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Heterogeneous catalytic hydrogenation of CO_2 by metal oxides: defect engineering – perfecting imperfection

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Metal oxides with their myriad compositions, structures and bonding exhibit an incredibly diverse range of properties. It is however the defects in metal oxides that endow them with a variety of functions and it is the ability to chemically tailor the type, population and distribution of defects on the surface and in the bulk of metal oxides that delivers utility in different applications. In this Tutorial Review, we discuss how metal oxides with designed defects can be synthesized and engineered, to enable heterogeneous catalytic hydrogenation of gaseous carbon dioxide to chemicals and fuels. If this approach to utilization and valorization of carbon dioxide could be developed at industrially significant rates, efficiencies and scales and made economically competitive with fossil-based chemicals and fuels, then carbon dioxide refineries envisioned in the future would be able to contribute to the reduction of greenhouse gas emissions, ameliorate climate changes, provide energy security and enable protection of the environment. This would bring the vision of a sustainable future closer to reality.

Key learning points

(1) Experimental and theoretical aspects of different types of defects in stoichiometric and non-stoichiometric metal oxides.
(2) Function of defects in metal oxides on the heterogeneous hydrogenation of CO_2.
(3) Adsorption and reaction of H_2 and CO_2 with defect-free and defect laden metal oxides.
(4) Thermochemical, photochemical and photothermal aspects of heterogeneous catalytic hydrogenation of CO_2 by metal oxides and support, promoter and inhibitor effects.
(5) Road-map for CO_2 utilization and champion CO_2 heterogeneous hydrogenation catalysts.

Introduction

Imagine a future, where a global network of pipelines delivers renewable fuels made from carbon dioxide, to power our industries, transportation systems, buildings and homes around the world. These renewable fuels will be made in carbon dioxide refineries using catalysts that are driven by renewable forms of electrical, solar and thermal energy, in a sustainable carbon-neutral carbon-cycle.

A global scale energy transition in which carbon dioxide is employed as a recyclable feedstock for making fuels, rather than treated as a waste product from the combustion of fossil fuels, will require technologies that can be scaled to handle hundreds of megaton carbon dioxide conversion processes, at an efficiency and cost that can compete with fossil resources.

In this regard, existing chemical and petrochemical industrial infrastructure, renowned for large-volume production of chemicals and fuels using heterogeneous catalysis, has the capacity to enable CO_2 utilization processes that can operate at such globally significant scales, to enable this perceived energy transition. The development of CO_2 refineries and other approaches to facilitate greenhouse gas reduction together are envisioned to play an important role in ameliorating climate change.

To realize this Utopian vision of a sustainable future in which fossil fuels are gradually replaced by renewable fuels using carbon dioxide as a feedstock, viewing it as an asset rather than a liability, there is an urgent need to discover and develop highly active, selective and stable heterogeneous catalysts that can power tomorrow's CO_2 refineries with an environmentally friendly energy balance, economic flow and carbon footprint.

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This need could be fulfilled by metal oxide nanomaterials. With their wide-ranging structures and myriad compositions, they are appealing targets for the development of high performance catalysts to facilitate heterogeneous hydrogenation reactions of gaseous CO_2 to chemical energy carriers. Notably, metal oxides have been the catalysts of choice for many large-scale industrial processes used for the manufacture of chemicals and fuels from non-renewable fossil resources, so why not adapt them to CO_2 as a renewable and recyclable feedstock.

Remarkably, it is the type and population of defects, which are intentionally incorporated into nanostructured metal oxides, that allow their catalytic behavior to be tailored and optimized.

In this Tutorial, we present a chemistry blueprint for the orchestration of different classes of defects in metal oxides that enable them to function as heterogeneous catalysts for the hydrogenation of gaseous carbon dioxide to energy carriers that include carbon monoxide, methane, methanol and dimethyl ether, at technologically significant conversions, rates, efficiencies and scales.

If CO_2 refineries can be developed that employ this class of defect-laden metal oxide catalysts for making renewable fuels from carbon dioxide and renewable forms of energy, and if they can be made economically competitive with non-renewable fossil fuels, then a transition from an unsustainable carbon-positive to a sustainable carbon-neutral future will be brought closer to reality.

Metal oxides – defects, defects, defects

It is striking that materials that display activity for the heterogeneous catalytic conversion of gaseous CO_2 to energy carriers

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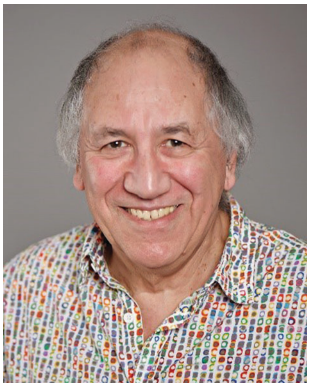

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are often based on metal oxides, with compositions that traverse large areas of the periodic table. This dominance is not only because of their earth abundance, stability, scalability, cost and ability to be synthesized in a nanostructured form but also because of the capacity of this class of materials to control the type, population and distribution of defects, which determines their properties, function and utility.

It is well known that defects control the properties of 'all' solid-state materials.[1–3] In the case of crystalline metal oxides, different kinds of point and extended defects, intentionally or unintentionally introduced into the lattice, determine their nucleation and growth, chemical reactivity, electrical, optical, magnetic, thermal and mechanical properties.[4] Perhaps less well known is the efficacy of surface defects in a periodic table of metal oxides, to heterogeneously catalyse a wide-range of chemical conversions.[5]

This perceived knowledge-gap has inspired the writing of this Tutorial with a particular focus on the heterogeneous catalytic hydrogenation of gaseous carbon dioxide by defect laden metal oxides. By drawing on the large body of work studying the chemistry and physics of different classes of defects, we show how the concepts from solid state science can be translated into the relevant thinking for heterogeneous catalysis with a focus on CO_2 fixation.

