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Surface Analogues of Molecular Frustrated Lewis Pairs in Heterogeneous CO_2 Hydrogenation Catalysis

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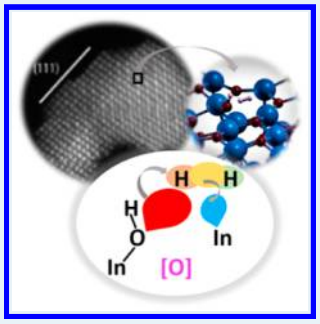

ABSTRACT: The discovery of homogeneous, solution-based molecular frustrated Lewis pairs, denoted FLPs, comprising main-group elements that can activate H_2 heralded a paradigm shift in chemistry and catalysis. In FLPs, unquenched Lewis base and Lewis acid sites (B···A) are able to polarize and dissociate H_2 heterolytically to form adjacent proton and hydride sites (BH^-···AH^+), which can enable reactions such as CO_2 reduction. In this paper, we draw attention to a relationship between these well-known molecular FLPs and the surface active sites comprised of proximal Lewis base and Lewis acid pairs, which have been reported multiple times in the literature to be responsible for driving various heterogeneous catalytic reactions. From our recent studies that described one such surface site in a nanostructured defect laden indium oxide, capable of activating H_2 and enabling the hydrogenation of CO_2, it was conjectured that these sites are surface FLPs. Significantly, the conversion rate for this hydrogenation reaction is observed to be more rapid in the light than in the dark. Kinetic measurements and density functional theory simulations are consistent with a reaction that proceeds via a surface FLP. It is found that the higher Lewis acidity and Lewis basicity in the excited state, which originates from trapping of the photogenerated hole and electron at the FLP acid and base sites, respectively, is responsible for the higher reactivity in the light in comparison to the dark. With the emerging experimental and theoretical understanding of the chemical and physical principles that underpin the reactivity of FLPs in both homogeneous and heterogeneous systems, it is now possible to rationally conceive and synthetically target heterogeneous FLP materials that bear a compositional and structural connection to homogeneous FLP molecules, and vice versa. This synergistic relationship between FLP molecules and materials could prove beneficial in future efforts aimed at expanding the accrued scientific knowledge on photochemical versus thermochemical activation of CO_2 and thereupon to exploit the perceived technological attributes of both systems in the catalytic conversion of carbon dioxide to value-added chemicals and fuels.

KEYWORDS: *frustrated Lewis pairs, homogeneous and heterogeneous catalysis, CO_2 reduction, molecules and materials, heterolytic H_2 splitting, surface chemistry*

■ PREAMBLE

Advances in the chemistry of molecules and materials often have a synergistic relationship, in that knowledge gained on the synthesis, structure, properties, functionality, and utility of one can impact the design, discovery, and development of the other. One can view this paradigm as a type of "chemi-mimetics", where lessons learned from molecules can inspire breakthroughs in materials and conversely information about materials can lead to progress in molecules.

In other words, understanding the physicochemical principles that underpin the behavior of molecules can be invaluable for creating materials that exhibit similar behaviors. Analogously, molecules can be crafted that emulate the characteristics of materials. In each case, the chemical and physical properties of one can benefit from the attributes of the other. In hybrid systems, which chemically integrate key traits of molecules and materials, new features can emerge which can transcend the sum of the component parts.

Nowhere is this relationship between the chemical and physical properties of molecules and materials more apparent than in the fields of homogeneous and heterogeneous catalysis. There are numerous documented examples where knowledge of one benefited advances in the other, such as leading to highly efficient and cost-effective heterogeneous and homogeneous catalysts for the synthesis of chemicals.[1]

In what follows we describe how recent developments in the chemistry and catalysis of molecules containing *frustrated Lewis pairs* (FLPs) have been recognized to have a natural

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Box 1. Heterogeneous Catalysis Basics

The chemical industry is one of the largest manufacturing sectors in the world, with global sales currently valued at around \$5B. Many manufactured products in the chemical industry are enabled by heterogeneous catalysts. These processes often involve chemical reactions of gaseous reagents on high-surface-area metal oxides. In the field of heterogeneous catalysis, with a long and stellar history of pioneering accomplishments, it has been well documented that surface acidity and basicity involving Lewis and Brønsted acidic and basic sites determine activity, selectivity, and turnover numbers and frequencies of catalytic reactions. The population, strengths, and electronic and steric effects of surface acid and base sites in metal oxide heterogeneous catalysts and the manner in which they influence activity−selectivity patterns have been investigated in great detail and correlated with their structure and composition and often discussed in terms of the electronegativity of element constituents. With the recent discovery of molecules containing frustrated Lewis pairs (FLPs), containing proximal nonbonded Lewis acid−Lewis base sites, which are able to heterolytically dissociate H_2 for subsequent reactions with CO_2, it is interesting to explore how homogeneous chemistry and catalysis of molecule FLPs relates to similar chemistry that occurs on metal oxide surfaces, which also contain proximal Lewis acid−Lewis base sites and may be considered as “surface FLPs”. This Perspective discusses whether or not thinking about surface acidity and basicity in terms of FLPs is something new or something old, is something useful and serves a practical purpose, or is something uninformative and unhelpful.

