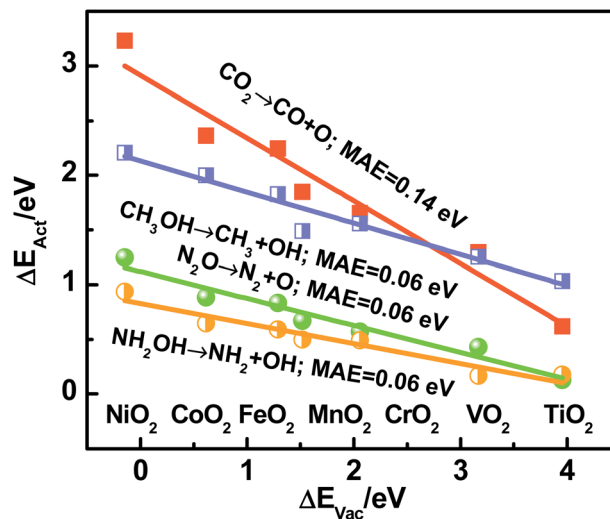


Fig. 3 Activation energy ( $\Delta E_{\text{Act}}$ ) for C–O and N–O bond scissions plotted as a function of the vacancy formation energy ( $\Delta E_{\text{Vac}}$ ) on MO<sub>2</sub>(110). The analyzed oxides are respectively marked in the trends. MAE: mean absolute error.

scission reactions indicate that  $\Delta E_{\text{Vac}}$  can be used as a single descriptor to analyze a number of dissociation reactions on rutile surfaces. According to Fig. 3, as  $\Delta E_{\text{Vac}}$  increases from NiO<sub>2</sub> to TiO<sub>2</sub>,  $\Delta E_{\text{Act}}$  gradually decreases, which suggests that strengthening bridge oxygen–metal bonds can significantly promote C–O and N–O bond scission reactions.

To further understand the nature of the bond between bridge oxygen and metal ions in rutile oxides, we calculated in Fig. 4 the differential charge density maps. It can be seen from Fig. 4a that there is considerable charge withdrawal from Ti by O in TiO<sub>2</sub>, which is indicative of rather ionic bonds. Fig. 4b–d show sizeable charge depletion from both M (M = Cr, Fe and Ni) and O centers and accumulation between them, meaning that the bonds are covalent. Furthermore, the charge withdrawn from O (blue part) gradually increases when moving from CrO<sub>2</sub> to NiO<sub>2</sub>, suggesting that more and more electrons contribute to the formation of the bond and lead to stronger covalent interactions. Therefore, these results show that the bridge oxygen–metal bond switches from ionic to covalent when moving from TiO<sub>2</sub> to NiO<sub>2</sub>, which is in turn responsible for the decrease in  $\Delta E_{\text{Vac}}$ .

In contrast, for N<sub>2</sub>O adsorption at the bridge O vacancy, we find charge depletion from metal centers and O centers in N<sub>2</sub>O and accumulation between them for all the rutile oxides studied, as shown in Fig. 4e–h, indicating that the bonds are covalent. Interestingly, the distance between M and O in N<sub>2</sub>O is closely related to the charge transferred. As the M–O distance increases from TiO<sub>2</sub> and CrO<sub>2</sub> (~2.5 Å) to FeO<sub>2</sub> and NiO<sub>2</sub> (~3.0 Å), the charge transferred markedly decreases. The similar bond nature between M and N<sub>2</sub>O also leads to a small variation in adsorption energies of 0.22 eV only. We note that this explanation based on bond ionicity and covalency is similar to that in previous studies on metalloporphyrins<sup>61</sup> and metals,<sup>7</sup> which grants generality to the analysis.

In brief, Fig. 2–4 show that reaction energies ( $\Delta E_{\text{Diss}}$ ), activation energies ( $\Delta E_{\text{Act}}$ ), oxygen vacancy formation energies





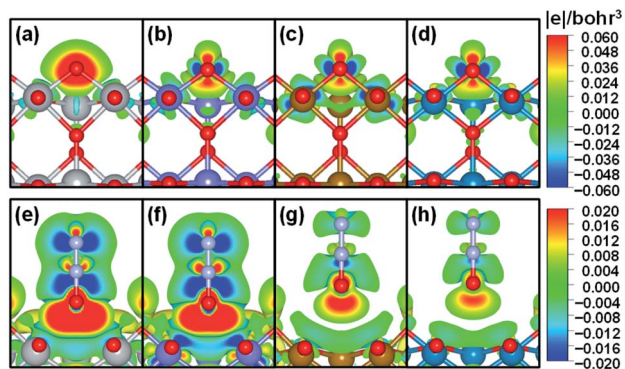


Fig. 4 Differential charge density map for adsorption of O (upper panels) and  $\text{N}_2\text{O}$  (lower panels) at the bridge O vacancy on  $\text{MO}_2(110)$ . (a and e)  $M = \text{Ti}$ ; (b and f)  $M = \text{Cr}$ ; (c and g)  $M = \text{Fe}$ ; (d and h)  $M = \text{Ni}$ . Grey, purple, orange, green, red and light purple spheres represent Ti, Cr, Fe, Ni, O and N, respectively. Blue and yellow-red isosurfaces indicate charge depletion and accumulation, respectively. The 2D profile is a cut along two bridge O–M bonds.

( $\Delta E_{\text{vac}}$ ), and electronic charges are all connected on rutile oxides, which holds promise for understanding and rationally capitalizing on the high activity of oxygen vacancies at rutile oxides observed experimentally.

We emphasize that  $\Delta E_{\text{vac}}$  is a more convenient descriptor than the others analyzed here in view of its straightforward calculation and experimental measurability.

## 4. Conclusions

By adsorbing and cleaving  $\text{CO}_2$ ,  $\text{CH}_3\text{OH}$ ,  $\text{N}_2\text{O}$ , and  $\text{NH}_2\text{OH}$ , we were able to construct linear BEP relationships for C–O and N–O bond scissions taking place at oxygen vacancies on rutile oxides. Interestingly, the analysis of the trends allowed us to identify the oxygen vacancy formation energy as a simple yet accurate descriptor for the transition-state energies of such scissions. This is important because oxygen vacancy formation energies are more easily calculated than transition-state energies and can be measured experimentally.

The nature of the bond between bridge oxygen and 3d metals in rutile oxides changes from ionic to covalent when moving from the left to the right of the periodic table (Ti to Ni), in line with the trends in formation energies of surface oxygen vacancies. The insight gained from this study can be used to enrich the design principles for oxide catalysts and simplify their modelling, particularly for those where lattice oxygen and/or oxygen vacancies participate in the catalytic cycles.

## Conflicts of interest

There are no conflicts to declare.

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