The majority of solid-state metal oxides with integral ratios of M : O are classified in terms of stoichiometry and when available a structure-type that include MO (rock salt, zinc blende), MO_2 (rutile, fluorite) M_2O (anti-fluorite), M_2O_3 (corundum, rare earth C), M_2O_5, M_2O_7, MO_3 (rhenium trioxide) M_3O_4 (spinel, inverse spinel), and MO_4.

Note that metal superoxides, peroxides, ozonides and sub-oxides are not included in this classification scheme or the discussion on CO_2 surface chemistry and catalysis that follows.

Hydrogenation of carbon dioxide by defect-laden metal oxides

In this Tutorial, we will first examine some key property–function relations that are realized by introducing different kinds of defects into stoichiometric metal oxides MO_x. Representative examples are illustrated in Fig. 1 by oxygen and metal vacancies, bridge and terminal bonded hydroxyls, and combinations thereof.

Thereafter, we will explore how these defects can be orchestrated to enable, tailor and optimise the heterogeneous catalytic hydrogenation of gaseous carbon dioxide to organic products of interest to the chemical and petrochemical industries, exemplified but not limited by the following list, together with their corresponding enthalpy of formation:

$$CO_2 + H_2 \leftrightarrow CO + H_2O \quad \Delta H_{298} = +41\ \mathrm{kJ\ mol^{-1}}$$

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \quad \Delta H_{298} = -49.1\ \mathrm{kJ\ mol^{-1}}$$

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O \quad \Delta H_{298} = -165\ \mathrm{kJ\ mol^{-1}}$$

While binary metal oxides will be the focus of this Tutorial, it will become apparent that many of the concepts can be expanded to include multinary complex metal oxides, exemplified by perovskites and spinels, garnets, polyoxometallates, aluminosilicates, layered metal oxides and hydroxides and brownmillerites. And because electrochemistry and photoelectrochemistry, photocatalysis, biocatalysis and homogeneous catalysis strategies for reducing carbon dioxide to chemicals and fuels are distinct from the gas-phase approach described herein, they will not be covered in this Tutorial.

Stoichiometric MO_x

The archetype is represented by the stoichiometric binary metal oxide MO_x, such as TiO_2, ZnO, WO_3, Nb_2O_5, SnO_2, NiO, MgO, V_2O_5 and Fe_2O_3, in which crystal lattice sites are composed of metal and oxygen.[4,5] This perfect crystal is devoid of defects, such as vacancies and hydroxyls, which prove to act as central players in this Tutorial. Depending on the constituent metallic element in stoichiometric MO_x, they can be classed as metals, semiconductors, insulators, and in special cases low-temperature superconductors. Their bonding can be described as metallic, ionic or covalent or something in between, the latter arising from the contribution of other interactions. This class of MO_x can be Lewis acidic or Lewis basic or neutral in character, whereby the coordinately unsaturated metal surface sites function as the former and the surface oxygen sites as the latter. The surface Lewis acidity and basicity can be tuned by the nature of the metal site, control being related to the size, charge, coordination number, geometry and electronegativity of the metal in a particular oxidation state.

Two factors are of the utmost importance in determining the properties of a given defect: the formation energy and the defect energy levels associated with electronic transitions. The formation energy determines the equilibrium concentration of a defect. The defect energy levels characterise the electron chemical potential at which the defect changes its charge state; for example, an oxygen vacancy can exist in a neutral (V_O^0), singly ionized (V_O^+), or doubly ionised (V_O^{++}) state. In the field of metal oxide semiconductors, the means to engineer defect properties and reactions have been well studied – they are less well explored in the context of heterogeneous catalysis. To amplify, the position and nature of the defect level in the electronic band gap of a material will determine whether a defect behaves as an electron acceptor (Lewis acid) or an electron donor (Lewis base), as well as the strength of its acidity or basicity. Understanding and controlling these properties is at the heart of designing new defect-based heterogeneous catalytic materials. Both of these critical properties are accessible from atomistic simulations, through *ab initio* thermochemistry.[6,7]

The diversity and tunability of the chemical and physical properties of defects in metal oxides can be understood in terms of the electronic and geometric structure, and frontier orbitals of the crystal lattice.[8] Typically, oxygen 2p-orbitals dominate the upper valence band (highest occupied states) and metal based orbitals dominate the lower conduction band (lowest unoccupied states). When a defect is formed its defect levels often fall within the electronic band gap, which can be understood in terms of changes in local bonding (hybridisation),

