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Review

Frustrated Lewis Pairs in Heterogeneous Catalysis: Theoretical Insights

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Abstract: Frustrated Lewis pair (FLP) catalysts have attracted much recent interest because of their exceptional ability in activating small molecules in homogeneous catalysis. In the past ten years, this unique catalysis concept has been extended to heterogeneous catalysis, with much success. Herein, we review the recent theoretical advances in understanding FLP-based heterogeneous catalysis in several applications including metal oxides, functionalized surfaces, and two-dimensional materials. A better understanding of the details of the catalytic mechanism can help in experimental design of novel heterogeneous FLP catalysts.

Keywords: heterogeneous catalysis; frustrated Lewis pairs; hydrogen dissociation, alkynes hydrogenation; density functional theory

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1. Introduction

Noble metal based catalysts have been an indispensable part of modern industrial catalysis [1-4]. However, their high cost and geopolitical risk have always placed a severe constraint on their applications. Considerable efforts have been made to reduce [5-7] and/or eliminate the use of noble metals in catalysts [8-10]. The former approach has greatly benefited from various strategies and concepts recently developed to improve the atomic efficiency and reactivity of active sites, such as alloyed catalysts [11-13], atomic dispersed catalysts [14-16], and surface defect engineering [17-19]. Meanwhile, significant efforts have been made to achieve similar activity of noble metals by utilizing other materials (e.g., earth-abundant transition metals and main-group elements) [20-23]. One such strategy is frustrated Lewis pairs (FLPs), which have attracted much recent attention thanks to its superior performance in homogenous small molecule activation [20, 24, 25]. As shown in Figure 1, an FLP assembles a pair of Lewis acid (LA) and base (LB) in proximity, but with steric hindrance to prevent them from recombining, so as to activate small molecules [26-28]. Besides catalyzing heterolytic H_2 dissociation [29, 30], FLP catalysts have also been demonstrated in activation of other molecules (e.g., alkenes, aldehydes and CO_2) [31-34], thus providing a new strategy for synthetic chemistry. Inspired by unique FLP-based catalysts in homogenous catalysis, this concept has recently been extended to heterogeneous catalysis [35, 36].

Solid surfaces provide a template for designing FLPs, which can be used to aid heterogeneous catalysis [37-39]. An early example involved the γ-alumina catalyzed low-temperature activation of CH_4 by Wischert et al. [40], who identified a surface FLP made up of LA and LB sites. The former is the tri-coordinated Al_{III}, while the later is O, and the dissociation of CH_4 led to Al-CH_3 and O-H. In another case, Shi et al. observed chain structures on the ZnO($10\bar{1}0$) surface [41], formed at an extremely low temperature (~20 K) by

the heterolytically dissociative adsorption of H_2, leading to a zinc hydride and a hydroxyl. Density functional theory (DFT) calculations found two kinds of Zn-O pairs on the surface. One has a bond formed between the Zn and O sites, which can be classified as classical Lewis pairs (CLPs). The other type of Zn-O pairs has the Zn and O sites well separated, thus forming FLPs. DFT calculations suggested that the H_2 dissociation on the FLP is more favorable than on the CLP. Similar FLPs have been found on ceria (CeO_2) [42, 43], which was reported recently to catalyze the selective hydrogenation of unsaturated hydrocarbons [44]. In this case, the FLP, formed between a Ce^{3+} (LA) created near an oxygen vacancy (O_v) and a nearby oxygen (LB), is shown to catalyze the heterolytic H_2 splitting [43]. These surface species have indeed been identified experimentally [45, 46], confirming the hypothesis. DFT calculations demonstrated that these species catalyze the subsequent hydrogenation [43].

Driven by these early success, a large number of theoretical studies have recently been carried out to gain insights into heterogeneous FLP catalysis and to predict new heterogeneous FLP catalysts. The LA and LB sites that make up heterogeneous FLPs may be the electron-deficient and electron-rich atoms and groups externally introduced, or sites with different electronic properties constructed by surface engineering. Among the proposed heterogeneous FLPs, metal organic frameworks (MOFs) and modified metal surfaces have been studied via density functional theory (DFT) calculations [47-50], while those based on two-dimensional (2D) materials and metal oxides have started to attract theoretical attention [17, 51, 52]. It is easy to understand why MOFs are good candidates for FLP-based catalysts, as various functional groups can be designed within a MOF with desired distances. On the other hand, metal oxides are naturally rich in LA (metals) and LB sites (oxygens) and surface vacancies can be leveraged in designing FLPs. The design of FLPs on 2D materials is even more versatile, a usual practice is to dop electron-deficient and electron-rich atoms to change the local environments [51-53]. These studies have greatly advanced our abilities to activate small molecules with surface FLPs. However, experimental conditions are often more complicated than theoretical models. Although several strategies, mechanisms, and structure-reactivity relationships have been proposed based on these theoretical studies, there is still a lack of consensus on how to design highly efficient FLP catalysts.

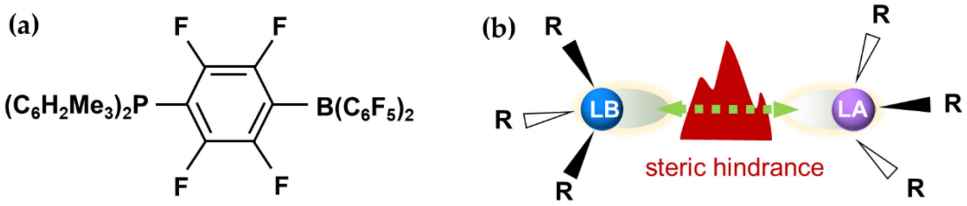

Figure 1. (a) Structure of the first reported homogeneous FLP. (b) Scheme of the common strategy for constructing homogeneous FLP catalysts. (a) is reproduced from Ref. 24 with permission.

