

Structure–Activity Relationships in Lewis Acid–Base Heterogeneous Catalysis

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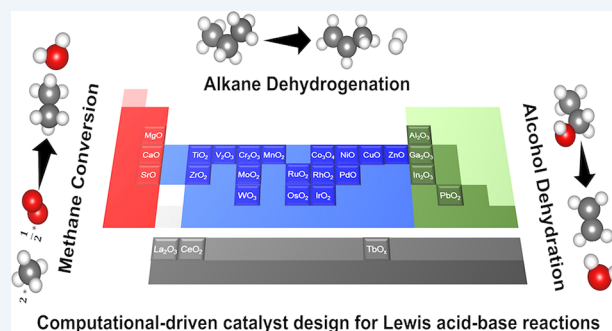
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ABSTRACT: Heterogeneous catalysts are the key components in industrial chemical transformations. Metal oxides are particularly appealing as catalysts owing to their inherent Lewis acid–base properties that facilitate the activation of chemically inert paraffinic C–H bonds. Computational chemistry provides a rich mechanistic understanding of catalyst functionality through the calculation of accurate thermodynamic and kinetic data that cannot be experimentally accessible. Using these data, one can relate the energy needed for elementary reaction steps with properties of the catalyst, paving the way for computational catalyst discovery. At the heart of this process is the development of structure–activity relationships (SARs) that facilitate the rapid prediction of promising catalytic materials for energy intense industrial transformations, guiding experimentation. In this review article, we highlight SARs on oxides for chemical reactions of high industrial relevance including (i) methane activation and conversion, (ii) alkane dehydrogenation, and (iii) alcohol dehydration. We also discuss current limitations and challenges on SARs and propose future steps to advance catalyst discovery.

KEYWORDS: C–H activation, catalyst screening, metal oxides, density functional theory, reactivity and selectivity descriptors



INTRODUCTION

Heterogeneous catalysis finds tremendous applications in modern industry, ranging from the production of commodity chemicals and pharmaceuticals to fertilizers and fuels.^{1–3} Around 80–90% of industrial chemical processes rely on heterogeneous catalysts with an estimated global market share of 1.5 trillion USD.^{1,3} Two major benefits of using heterogeneous catalysts include the facile separation of gaseous or liquid products from the solid catalyst and high catalytic stability under harsh reaction conditions (high temperatures and pressures).^{1–3} Among the most frequently used heterogeneous catalysts are metal oxides (MOs).⁴ MOs gained attention in the mid-1950s due to their potential in catalyzing acid–base reactions by the simultaneous participation of dual acid–base sites in catalytic events.⁴ Generally, the catalytic surface of MOs consists of anionic oxygen centers as Lewis base sites (O^{2-}) and coordinatively unsaturated cationic metal centers as Lewis acid sites (M^{n+}). The anionic oxygen centers have high electronegativity and can form both covalent and ionic bonds when interacting with nonmetals and metals, respectively.⁵ The electronegativity of cationic metal centers depends on their oxidation state, where higher oxidation states result in higher electronegativity. MOs are classified as acidic, basic, or amphoteric, depending on the oxidation state of the cation. Cations of

high oxidation states, such as V^{5+} , form covalent bonds with the oxygen anions, and behave as acidic oxides.⁵ Basic oxides entail cations at low oxidation states, such as Mg^{2+} , and form ionic metal–oxygen bonds.⁵ Amphoteric oxides, such as Al_2O_3 and Ga_2O_3 , show both acidic and basic properties. In acid–base reactions, Lewis acid sites of the MO (cationic metal centers) accept electrons from the reacting base, whereas Lewis base sites (anionic oxygen centers) donate electrons to the reacting acid.⁶ Surface hydroxyl groups can act as Brønsted acid or base as they can donate or accept a proton, respectively. The oxide surface is usually hydroxylated under normal conditions unless treated at elevated temperatures.^{5,7}

The promising catalytic properties of MOs have been attributed to their inherent Lewis acidity and basicity,⁶ thermal and chemical stability, and redox characteristics.⁴ These properties are crucial for numerous industrial processes including the direct activation of the chemically inert

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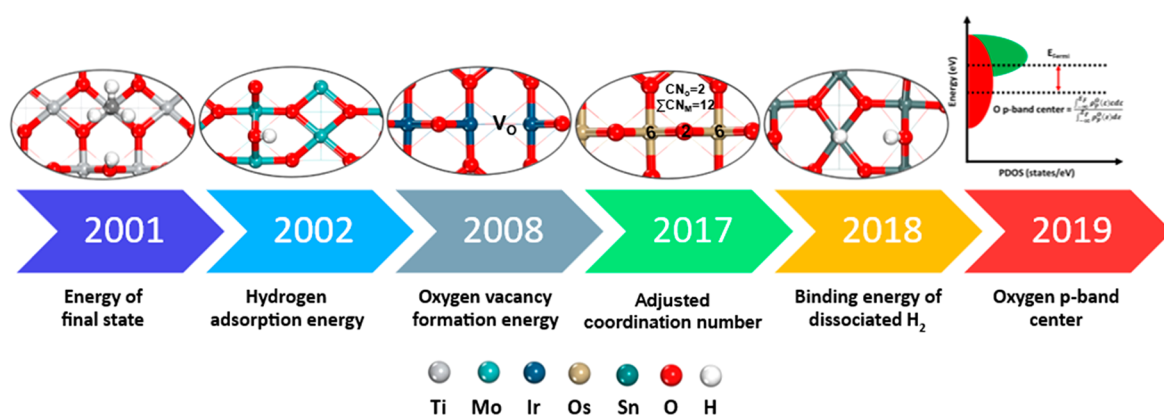


Figure 1. Timeline of fundamental reactivity descriptors development in Lewis acid–base heterogeneous catalysis. Rutile-type metal oxides (MO_2 structure) are used as an example to represent the descriptors.

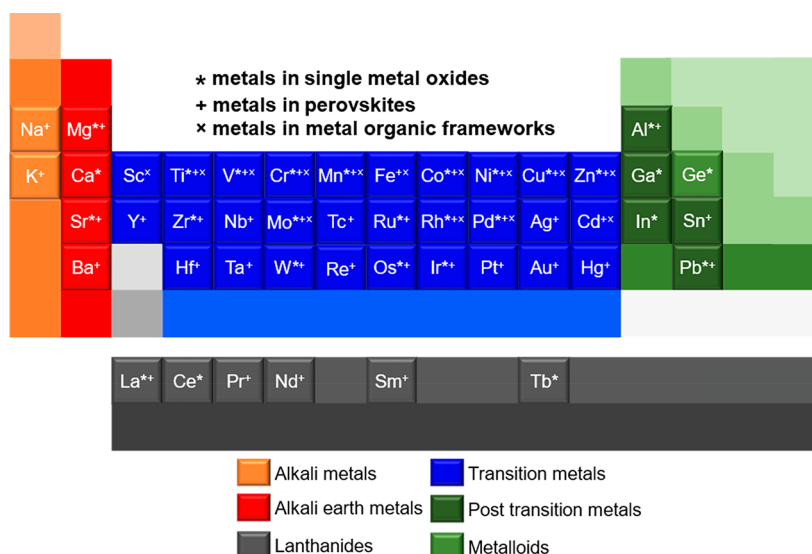


Figure 2. List of metals in various metal oxide types considered in this review. Metals in single metal oxides are denoted with *, in perovskites with +, and in metal organic frameworks with the x symbol.

paraffinic C–H bond, one of the most active research topics in chemistry due to its importance in upgrading shale and natural gas to fuels and chemicals.^{8–10} Hydrocarbons can interact with the oxide transition metal cation through one, two, or three hydrogen atoms, forming activated sigma complexes.⁵ Sigma complexes entail the donation of electron density from the σ orbital of a C–H bond into an empty d-orbital of the oxide transition metal cation.¹¹ However, just by exploring their structural characteristics, MOs are highly complex materials due to the high degree of surface heterogeneity.¹² In particular, the existence of diverse coordination environments and multiple oxidation states (the latter additionally affecting the electronic structure of MOs) results to exposure of sites with different Lewis acidity and basicity for catalysis. Therefore, identifying an active and selective oxide catalyst for a targeted chemical reaction becomes a significantly complex task.

Historically, selecting viable catalysts for a particular reaction relied on chemical intuition and/or “trial-and-error” experimentation.^{2,13,14} For instance, the first economical catalyst for the Haber–Bosch (ammonia synthesis) process was identified after more than 20 000 experiments covering a vast space of catalytic materials.¹⁵ Alternatively, computa-

tional-driven catalyst design is an emerging field for developing novel catalysts without painstaking and costly experimentation.^{16–18} In particular, computational chemistry provides atomic-level insights into catalytic reaction mechanisms, rationalizes puzzling phenomena in catalysis^{19–21} and identifies promising catalysts for targeted catalytic reactions.^{17,22} Density functional theory (DFT) is the most common approach among all computational modeling methods, because chemical reactions involve the formation and breaking of chemical bonds and need to be investigated with electronic structure methods that can accurately describe electron transfer processes. Nevertheless, large-scale DFT calculations are computationally expensive making the catalyst discovery based solely on DFT, a very challenging task due to the vast materials space of potential catalysts. The challenge becomes even higher when simulating realistic industrial processes that can involve numerous elementary reaction steps.^{19–21} For each elementary reaction step, a DFT calculation typically involves optimization of reactants and products on the catalyst surface, location of transition states (tedious process), and verification of these states (with vibrational frequencies calculations) as energy minima/maxima along the reaction coordinate of interest. Thus,

introducing faster approaches to accelerate catalyst screening has been a highly sought-after research goal.

A significant step toward establishing high-throughput computational catalyst design tools is the development of the Brønsted–Evans–Polanyi (BEP) scaling relationships. BEP relations correlate the energies of transition states (TSs) to the thermodynamics of elementary reactions.^{23–33} Such relationships motivated the development of reactivity descriptors, which are simple physical and/or chemical properties related to key elementary catalytic events and can be calculated faster. Examples of these reactivity descriptors are highlighted in Figure 1. Using such descriptors typically results in a description of catalytic performance that follows a volcano-shaped activity behavior.^{34–36} The volcano-shaped activity plot facilitates the identification of superior catalytic materials; in particular, candidates near the volcano maximum exhibit high catalytic activity and moderate adsorption strength of reaction intermediates (neither too weak to desorb, nor too strong to poison the catalyst), in line with the Sabatier principle.^{34,35,37} Subsequent exploitation of reactivity descriptors has ultimately enabled the construction of structure–activity relationships (SARs).³⁴ Broadly speaking, SARs are mathematical expressions that correlate catalytic activity with inherent catalyst-adsorbate physicochemical properties and can aid the screening and discovery of new catalysts.

In this review article, we summarize the current state-of-the-art in SARs for Lewis acid–base reactions. Specifically, we highlight noteworthy reactivity descriptors in (i) methane activation and conversion, (ii) alkane dehydrogenation, and (iii) alcohol dehydration. The main families of MOs reviewed in this article, as highlighted in Figure 2, include (i) single MOs (i.e., oxides that contain cations of one chemical element) such as alkaline earth MOs (AEMOs), transition MOs (TMOs), group IIIA MOs, and lanthanum MOs, (ii) multicomponent mixed MOs (i.e., oxides that contain cations of more than one chemical element) such as perovskites, and (iii) porous oxides, such as metal organic frameworks (MOFs). Finally, we address current limitations and challenges in SARs and propose potential steps for their effective and practical use for catalyst discovery.