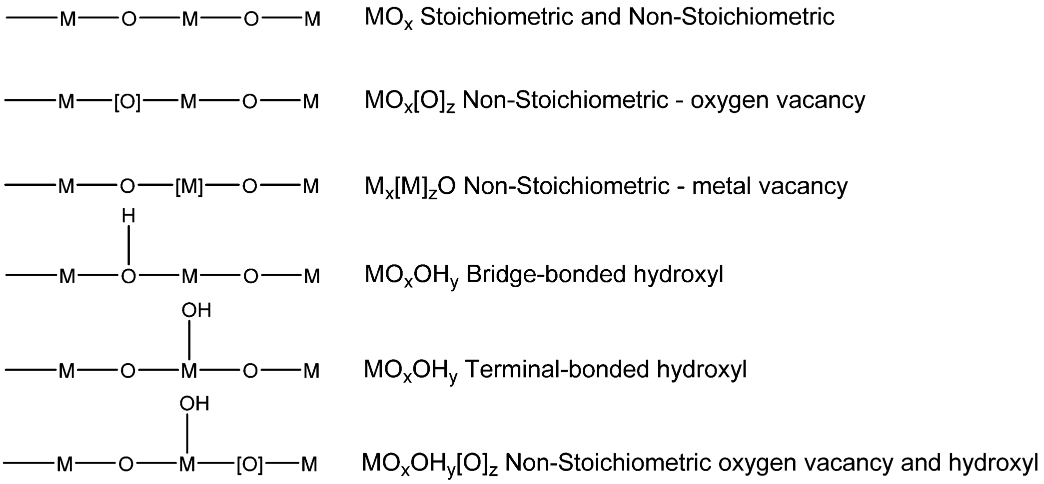

Fig. 1 Classes of defects that can be intentionally introduced into stoichiometric metal oxides, exemplified from top to bottom by oxygen and metal vacancies, bridge and terminal bonded hydroxyls, and combinations thereof.

structure, and polarisation of the lattice. Due to the high ionicity of metal oxides, the local Madelung potential has a significant role to play, *e.g.* the electrostatic potential can be strong enough to localise electrons at vacant sites, forming color centres;[9] the local Madelung potential has been shown to be a key driver of active sites for catalysis in MgO.[10] Due to this sensitivity to the local electronic and structural environment, the same type of defect present in different metal oxides can exhibit distinct properties and reactivity.

In the context of heterogeneous catalysis, the extent to which defects partition between the bulk and the surface is also of vital importance.[11] The degree of surface segregation and the charge state of defects in metal oxides depend on the doping (intentional or unintentional) of the material. Due to the lower coordination numbers found at the surface, point defects have a reduced formation energy, and thus the upper layers of a crystal can act as a reservoir with a high concentration of defects that migrate to and from the bulk material.[12] Even for a stoichiometric bulk metal oxide, it is common to find non-stoichiometry at the surface, which leads to electron accumulation or depletion layers.[13] In extreme cases, a two-dimensional electron gas is formed. This can become even more pronounced for nanostructured forms of metal oxides.

The morphology of the metal oxide will also play a role in that the composition and structure of an exposed crystal face, and the type and population of defects occupying that face, will determine which surface sites are exposed and catalytically active, as well as the effective work function, electronic band gap and density of states of the sample. An archetypal example of surface dependency is ZnO, which is present in the majority of leading industrial methanol catalysts.[14–16] Despite its widespread application, the exact mode of action of ZnO is a subject of debate.[17] Modern quantum mechanical/molecular mechanical approaches have been used to provide insights into the mode of action of ZnO in CO_2 reduction. In ZnO the lack of crystal inversion symmetry means that the (0001) surface has an electric dipole, which is quenched by the formation of surface vacancies. These sites, unlike bulk vacancies do not carry a charge, but can act as traps for carriers (electrons or holes) and thereby become highly active catalytic centres.[17]

Nano-structuring will regulate the surface area and therefore the population and kind of surface active sites available for the adsorption, reaction and desorption steps that define the surface chemistry and catalysis. TiO_2 is widely used for water splitting, but less commonly applied for CO_2 reduction, owing to an electron affinity that is too large for most CO_2 reduction processes. Nonetheless, by forming TiO_2 nanocrystals, with carefully tailored surface terminations, it is possible to construct nano-crystal heterojunctions, with midgap states, which result in greatly enhanced photocatalytic performance.[18] Specifically TiO_2 with (001) and (101) surfaces exposed is known to show enhanced quantum yields;[19] this is due to the increased number of active under-coordinated Ti sites (see the section on CO_2 activation by stoichiometric and non-stoichiometric metal oxides) and due to the formation of a semiconductor heterojunction, with favourable charge transfer effects (see the section on Metal oxide heterojunctions).

As mentioned above, the 'so-called' stoichiometric metal oxides might actually be slightly deficient in oxygen. The equilibrium concentration of point defects is sensitive to the growth and processing environment, including temperature and oxygen partial pressure. Under standard processing conditions, low concentrations (10^{15}–10^{18} cm^{-3}) of vacancies can provide metal oxides with excess electrons, thereupon giving them the properties expected of an n-doped or mixed-valence semiconductor.

Similar doping and redox effects can be achieved intentionally by aliovalent substitution of lattice O, for example, by F (donor) or N (acceptor). In all of these cases, the dopant and mixed valence energy states will exist in the electronic bandgap, endowing the metal oxide with new and interesting electrical and optical properties that can also influence surface adsorption, chemistry and catalysis, and in the case of photocatalysis, charge carrier dynamics (see the section on Non-Stoichiometric $MO_x[O]_z$).

Non-stoichiometric MO_x

Not all metal oxides are stoichiometric. There exist two main classes of non-stoichiometric metal oxides, those with defects and those without.[20] The latter class includes metal oxides where defects created during their synthesis have been eliminated by various processes.[11] A classic example is the crystallographic shear phases of tungsten oxides, WO_{3-x}, which are formed by creation of oxygen vacancies in the original WO_3 lattice by either thermal vacuum and/or hydrogen post-treatment. Through crystallographic shear of planes of corner-sharing WO_6 octahedral building blocks, displacement induced oxygen vacancies are eliminated and the structure adjusts to create line defects, built of regular groupings of reconstructed corner and edge sharing WO_6 octahedral blocks.[21]

The number of oxygen vacancies created and the shear-type reconstruction that ensues determine the value of x and the population, orientation, organization and periodicity of these line defects in the WO_{3-x} lattice. The value of x also establishes the electrical, optical and chemical properties of WO_{3-x}. The loss of oxygen from the lattice creates a charge imbalance, which must be counteracted in order to maintain charge neutrality. There are a large number of charge compensation mechanisms available, including metal vacancies, oxygen interstitial ions, and species substitution on the cation site. Which mechanism is preferred is determined by the formation energy of the defect–compensation pair for a given set of processing conditions. These formation energies can be probed directly by the application of atomistic modelling techniques.