Here, we review the recent advances in theoretical studies of FLPs at gas-solid interfaces and discuss their roles in heterogeneous catalysis. We strive to survey the recent theoretical studies of heterogeneous FLP catalysis, aiming to classify various types of heterogeneous FLP catalysts and strategies for creating surface FLPs. We also discuss mechanisms and structure-reactivity relationships that could potentially assist experiments in the rational design of the corresponding catalysts.

This review is organized into four sections. In Section 2, we briefly introduce the original concept of FLPs and the mechanism for small molecule activation by homogeneous FLP catalysts. Several FLP based heterogeneous catalysts are discussed in Section 3. In Section 3.1, we present our current understanding of several metal oxides-based FLP catalysts with the relevant catalytic mechanisms. Section 3.2 focuses on the progress of

FLP-facilitated catalysis on functionalized surfaces, including MOFs, metal surfaces and 2D materials. Finally, design strategy, challenges, and outlook are discussed in Section 4.

2. Mechanisms of FLP catalysis

H_2 activation has traditionally been catalyzed by noble metals. In 2006, Stephan and coworkers opened a door to metal-free activation of H_2 by introducing an FLP-based homogeneous catalyst $(C_6H_2Me_3)_2PH(C_6F_4)BH(C_6F_5)_2$ [24], shown in Figure 1(a). A common form of the FLP consists of an electron-deficient atom (or group) and electron-rich atom (or group) in one molecule or in a molecular pair, which are prevented from neutralization by utilizing geometry and/or steric hindrance. The role of the FLP is to promote H_2 dissociation into protonic (H^+) and hydridic (H^-) species. Since then, homogeneous FLP catalysts have been developed to activate other molecules such as N_2 and CO_2 [34, 54], and much effort has been devoted to the understanding of the mechanism [55-57].

Theoretical studies have provided valuable insight into the mechanism of FLP catalyzed H_2 dissociation. The importance of the "frustration" between the LA/LB sites, namely their spatial/steric separation, was confirmed by a theoretical study of Rokob et al [58]. The resulting FLP differs from its classical counterpart, CLP, which is stable with low catalytic activity, by creating a pre-organized and strained environment for catalysis, thus lowering the activation energy for hydrogen splitting, as shown in Figure 2(a). Specifically, these authors attributed the catalysis to a covalent transition state involving electron transfer (ET) between the LA/LB pair and the H_2 molecule. However, later theoretical studies by Grimme et al. [59] found little evidence for an activated complex LA–H–H–LB and the associated lowered barrier. Instead, the H_2 molecule inserted into the FLP cavity dissociates spontaneously and the activation is essentially the energy cost for H_2 to enter the electric field (EF, Figure 2(b)) generated by the FLP, see Figure 2(b). Both the ET and EF mechanisms, which are illustrated in Figure 2(c)-(d), are probably operative to some extent, but their importance might depend on the specific system [60] .

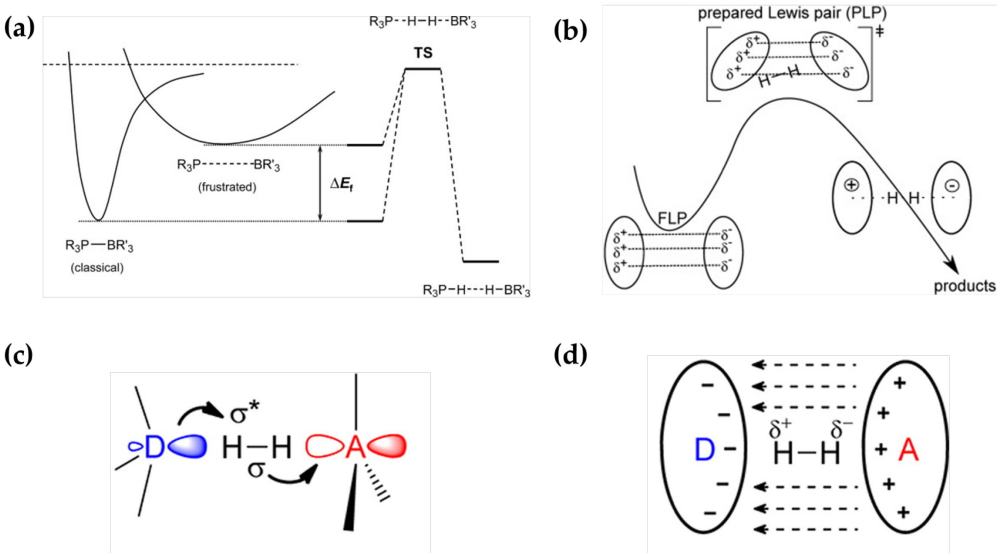

Figure 2. Role of (a) frustration and (b) electron field in mechanisms of H_2 activation catalyzed by FLPs proposed by Rokob et al. and Grimme et al., respectively. Schemes of FLP catalyzed H_2 dissociation via (c) the ET mechanism and (d) the EF mechanism. (a), (b) and (c)-(d) are from Refs. 59, 60, and 61, respectively, with permission from John Wiley and Sons and American Chemical Society.

The situation in heterogeneous FLP catalysts is expected to be similar to its homogeneous counterpart. The possible mechanisms and corresponding applications of FLPs in heterogeneous catalysis are discussed in detail in the following sections.

3. Current developments of heterogeneous FLP catalysts

3.1. FLPs based on metal oxides

Metal oxides, possessing natural LA and LB sites on their surfaces, are known as heterogeneous catalysts for C-H and H-H bond activation. Studies suggested that Lewis acid-base properties of the active sites on metal oxide surfaces could provide a unique perspective to obtain an in-depth understanding of the catalysis.