METHANE ACTIVATION AND CONVERSION

Methane is the primary constituent of natural gas with a concentration ranging between 70 and 90% by volume.^{38–40} The amount of methane uncaptured in the earth's crust is around 200 trillion cubic meters.³⁸ Considering methane hydrates, the methane stock could be as high as 15 quadrillion cubic meters.³⁸ This enormous reserve establishes methane as an undeniably major energy feedstock. Notably, methane reserves are distributed in remote areas of the United States, Russia, China, the Middle East, and other regions.^{39–42} Because of the low volumetric energy density of gaseous methane, its long-distance transportation necessitates energy intensive storage conditions at low temperatures and high pressures.^{39–43} Alternatively, methane can be converted directly into value-added liquid chemicals, thereby avoiding technical transportation hurdles.^{44–50} Owing to the high stability and strong C–H bonds (~ 440 kJ mol^{−1}), together with the absence of dipole moment, extreme reaction conditions are required to activate methane.^{40,51} Additionally, harsh reaction conditions in the presence of oxygen promote overoxidation and lower the selectivity toward desired

oxygenated products.³⁹ Therefore, designing active, selective and stable catalytic materials for the direct conversion of methane into valuable chemicals, is the holy grail in catalysis of the twenty-first century. In this section, we summarize reactivity descriptors according to the type of the oxide catalyst, starting with single MOs followed by mixed MOs in the perovskite ABO₃ structure and MOFs.

MOs are well-established catalysts for methane activation and conversion.^{52–56} Methane activation on MOs takes place through two competing mechanisms: radical and surface-stabilized, as illustrated in Figure 3.^{57,58} The former is

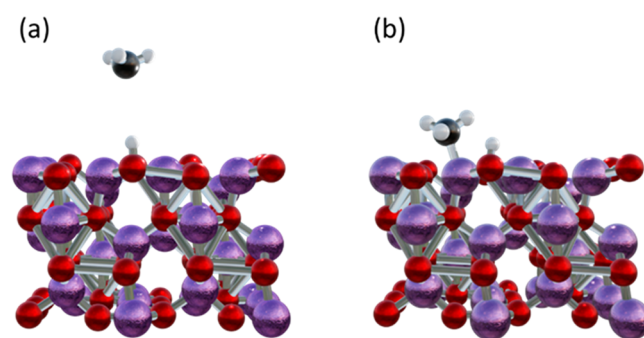


Figure 3. Two primary methane activation mechanisms on the (100) γ -Al₂O₃ surface: (a) radical and (b) surface-stabilized mechanism. Key: Al, magenta; O, red; H, gray; C, black.

characterized by the formation of methyl radical and surface hydroxyl species.⁵⁷ In the surface-stabilized mechanism, methane can either dissociate into methyl-hydroxy (M–CH₃, O–H) or methoxy-hydride (O–CH₃, M–H) surface intermediate pairs.^{58–60} However, the TS of the latter has higher energy than that of the methyl-hydroxy pathway.^{59,60} This can be attributed to the electrostatic interaction between the dipoles of the C–H and M–O bonds of the methoxy-hydride pathway, inducing a charge distribution that results in a negatively charged hydrogen (H^{δ−}).^{59,60} In the methyl-hydroxy pathway, the electrostatic interaction at the TS is favored, and no additional charge distribution occurs, leading to a TS with lower energy.^{59,60} Additionally, Lewis basic oxygen atoms have higher binding affinity to hydrogen than to methyl group, resulting in a more stable methyl-hydroxy surface intermediate pair.⁵⁶ Generally, the initial C–H bond activation of methane is postulated to be the rate-limiting step in oxidative coupling of methane (OCM), methane combustion, and methane reforming.^{61–67} Consequently, the ability of the catalyst to activate the methane C–H bond is an essential property of an ideal methane conversion catalyst.

One of the key descriptors in methane activation is the hydrogen affinity (E_H). E_H probes the ability of the MOs to abstract atomic hydrogen from the reacting methane, and is defined as the formation energy of adsorbed hydrogen relative to gas phase H₂O and O₂.³⁶ E_H was initially used as a reactivity descriptor for radical C–H bond activation.^{36,68} However, the use of this descriptor was limited to a single class of materials—that is, TMOs such as Cr₂O₃, V₂O₅, Co₃O₄, V₂O₅, W₂O₅, and Mo₃O₉.^{68,69} A landmark publication by Nørskov and co-workers established simplified SARs (eq 1) as a function of E_H to predict methane C–H bond activation energies on a broad family of materials containing oxygen atoms such as MOs, MOFs, zeolites, and graphene, as depicted in Figure 4.³⁶ Upon shifting to Gibbs free energies

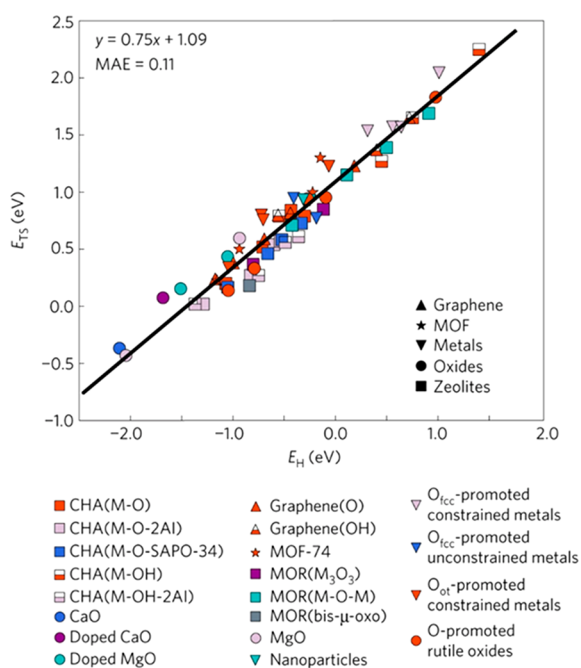


Figure 4. Universal scaling relationship for methane C–H bond activation that proceeds via a radical-like TS. Filled symbols correspond to M_mO_x active sites, while half-filled symbols correspond to M–OH active sites. The legend shows the classes of materials explored, and within each class several metals or cations were considered. The maximum absolute error is 0.30 eV and the mean absolute error (MAE) is 0.11 eV. Reprinted by permission from the Springer Nature Customer Service Centre GmbH: Springer Nature, Nature Materials, ref 36. Copyright 2017.

(G) to account for experimental reaction conditions, a scaling relation between G_H and the formation energy of the active sites (G_f) was obtained. Importantly, an enhanced catalytic activity toward methane activation may be achieved through tuning G_f by altering the catalyst physical properties, such as the ability of the catalyst to delocalize charge following the formation of the active site.³⁶ Interestingly, a volcano-shaped plot for the intrinsic rate of methane activation as a function of G_f was identified, with IrO_2 (located at the peak of the volcano) showing potential in activating methane at low temperatures.³⁶ Inspired by this work, Prats et al. identified a linear correlation between E_H and the logarithm of methane C–H activation energy barriers on Ni clusters dispersed on titanium carbide.⁷⁰ It is worth noting that E_H scaled linearly with the energy barrier of methane dissociation and not the formation energy of the TS as in the case of MOs, indicating somehow different chemistry (i.e., radical-like vs surface stabilized TS) governing methane C–H bond scission on carbide-based systems.⁷⁰

Additionally, the energy of final state (E_{FS}) was suggested to predict TS energies of MO systems that proceed through the surface-stabilized mechanism, eq 2.^{43,71–76} Notably, the distance between the active sites of rutile-type MOs (i.e., Lewis acidic M_{cus} and Lewis basic O_{br} sites) is relatively large (~ 3.00 Å) compared to the C–H bond of methane (~ 1.10 Å), leading to weak interactions between the final coadsorbed dissociated products, CH_3^* and H^* .⁷⁴ Hence, E_{FS} of methane activation on rutile MOs, through the surface-stabilized mechanism, might be approximated as the sum of methyl and hydrogen adsorption energies ($E_{FS} \approx E_{CH_3} + E_H$).⁷⁴ It is

noteworthy that the adsorbate–adsorbate interactions in insulating MOs are significant, hence the total energy of the true final state in these systems is E_{CH_3+H} rather than $E_{CH_3} + E_H$.^{71,77} Furthermore, a BEP relationship was identified between the dissociation energy of chemisorbed CH_4 and first C–H bond activation energy on rutile TiO_2 doped with a single transition metal (TM) atom.⁷⁸ Additionally, a linear scaling relationship between methane chemisorption energy and C–H $\sigma-\sigma^*$ occupancy (a quantitative measure of C–H bond strength) was obtained on doped rutile TiO_2 .⁷⁸

$$E_{TS,radical} = 0.75E_H + 1.09 \quad (1)$$

$$E_{TS,surface-stabilized} = 0.67E_{FS} + 1.04 \quad (2)$$

Abild-Pedersen and co-workers applied the radical (eq 1) and surface-stabilized (eq 2) SARs to predict methane C–H bond activation energies on AEMOs doped with either an alkaline earth metal (AEM) or a TM.⁷⁵ These SARs, although promising, underpredicted most of the TS energies by 0.20 eV compared to the DFT-calculated energies.⁷⁵ Recently, the surface-stabilized BEP scaling relationship (eq 2)³⁶ was extended to include dispersed Ni and Co monomers on (111) CeO_2 surfaces.^{79,80} However, less success has been achieved in applying these scaling relations to Ni clusters (e.g., Ni_4 and Ni_{13}) dispersed on CeO_2 , leading to significant overestimation of the TS energies by 0.29 to 1.06 eV. Additionally, the TOF of methane to methanol and methane dry reforming on Ni/CeO_2 increased as Ni coverage increased, then it dropped rapidly once the minimum heat of Ni atom adsorption was reached, providing a concrete example of the strong correlation between the thermodynamic stability of the dispersed metals on oxides and the catalytic activity.⁷⁹ Lustemberg et al. revealed that the existence of metal–support interactions in low-loaded metal clusters on CeO_2 ($M = Pt, Co, \text{ or } Ni$) results in substantial deviations from the surface-stabilized scaling relationship for the prediction of methane C–H bond activation energies.⁸⁰ In particular, these strong interactions result in extra stabilization for both the molecular methane and the dissociated product ($CH_3^* + H^*$), leading to active and stable catalysts for methane activation and conversion under very mild conditions.⁸⁰ It is, therefore, notable that such scaling relations may not be able to capture large materials space and may be limited to specific type of catalysts.

Li et al. correlated the methane dissociation energy barriers on PdO with E_{FS} .⁷² However, the correlation was weak ($R^2 = 0.73$) due to the weak methyl interaction with the catalytic surface (weak Pd–C bonding at the TS). Additionally, the O–H interaction was strong, suggesting that methane C–H bond scission on PdO occurs mainly due to coupling between the H of CH_4 species and the surface Lewis basic oxygen atoms. Therefore, hydrogen adsorption energy (HAE, similar to E_H but calculated relative to molecular H_2) was proposed as an alternative descriptor ($R^2 = 0.97$) for methane activation on PdO. Further, Tsai and co-workers developed E_{FS} -based SARs to predict TS energies for methane activation on metal sulfides and rutile MOs, with MAE of 0.11 eV.⁸¹ A linear scaling relationship between HAE and E_{FS} was obtained for Ni-containing CeO_2 catalysts (MAE = 0.16 eV).⁷⁹ Together, the above-mentioned descriptors, E_H and E_{FS} , can potentially predict methane activation TS energies on MOs (Figure 5), thereby avoiding computationally time-consuming and expensive TS barrier calculations.⁷¹

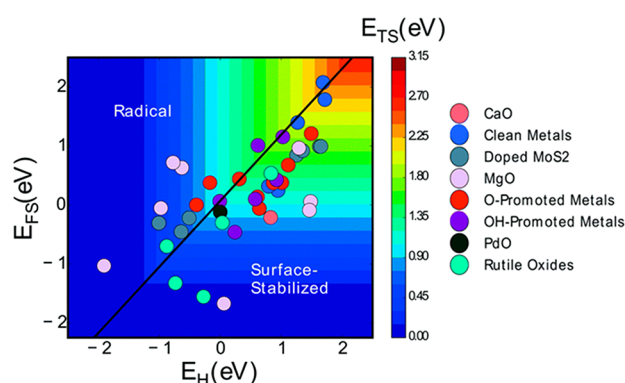


Figure 5. Methane activation TS energies, E_{TS} , as a function of two descriptors, E_{FS} and E_H . The equation of the black line is $E_{FS} = 1.12E_H + 0.07$, which marks the points where the two scaling relationships predict equal TS energies. Adapted with permission of The Royal Society of Chemistry, from ref 71. Permission conveyed through Copyright Clearance Center, Inc.