In for example WO_{3-x} the loss of oxygen from the lattice is compensated for by conversion of W(VI) to W(V), which form defect states in the electronic bandgap of WO_3 below the conduction band. At low values of x these W(V) states contain a single d-electron and are localized as small polarons, giving it the character of a mixed valence semiconductor. It displays strong visible absorption often in the red or near infrared, assigned to a W(V) → W(VI) inter-valence charge transfer electronic excitation. As x increases, the density of W(V) d-electron states grows and forms a partially filled band giving WO_{3-x} the character of a delocalized metal, with a non-integral oxidation state W(VI-x). It now displays a diagnostic plasma edge in the optical spectrum arising from the conduction electrons, hence this class of non-stoichiometric metal oxides is dubbed a bronze.[22] The ability to reversibly add and remove oxygen from the WO_{3-x} lattice with concomitant control over its physical and chemical properties has provided this class of non-stoichiometric materials with many interesting opportunities for enabling different kinds of heterogeneous catalytic reactions, including CO_2 activation.

Non-stoichiometric $MO_x[O]_z$

By contrast to the preceding case of non-stoichiometric metal oxides MO_x, in which oxygen vacancies are eliminated by a defect reconstruction, $MO_x[O]_z$ represents a class of non-stoichiometric metal oxides which retain oxygen vacancies, such as TiO_{2-x}, Nb_2O_{5-x}, ZrO_{2-x}, V_2O_{5-x} and CeO_{2-x}. Again, the electro-neutrality principle dictates that the metal oxidation state is reduced to charge-balance the loss of lattice oxygen and depending on the population of oxygen vacancies, either semiconducting or metallic character results. The nature of conduction will depend on whether the material has localized or delocalized electron states and may exhibit a temperature dependent metal–non-metal transition. The oxygen vacancies exist as donor defect states in the electronic bandgap giving rise to diagnostic features in optical absorption-emission, photoconductivity and X-ray photoelectron spectra. They can be observed by scanning transmission electron microscopy electron energy loss spectroscopy. These vacancies can function as traps for excited electronic charge as well as binding sites for surface adsorbed species and associated charge transfer – the degree to which they trap or transfer charge is determined by the defect level.

Surface located oxygen vacancies also serve to make coordinately unsaturated surface metal sites even more unsaturated and hence more Lewis acidic. Together these qualities provide this class of non-stoichiometric metal oxides with interesting opportunities in surface chemistry and catalysis. The conduction electrons associated with the oxygen vacancies can give rise to localized surface plasmon resonances in the near infrared spectral region.[23] An interesting question in the context of heterogeneous catalysis is whether near infrared excitation of the conduction electron resonance in these defect-laden nanostructured metal oxides can relax non-radiatively and thereby cause local heating that can drive a photo-thermal catalytic reaction – see photothermal catalysis later.

Another point about oxygen vacancies in metal oxides is their ability to trap photoexcited charge carriers and enable persistent photo-conductivity, which can last seconds to minutes. Such long excited-state lifetimes are potentially beneficial when trying to enhance the chemical reactivity of photogenerated electron–hole pairs in heterogeneous catalytic conversions. Oxygen vacancies can also enable oxide ion transport,[24] making this class of non-stoichiometric metal oxides of interest in chemical sensors and fuel cells, as well as heterogeneous catalysis that benefits from labile reactive lattice oxygen.

In the context of surface chemistry and catalysis, oxygen vacancies that exist on the surface of non-stoichiometric WO_{3-x} nanowires and TiO_{2-x} nanocrystals have been proposed to be photoactive for the abstraction of oxygen from adsorbed CO_2 to make CO, which can be desorbed as product CO or further reduced with adsorbed H_2O to form CH_4. Both of these non-stoichiometric metal oxides are bright blue, the color of which originates from inter-valence charge transfer optical excitation between mixed valence W(V,VI) and Ti(III,IV).

In these nanostructures, the reduced metal oxidation states and oxygen vacancies in WO_{3-x} and TiO_{2-x} exist as mid-gap defect states, which facilitate visible light absorption, charge separation of photo-generated electrons and holes, and adsorption and reaction of CO_2 and H_2O to produce CO or CH_4, respectively.

A challenge with this class of nanomaterials is to re-instate the non-stoichiometry after the first reaction cycle to make them catalytic. Possible approaches to overcome this impediment include operating at higher temperature or light intensities, the addition of H_2 dissociation-spillover catalysts, and/or the use of H_2 as the hydrogen source.

Non-stoichiometric $MO_x[M]_z$

By comparison with the previous case, lattice vacancies can also exist on the metal site in the $MO_x[M]_z$ class of non-stoichiometric metal oxides, representative examples being $Fe_{1-x}O$ and $Ni_{1-x}O$. To balance the loss of metal sites and overall charge reduction, the oxidation state of the remaining metal must be increased, or oxygen vacancies must be formed, the preferred mechanism depending on thermodynamics. Wüstite $Fe_{1-x}O$ is a classic case in point, which at low values of x can lead to local reconstruction and at high values of x, clustering of metal vacancies. The former looks like a modified version of rock salt FeO, while the latter looks more like the inverse spinel Fe_3O_4, end members. Early materials simulation work probed the thermodynamics of defect clustering in this system.[25] Again semiconductor–metal character depends on whether the material has localized or delocalized electron states and may exhibit a Peierls-type of metal–non-metal transition. Another example in this class of materials is the black colored, mixed valence, polaron-hopping semiconductor, $Ni_{1-x}O$.