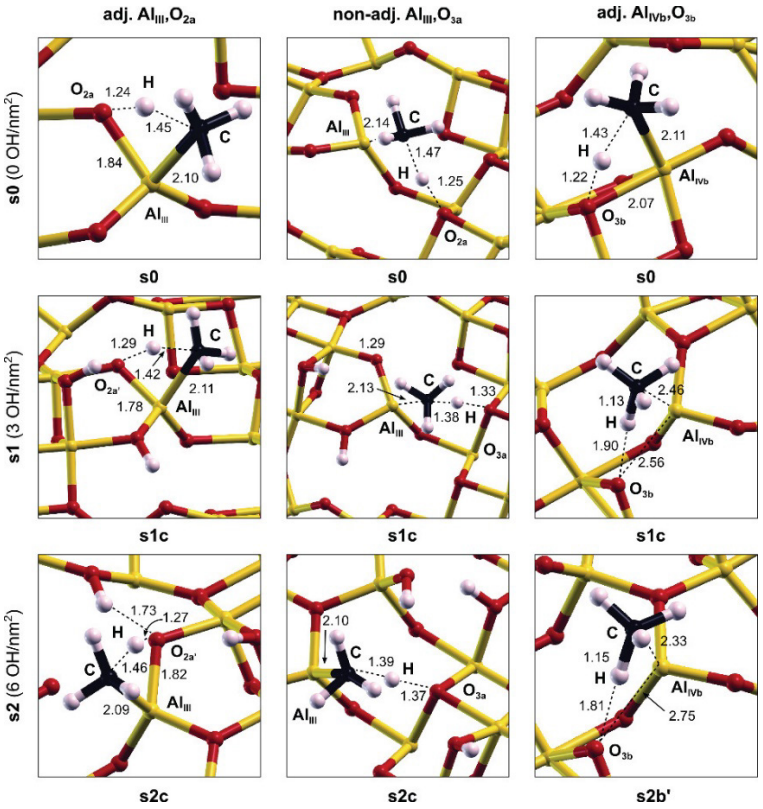

Figure 3. Configurations of the transition states for CH_4 dissociation on various surface Al-O pairs for surfaces at different OH coverages (0, 3 and 6 OH/nm²). Adapted from Ref. 62 with permission.

γ-alumina (γ-Al_2O_3) is considered as a heterogeneous FLP catalyst for C-H bond activation in CH_4. In a combined experimental and first-principles study, Wischert et al. revealed that low-temperature heterolytic C-H bond cleavage in CH_4 on a hydroxylated γ-Al_2O_3(110) to form Al-CH_3 and O-H can be ascribed to the co-action of non-adjacent Lewis acid-base pairs consisting of surface Al_{III} (LA) and O (LB) sites [40]. These two sites are separated by 4.1 Å on the hydroxylated alumina surface, forming a cavity for the adsorption and activation of CH_4, leading to Al-CH_3 and O-H. They also speculated that such FLP catalysis might be general for different oxides towards other molecules with polarizable X^+-Y^- bonds. In the subsequent study by the same group, the authors theoretically compared the C–H or H–H bond cleavage of CH_4 or H_2 catalyzed by a frustrated Al-O pair over the γ-Al_2O_3(110) and γ-Al_2O_3(100) surfaces as a function of hydroxyl coverage [61], see Figure 3. Similar to the case of CH_4 activation, the activation of the H-H bond in H_2 leads to Al–H and O-H species. The activation of H_2 is more facile because of the lower dissociation barrier than that for CH_4 activation. Importantly, these studies demonstrated that the reactivity of Al and O sites is affected by partial hydroxylation, which stabilizes the metastable (110) surfaces and tunes the electronic structures of the Al-O FLP by increasing the acidity of Al and the basicity of O. Hence, surface hydration can be used as an effective strategy to create and stabilize surface FLPs on (nonreducible) metal oxide surfaces.

Another example of FLP facilitated heterolytic dissociation of H_2 was reported on hydroxylated indium oxide ($In_2O_{3-x}(OH)_y$) which catalyzes the Reverse Water Gas Shift

(RWGS) reaction, whereby CO_2 is reduced by H_2 to CO ($CO_2 + H_2 \rightarrow CO + H_2O$). In DFT calculations of this reaction combined with in situ spectroscopic and kinetic studies by Ghuman et al. [62], the activation of H_2 was attributed to surface FLPs consisting of non-adjacent hydroxide (LB) and indium (LA) pairs, with the later exposed at a surface oxygen vacancy. The proposed mechanism leads to the formation of surface O-H_2 and In-H species, which subsequently attack the adsorbed CO_2 to produce CO and H_2O.

The existence of FLPs is of course not restricted to the two examples discussed above. Ceria (CeO_2) has long been used as a support of metal catalysts, thanks to its strong reducibility [63]. The recent discovery by Vilé et al. that ceria alone is capable of catalyze selective hydrogenation of unsaturated hydrocarbons [44, 64, 65] has stimulated considerable interest to understand its reactivity and selectivity [66]. The initial proposal of the mechanism for partial acetylene hydrogenation contained a relatively high barrier (2.86 eV) [64], which is kinetically unattainable. The key flaw of that mechanism was the assumption of homolytic activation of H_2, leading to the formation of two surface OH species, which are responsible for the high barrier in the hydrogenation step. Interestingly, other DFT studies showed that heterolytic activation of H_2 has a significantly lower barrier [67]. In this case, an exposed Ce serves as the LA for accepting the hydride (H^-) species from the dissociating H_2, while a surface O can serve as the LB for the proton (H^+). Subsequent DFT calculations revealed the crucial role of O vacancies in forming the surface FLPs [42, 68], and mechanism investigation suggest that the energy barrier of the rater-determining step of acetylene hydrogenation catalyzed by the FLP is lower than that by a CLP on CeO_2(110) facets (Figure 4(a)). One can see from the charge density difference (CDD) in Figure 4(b) that in the TS of H_2 activation, electron density was increased around H on Ce while decreased around H on O with both CLP and FLP. Meanwhile, it can be inferred from the electron localization function (ELF) maps that there are some highly delocalized regions between H^- and Ce and the region between O and H^+ show a strong covalent property. All these suggested that both the local electric field on surface and electron transfer between H_2 and FLP/CLP contribute the reactivity. Based on our DFT calculations on CeO_2(111), the proton and hydride species are crucial for the subsequent hydrogenation steps [43, 69], leading to a mechanism that is consistent with experimental observations [46]. All the above studies suggested that the surface FLPs are crucial for the heterolytic H_2 dissociation. Recently, Wu et al., using in situ inelastic neutron scattering spectroscopy (INS) revealed that the hydride (Ce-H) species is indeed present during the acetylene hydrogenation catalyzed by ceria [45]. In the meantime, Moon et al. detected surface OH species on the ceria catalyst using in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) [70]. These experimental data thus provided strong supporting evidence for the heterolytic dissociation mechanism catalyzed by surface FLPs.