It becomes important to understand the factors that determine the dominant mechanism in methane activation processes because selecting reactivity descriptors depends on the reaction mechanism. Previous studies showed that methane activation on catalysts with a high density of active sites favors the surface-stabilized mechanism, whereas the radical mechanism is dominant in catalysts with isolated active sites (i.e., large distance between the active sites).^{82,83} Latimer et al. demonstrated that both catalyst reactivity and geometry influence the dominant mechanism.⁷¹ For instance, catalysts in which the surface-stabilized mechanism is geometrically accessible will prefer the radical pathway if $E_{TS, \text{radical}}$ scaling relationship results in a lower TS energy than $E_{TS, \text{surface-stabilized}}$. Aljama and co-workers showed that dual Lewis acidic (cationic metal) and basic (anionic oxygen) sites participate in stabilizing the C–H activation TS on pure AEMOs, resulting in a clear correlation between E_{FS} and TS energy.⁸⁴ However, upon doping the surface with an alkali metal (AM) such as lithium, a TS with a radical behavior (no interaction between the active Lewis acidic metal center and CH_3 fragment) was observed. Specifically, the geometry of doped AEMO catalyst forces the TS structure to interact mainly with lattice Lewis basic oxygen atoms. This shift in the reaction mechanism establishes HAE as the only suitable descriptor for methane activation on AM-doped AEMOs.⁸⁴ Methane activation on AEMOs doped with either TM or AEM follows the surface-stabilized pathway, with SARs similar to those established for pure AEMOs.⁷⁵

Interestingly, doping MOs with heterometals can tune the catalytic activity via altering the acidic properties and electronic structure of the catalyst.^{75,78,85,86} For instance, doping La_2O_3 with lower-valence dopants (such as Cu, Mg, Zn, and Fe) was found to increase the reactivity of Lewis basic oxygen atoms, leading to lower C–H bond activation energies.⁸⁶ The decrease in the activation energy for dissociative adsorption of methane was also observed for Pt-doped CeO_2 ⁸⁷ and lanthana doped with Cu, Mg, or Zn, owing to the substantial activation of neighboring surface Lewis basic oxygen atoms.⁸⁸ Additionally, single TM atoms (e.g., Pd, Rh, Os, Ir, and Pt) doped on rutile TiO_2 exhibited a substantially beneficial effect on the heterolytic dissociation of methane at temperatures below 25 °C.⁷⁸ More specifically, DFT calculations showed that low temperature methane

activation occurs when the energy of methane desorption to the gas phase exceeds the energy of C–H activation TS.⁷⁸ Lithium doping on NiO was found to increase the surface lattice oxygen Lewis basicity, leading to stronger hydrogen chemisorption and lower C–H activation energy barriers.⁸⁹ Likewise, doping CaO, MgO, or SrO with either a TM or an AEM enhances the catalytic activity toward OCM via increasing HAE (becomes more exothermic) and decreasing the C–H activation barriers.⁷⁵ However, previous work showed that the strong binding of hydrogen on Li-doped and Au-doped MgO may result in undesired coke formation due to poisoning of active sites.^{75,84,90} Consequently, ideal catalysts for methane activation should exhibit mild hydrogen binding energy, consistent with the Sabatier principle.

As the acid–base properties are key characteristics of MOs, it is, therefore, possible to use them as reactivity descriptors for paraffinic C–H bond activation.⁶ Cholewinski et al. used the binding energy of dissociated hydrogen (BE_{H_2}) as descriptors for Lewis acidity and basicity of oxides, which is probed by local band centers on the binding sites (i.e., the unoccupied s-band center of the metal and occupied p-band center⁹¹ of lattice oxygen).⁴³ Linear correlations were demonstrated between methane C–H activation barriers and both the BE_{H_2} and E_{FS} (energy of final state) on γ - Al_2O_3 . Thus, strong Lewis acid–base active sites (with more exothermic BE_{H_2} and E_{FS}) exhibit low C–H activation barriers, whereas weak Lewis acid–base site pairs exhibit high C–H activation barriers. The Bader charge, projected band centers (i.e., O p-band and W d-band centers), and binding energy of hydrogen within intercalated H_xWO_3 lattice have been used to probe Lewis acid–base properties of tungsten trioxide.⁹² Shen et al. identified a linear correlation between methane adsorption energy and the p-band center difference between the spin-up and spin-down channels of the active Lewis basic oxygen atom of magnetic TM-doped $[\text{V}_2\text{O}_5]_n$ clusters ($n = 2, 3, 4$).⁹³ Further, methane C–H bond activation energy was found to correlate linearly with the Lewis acidity (through fluoride affinity) of the La^{3+} and Brønsted basicity (through proton affinity) of O^{2-} of La_2O_3 .⁹⁴ Furthermore, chemisorption of CO_2 at $\text{La}^{3+}\text{--O}^{2-}$ site pair was identified as a robust descriptor for methane C–H activation.⁹⁴ Interestingly, this descriptor represents a combined measure of acid–base properties of La_2O_3 active sites. Specifically, stronger CO_2 chemisorption (i.e., higher Lewis acidity and Brønsted basicity of the active site) leads to higher catalytic activity and lower C–H activation energy barriers.⁹⁴

Redox reactions of MOs are crucial for the overall methane oxidation activity. In the first stage of OCM, methane can be oxidized by lattice oxygen and further converted into ethane and water, creating an oxygen vacancy on the surface. In the second stage, gaseous oxygen can heal the oxygen vacancy, forming surface peroxide O_2^{2-} . The O_2^{2-} can further oxidize methane and recover the surface, following the Mars–van Krevelen mechanism.⁹⁵ Oxides are divided into the following two main families, depending on their chemical behavior: nonreducible and reducible MOs. Nonreducible oxides are highly ionic, with a wide band gap, and behave as insulators. These oxides are commonly derived from alkaline earth metals or aluminum. On the contrary, reducible oxides typically have narrower band gaps and behave as semiconductors. Upon oxygen vacancy formation on reducible

oxides, the two electrons engaged in the bond between the removed oxygen and the surface tend to localize at the Lewis acidic metal centers and populate otherwise forbidden electronic states.⁹⁶ The change in electron occupation upon vacancy formation typically influences the catalytic activity of the oxide. Experimental studies revealed that partially reduced PdO are more reactive for methane activation than PdO.⁹⁷ Additionally, the existence of oxygen vacancy in α -Fe₂O₃ (001) promoted methane dissociation substantially via lowering the dehydrogenation barriers of CH_x ($x = 1-3$).⁹⁸

In an effort to develop SARs with descriptors based only on catalyst properties (i.e., no interactions with adsorbates), researchers have successfully correlated the methane C–H bond activation with the surface reducibility of pure CeO₂,^{99,100} metal-doped CeO₂,^{73,100} lithium-doped MgO,⁹⁰ and metal-doped La₂O₃.^{86,101} Kumar et al. extended the correlation to other oxides, including TiO₂, MgO, ZnO, and TbO_x, in their pure and doped states.¹⁰² The surface reducibility may be quantified by two stability descriptors: oxygen vacancy formation energy (OVFE) and work function (Φ). The OVFE is defined as the energy required to create an oxygen defect on the oxide surface by losing an oxygen atom, whereas Φ is the minimum amount of energy required to discharge an electron from the oxide surface to vacuum.¹⁰² OVFE was established as a more significant surface reducibility and methane activation descriptor than Φ .¹⁰² This is because OVFE offers additional information regarding the (i) structural reorganization upon oxygen vacancy formation and (ii) strength of diatomic M–O bonds. For instance, OVFE correlates linearly with M–O bond strength, meaning that a higher diatomic M–O bond enthalpy leads to more endothermic OVFE.⁷³ Consequently, MOs that are hard to reduce (with a highly endothermic OVFE) show higher barriers for methane C–H activation as compared to reducible MOs. Mayernick and Janik showed that incorporation of rare-earth (such as Zr) or noble metals (such as Pd) into the CeO₂ lattice can alter the redox properties of the catalyst (as quantified by OVFE) and hence its catalytic activity toward methane activation.⁹⁹ Therefore, the design principle for enhancing methane activation on reducible MOs is to tune OVFE. Krcha et al. identified a volcano activity plot using OVFE versus C–H bond activation energy and vacancy refilling energy.⁷³ It was concluded that dopants offering OVFE between -0.50 and $+1.00$ eV, such as Ag, Au, Ni, Co, Pt, Pd, and Mn, will likely be located at the volcano summit for hydrocarbon conversion on TM-doped CeO₂.⁷³

Recently, Huang and co-workers found a strong linear correlation between OVFE and both heterolytic (CH₄* $\rightarrow$ CH₃*(Ce) + H*(O)) and homolytic (CH₄* $\rightarrow$ CH₃*(O) + H*(O)) methane C–H bond cleavage on solid frustrated Lewis pairs of CeO₂.¹⁰⁰ It is of interest that heterolytic dissociation of methane exhibited a negative linear correlation with OVFE, whereas the homolytic methane activation barriers showed a positive linear correlation with OVFE.¹⁰⁰ The reversed trend is due to the difference in electron transfer between the catalyst and reacting methane during the chemical reaction. The above-mentioned OVFE-based SARs have been successfully confirmed experimentally. In particular, Derk et al. found a linear correlation between OVFE and experimentally measured activation energies for methane oxidation catalyzed by metal-doped La₂O₃.⁸⁶ It was suggested that smaller OVFE (corresponds to higher reactivity of lattice oxygen) leads to lower C–H activation barriers.

The binding energy of surface lattice oxygen on CuO catalyst was found to significantly influence the ability of the surface to chemisorb hydrogen and activate methane.¹⁰³ Varghese and Mushrif studied methane activation on the (110) and (100) NiO surfaces and proposed HAE on surface Lewis basic oxygen atoms and binding strength of corresponding surface oxygen as reactivity descriptors for methane activation.⁸⁹ More specifically, strong binding of the surface Lewis basic oxygen centers with the Lewis acidic metal centers lowers their basicity and weakens the HAE on the oxygen sites, leading to high C–H activation barriers.⁸⁹ From an experimental perspective, it is important to note that HAE serves as a better descriptor for the oxide reactivity because it is a directly measurable quantity, unlike the lattice oxygen binding strength. Additionally, a linear correlation between the homolytic methane C–H bond activation energy barrier and HAE on active oxygenated FeN₄ sites embedded on graphene carbon nanosheets, was obtained.¹⁰⁴ Similarly, a BEP relationship was identified between HAE and methane C–H activation energy on single TM atoms anchored at the N-doped graphene.¹⁰⁵ Importantly, a 2D volcano-shaped relationship was identified for methane activation at 150 °C as a function of metal-oxo formation energy and HAE.¹⁰⁵ As expected, the aforementioned descriptors exhibited an inverse correlation, explaining the trade-off between the stability and reactivity of the oxygenated active site. Interestingly, the coordination number of the active site (CN) can be tuned to enhance the reactivity for methane activation; more specifically, lowering the CN results in superior catalysts for methane activation.¹⁰⁵

The band gap has been also identified as a surface reactivity descriptor that correlates with the activation barrier for heterolytic methane C–H bond cleavage on TMOs and their supported single-atom catalysts.¹⁰⁶ In this study, Xu et al. demonstrated a linear relation between HAE on bridging Lewis basic oxygen atom of rutile (110) TiO₂ and its band gap. In particular, a smaller band gap promotes oxygen reactivity and enhances catalytic performance toward methane activation.¹⁰⁶ Tsuji and Yoshizawa found a BEP relation between the metal–CH₃ bond strength (quantified by the integrated crystal orbital Hamilton population, ICOHP) and the activation energy of methane C–H bond scission on rutile type of TMOs (e.g., PtO₂, CrO₂, and IrO₂).¹⁰⁷ Interestingly, the Pt–CH₃ bond was the strongest, which was due to the significant charge transfer from the CH₃ fragment (acts as a Lewis base) to Pt atom (acts as a Lewis acid), revealing PtO₂ as a more active catalyst than CrO₂ and IrO₂.¹⁰⁷

Though a large fraction of the developed descriptor-based SARs in methane activation has been focused on single MOs such as TMOs and AEMOs, there have been several extensions of these SARs to other catalytic materials, such as multicomponent mixed MOs (e.g., oxide perovskites). Unlike single MOs, mixed MOs exhibit diverse chemical and physical properties due to compositional variation, including variation in metals and ratios (both stoichiometric and nonstoichiometric).^{108–110} The metal–metal and metal–oxygen interactions in mixed oxides can give rise to different electronic states not observed in single MOs, leading to substantial variations in the electronic and chemical properties of the oxide, especially in the case of ABO₃ perovskites (A denotes AM or AEM and B denotes TM).^{111,112} For instance, the strong metal–oxygen–metal interactions in SrTiO₃

substantially alter the electron density of Ti leading to better catalytic activity of SrTiO₃ as compared to TiO₂. Additionally, introducing dopants into the oxide lattice can induce stress into the host oxide, which promotes the formation of highly reactive defects.^{111,112} The Zr-stabilized defects in ceria lead to high thermal stability and enhanced redox properties of the Ce_{1-x}Zr_xO₂ mixed oxide.^{111–114} On the other hand, the host metals can impose unusual coordination modes on the doped metals, resulting in large variations in the chemical properties of the dopant metals.¹¹¹ Upon the addition of Zr to CeO₂, different types of Zr–O distances are produced, and the Zr positive charge in Ce_{1-x}Zr_xO₂ was found to be smaller than that in pure ZrO₂, whereas the positive charge in Ce was larger than that in pure CeO₂.¹¹⁴ Hence, the enhanced chemical and electronic properties of mixed MOs can produce superior catalytic activity.