Bridge or terminally bonded hydroxyls MO_xOH_y

Stoichiometric metal oxide hydroxides, often in numerous polymorphic forms, are ubiquitous in the periodic table, representative examples from the main group and transition group elements being AlOOH, InOOH, FeOOH, NiOOH and solid-solutions such as $Fe_xNi_{1-x}OOH$. These can be made non-stoichiometric by thermally induced partial dehydroxylation.

Hydroxyls introduced into the lattices of metal oxides by this or other synthetic approaches bring forth interesting new chemical and physical properties. They can exist as terminal hydroxyls bonded to a single metal atom site or bridging hydroxyls spanning two or more metal atom sites and even participating in a bridge-terminal equilibrium.[26] The terminal hydroxyls can function as Brønsted acids or Lewis bases differentiated mainly by the radius, oxidation state and electronegativity of the adjacent metal sites.

Generally speaking, smaller higher charged metal sites favor the former, the opposite preferring the latter. Bridge-bonded hydroxyls normally exhibit Brønsted acid character. Chemical and electrochemical synthetic methods that inject protons and charge-balancing electrons into the metal oxide create Brønsted acid hydroxyls, while thermal dehydroxylation of metal hydroxide precursors can be used to make Lewis base hydroxyls.

These kinds of hydroxyl sites can appear as energy states in the electronic bandgap of the metal oxide lying closer to the oxide-like valence band and often serving as a trap for electronically generated holes. The protons on the Brønsted acid sites are often mobile. They can hop from one oxygen to a neighboring oxygen site enabling proton conductivity and provide application opportunities for fuel cells, displays and sensors.

The Brønsted acidity as well as Lewis basicity of these hydroxyls can also provide active sites for many heterogeneously catalysed organic transformations. In this context, it has been recently recognized that a Lewis basic hydroxyl proximal to a coordinately unsaturated Lewis acidic site constitutes a surface frustrated Lewis pair (SFLP) that is able to catalyze heterogeneous hydrogenation reactions of gaseous carbon dioxide,[27–29] a topic touched upon later in this article.

Non-stoichiometric $MO_xOH_y[O]_z$

In this category, a metal oxide material that provides a catalytically active surface, which judiciously integrates the chemical and physical properties of oxygen vacancies, hydroxyls and coordinately unsaturated metal sites, in principle can benefit from the attributes of all the aforementioned classes of metal oxides in a single platform.

One such material that has been the subject of much recent activity is $InO_xOH_y[O]_z$.[30] It can be synthesized by controlled thermal dehydroxylation of nanostructured $In(OH)_3$ according to the balanced equation: $2In(OH)_3 \rightarrow In_2O_xOH_{(6-2x)} + xH_2O \rightarrow In_2O_3 + 3H_2O$, where thermogravimetric analysis can provide the value of x at any point in the solid-state chemical transformation.

As discussed later in this article, the defect sites in this class of non-stoichiometric metal oxides play a pivotal role in the kinetics of the thermochemical and photochemical catalyzed transformation of $CO_2 + H_2 \rightarrow CO + H_2O$, the reverse water gas shift reaction.[29–31]

CO_2 activation by stoichiometric and non-stoichiometric metal oxides

CO_2 can adsorb on stoichiometric and non-stoichiometric MO_x surfaces, by coordination to one or two adjacent metal sites through the terminal oxygen atoms of the CO_2. The carbon atom of CO_2 can also interact with surface oxygen sites. In the case of non-stoichiometric $MO_x[O]_z$ the surface oxygen vacancies can serve as additional adsorption sites by interacting with the carbon and/or oxygen atoms of CO_2. Similarly, in non-stoichiometric $MO_x[M]_z$ the surface metal vacancies can serve as adsorption sites for the CO_2. Once hydroxides are introduced into MO_xOH_y and $MO_xOH_y[O]_z$ the CO_2 can bind to the surface, for example as bicarbonates and carbonates, in monodentate and bidentate modes. All of these adsorption modes for CO_2 on stoichiometric and non-stoichiometric metal oxides are illustrated in Fig. 2. The adsorption strength and mode of binding of CO_2 to the surfaces in all of the aforementioned cases will depend on the elemental composition and structure of the metal oxide, and the nature of the intrinsic and extrinsic defects. The CO_2 surface interactions can traverse weak physical to strong chemical forces, the magnitude of which will affect the structure and reactivity of the adsorbed CO_2 and the kinetics and mechanisms of surface chemical and catalytic reactions of CO_2 with a hydrogen source.

H_2 activation by stoichiometric and non-stoichiometric metal oxides

Stoichiometric and non-stoichiometric metal oxides are known to be able to heterolytically dissociate molecular H_2 into proton