counterpart in materials chemistry and catalysis. Herein we focus attention on FLP molecules and materials, which have the capacity to activate H_2 and CO_2 to form value-added chemicals and fuels.

To amplify, FLPs are generated when a main-group Lewis base and Lewis acid are combined without forming a “classical” Lewis base−Lewis acid adduct but instead leave the basicity and acidity unquenched due to the steric bulk of their substituent ligands. This unquenched nature of their nucleophilic and electrophilic sites leads to unusual but significant chemical reactivity of “frustrated” systems, making them capable of activating small molecules.[2] For example, molecular FLPs can induce the heterolytic cleavage of H_2, reversible binding and release of CO_2, and hydrogenation of CO_2 to CO. The combination of a phosphine and borane Lewis base and acid respectively was the first non transition metal based molecular system known to reversibly activate hydrogen.[3−6]

In this context, and as discussed in more detail in the closing section of this paper, this kind of activation of H_2 by Lewis acid and Lewis base sites on the surface of main-group-metal oxides has been well documented in the surface chemistry and heterogeneous catalysis literature, at least half a century prior to the discovery that molecular and surface FLPs can heterolytically split H_2 and activate CO_2 under mild conditions.[2−13]

What is interesting is the recently realized relationship of the reactivity of molecular FLPs with H_2 and CO_2 to similar kinds of surface chemical reactions, discovered for prototype nanostructured materials, exemplified by the metal oxide archetype $In_2O_{3-x}(OH)_y$ with H_2 and CO_2.[7−13] Similar to the case for molecular FLPs, the surface of $In_2O_{3-x}(OH)_y$ contains main-group elements arranged as spatially separated Lewis base and Lewis acid sites, denoted InOH···In, which comprises a surface FLP.

To amplify, in this surface FLP, the terminally bonded surface hydroxide group (OH) acts as a Lewis base and the coordinately unsaturated surface indium (In) site acts as a Lewis acid. They function synergistically to heterolytically dissociate adsorbed H_2 on the surface of $In_2O_{3-x}(OH)_y$, as seen in steps II and III in the reaction scheme shown in Figure 1.

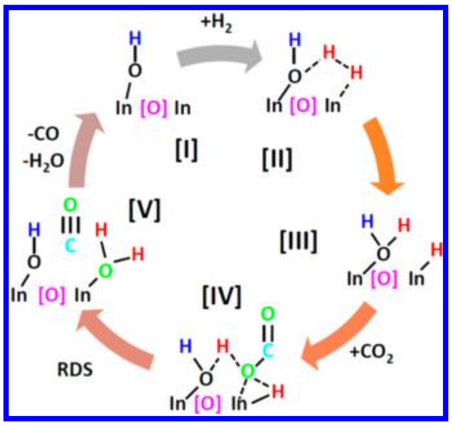

Figure 1. Proposed mechanism for the thermally enabled reverse water-gas shift (RWGS) reaction, $CO_2 + H_2 \rightarrow CO + H_2O$, by $In_2O_{3-x}(OH)_y$ nanostructured materials.[10] Reproduced from ref 10. Copyright 2015, Royal Society of Chemistry.

The so-formed protonic and hydridic surface FLP sites serve to capture and convert CO_2 to CO and H_2O, as seen in steps IV and V shown in Figure 1. While the attack of the negative hydride on the oxygen atom in IV rather than the carbon in the experimentally determined rate-determining step seems counterintuitive, it is possible that the proton attacks the O of adsorbed CO_2 first, which then reacts with hydride to form product water followed by release of CO. In situ FTIR studies will help clarify this key point.

The surface FLP catalyst can also be envisioned as a kind of surface-immobilized molecular catalyst,[14] a hybrid FLP, which combines the properties of both homogeneous and heterogeneous FLPs. This chemi-mimetic connection between FLP molecules and materials, as mentioned above, speaks well for the development of new classes of FLP heterogeneous catalysts built from molecules and materials, as well as hybrid combinations thereof.