Doping has been shown to enhance the FLP catalytic activity on ceria. For example, Ni doping promotes oxygen vacancies (Figure 4(c)), leading to effective Ce/O FLPs [43, 71] without directly participating in catalysis. Doping of Ga can also lead to novel single atom catalysts in which the LA is provided by the doped metal on ceria surfaces [69], and result in a lower barrier for H_2 activation and more active H species, as illustrated by Figure 4(d). Other dopants include copper [72, 73], for which DFT results show that atomic Cu promotes the formation of O_v [66], leading to Cu/O FLPs to catalyze the cleavage of the H-H bond. These Ce-O FLPs were also found to be active for CH_4 activation, thanks to the strong interaction between the CH_4 molecule and FLPs. In addition, the FLPs are shown to efficiently catalyze the non-oxidative coupling of CH_4 into C_2H_6 and C_2H_4 [74].

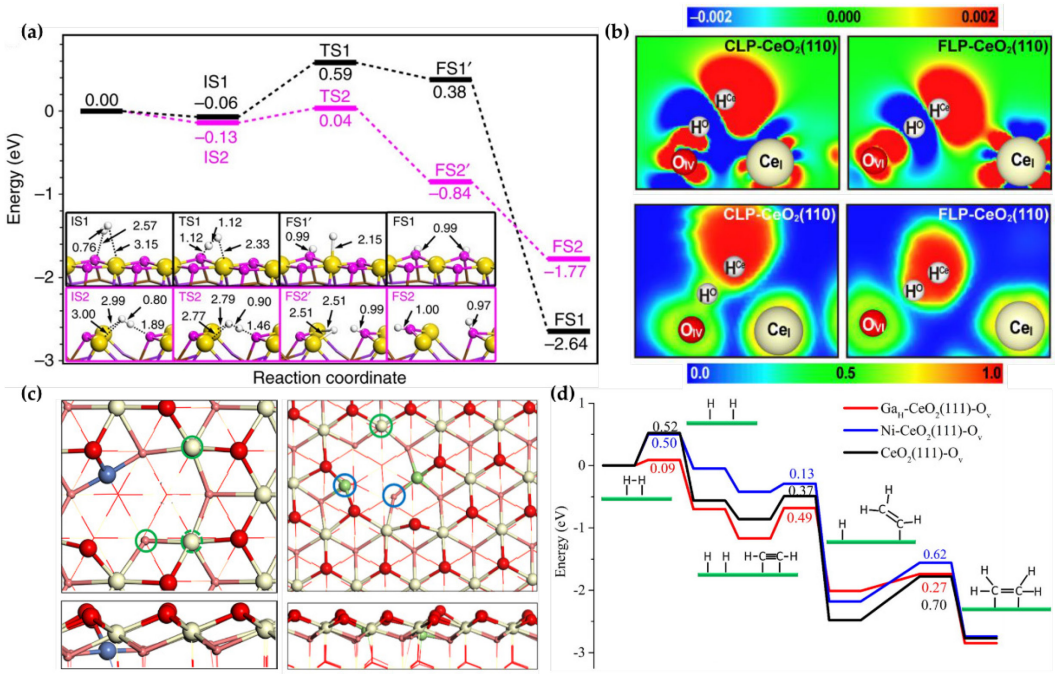

Figure 4. (a) Calculated energy profiles of the FLP (magenta line) and CLP (black line) catalyzed H_2 dissociation on CeO_2(110) with (magenta line) and without (black line) O vacancies. Color code: yellow, Ce; pink, O; white, H. (b) CDD (upper) and ELF (bottom) maps of H_2 activation TS on CeO_2(110). (c) Top and side views of Ni(left)/Ga(right) doped CeO_2(111), FLPs were marked by solid circles. Color code: yellow, Ce; red, O; blue, Ni; green, Ga. (d) Energy profiles of acetylene hydrogenation catalyzed by Ga/Ni-doped CeO_2(111) and defect CeO_2(111). (a), (b), (c), (d) are adapted from Refs. 43, 69, 44 and 70, all with permission.

We further notice a recent DFT study by Lin's group showing that Ti and O sites on anatase TiO_2(100) and TiO_2(110) surfaces can form diverse FLPs with different distance between Ti and O (Figure 5(a)) in the presence of oxygen vacancies [75]. These Ti-O FLPs can heterolytically cleavage H_2 to form Ti-H and O-H species, which then react with acetylene to produce ethylene. Interestingly, the calculation results showed a volcano-shaped relationship between the H_2 activation energy and the strength of the O-H bond (Figure 5b), while the barriers of the first and second steps of acetylene hydrogenation are positively correlated to the strength Ti-H bonds and C_2H_3 adsorption energy, respectively. Importantly, this theoretical prediction on the hydrogenation reactivity of TiO_2 was confirmed by experiment [75], thus providing useful insights for the future development of metal oxide-based FLPs catalysts.