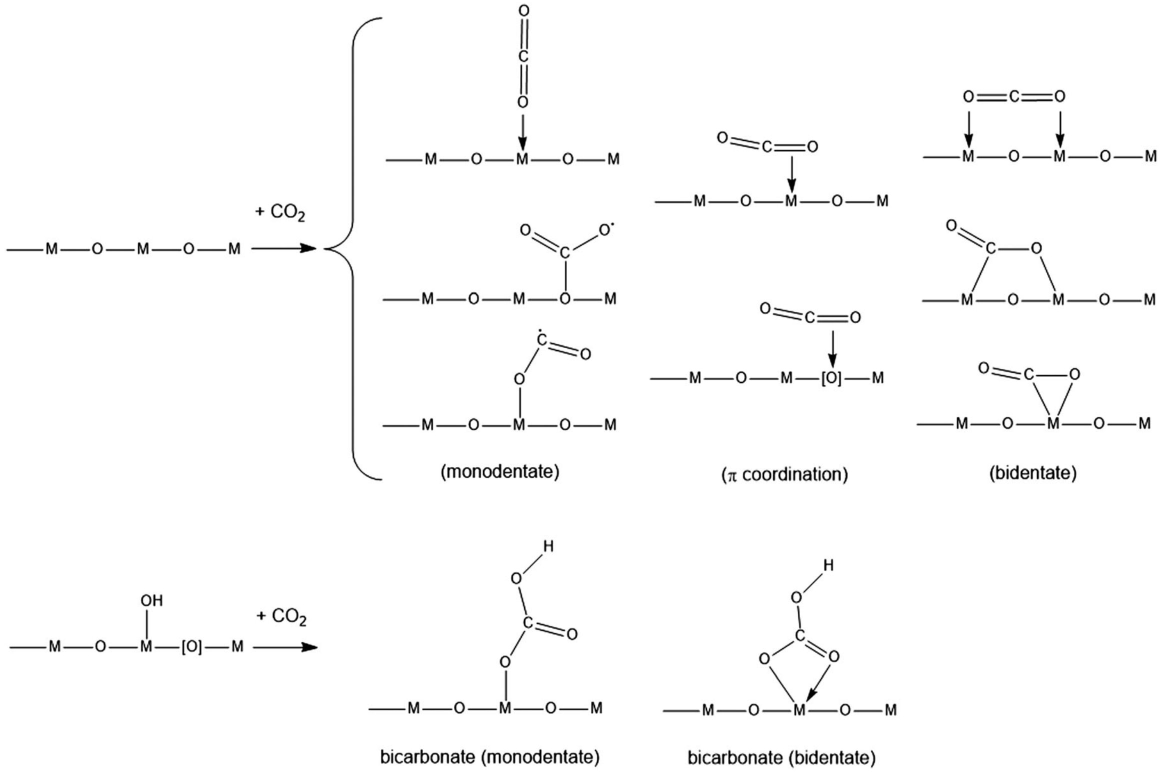

Fig. 2 Modes of adsorption for CO_2 on the surfaces of stoichiometric and non-stoichiometric metal oxides.

and hydride sites, and homolytically into two proton sites. These modes of activation are illustrated for some representative defect-free and defect-containing metal oxides in Fig. 3.

In the case of a stoichiometric metal oxide shown on the top of Fig. 3, the electric polarization of an adsorbed H_2 at an anisotropic and proximal metal–oxygen M–O surface site can weaken the H–H bond causing it to split heterolytically into a hydridic and a Brønsted acidic MH···OH site, exemplified by H_2–ZnO thermochemical and H_2–MgO photochemical activation, as depicted at the top of Fig. 3. This same type of H_2 dissociation can occur at an electrically anisotropic and proximal MOH···M site, exemplified by H_2–$In_2O_{3-x}OH_y$,[29] shown at the bottom of Fig. 3, to create a MOH_2···MH site. Both of these cases can be likened to the chemical reactivity of a surface frustrated Lewis pair (SFLP).

One can think of both of these dissociations in terms of weakening of the H_2 bond by removing the sigma bonding charge through interaction with the electron withdrawing Lewis acidic metal site with concomitant addition of a sigma antibonding charge by way of the electron donating

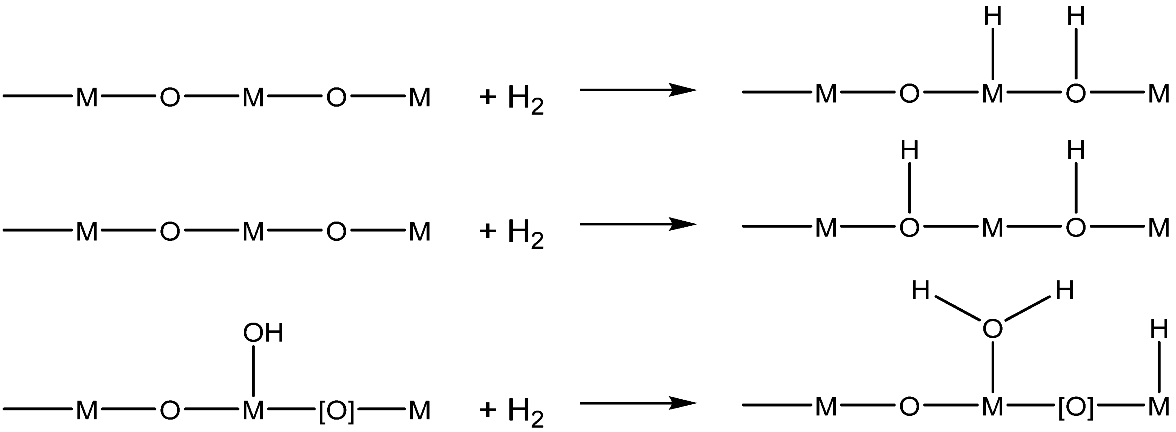

Fig. 3 Different modes of activation of H_2 by stoichiometric and non-stoichiometric metal oxides, respectively from top to bottom, heterolytic, homolytic and heterolytic dissociation of H_2.

Lewis basic oxygen or hydroxide sites. In both of these cases, charge balance between the surface hydride and proton means that the state of oxidation of the metal does not change.

It is worth pointing out that metal oxides containing both proton and hydride sites are not that common. An interesting recent report shows how lattice oxide in $BaTiO_3$ can be replaced by hydride enabled by heating it with CaH_2 to make the new class of metal oxide-hydrides, $BaTiO_{3-x}H_{2x}$.