HETEROGENEOUS−HOMOGENEOUS FLP ANALOGY

Recent DFT analyses of molecular FLPs provided a thought-provoking insight into the “FLP advantage” in the case of the activation of H_2 on the archetype $R_3P\cdots BR'_3$.[15] The origin of this FLP advantage was described in terms of ΔE_f, the energy of frustration. This represents the difference in energy between the classical Lewis base−Lewis acid complex $R_3P\rightarrow BR'_3$ and the FLP equivalent $R_3P\cdots BR'_3$, in which sterically demanding R and R′ organic groups prevent the formation of a normal donor−acceptor dative bond. Instead, the donor and acceptor are kept apart but are at a nonbonding distance and function thereby as loosely bound, energetically challenged, and highly reactive species for enabling H_2 activation. The resultant effect is to destabilize $R_3P\cdots BR'_3$ with respect to $R_3P\rightarrow BR'_3$, causing a reduction of the activation barrier ΔE_f for the heterolytic dissociation of H_2. The resulting zwitterionic complex $R_3PH^+\cdots^-HBR'_3$ can then bind and participate in reactions with CO_2 to form reduction products such as CO, HCO_2H, and CH_3OH in a stoichiometric or catalytic manner.

A similar energy advantage was found for surface FLPs. Our previous analysis showed that not every O vacancy site substituted with OH to form $In_2O_{3-x}(OH)_y$ was active for H_2 dissociation.[7−13] Only those sites that were able to make surface FLPs InOH···In were active; others acted as the classical Lewis base−Lewis acid complex InOH→In. The postulated "surface FLP frustration energy advantage" in this situation, denoted ΔE_{sf}, is the difference in the activation barrier for the heterolytic dissociation of H_2 on the classical Lewis base−Lewis acid complex InOH→In and the FLP analogue InOH···In, illustrated in Figure 2. The preliminary results of this theoretical analysis have estimated ΔE_{sf} as 1.15 eV for the $In_2O_{3-x}(OH)_y$ system.[16]

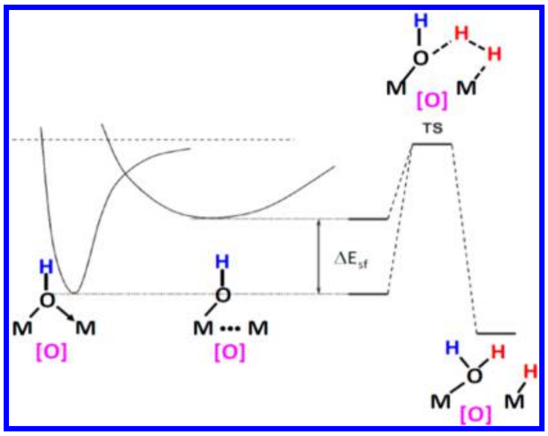

Figure 2. Tuning the reactivity of surface frustrated Lewis pairs (FLPs) in $M_2O_{3-x}OH_y$, where M = In and ΔE_{sf} = surface frustration energy advantage, which can be tuned through chemistry control of the Lewis acidity and Lewis basicity of surface metal M (acceptor) and surface hydroxide OH (donor) sites, respectively. In this diagram MOH→M represents a conventional Lewis base−Lewis acid surface complex, whereas MOH···M depicts the surface FLP. Graphic adapted from ref 11. Copyright 2016, American Chemical Society.

This model nicely explains the energy landscape and origin of the reactivity of molecular FLPs. It can provide a rationalization of the energetics and dynamics that underpin the surface chemistry responsible for the recently discovered reverse water-gas shift (RWGS) reaction, $CO_2 + H_2 \rightarrow CO + H_2O$, catalyzed by nanostructured forms of $In_2O_{3-x}(OH)_y$ illustrated in Figure 1. The mechanism, which is founded upon DFT analysis, supports the proposal that an active FLP surface site comprised of proximal and spatially locked Lewis acid In(III) and Lewis base OH(−I) sites enables the RWGS reaction.[7−13]

Significantly, it is found that stoichiometric In_2O_3 nanocrystals with the bixbyite crystal structure are inactive for the $CO_2 + H_2 \rightarrow CO + H_2O$ reaction in the dark and in the light. Hence, this is justification for the use of the notation InOH→In for the surface site analogous to $R_3P\rightarrow BR'_3$. In contrast, nonstoichiometric $In_2O_{3-x}(OH)_y$ with hydroxyl groups is very active, much more so in the light than the dark, supporting the use of the notation InOH···In for the surface FLP site analogous to the FLP in $R_3P\cdots BR'_3$. These observations strongly suggest that the presence of both the Lewis acid In(III) and the Lewis base OH(−I) surface sites is a prerequisite for the RWGS reaction and a rationale for the origin of the activity of $In_2O_{3-x}(OH)_y$ in comparison to the inactivity of In_2O_3 for this reaction.