Oxide perovskites have emerged as active catalysts for methane activation because of their thermal and chemical stability, as well as flexible optimization of their Lewis acid–base and redox properties through controlling the surface composition, the relative size of the cations in the bulk crystal, and surface reconstruction.^{115–117} Importantly, methane activation on perovskites occurs mainly on the basic oxygen atoms via homolytic C–H bond cleavage.¹¹⁸ Recently, Fung and co-workers proposed HAE and OVFE (aforementioned on methane activation on MOs) as descriptors for methane activation on ABO₃-type perovskites.¹¹⁸ Furthermore, the ICOHP of the B–O bond was used as a bulk stability descriptor for surface oxygen reactivity, correlating linearly with OVFE and HAE.^{119,120} The less exothermic ICOHP of the B–O bond implies a weaker B–O bond. Consequently, the corresponding lattice oxygen exhibits high reactivity, owed to the availability of free valence electrons to interact with hydrogen, resulting in stronger hydrogen adsorption.^{119,120} Additionally, oxide band gaps and enthalpy of formation were identified as combined descriptors of metal–oxygen bond strength in lanthanum strontium TMO perovskites, where a linear combination of the two descriptors scaled linearly with OVFE.¹²¹ The cation electronegativity difference (ΔX_{B-A}) can also describe the HAE on oxide perovskites, where a larger electronegativity difference between the two cations results in stronger hydrogen adsorption.¹²⁰ The electronegativity difference is mainly driven by the B cation, meaning that the more electronegative the B cation, the weaker the B–O bond and the more reactive the lattice oxygen toward hydrogen adsorption.¹²⁰ Recently, Lim et al. proposed a set of catalytic descriptors for OCM on perovskites via combined DFT calculations and experiments.¹²² The C–H bond dissociation energy (BDE), methyl radical adsorption energy ($E_{CH_3^*}$), and OVFE were identified as reactivity and selectivity descriptors in OCM catalysis.¹²² For instance, a low C–H BDE facilitates the activation of methane on doped and undoped SrTiO₃ perovskites. On the other hand, $E_{CH_3^*}$ and OVFE exhibited volcano-shaped correlations with the selectivity toward C₂₊ and CO_x products, respectively.¹²² Chang et al. revealed a linear correlation between the OVFE and the effective Bader charge on the Lewis basic oxygen ion in perovskite ($|q_O|$); the less negative $|q_O|$, the weaker the interaction between the oxygen and the Lewis acidic TM ions of the perovskite, facilitating the formation of oxygen vacancies.¹²³ Notably, substitution of Sr²⁺ for La²⁺ at the A site and Co³⁺ for Fe³⁺ at

the B site of the LaFeO₃ perovskite reduces the OVFE and enhances the oxygen mobility, leading to improved catalyst selectivity toward methane total oxidation.¹²³ On the contrary, perovskites with low oxygen mobility are selective for partial oxidation processes.

Descriptor-based SARs for methane activation on MOFs have also been established.^{124,125} Rosen et al. investigated the oxidative activation of methane on a series of experimentally derived MOFs via the radical-rebound mechanism, an accepted mechanism for catalysts with isolated active sites.¹²⁴ The radical-rebound mechanism comprises five consecutive steps. The first step is the oxidation of the MOF surface to form a metal-oxo active site, followed by methane adsorption on the oxygen atom of the active site. Then, a hydrogen atom is abstracted from methane, releasing the methyl radical. Finally, the methyl radical rebounds to the oxygen site and methanol molecule desorbs to regenerate the MOF surface. The metal-oxo formation energy, ΔE_O , was found to correlate with HAE, suggesting the binding strength of the active sites as a reliable and robust descriptor for methane C–H activation on MOFs. More endothermic ΔE_O values (lower metal-oxo stability) indicate higher reactivity of the active site toward hydrogen (more exothermic HAE) and lower methane C–H bond activation energy barriers. An ideal MOF catalyst should exhibit a ΔE_O value that is neither too endothermic such that the population of the active sites is too low to achieve sufficient methane conversion, nor too exothermic such that methane C–H activation requires high energy barriers.¹²⁴ It should be noticed that the stability of active sites appears as a descriptor for the binding energy of various adsorbates, including the methyl species, on metal nanoparticles and not only on metal oxides, demonstrating a more general concept in catalysis.¹²⁶ Furthermore, Pahls et al. showed a linear correlation between the TS C–H bond length and methane C–H activation free energy barriers on Cu-based bimetallic MOFs, with shorter C–H bonds associated with lower activation free energy barriers.¹²⁵ The spin density of the reacting oxyl atom and the sum of all oxygen atoms bounded to Cu and the second metal (Lewis acidic metal site), were used as informative quantitative descriptors for methane C–H bond activation.¹²⁵ The promising results of descriptor-based SARs of methane activation on MOs reveal their potential as screening tools to facilitate the design of improved methane activation catalysts.

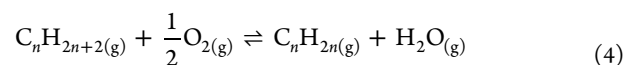
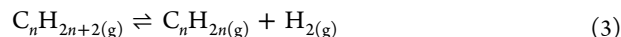
However, just by designing catalysts that can activate methane does not address the methane conversion issue in the chemical industry, since the high reactivity of the desired products results to nonselective chemical processes. Up to now, there exists no industrial process capable of directly converting methane to methanol,⁶⁶ and even if methanol is produced, it is thermodynamically challenging to prevent its C–H bonds from further oxidation under harsh reaction conditions (methanol C–H BDE is 0.49 eV lower than that of methane), highlighting the trade-off between product selectivity and reactant conversion.¹²⁷ Latimer et al. found a linear correlation between the activation energies of radical C–H bond scission of methane and methanol ($\Delta G^\ddagger$) on different types of catalysts (e.g., rutile MOs, MOFs, graphene, metals, etc.).⁶⁶ The authors built a simple kinetic model based on $\Delta G^\ddagger$ to quantify the selectivity–conversion trade-off. It was found that methanol selectivity is catalyst-independent and it depends solely on methane conversion and temper-

ature.⁶⁶ The following potential strategies were suggested to increase the methanol selectivity: (i) aqueous reaction conditions to lower the free energy of methanol while increasing methanol activation barrier compared to methane, (ii) diffusion-limited systems to activate methane and methanol at similar rates, and (iii) designing materials with a strong affinity to methanol (CH_3OH^*) but low reactivity toward oxidizing agents (O^*) to prevent overoxidation reactions.⁶⁶ It should be noted that correlations between methanol and oxygen (CH_3OH^* vs O^*) binding energies on MOs are not relevant for catalyst screening due to different binding mechanisms.⁶⁶ Specifically, oxygen binding on MOs depends on charge transfer between the substrate and the O 2p states,³⁰ while adsorption of methanol (electron-pair donor, Lewis base) is stabilized by Lewis acid–base interactions with the substrate (i.e., metal centers). Although there is a lack of correlation between the two quantities, catalysts with similar characteristics were found to exhibit similar binding affinity. Metallic ionic oxides, such as IrO_2 and RuO_2 , tend to have a strong affinity to both oxygen and methanol, while oxide insulators, such as GeO_2 , ZnO , and $\alpha\text{-Al}_2\text{O}_3$, have a weak and strong affinity to oxygen and methanol, respectively. Consequently, it is essential to design catalysts that can effectively activate methane and simultaneously inhibit product overoxidation.

LIGHT ALKANE ($\text{C}_2\text{--C}_4$) ACTIVATION AND DEHYDROGENATION TO OLEFINS

The efficient conversion of light alkanes into olefins is of great importance to the modern chemical industry.^{8,128,129} Olefins, the essential building blocks for the production of polymers and daily use commodities, are produced primarily from steam cracking and fluid catalytic cracking of naphtha.^{34,85,130–133} However, these unit processes are limited by the low product selectivity, high-energy cost, and use of nonrenewable fossil fuel resources.^{34,85} Fortunately, the increased production of shale gas reduced the price of light alkanes and established them as an attractive feedstock for olefins production.^{34,85} Alkanes can be dehydrogenated to olefins via nonoxidative (ADH, eq 3)^{34,85} and oxidative (ODH, eq 4) routes.^{130–135} The former is an endothermic reaction that requires energy intensive operating conditions (i.e., high temperatures between 500 and 700 °C).^{130,131,133} These harsh conditions can promote coke formation, thermal cracking, and catalyst deactivation, increasing the hurdle to produce olefins.^{85,130,131} On the contrary, ODH is an exothermic reaction that proceeds at low temperatures; thereby the catalyst life is prolonged.^{130,131} ODH overcomes most of the ADH hurdles due to the use of oxidants, such as O_2 and CO_2 , in the reacting stream.^{85,130,131} However, ODH is associated with unavoidable overoxidation which limits the selectivity toward olefins.^{85,130,131,134,136} Irrespective of the dehydrogenation route, these reactions are initiated by alkane activation—that is, scission of an alkane C–H bond. The acid–base properties of oxides can influence the type of alkane activation mechanism. For heterolytic C–H bond activation, the mechanism may involve (i) proton abstraction by Lewis basic oxygen site and carbanion formation on the Lewis acidic metal site, (ii) hydride abstraction by Lewis acidic metal site and carbocation complex formation on the Lewis basic oxygen site, or (iii) formation of a radical fragment through H atom abstraction.⁵ Generally, paraffinic C–H bonds are more reactive than C–C bonds, therefore, an

ideal dehydrogenation catalyst should exhibit high selectivity toward C–H bond cleavage.⁸ It is, therefore, important to develop SARs for alkane C–H bond activation to further accelerate the design of improved dehydrogenation catalysts.