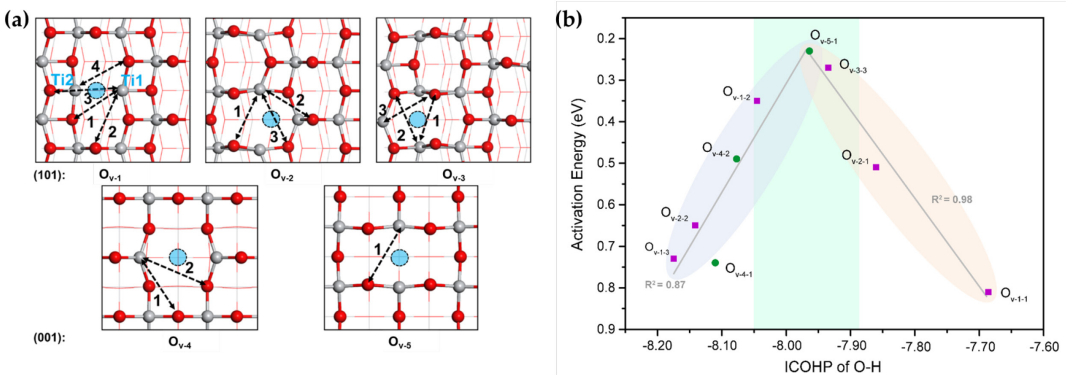

Figure 5. (a) Potential FLPs assembled by Ti and O on anatase TiO_2(101) and TiO_2(001) with O_vs (denoted by blue circles). (b) Correlations between integration of crystal orbital Hamilton population (ICOHP) of O-H with H_2 activation energy. Adapted from Ref. 76 with permission.

It is important to recognize that the FLP is a dynamic entity, whose properties can be altered by external parameters such as temperature. Indeed, the impact of temperature on the surface In/O FLPs in catalyzing RWGS was investigated in the temperature range from 20 to 180°C by using the metadynamics-biased ab initio molecular dynamics (metaD AIMD) [76]. The FLPs were found to be structurally altered at the high temperature (180°C) with the distance between the LA and LB fluctuating by 0.04 Å. This leads to a reduction of the barrier of the heterolytic H_2 dissociation by 0.15 eV compared to that at 20 °C (Figure 6(a)). While the reduction of CO_2, considered as the rate-limiting step, is not sensitive to temperature changes, the calculated energy barrier for the adsorption of CO_2 at the FLPs is reduced by 0.19 eV (Figure 6(b)). The results highlight the important role of thermal fluctuation in the spatially separation of FLPs, which is closely related to the enhanced reactivity.

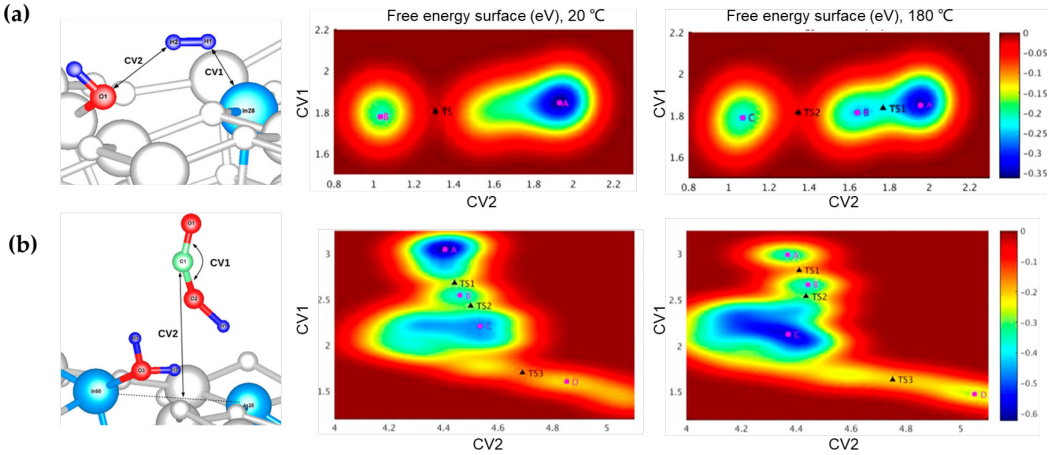

Figure 6. Collective variables (CVs) that used in metaD AIMD simulation of the free energy surfaces of (a) H_2 dissociation and (b) CO_2 reduction catalyzed by In/O FLP under 20 and 180 °C. Color scheme: catalyst surface, white; LA (In), light blue; H, blue; O, red. Adapted from Ref. 77 with permission.

In another example, Fabris and workers computed the free energy surface for H_2 activation on CeO_2(111) using metadynamics [77]. Although no oxygen vacancy was included in the simulation, this study also demonstrated that the barrier (0.73 eV) is significantly reduced at the simulation temperature (350 K) relative to the 0 K result (0.99 eV), due apparently to the thermal fluctuation of the surface O species.

The temperature dependence of stable Ce-O FLPs on CeO_2(110) was discussed by Huang et al., who reported that the formation of surface FLPs is dependent on the number of oxygen vacancies [74]. Although static DFT calculations indicated that the FLPs in the presence of less oxygen vacancies were unstable, AIMD results showed that the FLP sites can dynamically regenerate at high temperatures.

3.2. FLPs based on functionalized surfaces

As discussed in the above section, heterogeneous FLPs on metal oxides are assembled from pre-existing Lewis acid and base sites. However, for most solid surfaces, the chemical environment is relatively simple and does not allow natural formation of FLPs. Therefore, introduction of foreign species as the LA or LB on the surface is an effective strategy to construct surface FLPs. These studies not only provide us with alternative perspectives to understand the processes involved in heterogeneous catalysis, but also extend the application of heterogeneous FLP catalysis and design strategies for future FLP-based catalysts.