By analogy with the reactivity of the molecular FLP, the resulting zwitterionic surface site denoted $InOH_2^+\cdots^-HIn$ that results from the adsorption and heterolytic dissociation of H_2 on the FLP InOH···InH site (Figure 2) is then able to bind and react with CO_2 to form reduction products as illustrated in Figure 1. Even though, in this particular example, there exist activation barriers for the H_2 heterolytic dissociation at the pristine FLP InOH···InH site (DFT, E_a = 0.6 eV) as well as the CO_2 adsorption reaction at the FLP $InOH_2^+\cdots InH^-$ site (DFT, E_a = 1.0 eV), the rate-determining step (RDS) is controlled by the higher E_a process, namely IV → V in Figure 1, in agreement with kinetic measurements.[7−13] A key point is that In_2O_3, devoid of Lewis base hydroxide groups is not able to heterolytically split H_2, whereas the $In_2O_{3-x}(OH)_y$, which contains hydroxides, is the active form able to do so.

It is now apparent that the reactivity of surface FLPs for the reduction of CO_2 by H_2 can in principle be rationally and systematically fine tuned by judicious control of the Lewis basicity and Lewis acidity of proximal surface hydroxide and coordinately unsaturated metal sites, respectively, in nanostructured metal oxide materials, as illustrated in Figures 1 and 2.

■ THERMOCHEMICAL VS PHOTOCHEMICAL CO_2 REDUCTION

To the best of our knowledge, there are no reported examples of light-activated hydrogen reactions of CO_2 by molecular FLP.[2] In contrast, the $In_2O_{3-x}(OH)_y$ nanostructured material has been found to drive the RWGS reaction illustrated in Figure 1 by many orders of magnitude faster in the light than in the dark, with a corresponding reduction in measured activation energy of 20 kJ/mol.[7−13]

To delve more deeply into this key observation, we investigated, theoretically and experimentally, the unique photoactive behavior of pristine and defected indium oxide surfaces. These studies provided a fundamental insight into their excited state properties as well as an explanation for the experimentally observed enhanced activity of defected indium oxide surfaces for the gas-phase RWGS reaction, $CO_2 + H_2 \rightarrow CO + H_2O$, in the light in comparison to the dark.[7−13]

To this end, a detailed excited state study of pristine and defected forms of indium oxide (In_2O_3, In_2O_{3-x}, $In_2O_3(OH)_y$, and $In_2O_{3-x}(OH)_y$) surfaces was performed using time-dependent density functional theory (TDDFT) calculations, the results of which were supported experimentally by transient absorption spectroscopy and photoconductivity measurements.[11,12]

It was found that the surface FLPs created by a Lewis acidic coordinately unsaturated surface indium site situated proximal to an oxygen vacancy and a Lewis basic surface hydroxide site in $In_2O_{3-x}(OH)_y$ become more acidic (hole trapping) and more basic (electron trapping), respectively, and hence more active in the ES in comparison to the GS, as illustrated in Figure 3. This description of the ES in comparison to the GS provides a rationale for the enhanced activity and reduced activation energy of the photochemical RWGS reaction observed experimentally for $In_2O_{3-x}(OH)_y$ in comparison to the thermochemical reaction.[11,12]

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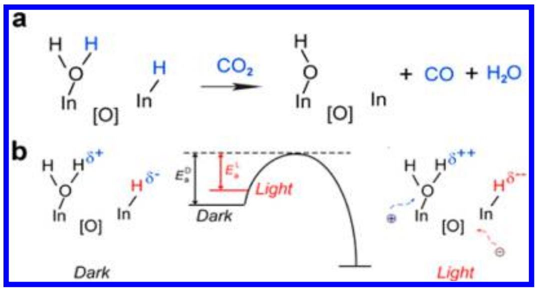

Figure 3. Schematic illustration of the origin of the difference in the experimental activation energy $(\Delta E_a)_{exptl}$ for the RWGS reaction, $CO_2 + H_2 \rightarrow CO + H_2O$, involving the GS surface FLP in the dark and ES surface FLP in the light. The computational analyses of the GS and ES of the $In_2O_{3-x}(OH)_y$ cluster model showed that for the rate-determining step the photogenerated electrons and holes trapped at the Lewis acid and Lewis base sites of an ES surface FLP enhance their Lewis acidity and Lewis basicity in comparison to the GS surface FLP. This increased frustration of charges at the surface Lewis pair consequently decreases the activation barrier for the overall CO_2 reduction reaction, which is supported by experimental measurements.[10−13,16,17]