Several groups have computationally investigated ADH with a focus on identifying descriptor-based SARs. Kostetsky et al. developed an ADH model on MOs inspired by an alcohol dehydration model (*vide infra*).¹³⁷ The model captures the effect of alkane substitution (i.e., alkane branching) through carbenium ion stability (CIS) and catalyst Lewis acidity and basicity through alkane binding energy (BE) and proton affinity (PA), respectively.¹³⁷ The model serves as a preliminary screening tool to discover highly active catalytic MOs and light alkanes for their dehydrogenation to olefins. Dixit et al. revealed site-dependent ADH mechanisms on $\gamma\text{-Al}_2\text{O}_3$ and identified BE_{H_2} as a quantitative activity descriptor for the concerted ADH (i.e., simultaneous cleavage of two paraffinic C–H bonds to form an olefin and two surface-bound hydrogen atoms which further recombine to form molecular H_2) that is favored on strong Lewis acid–base surface pairs.³⁴ In addition, turnover frequencies (TOFs) of propane dehydrogenation (PDH) on $\gamma\text{-Al}_2\text{O}_3$ acid–base site pairs were plotted vs BE_{H_2} and a volcano activity plot was revealed, as depicted in Figure 6, clearly demonstrating a site-

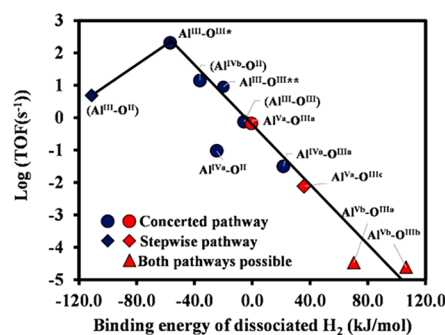


Figure 6. Log(TOFs) of propane DH on different site pairs for the mechanism exhibiting the highest TOFs vs H_2 binding energy. Red points represent sites on the (100) and blue points on (110) facets of $\gamma\text{-Al}_2\text{O}_3$. The aluminum atoms of the site pairs shown in parentheses are expected to be hydroxylated (blocked) under experimental dehydrogenation conditions. Reproduced from ref 34. Copyright 2018 American Chemical Society.

dependent catalytic behavior on $\gamma\text{-Al}_2\text{O}_3$. Importantly, ab initio molecular dynamics showed that catalyst poisoning through strong hydrogen dissociation on the most active site (located at the top of the volcano plot) is unlikely under experimental conditions.³⁴ Very recently, Xiao and co-workers adopted a similar paradigm for studying the influence of oxygen vacancy formation on coordinatively unsaturated $\text{Al}_{\text{cu}}\text{--O}$ sites of the (110) $\gamma\text{-Al}_2\text{O}_3$ for PDH.¹³⁸ The intrinsic Lewis acidity and basicity of the (110) $\gamma\text{-Al}_2\text{O}_3$ surface were evaluated using combined BE_{H_2} and the center of unoccupied bands of surface aluminum 2s and 2p orbitals, descriptors that have been previously suggested to probe Lewis acid–base surface properties.^{34,43,138} A strong correlation between C–H

bond activation and BE_{H_2} was confirmed and a volcano-shaped dehydrogenation activity vs BE_{H_2} was also verified.¹³⁸

Recently, Abdelgaid et al. investigated the nonoxidative dehydrogenation of ethane, propane, and isobutane on undoped and gallium-doped (100) γ - Al_2O_3 surfaces.⁸⁵ A comprehensive alkane dehydrogenation model that captures the catalyst acid–base surface properties (through BE_{H_2}) and alkane substitution (through CIS) was developed.⁸⁵ The model facilitates the prediction of the activation barriers of ADH on group IIIA MOs, in their doped and undoped states. Batchu et al. calculated the free energies of H_2 chemisorption on different Lewis acid–base site pairs to understand the higher activity of the gallium-doped (110) γ - Al_2O_3 surface as compared to the undoped (110) γ - Al_2O_3 .¹³⁹ More specifically, a more exothermic H_2 adsorption energy indicates an extra stabilization of the metal-hydride intermediate, leading to higher activity of the Ga^{III} -doped γ - Al_2O_3 as compared to the undoped surface. However, under dry conditions, the strong affinity of undercoordinated Ga^{III} for hydride resulted in (i) substantial site blocking with hydride species, especially at high conversions of ethane where a considerable amount of H_2 forms, and (ii) low partial reaction order with respect to ethane (0.40 vs 1.00 in case of pristine γ - Al_2O_3). Song et al. performed both experimental and computational studies on PDH using TiO_2 doped with fifth-period TMs and found a linear relationship between PDH TOFs and BE_{H_2} , where the dissociated hydrogens were both bounded to the dopant TM (Lewis acid site) of the oxygen-deficient $TM-TiO_{2-x}$.¹⁴⁰ The more exothermic the BE_{H_2} , the lower the barrier for the first C–H bond activation and the higher the PDH rate.

Chang et al. identified the coadsorption energy of 2-propyl and H ($E_{2\text{-propyl}\&H}$) as an activity descriptor for PDH on reducible and nonreducible MOs.¹⁴¹ Although the $E_{2\text{-propyl}\&H}$ descriptor is based on BEP relationships where the intermediate reaction energy correlates with the catalytic activity, one would expect ($E_{2\text{-propyl}\&H}$) to correlate with the aforementioned BE_{H_2} .¹⁴⁰ Similarly, Xiao et al. obtained a linear relationship between PDH TOF and $E_{2\text{-propyl}\&H}$ on TiO_2 -based catalysts.¹⁴² Vanadium-doped TiO_2 was further identified as an effective PDH catalyst (with a C–H activation energy barrier of 0.93 eV) through a computational screening of TiO_2 doped with fourth-period TMs.¹⁴² A similar BEP relationship was obtained for PDH on oxygen-deficient $TM-TiO_{2-x}$ where $Ru-TiO_{2-x}$ exhibited the highest PDH activity.¹⁴⁰ Additionally, a linear relationship was identified between the d-band center of the TM dopant on TiO_2 -based catalysts and the adsorption energy of (i) 2-propyl and (ii) 2-propyl&H in the TS, which in turn affect the activation barrier of the first C–H bond activation on propane.¹⁴⁰ The HAE on surface oxygen was found to scale linearly with the p-band center of the oxygen sites of V_2O_5 -based catalysts.¹⁴³ A higher oxygen p-band center (i.e., higher basicity) results in stronger hydrogen chemisorption on surface oxygen atoms. Xiong et al. identified correlations between both the surface oxygen p-band center (negative correlation) and HAE (positive correlation) with the propane dehydrogenation energy barriers on supported vanadium oxides.¹⁴⁴

Recently, the formation energy of adsorbed H on the Lewis basic oxygen site ($E_{H@O}$) and the formation energy of adsorbed 2-propyl on the Lewis acidic metal site ($E_{\text{propyl}@M}$) were used as reactivity descriptors for PDH on ZnO doped

with single atoms.¹⁴⁵ Specifically, the two descriptors scaled linearly (either as a single quantity or their combinations) with the formation energies of relevant reaction intermediates and activated complexes. As a result, the formation energies of the TS for propane first C–H bond scission and H–H recombination to form molecular H_2 also correlated with the linear combination of the two descriptors. It was shown that hydrogen binds very strongly to the Lewis basic oxygen centers on Ag- and Au-doped ZnO catalysts, with a surface coverage of ~ 1.00 , leading to poor PDH catalytic activity regardless of the low C–H bond activation energy barriers.¹⁴⁵ Through descriptor-based microkinetic analysis, Mn- and Cu-doped ZnO were proposed as potential low-cost catalysts for PDH reaction with enhanced selectivity and catalytic activity.¹⁴⁵ It should be noted that Mn-doped ZnO is an example of a MO catalyst where Lewis acid–base interactions between coadsorbed amphoteric species occur. As schematically shown in Figure 7a, there is an apparent charge

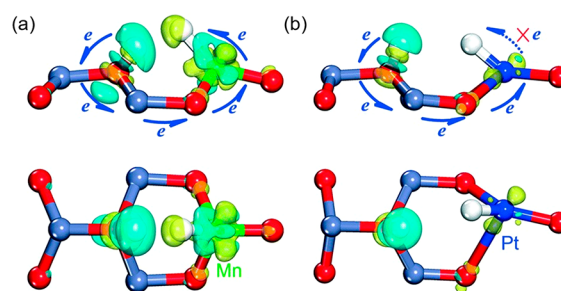


Figure 7. Side and top views of the computed charge density difference for coadsorption of two hydrogen atoms on (a) Mn_1 -ZnO and (b) Pt_1 -ZnO. Charge accumulation and depletion are colored yellow and cyan, respectively, with the isosurface value being $0.05\ e\ \text{\AA}^{-3}$. Adapted with permission of The Royal Society of Chemistry, from ref 145. Permission conveyed through Copyright Clearance Center, Inc.

accumulation around the H atom adsorbed at the Mn site. On the contrary, no apparent electron transfer between adsorbates takes place on Pt-doped ZnO (Figure 7b). Bader charge analysis revealed that adsorbed hydrogen at Mn site gains 0.20 electrons upon coadsorption of a second hydrogen at the next-nearest neighboring oxygen site, whereas charge on adsorbed hydrogen at the Pt site remains nearly constant even after coadsorption of a second hydrogen atom at a neighboring oxygen site.¹⁴⁵ This type of interactions between surface adsorbates do not hold on Cr_2O_3 because Cr ions can exist in a lower oxidation state of +2 and hence withdraw electrons from the reacting Lewis base and the underlying oxygen site.¹⁴¹

Subsequent studies by Chang et al. identified $E_{H@O}$ as a PDH reactivity descriptor for Ga_2O_3 doped with Ni, Pd, Pt, Cu, Ag, and Au (Figure 8a), resulting in a volcano-shaped activity plot (Figure 8d).¹⁴⁶ Notably, Lewis acid–base interactions between coadsorbed species are absent in these catalysts because electronic structure analysis revealed the neighboring oxygen to be too electron-deficient, limiting the ability of the oxygen site to transfer electrons to the adsorbates on the metal site. When the Lewis acid–base interactions are present, the formation energy of a coadsorbed pair of H atoms at the M–O site ($E_{H\&H@M-O}$, similar to the BE_{H_2}) becomes the descriptor for PDH (Figure 8b,c), resulting in a straight-line activity plot (Figure 8e).¹⁴⁶

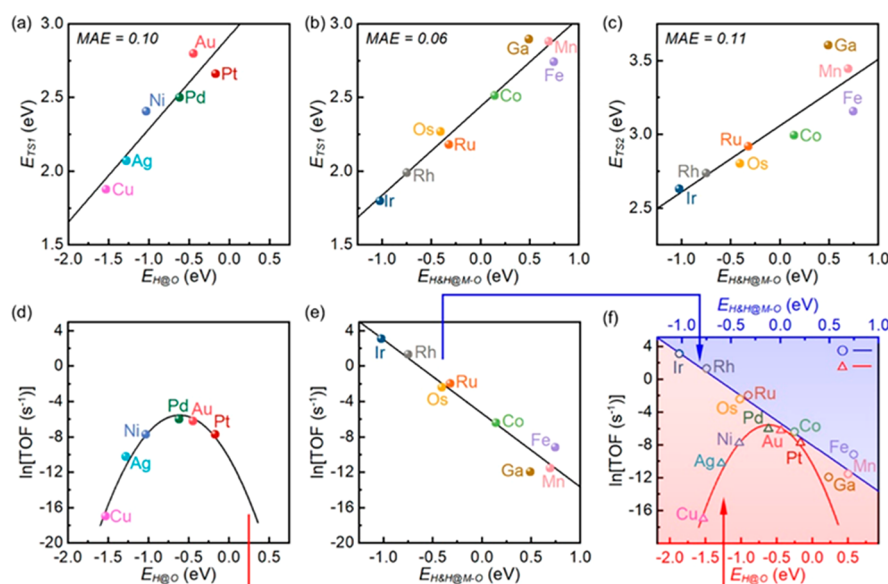


Figure 8. (a) Calculated E_{TS1} as a function of $E_{H@O}$, calculated (b) E_{TS1} and (c) E_{TS2} as a function of $E_{H\&H@M-O}$, volcano plot of the logarithm of TOF for PDH at 848.15 K, 0.20 bar of C_3H_8 , and 0.16 bar of H_2 as a function of (d) $E_{H@O}$, (e) $E_{H\&H@M-O}$, and (f) $E_{H@O}/E_{H\&H@M-O}$. Reprinted from ref 146. Copyright 2021 American Chemical Society.