The simplest case would be pre-absorption of LAs and LBs on surfaces as the electron acceptor or donor, respectively. Lu et al., found that the pre-adsorption of imine or nitrile

as LBs can enable the efficient H_2 activation on the modified gold surface, where the gold atom serves as LA [47] (Figure 7(a)). The DFT calculation results suggested that the enhanced reactivity of the functionalized gold surface can be ascribed to synergetic effects of the frustrated LA and LB sites, on which the partially filled *s*- and *p*- states of gold accept the electrons from the H_2 σ orbital (Figure 7(b)). Similarly, Fiorio et al. reported that the pre-adsorption of nitrogen-containing Lewis bases on Au nanoparticles can also couple with surface Au atoms to generate heterogeneous FLPs [48, 49]. Interestingly, they found that FLPs composed of Au LA sites and amine species with different basicity can be used to tune H_2 heterolytic activaction, consistent with the experimental observations. Besides, a reaction intermediate can also act as LB. For example, by a first-principles study, Jian et al., demonstrated that $Ni_1(OH)_2/TiO_2$ possess superior reactivity and selectivity for acetylene hydrogenation [78], in which the adsorbed C_2H_3 and C_2H_5 intermediates produced during the acetylene hydrogenation can serve as LBs to form FLPs with the surface Ni sites to accelerate the heterolytic H_2 cleavage. The enhanced reactivity of metal surfaces by the introduction of foreign species to create new FLPs offers a useful strategy for the development of other metal-based hydrogenation catalysts.

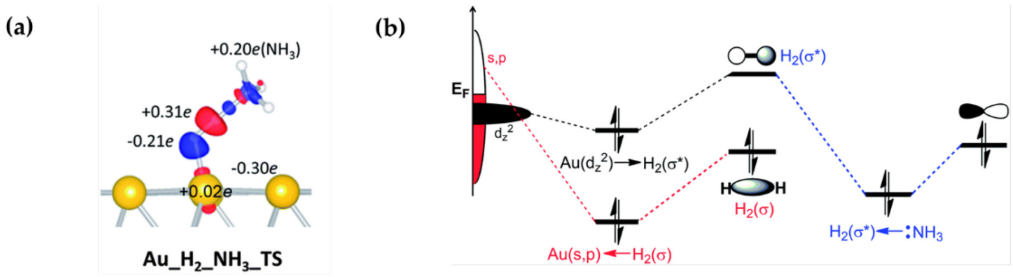

Figure 7. (a) Charge density difference map of the transition state of H_2 activation catalyzed by the Au/NH_3 FLP. (b) Schematic illustration of the favorable interactions among Au, H_2, and NH_3. Adapted from Ref. 48 with permission.

Porous MOFs provide a flexible template and suitable nanospace to create FLPs. For example, Ye et al. reported that 1-(difluoroboranyl)-4-methyl-1H-pyrazole molecule grafted in the MOF of UiO-66 exhibits the characteristics of an FLP formed by P (LB) and B (LA) atoms [79]. From first-principles calculations, the authors found that this FLP has the capacity to catalyze the heterolytic H_2 dissociation to form P-H and B-H species, the key step in the CO_2 reduction with H_2. The calculated minimal energy reaction pathway indicates that the CO_2 is hydrogenated with the pre-adsorbed H species at FLP sites. Such a heterogeneous FLPs (UiO-66-P-BF2) shows a higher reactivity than the homogeneous FLPs catalyst (1-[bis(pentafluorophenyl)boryl]-3,5-aditert-butyl-1H-pyrazole).

In addition, FLPs can also be created via engineering the interface between metal and metal oxide. For example, Zhao et al. reported that interfaces between metallic or oxidized nickel species and a Au surface (Figure 8(a)) are active for H_2O dissociation [80]. Furthermore, their DFT results showed that the $Ni_{13}O_{13}$/Au(111), Ni_{10}/Au(111), $Ni_{10}O_6$/Au(111) and $Ni_{10}O_6$-Ni_6/Au(111) interfaces have different adsorption strengths for the adsorption of H_2O (Figure 8a). Among them, the NiO_x-Ni interface possessed the strongest adsorption of H_2O, which is controlled by the Lewis acidity of the Ni site. In particular, H_2O dissociation at the NiO_x-Ni interface is a spontaneous process (Figure 8(b)) in which metallic Ni acts as an LA to accept the hydroxyl while the O serves as LB to capture proton with the frustrated LA-LB distance of 3.41 Å (Figure 8(c)). This work points out that the heterogeneous FLPs can also be constructed at metal and metal-oxide interfaces, extending the applications of FLP in heterogeneous catalysis.