■ ACTIVE SURFACE LB···LA FLPS VERSUS INACTIVE SURFACE LB→LA PAIRS

Another enquiry concerns the factors which control the observed "volcano" dependence of the gas-phase light-assisted CO_2 to CO hydrogenation rate on the temperature of dehydroxylation of the $In(OH)_3$ precursor.[8,10] Pivotal is the balance between terminally bonded InOH···In versus bridge-bonded InOH→In moieties for $In_2O_{3-x}(OH)_y$, where the former is considered akin to an active P···B FLP while the latter is closer to an inactive P→B FLP, as illustrated in Figure 4.

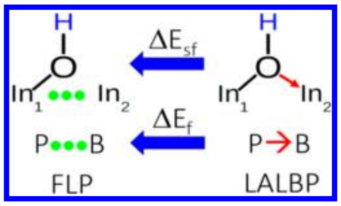

Figure 4. Tailoring the reactivity of a surface FLP: active surface FLP and inactive surface LALBP (top left and right) versus active molecule FLP and inactive molecule LALBP (bottom left and right), where ΔE_{sf} and ΔE_{mf} are the frustration energies for the surface and molecule cases, respectively.

Conceptualizing this problem can be viewed as a piece of classical inorganic chemistry: the stronger the Lewis acid (LA) of the In coordinately unsaturated site, the more it will want to accept charge from the neighboring InOH Lewis base (LB) hydroxyl group to form a bridge bond. This situation will be favored for an InOH group in the proximity of an oxygen vacancy [O] site where the neighboring "super-coordinately unsaturated" In site will be a stronger LA.

In this way one can begin to appreciate why the temperature and time profile of the dehydroxylation of the $In(OH)_3$ precursor, written in the balanced stoichiometric form $2In(OH)_3 \rightarrow In_2O_xOH_{6-2x}[O]_{(6-x)/3} + xH_2O \rightarrow In_2O_3 + 3H_2O$, will control the precise O:OH:[O] ratio in the thermally produced catalyst, denoted $In_2O_xOH_{6-2x}[O]_{(6-x)/3}$. This thermal treatment in turn will determine the local structural and electronic environment and the Lewis acidity and Lewis basicity in the immediate vicinity of the proximal In and InOH sites, all of which will most likely be crystal face dependent.

Experimentally and theoretically it is found that low-index (111) faces are favored and the activity for the RWGS reaction is maximized for a dehydroxylation temperature of 250 °C with "volcano" dependence for the CO_2 hydrogenation rate in the dihydroxylation range of 200−350 °C. This is the temperature regime where the bixbyite structure is favored, nanocrystal sintering does not occur, the surface area remains essentially the same, and the CO_2 adsorption capacity is optimized.[8,10]

So this raises the following question: what is special about 250 °C? It is all connected to the value of x at this particular temperature in the nanostructured $In_2O_xOH_{6-2x}[O]_{(6-x)/3}$ catalyst, which can be established by quantification of the intensities of the XPS ionization potentials for O:OH:[O].[18−22] In the dehydroxylation of the $In(OH)_3$ precursor, bridging OH groups existing between every octahedral In site gradually transform into bridging O, terminal-bridge OH, and [O] vacancies in $In_2O_xOH_{6-2x}[O]_{(6-x)/3}$ to form just bridging O and [O] vacancy sites in fully dehydroxylated In_2O_3. A value of x must therefore exist at 250 °C, where the charge density around the LA In and LB InOH favors an active FLP with a terminal InOH denoted InOH···In rather than an inactive LA and LB pair with a bridge-bonded InOH→In, as illustrated in Figure 4.

■ TAILORING THE REACTIVITY OF SURFACE FLPS

With the information accrued on the structure, property, and surface chemistry relations that appear to govern the thermochemical and photochemical activity of $In_2O_{3-x}(OH)_y$ for the RWGS reaction, one can begin to think about how to systematically tune the elemental composition of the material to improve the efficiency of this conversion process.

Because proximal LA and LB surface sites in an FLP configuration have been implicated in the ground and excited state RWGS reactivity of $In_2O_{3-x}(OH)_y$, a logical approach to tailor its activity is to tune the LB of the InOH site and the LA of the coordinately unsaturated In site. The LB of the InOH sites will be largely determined by the electronegativity of the In to which the donor OH is bonded, while the LA of the coordinately unsaturated In will be finely influenced by the population of [O] vacancies.