By contrast, H_2 can homolytically dissociate on stoichiometric and non-stoichiometric metal oxides as illustrated in the middle example shown in Fig. 3. The dissociation of H_2 in this instance results in the formation of surface $\cdots HO\cdots M\cdots OH\cdots$ sites, examples being H_xMoO_3, H_xWO_3 and $H_xNb_2O_5$.

This process entails the reaction of two protons with two Lewis basic oxygen sites with simultaneous injection of the corresponding amount of electron charge into the metal to generate lower oxidation states. This process creates a mixed valence localized semiconductor or delocalized metal, respectively for lower and higher levels of H_2 incorporation into the electronic band structure. A metal–metal oxide heterostructure, such as $Pd@Nb_2O_5$ described later in this article, may be required to facilitate the H_2 dissociation by spillover from the metal to the metal oxide.[32]

CO_2 and H_2 activation by stoichiometric and non-stoichiometric metal oxides

Metal oxides have the capacity to simultaneously or sequentially dissociate H_2 homolytically and heterolytically, and adsorb, activate and react with CO_2 at one or a combination of surface Brønsted acid and Brønsted base, Lewis acid and Lewis base, metal hydride, oxygen vacancy and coordinately unsaturated metal sites. This capability provides many opportunities for tailoring the adsorption, reactivity and selectivity behavior of metal oxides for the hydrogenation of carbon dioxide to fuels, as illustrated in Fig. 4.

Possible reaction intermediates involved in the heterogeneous catalytic hydrogenation of carbon dioxide include surface bound bicarbonate, formate, carbide, carbonyl, and methoxy groups, as illustrated in Fig. 4. These can react further and desorb as products that include formic acid, formaldehyde, methanol, carbon monoxide and methane.[33]

The surface chemistry and catalysis challenge in this endeavor figures out how to synthesize a metal oxide catalyst with the optimal combination of these surface features, to favor the formation of one particular carbon dioxide hydrogenation product, at the highest possible conversion rate and without inhibition by products, such as CO or H_2O, or deactivation by sintering or poisoning, to provide a catalyst with long-term stability.

Whilst this challenge may seem daunting at first, decades of research into defect properties of oxides and recent advances in synthetic, characterisation and computational techniques mean that rational design of high-performance, defect-mediated metal oxide heterogeneous catalysts for CO_2 fixation is not an impossible dream.

The power of materials theory and simulation in this field has been elegantly demonstrated by the work of Nørskov and colleagues on screening new electrocatalysts,[34] mechanistic insights into catalyst operation,[35] and the development of new multi-scale techniques for describing surface defect reactions.[36]

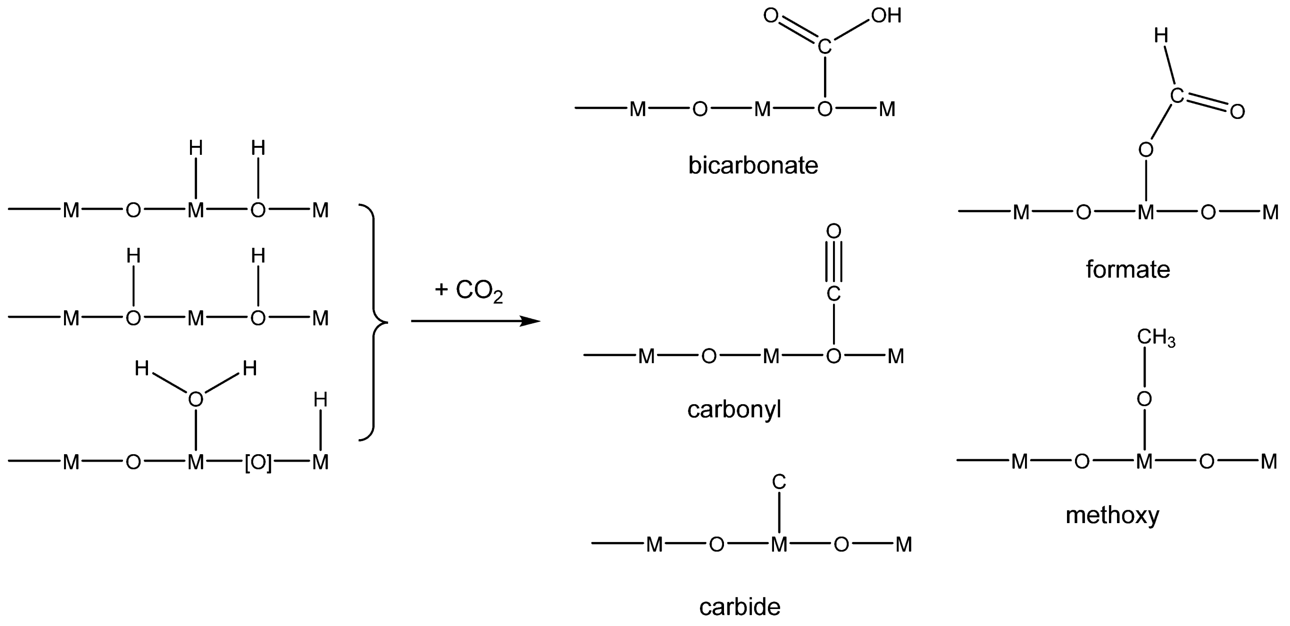

Fig. 4 Illustration of the structure and bonding of possible surface reaction intermediates that can form during the heterogeneous catalytic hydrogenation of carbon dioxide on metal oxides with designed defects. These surface species can react further with protons, hydrides and hydroxyls, to form products that include formic acid, formaldehyde, methanol, carbon monoxide and methane.