Consequently, the authors revealed that volcano-shaped activity plot can be broken through by Lewis acid–base interactions (Figure 8f), leading to catalysts with higher activities (e.g., Ir-doped Ga_2O_3) than that of the summit of the volcano.¹⁴⁶ Additionally, a negative linear scaling correlation was obtained between $E_{H@O}$ and Bader charge carried by the surface oxygen site. Further, the O p-band center exhibited a good linear scaling relation with the $E_{H@O}$.¹⁴⁶ More importantly, calculated coverage of intermediates on Ni-, Cu-, and Ag-doped catalysts (with $E_{H@O}$ values stronger than -1.00 eV as shown in Figure 8d) revealed that the majority of active sites are occupied by dissociated hydrogen species, explaining the decrease in the PDH TOFs, although the binding of hydrogen atoms on the oxygen centers is strengthened.¹⁴⁶

Furthermore, E_H was identified as a catalytic activity descriptor for PDH on MXenes, a family of 2D materials with a formula of $M_{n+1}X_nT$ where M is an early TM, X is C and/or N, T is a termination group such as O and OH, and n equals 1, 2, or 3.¹⁴⁷ More explicitly, E_H correlates linearly with the dehydrogenation energy barriers where low hydrogen affinity results in lower C–H activation barriers of both terminal methyl and middle methylene bridge groups of propane on $Ti_2CO_{2-z}(OH)_z$ ($0 \leq z \leq 2$). The BEP scaling relationship was extended to include Ti_2C MXenes terminated with a F group (i.e., Ti_2CF_2).¹⁴⁸ The adsorption energy of pyridine molecule has also been used to probe the surface acidity and coordination geometry of Ga sites in β - Ga_2O_3 nanoparticles.¹⁴⁹ It was shown that weak Lewis acid sites (attributed to tricoordinated Ga sites created upon vacancy formation on the (100) β - Ga_2O_3) with lower pyridine adsorption energies, promote propylene production over cracking products in PDH reaction on the fully dehydroxylated oxygen-deficient β - Ga_2O_3 surface.¹⁴⁹

Jiang et al. identified the adjusted coordination number (ACN) as a structural descriptor to predict the catalytic performance of TMOs (such as Cr_2O_3 , V_2O_5 , Co_3O_4 , and NiO) toward alkane activation.¹⁵⁰ It is worth noting that

ACN ($ACN = CN_O^* \lambda - \sum CN_M$) is a function of CN of the active oxygen in question and CN of neighboring metal atoms, which resembles the generalized coordination number concept on metals.¹⁵¹ Furthermore, linear correlations between ACN and (i) OVFE (ii) HAE, and (iii) ethane C–H activation energy barriers were obtained. In this way, oxygen sites with low ACN are more reducible and further reactive toward paraffinic C–H bond activation.¹⁵⁰ Zhou et al. confirmed a linear correlation between HAE and ACN on Ce_nO_{2n} ($n = 1-10$) sub-nano-clusters.¹⁵² The authors further proposed a sigmoid-function-based structural descriptor, namely, the sigmoid coordination number (i.e., $f(SCN)$) to predict the HAE on Ce_nO_{2n} clusters. An excellent agreement between the DFT-predicted HAE and model-predicted HAE was obtained with $RMSE = 0.02$ eV.¹⁵²

It should be recognized that oxygen vacancy on metal oxides plays a major role in the dehydrogenation of alkanes by enhancing the catalytic properties of reducible oxides.^{141,153,154} Zhang et al. revealed high activity of the oxygen-deficient ZrO_2 toward PDH reaction, with lower C–H activation barriers than pristine ZrO_2 .¹⁵³ Importantly, an alternative pathway for PDH was suggested, which requires the participation of two unsaturated Lewis acidic Zr sites in the homolytic activation of the C–H bonds, while propane activation on pristine ZrO_2 occurs via heterolytic C–H bond cleavage by dual Lewis basic oxygen and Lewis acidic Zr sites. Zeeshan et al. investigated PDH on oxygen-deficient CeO_2 and demonstrated that the presence of oxygen vacancies promotes Lewis acid–base interactions between surface adsorbates and reduces the second dehydrogenation energy barrier as compared to pristine ceria.¹⁵⁴ Chang et al. found that vacancy formation on the (0001) Cr_2O_3 surface enhances the catalytic activity by reducing the energy barriers of first and second dehydrogenation steps as compared to the pristine Cr_2O_3 surface.¹⁴¹ On the contrary, oxygen vacancy resulted in a negative effect on the reactivity of ZnO toward PDH (i.e., increased PDH barriers) because ZnO is an irreducible MO where Zn has only one stable cationic

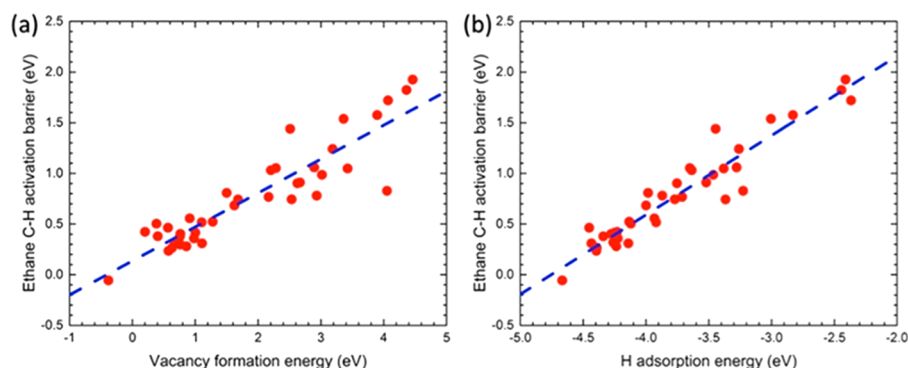


Figure 9. Correlation of the ethane C–H activation energy with (a) vacancy formation energy; (b) H adsorption energy. The blue dashed lines represent the linear best fit for the points. Reprinted with permission from ref 157. Copyright 2018 Wiley-VCH Verlag GmbH & Co. KGaA.

oxidation state, Zn^{2+} .¹⁴¹ It is worth noting that the correlations between $E_{2\text{-propyl}\&\text{H}}$ and PDH rates on nondefect MOs were found to hold true on pristine oxides.¹⁴¹ Together, oxygen vacancies can modify the electronic structure of the active sites, open alternative PDH reaction pathways, and modify the reactivity of reducible oxides.

Progress has been also made in developing SARs for oxidative C–H activation of light alkanes on reducible MOs.^{68,155–159} Vajda and co-workers developed simplified descriptor-based SARs for oxidative dehydrogenation of propane on Co_3O_4 .⁶⁸ In this study, HAE on the most Lewis basic oxygen sites was established as reactivity descriptor, such that a high HAE denotes high oxygen reactivity toward oxidative C–H bond activation.⁶⁸ The CN of active vanadium sites was identified as a structural descriptor in predicting catalytic activity of the anatase TiO_2 (001) surface supported on the VO_x catalyst toward propane oxidative dehydrogenation.¹⁵⁶ Subsequent work by Fung et al. studied ethane activation on the Co_3O_4 (111) and (311) facets doped with a wide range of metals (K to Ge). OVFE (Figure 9a) and HAE (Figure 9b) are shown to be powerful stability and reactivity descriptors, respectively, for oxidative alkane C–H bond activation on Co_3O_4 . In particular, a strong HAE and a low OVFE (facile surface reduction) result in decreased ethane C–H activation energy barriers.¹⁵⁷

In 2008, Fu et al. investigated the selective oxidation of light alkanes on TMOs through the radical mechanism (C–H bond cleavage to an alkyl radical and surface hydroxyl species).⁶⁹ Interestingly, the strength of the O–H bond was suggested as an activity descriptor for surface oxygen reactivity, correlating with both proton and electron affinities of the H atom. Further, a relationship was identified between the energy gaps of TMOs frontier orbitals and the C–H activation of lower alkanes ($\text{C}_1\text{--C}_4$) by terminal oxygen. Additionally, the singlet–triplet excitation energy (a descriptor used to estimate the M–O π bond strength and involves promoting an electron from the highest occupied molecular orbital to the lowest unoccupied molecular orbital) correlated linearly with the energy gaps of the oxides, and hence the activity of TMOs toward oxidative C–H bond activation.⁶⁹ Deshlahra and Iglesia developed SARs for oxidative C–H activation of light alkanes on oxides using fundamental descriptors that include (i) BDE, (ii) HAE, and (iii) interaction energy between organic radicals and surface hydroxyl species at the TSs.¹⁵⁸ Moreover, the binding energy of oxygen to the metal site of MOFs was identified as an activity descriptor for ODH.¹⁵⁹ More specifically, weaker

oxygen binding to the metal site facilitates the hydrogen abstraction from the reacting alkane, lowering the C–H bond activation energy barriers.¹⁵⁹

As reactivity descriptors facilitate the screening and design of catalysts with optimized activity toward a given reaction of interest, selectivity descriptors are equally important in the rational design of catalysts. The desired products in alkane dehydrogenation (i.e., olefins) interact more strongly with the oxide surface than the alkanes themselves and occupy well-defined sites (i.e., on top of the Lewis acid site through the π -electrons of the double bond).^{160–163} Thus, olefins have a high tendency to get further dehydrogenated to alkynes and other cracking products, depending on the Lewis acid–base properties of the oxide. To measure the oxide selectivity to olefins, the difference between alkene deep dehydrogenation activation energy (E_{deh}) and alkene desorption energy barrier (E_{des}) was identified as a selectivity descriptor ($E_{\text{deh}} - E_{\text{des}}$).^{141,145,146,154,164} Deep dehydrogenation of propene on CeO_2 was found to be less favored, by 1.17 eV, than propene desorption, whereas creating an oxygen vacancy and doping with Pt reduced the $E_{\text{deh}} - E_{\text{des}}$ to 0.90 and 0.46 eV, respectively, due to the higher adsorption stability of propylene on the modified catalyst.¹⁵⁴ Similarly, $E_{\text{deh}} - E_{\text{des}}$ was positive (i.e., higher selectivity to olefin desorption) on nondefect, oxygen-deficient, and Pt-doped Cr_2O_3 (0001) and ZnO (1010) surfaces,¹⁴¹ consistent with experimental findings that propylene selectivity can be greater than 90% on these oxides.^{8,165} Additionally, propylene desorption was kinetically favored over deep dehydrogenation on pristine and single-atom-doped Ga_2O_3 , in accordance with the experimentally measured selectivity of 95% over $\beta\text{-Ga}_2\text{O}_3$.^{146,164}

ALCOHOL DEHYDRATION

Although alcohol dehydration has been a subject of catalysis studies for over half a century,¹⁶⁶ it has attracted significant attention lately due to its importance in the production of value-added chemicals, such as olefins and ethers, from biomass derived oxygenates.¹⁶⁷ MOs are traditionally active and selective catalysts for alcohol dehydration due to their Lewis acidity and basicity and good thermal stability.^{168–174} Alcohol dehydration on MOs occurs via two competing mechanisms, namely, E1 and E2.^{170,172,175,176} The first step in both mechanisms is the adsorption of alcohol on the Lewis acidic metal site. The E1-type mechanism is characterized by the formation of alkoxide species via O–H dissociation, followed by an olefin formation through β -hydrogen transfer to the alkoxy oxygen to generate a hydrated MO surface. In

Table 1. Summary of Lewis Acid–Base Reactivity Descriptors Established on Metal Oxides^a