Mechanistically, it is known that the activation energy for the adsorption and heterolytic splitting of gaseous H_2 on the InOH···In surface FLP, the first step in the RWGS reaction, will depend on the electrostatic polarization created by the adjacent LB and LA sites. This implies that an increase in either LB and/or LA in the ground or excited state will serve to decrease the activation barrier for the H_2 dissociation step.

This initial step in the RWGS reaction creates a modified FLP surface, denoted $InOH_2^+$···InH^-, which subsequently serves to adsorb gaseous CO_2. It is known that the CO_2 bends and through one of its oxygens binds to the proton and hydride sites of the surface FLP. In the rate-determining step that follows, proton and hydride transfer to the bonded oxygen of adsorbed CO_2 produces CO and H_2O, the latter being adsorbed to the surface at the LB, LA, or [O] site. The adsorbed product H_2O must be desorbed for the RWGS reaction to proceed; hence, its strength of binding to these surface sites is another materials parameter that needs to be considered and tuned for optimization of conversion rate and yield.

Each of the above steps in either the thermally and/or photochemically driven RWGS reaction of $In_2O_{3-x}(OH)_y$ will be affected by the LA and LB of the surface FLP in its ground and excited state. Therefore, to tailor the reactivity to advantage, it is important to understand how element variations of the ground and excited state surface FLP InOH···In, designed to partially or completely substitute for the metal and oxygen sites and control the population of [O], ultimately affect the energetics and dynamics of H_2 dissociation, CO_2 adsorption and reaction, and H_2O and CO desorption. An interesting question is whether there is an optimal distance to activate hydrogen and how this activation changes as the distance between the LA and LB sites changes. This point has been addressed in a recent meta-dynamics-biased ab initio molecular dynamics study that investigated the free energy landscape of the multistep RWGS reaction on $In_2O_{3-x}(OH)_y$ at 20 and 180 °C and explained the effect of temperature on the geometry of the FLP surface FLP site.[13] Interestingly, it was found that, because the lattice of $In_2O_{3-x}(OH)_y$ expands with increasing temperature, the separation between the LB InOH and LA In sites of the surface FLP increases, which contributes to the experimentally observed enhanced reactivity. In this context, it is noteworthy that some homogenerous systems form classical Lewis acid–base adducts but only access FLP reactivity by a dissociative equilibrium.[23]

Another key point to consider in the dynamics of the gas-phase light-assisted RWGS reaction is the lifetime of the photogenerated electron–hole pair responsible for the excited state reactivity. This lifetime appears to depend on electron and hole trapping in oxygen vacancies and surface hydroxide groups, respectively. It is believed that photogenerated electron and hole localization in these surface sites enhances their Lewis acidity and basicity, lowering the activation energy for the RWGS reaction under illumination.[11,12] Therefore, the type and population of LB, LA, and [O] sites in the surface FLP matter, where the longer the photogenerated electron and hole pair survive, the greater the probability of their surface chemical reactions with CO_2 and H_2 in the RWGS reaction to produce CO and H_2O. In this respect, the photoexcitation and -relaxation processes involving a large number of defect states are highly complex, as illustrated in Figure 5 for the $In_2O_{3-x}(OH)_y$ surface,[17] and it is currently very difficult to draw conclusions about the specific relaxation pathways and lifetimes of the charge carriers in these materials.

How then can one achieve the above reactivity enhancement in practice? Through rational composition variations in the direct synthesis one can expect to partially or completely substitute the surface In(III) cation sites for metals $M(q+)$ or the $O(-II)$ anion sites for $E(q-)$ with the same or different oxidation states, (Figure 6). Controlling the distribution of metal sites within these new materials will be synthetically challenging and will likely require some trial and error; however, computational simulations may help to more rationally guide materials selection and reduce the number of elements to explore.

In this way it is possible to synthesize surface FLPs MOH··· M in which the LA and LB of the cation and anion sites can be systematically altered to optimize their reactivity in the gas-phase light-assisted RWGS reaction. Some proposed variations of the composition field through the direct synthesis pathway include the following:

$MOH{-}In(OH)_3 \quad M = Li, Na, K, Rb, Cs$

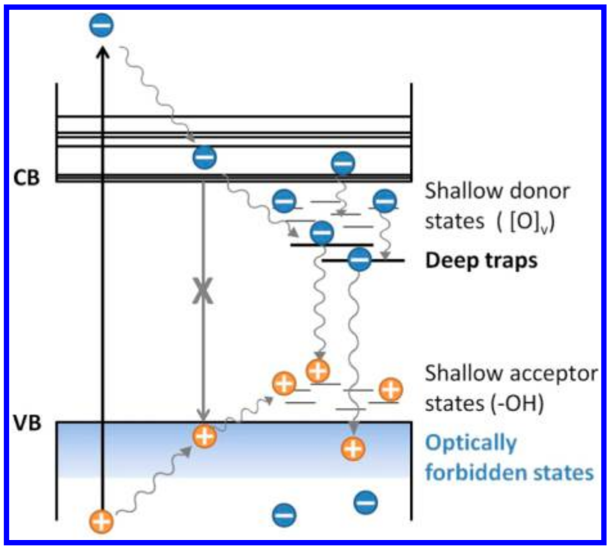

Figure 5. Schematic illustration of charge carrier recombination pathways in $In_2O_{3-x}(OH)_y$ nanoparticles. The vertical black arrow indicates initial excitation from the pump pulse. The wavy gray arrows illustrate different nonradiative relaxation processes.[17]

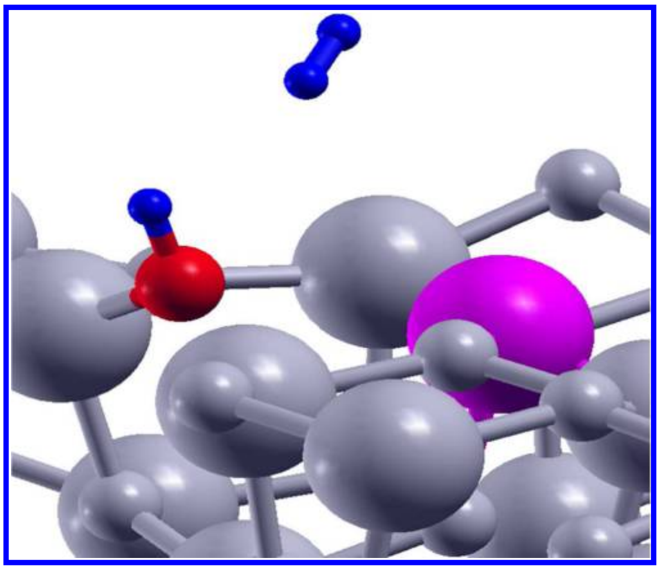

Figure 6. Tailoring the reactivity of a surface FLP in $In_2O_{3-x}(OH)_y$ with H_2 and CO_2, through isomorphous substitution of the Lewis acid In(III) site (large white sphere) and/or the Lewis base InOH site by $M(q+)$ (large purple sphere). Reproduced from 13. Copyright 2016, American Chemical Society.

$M(OH)_2{-}In(OH)_3$

$M = Zn, Cd, Hg, Sn, Pb, Mn, Ni, Cu$

$M(OH)_3{-}In(OH)_3 \quad M = Sb, Bi, Fe, Co$

$M(OH)_4{-}In(OH)_3 \quad M = Sn, Ti, Ce$

SURFACE FLPS: SOMETHING NEW, SOMETHING OLD?

A periodic table of metal oxides has enabled a wide range of heterogeneous catalytic reactions.[18−20] The kinetics and mechanisms of reactions that are thermally enabled are intimately related to how surface acidity and basicity affect the processes of adsorption, reaction, and desorption of reactants, intermediates, and products with solid surfaces. To this end, the acidity and basicity of surface sites, hydroxyl groups, and oxygen vacancies have always played a central role in the annals of heterogeneous catalysis and there exists a vast and impressive literature spanning more than half a century that describes in detail their effect on a myriad of surface chemical and catalytic processes.[18−22,24−28] By comparison, in light-assisted heterogeneous catalysis, the effect of photogenerated electrons and holeson surface acidity and basicity, hydroxyl groups, and oxygen vacancies is of a more recent vintage and under active investigation.[11,12]

With this history of early accomplishments one can justifiably ask the following: what new insight does the FLP paradigm bring to the subject of surface chemistry and heterogeneous catalysis generally and specifically how does the FLP way of thinking help with the challenge of understanding the underlying chemical and physical principles that underpin the use of solar power for converting gaseous CO_2 to fuel? Is the concept of surface FLPs applied to the gas-phase light-assisted hydrogenation of CO_2 something new and exciting or just a rethinking of existing ideas and normal practice of surface acidity and basicity?