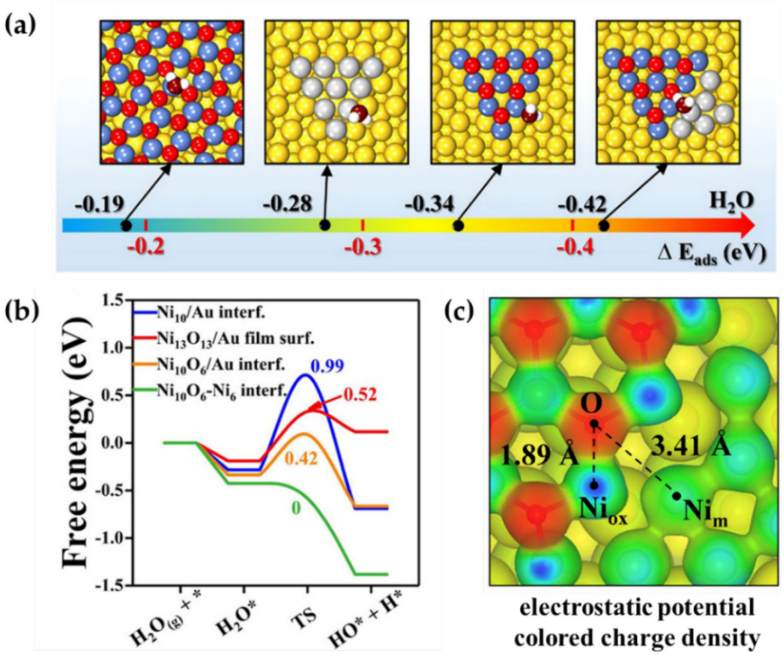

Figure 8. (a) Structures and adsorption of H_2O on $Ni_{13}O_{13}$/Au(111), Ni_{10}/Au(111), $Ni_{10}O_6$/Au(111) and $Ni_{10}O_6$-Ni_6/Au(111). Color code: Au, yellow; metallic Ni, grey; oxidized Ni, blue; oxygen in NiO_x, red; oxygen in H_2O, brown; hydrogen, white. (b) Gibbs free energy diagram of H_2O dissociation on the four surfaces. (c) Electrostatic potential colored electron density of $Ni_{10}O_6$-Ni_6/Au(111). Adapted from Ref. 81 with permission.

Besides the surface FLPs mentioned above, FLPs based on nanostructured carbon materials have also been reported recently. As mentioned above, Primo et al. demonstrated that graphene can hydrogenate the C_2H_2 to C_2H_4 with high conversion rates and selectivity in the absence of noble metals [81]. Interestingly, the addition of metal impurities (e.g., Mn, Pd) affects little the hydrogenation performance, even sometimes decreases the reactivity. The comparison between the performance of graphene, graphene oxide, reduced graphene oxide, and N/P/S-contained graphene also suggested the reactivity originates from intrinsic sites of graphene. More interestingly, the reactivity of graphene was significantly and reversibly affected by the pre-adsorption of CO_2 and NH_3. Based on these observations, Primo et al. concluded that the hydrogenation reactivity can be ascribed to surface FLPs. However, the mechanism from the perspective of FLPs is still unexplained.

Of course, FLPs can also be created by substitutive doping, which changes the chemical structure of graphene. Sun et al. proposed an FLP catalyst for H_2 activation by boron and nitrogen co-doping the bilayer graphene (BN-G) [82]. From DFT calculations, three BN-G configurations were obtained, including AA-stacking (AA-01), AB-stacking (AB-01), and AB-stacking (AB-02). H_2 activation in the interface between the two layers of these three structures was further investigated and compared with the process catalyzed by pristine bilayer graphene. The calculated activation energy of H_2 dissociation on pristine bilayer graphene is 2.3 eV, while 0.99, 1.05 and 1.36 eV on AA-01, AB-01 and AB-02, respectively. It was thus proposed that the FLP formed by B and N catalyzes the heterolytic H_2 cleavage. Furthermore, Sun et al., found that dopants at the graphene edge possess higher reactivity towards H_2 dissociation, H_2 could spontaneously dissociate at the B site on the edge, reveal that the dopants at the edge could contribute more reactivity than that of the dopants in the basal plane.

Besides 2D carbon-based materials, other 2D structures have also been investigated for constructing FLP-based catalysts. Zhao et al. reported an FLP catalyst based on phosphorene via a doping strategy [51]. In particular, the introduced B in the phosphorene

monolayer serves as the LA while P acts as the LB, (Figure 9(a), left). The charge transfer can be seen from the ELF results (Figure 9(a), right): the electron density on the B atom is highly delocalized, indicating it is charge-deficient, while the electron density on the P atom is strongly localized, suggesting that it has lone pair electrons. H_2 activation catalyzed by such an FLP would results in a much lower barrier of 0.59 eV (Figure 9(b)) compared to 2.25 eV on pristine phosphorene, suggesting a high activity of the newly formed FLPs for H_2 activation. They also found that, using Me_2C=O, HCN, and C_2H_4 as probe molecules, the produced H species over the FLPs can attack the unsaturated molecules to complete the hydrogenation catalysis.

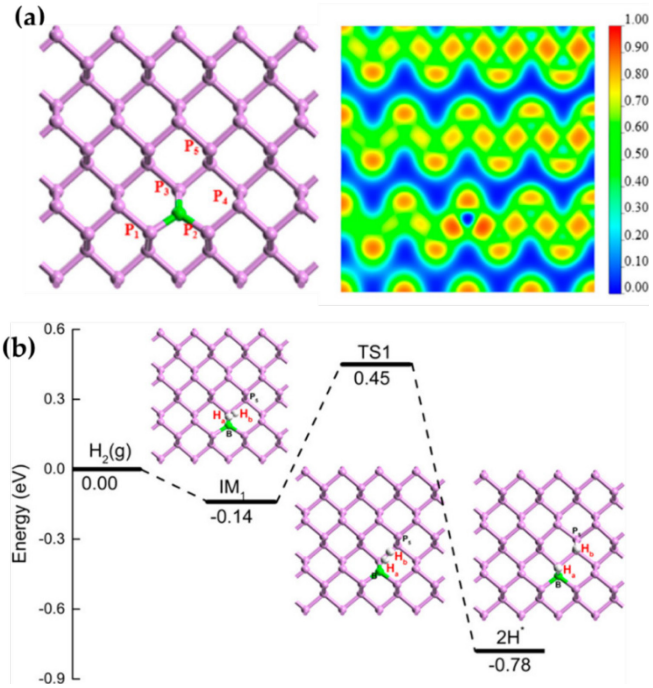

Figure 9. (a) Structure and electron localized function (ELF) diagram of B doped phosphorene. (b) Energy diagram of H_2 activation catalyzed by B doped phosphorene. Adapted from Ref. 52 with permission.