Entry	Descriptor	Descriptor type	Acid–base reaction	Catalyst
1	Hydrogen affinity (E_H)	Electronic	Methane activation and conversion Alkane dehydrogenation	MgO, ^{36,71} CaO, ^{36,71} IrO ₂ , ^{36,71} PdO, ^{36,71} rutile oxide, ^{36,71} MOF, ^{36,71} MXene, ^{147,148} Ni/TiC ⁷⁰
2	Hydrogen adsorption energy (HAE)	Electronic	Methane activation and conversion Alkane dehydrogenation	TiO ₂ , ¹⁰⁶ MgO, ^{75,84} CaO, ^{75,84} SrO, ^{75,84} IrO ₂ , ^{74,81} PdO, ⁷² rutile oxides, ⁷⁴ Ni-containing CeO ₂ , ⁷⁹ metal-doped La ₂ O ₃ , ⁸⁶ ABO ₃ -type perovskites, ^{118–120} MOFs, ¹²⁴ Co ₃ O ₄ , ^{68,150,157} V ₂ O ₃ , ^{143,150} Cr ₂ O ₃ , ¹⁵⁰ NiO, ^{89,150} WO ₃ , ⁹² Kegging polyoxometalate, ¹³⁸ graphene, ^{104,105} Ce _n O _{2–n} , ⁵² single-atom-doped on ZnO, ¹⁴⁵ Ga ₂ O ₃ -based catalysts, ¹⁴⁶ supported vanadium oxides ¹⁴⁴
3	Final state energy (E_{FS})	Electronic	Methane activation and conversion Alkane dehydrogenation	γ -Al ₂ O ₃ , ⁴³ MgO, ^{71,75,83,84} CaO, ^{71,75,83,84} SrO, ^{71,75,84} PdO, ^{71,72} metal-doped CeO ₂ , ⁷³ low-loaded M/CeO ₂ , ^{79,80} rutile oxides, ^{71,74,81} metal-doped La ₂ O ₃ ⁸⁶
4	Carbenium ion stability (CIS)	Binary (Reactant)	Alkane dehydrogenation Alkane dehydrogenation Alcohol dehydrogenation	γ -Al ₂ O ₃ , ^{85,137,168–170,178} β -Ga ₂ O ₃ , ¹⁷⁷ In ₂ O ₃ ¹⁷⁷
5	Proton affinity (PA)	Electronic	Alkane dehydrogenation Alcohol dehydrogenation	TiO ₂ , ¹⁷⁸ ZrO ₂ , ¹⁷⁸ γ -Al ₂ O ₃ , ^{85,137,170,177,178} β -Ga ₂ O ₃ , ¹⁷⁷ In ₂ O ₃ ¹⁷⁷
6	Reactant binding energy (BE)	Electronic	Alkane dehydrogenation Alcohol dehydrogenation	TiO ₂ , ¹⁷⁸ ZrO ₂ , ¹⁷⁸ γ -Al ₂ O ₃ , ^{137,177,178} β -Ga ₂ O ₃ , ¹⁷⁷ In ₂ O ₃ ¹⁷⁷
7	Binding energy of dissociated hydrogen (BE_{H_2})	Electronic	Methane activation and conversion Alkane dehydrogenation	γ -Al ₂ O ₃ ^{34,43,85,138–140}
8	Coadsorption energy of 2-propyl and H ($E_{2\text{-propyl}\&\text{H}}$)	Electronic	Alkane dehydrogenation	Oxygen vacancy TM–TiO _{2–x} , ¹⁴⁰ reducible and nonreducible MOs: Cr ₂ O ₃ , Pt–Cr ₂ O ₃ , ZnO, Pt–ZnO, ¹⁴¹ TM-doped TiO ₂ , ¹⁴²
9	Coadsorption energy of a pair of H atoms ($E_{\text{H}\&\text{H}(\text{M}-\text{O})}$)	Electronic	Alkane dehydrogenation	Ga ₂ O ₃ -based catalysts ¹⁴⁶
10	Local band centers	Electronic	Alkane dehydrogenation Methane activation and conversion	γ -Al ₂ O ₃ , ^{43,138} V ₂ O ₃ , ¹⁴³ supported vanadium oxides, ¹⁴⁴ TM-doped V ₂ O ₅ clusters, ⁹³ WO ₃ , ⁹² oxygen-deficient TM–TiO _{2–x} , ¹⁴⁰ Ga ₂ O ₃ -based catalysts ¹⁴⁶
11	Bader charge	Electronic	Alkane dehydrogenation Methane activation and conversion	WO ₃ , ⁹² La–Fe-based perovskites, ¹²³ Ga ₂ O ₃ -based catalysts ¹⁴⁶
12	Adjusted coordination number (ACN)	Geometric	Alkane dehydrogenation	TMOS: ¹⁵⁰ V ₂ O ₃ , Cr ₂ O ₃ , Co ₃ O ₄ , NiO, Ce _n O _{2–n} , ¹⁵²
13	Sigmoid coordination number (SCN)	Geometric	(De) hydrogenation	Ce _n O _{2–n} , ¹⁵²
14	Coordination number (CN)	Geometric	Methane activation and conversion	Graphene, ¹⁰⁵ TiO ₂ supported on VO _x ¹⁵⁶
15	Oxygen vacancy formation energy (OVFE)	Binary	Alkane dehydrogenation Methane activation and conversion	TiO ₂ , ¹⁰² ZnO, ¹⁰² TbO ₂ , ¹⁰² MgO, ^{75,84,102} CaO, ^{75,84} SrO, ^{75,84} Co ₃ O ₄ , ^{150,157} ABO ₃ -type perovskites, ^{118–120} V ₂ O ₃ , ¹⁵⁰ Cr ₂ O ₃ , ¹⁵⁰ NiO, ¹⁵⁰ CeO ₂ , ^{73,99,100} La ₂ O ₃ , ⁸⁶ La _{1–x} Sr _x BO ₃ , ¹²¹ SrTiO ₃ perovskites ²²

Table 1. continued

Entry	Descriptor	Descriptor type	Acid–base reaction	Catalyst
16	Reduced surface work function (Φ)	Electronic	Alkane dehydrogenation	TiO ₂ , ¹⁰² ZnO, ¹⁰² TiO ₂ , ¹⁰² MgO ¹⁰²
17	Methane/methyl adsorption energy ($E_{\text{CH}_4^*}/E_{\text{CH}_3^*}$)	Electronic	Methane activation and conversion	Doped rutile TiO ₂ , ⁷⁸ ABO ₃ -type perovskites ¹²²
18	Singlet–triplet excitation energy (ΔE_{ST})	Electronic	Alkane dehydrogenation	TMOs; ⁶⁹ CrO ₃ , VO ₃ Cl, WO ₃ , and MoO ₃
19	C–H Bond Dissociation Energy (BDE)	Electronic	Methane activation and conversion	ABO ₃ -type perovskites, ¹²² Kegging polyoxometalate ¹⁵⁸
20	Oxygen binding energy	Electronic	Alkane dehydrogenation	MOFs, ¹²⁴ NiO, ⁸⁹ single TM atoms anchored at the N-doped graphene, ¹⁰⁵ rutile MOs ⁶⁶
21	Energy weighted mean of the s-conduction band states (E_s^*)	Electronic	Methane activation and conversion	γ -Al ₂ O ₃ ¹⁷¹
22	Band gap	Electronic	Alcohol dehydration	Rutile TMOs; ¹⁰⁶ TiO ₂ , Pt ₁ –TiO ₂
23	Integrated crystal orbital Hamilton population (ICOHP)	Electronic	Methane activation and conversion	La _{1-x} Sr _x BO ₃ , ¹²¹ TMOs; ⁶⁹ CrO ₃ , VO ₃ Cl, WO ₃ , and MoO ₃
24	Electronegativity difference ($\Delta X_{\text{B-A}}$)	Electronic	Alkane dehydrogenation	Rutile MOs; ¹⁰⁷ PrO ₂ , IrO ₂ , CrO ₂ , ABO ₃ -type perovskites, ^{118–120}
25	Difference between alkene deep dehydrogenation activation energy and alkene desorption energy barrier ($E_{\text{deh}} - E_{\text{des}}$)	Electronic	Methane activation and conversion	ABO ₃ -type perovskites ¹²⁰
26	Difference between methane and methanol activation energies (ΔG^*)	Electronic	Alkane dehydrogenation	CeO ₂ , ¹⁵⁴ Cr ₂ O ₃ , ¹⁴¹ ZnO, ¹⁴¹ β -Ga ₂ O ₃ ^{146,162}

^aDescriptors are classified as electronic (i.e., catalyst electronic properties), geometric (i.e., catalyst surface structure), and binary (i.e., considering both catalyst electronic and structural properties) correlating with catalytic behavior. Descriptors 1–24 address activity, whereas 25 and 26, selectivity.

the concerted E2-type mechanism, β -hydrogen is abstracted by surface Lewis basic oxygen site, followed by a simultaneous cleavage of C–OH bond to form desorbed alkene product and a hydrated surface Lewis acid–base pair. The catalytic cycle of the two mechanisms is completed via molecular water formation through the recombination of surface-bound hydroxyl and hydrogen species. Finally, molecular water desorbs to regenerate the MO catalyst.^{175,177,178} Notably, it has been suggested that the concerted E2-type mechanism is more energetically preferred on MOs than the E1-type mechanism, owing to the higher dehydration barrier of the latter.^{168,177,178} This is because inherently you have a C–H activation of a beta carbon (with respect to the hydroxyl position) and involving surface oxygens is preferable to the oxygen of the adsorbed alcohol due to their higher basicity and less strain at the TS. Importantly, both Lewis and Brønsted acid sites of the oxide can act cooperatively in alcohol dehydration.¹⁷⁹ For instance, the dehydration reaction can be initiated by the protonation of weakly basic OH group of the alcohol by the acidic proton of the Brønsted site to form water molecule and carbocation.¹⁶⁹ Hence, the nature of the acid site (either Lewis or Brønsted) can influence the reaction mechanism. By understanding the dehydration chemistry on MOs, SARs can be developed for the effective screening of alcohol dehydration catalysts.

Roy and co-workers studied the dehydration of several alcohols with varying size and degree of alcohol substitution on γ -Al₂O₃ using both experiments and theory.¹⁷⁰ The TS exhibited carbenium ion character with the enhanced catalytic performance of tertiary alcohols correlating with a decrease in alcohol stability, as quantified by the CIS.¹⁷⁰ Kostestkyy et al. studied the dehydration of primary, secondary, and tertiary alcohols on Al₂O₃, TiO₂, and ZrO₂ catalysts through a combination of temperature programmed desorption and DFT studies.¹⁷⁸ Descriptor-based SARs were then constructed to correlate the dehydration barriers with relevant physicochemical properties of both the alcohols and the MO catalysts as follows (i) alcohol reactivity, CIS;¹⁶⁸ (ii) surface oxygen basicity, PA of surface oxygens; (iii) surface metal acidity, binding energy of alcohols on Lewis acidic center (alcohol BE). Given the structural similarities at the concerted-elimination TS between alcohol dehydration and ADH, these descriptor-based SARs were successfully transferred to ADH reactions on MOs.¹³⁷ It should be noted that due to the hydroxyl groups of alcohols being a base, alcohols bind stronger to the Lewis acid sites of the oxide catalyst compared to alkanes (i.e., isopropyl alcohol BE on (110) γ -Al₂O₃ ranges from −0.70 to −1.30 eV,¹⁷¹ whereas propane BE ranges from −0.20 to −0.70 eV).³⁴ Thus, adsorption of alcohols can be used as a probe of the oxide Lewis acidity, while their decomposition to olefins probes both Lewis acidity and basicity of the oxide. Furthermore, an alcohol dehydration model was built on group IIIA MOs as a function of surface acidity and basicity (through alcohol BE and PA of surface oxygens) and degree of alcohol substitution (through CIS).¹⁷⁷ The model was in excellent agreement with the previous model on Al₂O₃, TiO₂, and ZrO₂.¹⁷⁸ Additionally, the authors studied olefin formation through ether decomposition and identified a correlation between alcohol dehydration and ether decomposition activation barriers.¹⁷⁷ Because of the similarities of the TS structures between the two different acid–base reactions (ether decomposition vs alcohol dehydration),

the dehydration model was extended to predict the ether decomposition activation barriers.