In the archives of metal oxide surface chemistry and catalysis, a theme running throughout the research and development of optimized systems has been understanding the origin, controlling the action, and tuning the efficacy of Lewis and Brønsted acid and base sites in thermally and photochemically enabled heterogeneous catalysis. The goal has always been the creation of rules for manipulating the acidity and basicity of surfaces to control activity and selectivity of chemical and catalytic reactions.[18−22,24−28]

In the context of metal oxides it has long been known that cationic surface sites can be viewed as Lewis acids whose acid strength will depend on their ionic potential (charge to radius ratio), coordination number and geometry, and electronic properties. Anionic oxide and hydroxide surface sites, on the other hand, can function as Lewis bases, the strength of which will depend on the properties of the cation and its local environment. Oxygen vacancies in the surface of a metal oxide are lattice sites that can behave as Lewis bases if the anionic electron charge is retained or Lewis acids if the charge is transferred locally to a reducible metal cation or delocalized into the conduction band.[29] The oxygen vacancies can be intrinsic in stoichiometric or extrinsic in nonstoichiometric metal oxides and their Lewis acid and Lewis base strength will depend upon their local environment. Surface hydroxyl groups can also serve as Brønsted acid or base sites being able to donate or accept a proton and are present to some extent in most metal oxides.[18−22,24−28]

Because of differences in the structure, bonding, and electronic properties of different crystal faces of metal oxides, the Brønsted or Lewis acidity or basicity of surface sites will be dependent on the crystal face and on how the surface structure relaxes due to surface reconstruction. Furthermore, adsorption on these surface acid or base sites is a cooperative process which will influence the acidity and basicity of neighboring sites.

The quantification of Brønsted and Lewis acid and base strength, as well as their population, can be achieved by one or a combination of indicator, molecule probe infrared spectroscopy, calorimetric enthalpy of adsorption, and temperature-programmed thermal desorption methods.[28,30] One can appreciate that, while the heterogeneous catalysis literature of metal oxide materials is replete with experimental and theoretical studies of Brønsted and Lewis acidity and basicity, there is no general theory able to predict their surface chemistry and reactivity.

Nanostructured metal oxide based heterogeneous catalysts are very appealing as platforms for driving thermochemical and photochemical gas-phase reduction reactions of CO_2 due to their stability under a range of operating conditions, ease of preparation with low-cost reagents, and ability to scale to technologically relevant proportions. With a century of heterogeneous catalysis in the chemical and petrochemical industries, the ability to integrate new CO_2 reduction materials and processes into a well-established infrastructure would remove many bottlenecks for establishing a CO_2-based chemical and petrochemical economy.[31]

■ OUTLOOK

While the past and present literature on this interesting topic clearly bear striking relationships, it is our contention that recognition and elaboration of the connection between molecular and surface FLPs in homogeneous and heterogeneous catalysis, respectively, specifically in the context of carbon dioxide hydrogenation, is not just a reframing of old ideas. Rather, the recognized symbiosis between FLP molecules and materials enables a new and fresh view of the surface chemistry and a deeper insight into how to chemically tailor, by design, the surface structure and composition of nanostructured metal oxides, to optimize the chemical and catalytic reactivity of the surface FLPs.

It is our view that what we have here is not simply a case of rediscovery of surface acidity and basicity in surface chemistry and catalysis. Instead, it represents a new way of thinking about old ideas in heterogeneous catalysis that have emerged from the recent discovery of FLPs. This paradigm can now be exploited in studies aimed at enhancing and enriching experimental and theoretical innovation in the burgeoning field of CO_2 fixation to chemicals and fuels.

The fundamental insight that has been accrued concerning the role of ground state and excited state surface FLPs for CO_2 reduction could lead to new ways of discovering improved photocatalysts for solar fuel production. While there is still much to do before large-scale solar fuel production becomes a commercially viable technology, it is our hope that the work described herein will provide some help and guidance in (i) elemental composition selection, (ii) materials design, and (iii) surface structural engineering, to enable discovery of the next generation of gas-phase CO_2 reduction photocatalysts.

It is exciting to note that around the time of our first report of surface FLPs in $In_2O_{3-x}(OH)_y$ and their participation in heterogeneous catalytic reactions of CO_2 and H_2,[10−12] others have discovered surface FLPs in other systems. These include H_2 activation by B,N-doped graphene[32] and small-molecule and organic hydrogenations by platinum-loaded zeolite Y.[33] Interestingly, molecular phosphine and borane Lewis acids and Lewis bases have been supported on silica, and this new type of homogeneous−heterogeneous hybrid FLP has been demonstrated to show unprecedented catalytic activity and stability in the *Z*-selective hydrogenation of 3-hexyne to (*Z*)-3-hexene with a selectivity up to 87%. This activity was found to be similar to that found for homogeneous FLP analogues.[34]

Altogether, the advances presented in this Perspective bode well for the future development of heterogeneous FLPs, as well as hybrid homogeneous−heterogeneous FLPs, in synthetic chemistry and catalysis.

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Notes

The authors declare no competing financial interest.

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