Doping of 2D materials by metals can also lead to FLPs. Chen et al., reported transition metals and boron co-doped phosphorene with promising N_2 reduction reaction (NRR) electrochemical performance [83]. Usually, it is well recognized that the electrocatalytic NRR performance can be improved by stabilizing the key N_2H intermediates [84]. These authors demonstrated an alternative strategy based on concept of FLPs. Accordingly, the B atom acts as the LA to provide an empty orbital while the transition metal acts as the LB to donate electrons for enhancing N_2H adsorption.

Carbon nitride group is another 2D material that is widely used in heterogeneous catalysis [85]. For example, Wan et al. reported Al/B doping C_2N and *g*-C_3N_4 to construct FLPs from their DFT calculations [52]. These theoretical results showed that Al-N FLPs were more active than B-N FLPs for H_2 activation. Introducing Al as the LA breaks the electron-rich environments at the pore edge and form several Al-N combinations with varying electronic structures as FLPs (Figure 10(a)). These FLPs could efficiently activate H_2 to form Al-H and N-H (Figure 10b), which can then hydrogenate C_2H_2 to C_2H_4. Similar to transition states on defect CeO_2(110) (Figure 4(b)), CDD and ELF maps in Figure 10(c) suggested the electron transfer between H_2 with the Al/N FLP. Both cases utilize the intrinsic LB sites of carbon nitride, taking advantage of the introduced electron-deficient LA, to achieve the small molecule activation in the absence of noble metals.

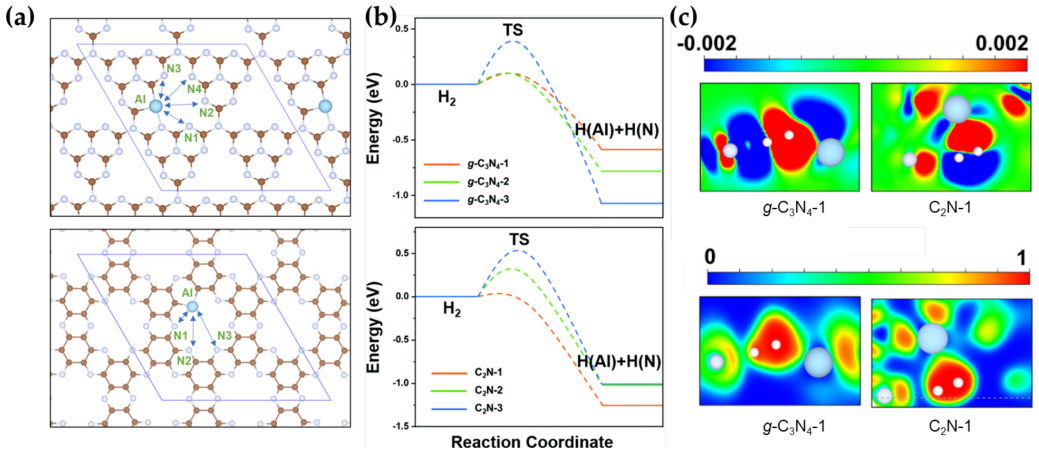

Figure 10. (a) Scheme of potential FLPs on Al-doped *g*-C_3N_4 (upper) and C_2N (bottom). (b) Energy profile of H_2 activation on Al/N FLPs. (c) CDD (upper) and ELF (bottom) maps for TSs of H_2 activation on *g*-C_3N_4-1 and C_2N-1. Adapted from Ref. 53 with permission.

4. Conclusions and prospects

Significant efforts have recently been made to explore the application of heterogeneous FLP catalysts for various reactions. Herein, we provide a comprehensive review of theoretical understanding of the mechanisms of FLP-facilitated heterogeneous catalysis. The insights provided by these theoretical results, coupled with experimental observations, offer a framework for in-depth understandings of heterogeneous FLP catalysis and design principles.

The key to heterogeneous FLP catalysis is the presence of spatially separated but adjacent surface active sites with electron rich and deficient properties, respectively. The geometric separation of these LA and LB sites is important because it prevents direct bonding that would neutralize them, as in a CLP, while offering a suitable cavity for the cleavage of the targeted bond. Hence, the optimization of the separation between the FLP sites and the acidity/basicity is essential for the catalyzed activation of molecules, such as H_2 and CH_4. The adjacent LA and LB sites also polarize the molecule, resulting in a lowered dissociation barrier. In the H_2 case, for example, its dissociation results in the formation of protonic and hydridic species, which can then be used to carry out subsequent reaction steps.

The heterogeneous FLP systems reported so far can be generally divided in to two categories based on materials. One class is based on metal oxides while another relies on functionalizing surfaces. The former has abundant LA(M) and LB(O) sites of its own and is subjected to modifications by external means such as substitutive doping. The doped metal can either serve as the LA, or help to create an LA site through promoting oxygen vacancies. Alternatively, one can also control the LB site by hydroxylation. On the other hand, the latter type relies on the introduction of LA and LB species through functionalization. This can be readily achieved in porous materials such as MOFs, where the distance between the LA and LB sites can be readily controlled. The functionalization can also take place on metal surfaces, where the introduction of LB species transforms metal atoms as LA sites. Non-metal FLPs can be created analogously by doping 2D materials such as graphene. These strategies provide a range of tools in designing FLPs in heterogeneous systems.

The rapid development of the field serves as a manifestation of the powerfulness and universality of the FLP concept in heterogeneous catalysis. We expect a more flexible ways to create FLPs in the future with traditional and novel LAs and LBs. Materials, such as metal-support interfaces and corrugated/reconstructed 2D materials, possessing regions with different electron gaining and losing abilities, might be leveraged to generate poten-

tial FLPs. Due to its outstanding performance in activating small molecules and the avoidance of nobel metals, FLPs have the prospect of wider applications in the future for heterogeneous catalysis. We expect robust future development in this field.

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