Jenness et al. investigated alcohol dehydration on γ -Al₂O₃ in the presence and absence of a coadsorbed water molecule.¹⁷¹ The authors proposed a descriptor termed the energy weighted mean of the s-conduction band states for the Al³⁺ centers (E_s^*) to be alcohol dehydration and Lewis acidity descriptor. Particularly, E_s^* acts as a means to quantify the ability of the reacting alcohol to transfer an electron charge to acidic Al³⁺ centers. A linear correlation between alcohol BE (e.g., ethanol, *tert*-butanol, and isopropyl alcohol) on the (100) and (110) γ -Al₂O₃ facets and E_s^* was observed. A near linear dependence of the ethanol dehydration barriers on the BE of ethanol was obtained, suggesting a significant influence of γ -Al₂O₃ Lewis acidity on the dehydration activity. Consequently, a similar linear dependence of ethanol dehydration barriers on E_s^* was demonstrated. Interestingly, hydration of (110) γ -Al₂O₃ caused a downshift in E_s^* and increased Lewis acidity strength, suggesting a decrease in the dehydration energy barriers.¹⁷¹ However, depending on the surface site, the ethanol dehydration energy barriers would change variably and in the opposite trends (i.e., from a negligible change of less than 0.10 eV to a significant increase of ~0.60 eV). This is because the neighboring surface oxygen atom already contains an adsorbed H from the dissociated surface waters, causing a significant reduction in the basicity of this site which diminishes its ability to accept a β -hydrogen from ethanol.¹⁷¹ Christiansen et al. demonstrated strong competitive adsorption of ethanol and water on the Lewis acid sites, supporting previous studies that propose adsorbed water as an inhibitor to alcohol dehydration activity.¹⁷²

Foo et al. investigated the reactivity and acid–base properties of perovskites, both experimentally and theoretically, using the conversion of 2-propanol as a probe acid–base reaction.¹⁸⁰ Perovskites exhibited intermediate to strong Lewis basicity together with weak Lewis acidity. Both alcohol dehydration and dehydrogenation competed on perovskites, with higher selectivity toward alcohol dehydrogenation due to the dominant surface basicity of perovskites. In addition, the adsorption energy of 2-propanol on the catalyst was correlated to both the tolerance factor (structural parameter) of the bulk perovskites and the synergism between acid and base sites.¹⁸⁰ Overall, both Lewis acidity and basicity of MOs are responsible for the dehydration activity.

■ LIMITATIONS AND OUTLOOK

Descriptor-based SARs enable the screening of potential Lewis acid–base catalytic materials for industrial relevant chemical conversions. In Table 1 and Figure 10, we summarize the descriptors used for specific reactions of interest in a wide range of oxide catalysts. A common reactivity descriptor, as summarized in Table 1 and Figure 10, is the adsorption energy of key surface reaction intermediates and activated complexes. HAE, BE_{H_2} , E_{FS} , $E_{2\text{-propyl\&H}}$, $E_{H\&H@M-O}$, BE, and $E_{CH_3^*}$ are examples of reactivity descriptors based on the adsorption strength of key reaction intermediates. These intermediates are often found to be rate-limiting species in a specific reaction of interest. For instance, coadsorbed 2-propyl and hydrogen are identified as rate-limiting intermediates in PDH on the ZnO (10 $\bar{1}$ 0) surface, and the overall PDH rate can be enhanced via stabilizing the adsorption of these intermediates on the surface.¹⁴⁵ As shown



Figure 10. Word cloud depicting the frequency of reactivity descriptors for Lewis acid–base reactions reviewed in this article.

in Figure 10, the most frequently used descriptors for paraffinic C–H bond activation include HAE, OVFE, and E_{FS} . We note that these descriptors correlate with each other and can be used to describe the reactivity of various types of catalysts. Additionally, some oxides can effectively catalyze a different set of reactions. For instance, $\gamma\text{-Al}_2\text{O}_3$ has emerged as an active catalyst for methane activation, alkane dehydrogenation, and alcohol dehydration reactions owing to its inherent Lewis acid–base surface properties.

As shown in this review, descriptor-based SARs are often limited to a single class of catalytic materials and/or a specific reaction. Developing universal reactivity descriptors that can simultaneously be used to screen many catalysts for different acid–base reactions has been the ultimate goal of researchers. Identifying universal descriptors, although promising, is a formidable task due to the enormous materials space of heterogeneous catalysts. There is structural diversity on Lewis acid–base sites that can affect SARs to a different degree with the following order of importance: (i) changing from one catalytic material to another, (ii) changing from one surface to another on the same catalyst, and (iii) changing from one site to another on the same catalytic surface. As a result, SARs should be sensitive to all these different degrees of freedom, so they are able to identify the exact catalyst and sites on its surface that are active and selective for a specific reaction of interest. SARs should also account for different reaction mechanisms since these can change on catalytic sites that exhibit different Lewis acid–base properties.³⁴ However, it is possible to build SARs for a subfield of reactions that share similar TS structures (e.g., alkane dehydrogenation–alcohol dehydration–ether decomposition).^{137,170,177,178} In addition,

some descriptors, such as the HAE and the BE_{H_2} , show some universality on describing C–H bond activation, as shown in Table 1 and Figure 10, while being very relevant to each other as descriptors.^{34,36,71,75,84,85,138,147} Descriptors that exhibit universality across different materials should comprise the basis for developing SARs. An additional parameter that needs to be taken into consideration in developing SARs is the experimental condition for a reaction of interest.¹⁸¹ For example, SARs are developed for energy intensive reactions that typically require high temperatures and/or pressures. Thus, the catalyst surface and associated properties may be completely different under realistic reaction conditions, especially in the presence of a reactive environment (e.g., presence of hydrogen in dehydrogenation reactions and water in dehydration reactions). For these reasons, SARs should be

able to capture surface site catalytic properties relevant to the experimental conditions.

Another complexity is that SARs typically originate from DFT calculations. Although DFT is instrumental in studying heterogeneous catalysis,¹⁸² an accurate description of MOs electronic structural properties is challenging.¹⁸³ A key hurdle is the direct dependency of the calculated electronic properties (e.g., OVFE)¹⁸⁴ on the DFT exchange–correlation functional, noting that a real functional is still unknown.^{185–188} Exchange–correlation functionals may cause erroneous self-interactions of electrons, especially in 3d and 4f metals, which contain highly localized d- and f-orbitals. One common approach to treat the self-interaction between correlated electrons is the Hubbard U model (i.e., DFT + U),^{189,190} which applies an onsite Coulomb correction potential term U and an exchange term J on the localized orbitals. The U value is most frequently selected based on its ability to reproduce the experimental bulk properties (e.g., band gap, lattice parameters, etc.). However, there is no single U value that can accurately capture all bulk properties of a specific oxide material.¹⁸⁹ It should be noted that U values optimized to reproduce bulk values may not be relevant for surface reactions simply because surface properties can differ from those in bulk.^{191,192} For instance, a U value of 7.00 eV for CuO (optimized based on bulk properties) results in underestimating the adsorption enthalpies of H_2 on CuO (111) by 0.32 eV.¹⁹⁰ In addition, DFT calculations are time-consuming and cost-ineffective when modeling complex reaction networks.^{193,194} This, in turn, slows down the pace of discovering reactivity descriptors for a gamut of reaction steps.

On the other side, machine learning (ML) is a powerful tool in rational catalyst design as it can quickly and accurately capture complex nonlinear correlations between catalytic activity and catalyst–reactant physicochemical properties.^{74,193,194} ML algorithms are fueled by rich training data sets to predict highly accurate electronic structures and reaction mechanisms.^{74,193,194} Nevertheless, ML has recently started to gain popularity in the screening of MO catalysts for acid–base reactions, but its wide application is limited by the lack of a consistent and easily accessible database. To overcome this hurdle, significant efforts have been made to develop public databases for catalytic surface reaction energetics including CatApp¹⁹⁵ and Catalysis-Hub.org.¹⁹⁶ Such databases can boost the application of ML algorithms in catalysis by avoiding expensive DFT calculations and offering a platform for model benchmarking. In addition, extraction of data from the literature^{188,197,198} and in-house^{74,199} data generation, have been also employed.²⁰⁰ For instance, Xu et al. selected suitable geometric and energetic descriptors by percentile-LASSO to improve the BEP relationship of methane activation on rutile-type TMOs, based on DFT-calculated activation energies for radical and surface-stabilized mechanisms.⁷⁴ Singh et al. developed several regression models (using literature database)⁷⁶ to predict TS energies of dehydrogenation reactions, among which an artificial neural network model resulted in the smallest test error of 0.22 eV.¹⁹⁸ Additionally, Zhang and Xu developed ML models to predict DFT-calculated adsorption energies of methane-related species on Cu-based alloy surfaces using a rich data set extracted from literature.¹⁹⁷ Importantly, highly accurate training data is necessary for ML application to avoid biased and chemically nonrealistic predictions. Ulissi et al.

showed that DFT uncertainty affects the ability of ML algorithms to select the most likely pathway for a certain reaction network.¹⁹³

Although most ML algorithms are commonly trained on computationally derived data sets, implementing experimental catalytic data has the potential to improve the overall performance of the ML models.^{201,202} Suzuki et al. developed a ML model based on an experimental catalytic data set on OCM, water gas shift, and CO oxidation reactions.²⁰³ The Yildirim group systematically reviewed literature and developed experimental databases for steam reforming²⁰⁴ and dry reforming of methane.²⁰⁵ Using ML, the authors identified the most active catalysts and reaction operational conditions that lead to high methane conversion.²⁰⁴ Additionally, some metal oxides do not retain their initial oxide phase under reaction conditions (e.g., oxides can be reduced or form surface hydroxide which hinders the catalyst's ability to activate hydrocarbons). Hence, it is crucial to gain atomic-level insights into the structure of the catalyst under operation to feed realistic structures in the DFT calculations and contribute toward gaining accurate information on catalyst behavior. Spectroscopic data mining is a powerful tool to obtain a comprehensive picture of the nature of the catalyst and the interactions of reactants and activated complexes with the oxide surface under reaction conditions. *In situ* and *operando* spectroscopies, including diffuse-reflectance infrared, steady-state isotopic transient kinetic analysis, mass, and X-ray spectroscopies, can provide quantitative information regarding the catalytically active species and reaction kinetic parameters which can be further used to identify relevant reaction mechanisms.²⁰⁶ Hence, spectroscopic data mining can inform the development of accurate SARs for relevant reaction mechanisms. These mechanisms should include experimentally observed reaction intermediates that participate in the reaction and do not act as spectator species, as well as experimentally relevant catalytic surfaces. Together, catalytic/spectroscopic data mining combined with DFT and machine learning can guide experiments for the identification of promising catalysts.²⁰⁷

In summary, a potential path forward to improve the screening of oxides toward acid–base heterogeneous catalysis includes the following:

- Developing universal reactivity descriptors that apply to diverse types of acid–base reactions on MOs exhibiting structural diversity (i.e., SARs capturing a wide range of materials space).
- Coupling machine learning with catalytic experiments and DFT calculations to automate the prediction of activity descriptors and screening of oxides.
- Incorporating the dynamic nature of heterogeneous catalysis under realistic experimental conditions into descriptor-based SARs to ensure effective screening of catalytic materials under industrial application.

CONCLUSIONS

First-principles-based computational modeling is a powerful tool that can contribute to understanding the reaction mechanisms in heterogeneous catalysis and identify active and selective catalysts for industrial application. Descriptor-based SARs offer a predictive screening tool that can potentially accelerate the discovery of novel catalysts for a wide range of chemistries. In this review article, we

highlighted acid–base SARs on MOs for reactions that are highly important to the industrial and energy sectors, such as methane activation and conversion, alkane dehydrogenation, and alcohol dehydration. Additionally, we discussed the current limitations of SARs and proposed future steps to advance the field.

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Notes

The authors declare no competing financial interest.

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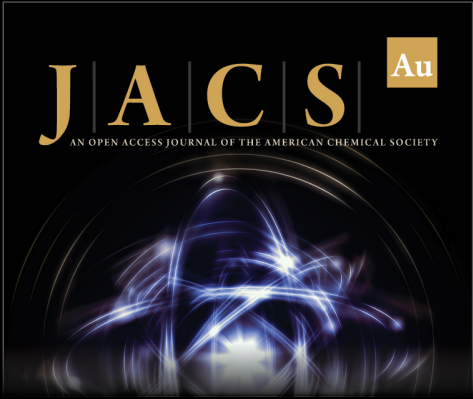
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