Thermochemical, photochemical and photothermal heterogeneous catalytic hydrogenation of CO_2

An interesting recent development concerns studies that are designed to compare the kinetics and mechanisms of heterogeneous catalytic hydrogenations of carbon dioxide driven thermochemically, photochemically or photothermally using the heat and/or light of the sun.[28,29,31,37]

In this context, detailed experimental and theoretical studies on a catalytically active, defect engineered, nanocrystalline form of bixbyite $In_2O_{3-x}OH_y[O]_z$ have revealed that oxygen vacancies and hydroxyls exist as mid-bandgap energy states, the former located below the conduction band and the latter above the valence band, Fig. 5.[31] Following band gap excitation, oxygen vacancies and hydroxyls serve as traps for photo-generated electrons and holes. This has the effect of slowing down carrier relaxation times – resulting in long-lived excited states.[31] Importantly, this also enhances the Lewis acidity and Lewis basicity of the defect centres in the excited state.[28] Together these two effects work synergistically for the reverse water gas shift reaction, $CO_2 + H_2 \rightarrow CO + H_2O$, enhancing the conversion rate and reducing the activation energy for the rate determining carbon dioxide hydrogenation step by 20 kJ mol^{-1}, in the light compared to the dark.[28]

To amplify, the first step in the catalytic cycle involves the heterolytic dissociation of H_2 on the surface frustrated Lewis pair $InOH\cdots In$ to form $InOH_2^{+}\cdots InH^{-}$.[27,29] The rate determining step involves the reaction of $InOH_2^{+}\cdots InH^{-}$ with gaseous CO_2 to form CO and H_2O.[28,29] Following band-gap excitation, electrons and holes relax into these mid-gap defect states, making the hydride on the InH^{-} more hydridic and the proton on the $InOH_2^{+}$ more acidic, respectively, thereby reducing the activation energy for the surface frustrated Lewis pair catalysed reverse water gas shift reaction, in the light compared to the dark.

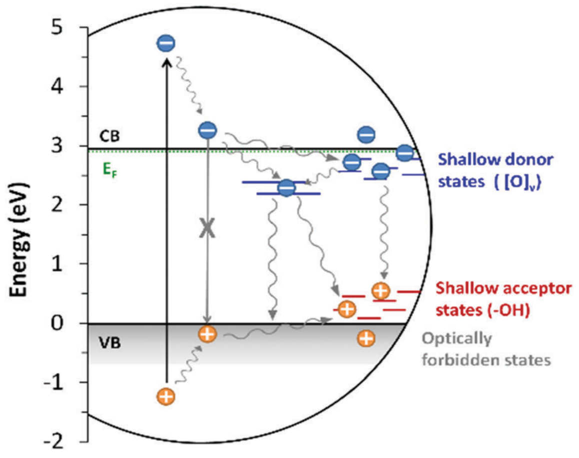

Fig. 5 Schematic diagram illustrating the different charge carrier relaxation processes in $In_2O_{3-x}(OH)_y[O]_z$.

Defect tailoring

The functional properties and the reactivity of catalysts can be tailored by defect engineering using several materials chemistry strategies. Taking the defect laden heterogeneous carbon dioxide hydrogen catalyst $In_2O_{3-x}OH_y[O]_z$ as a representative example, with detailed insight into the carrier dynamics as the background, in what follows, we briefly discuss each of these strategies, working left to right in Fig. 6.

Local acceleration by the photothermal effect

The enhanced activity for the photothermal approach using ultra-black, broad-band and highly absorbing supports for the catalyst, such as silicon nanorods or titanium sesquioxide,[38] is attributed to the effects of reduced light reflection losses, improved light harvesting efficiency and more efficient heat transfer from the ultra-black support to $In_2O_{3-x}(OH)_y[O]_z$.[39] These hybrid catalysts utilize the vast majority of the solar irradiance to simultaneously produce both the photogenerated charge carriers and local heating to accelerate the photocatalytic reaction.

These features are related to the band structures of the materials – silicon and titanium sesquioxide are indirect gap semiconductors, with strong optical absorption throughout the near infrared, visible and ultraviolet spectral range. The indirect nature of the optical transitions means that excited carriers are less likely to recombine radiatively, but rather relax to the band edges, dispersing their excess energy through electron–phonon interactions, resulting in localized heating. Together these effects have been found to enhance the heterogeneous photocatalytic reverse water gas shift reaction rate of nanocrystalline $In_2O_{3-x}(OH)_y[O]_z$ attached to the ultra-black silicon nanorod and titanium sesquioxide supports, illustrated on the left in Fig. 6.[39]

In this context, it's worth commenting on what makes photo-thermal heterogeneous catalysis so attractive. Being powered by both the heat and light from the Sun, with photons harvested across the entire solar spectral wavelength range, it turns the prevailing view of solar energy on its head.[32,38,39] Materials that have low performance metrics for making solar electricity can have a high efficiency for making solar fuels!

Charge transport and separation by superstructures

The performance of photocatalysts requires efficient charge separation and charge transport, which is closely related to defects and the associated concentration of excited carriers. The application of superstructures offers a possible route to maximising the harvesting of these mobile carriers to facilitate CO_2 chemistry, by ensuring that the excitation event takes place within the carrier diffusion length from an active surface site.[40] A classic case is nanorod superstructures made of self-assembled nanocrystalline $In_2O_{3-x}(OH)_y[O]_z$ with the observed correlation between rod length, e–h lifetimes and CO_2 to CO conversion rate, implying that improved charge transport and charge separation between nanocrystals in the nanorod are responsible for the observed enhancement of photoactivity, illustrated second left in Fig. 6.[40]

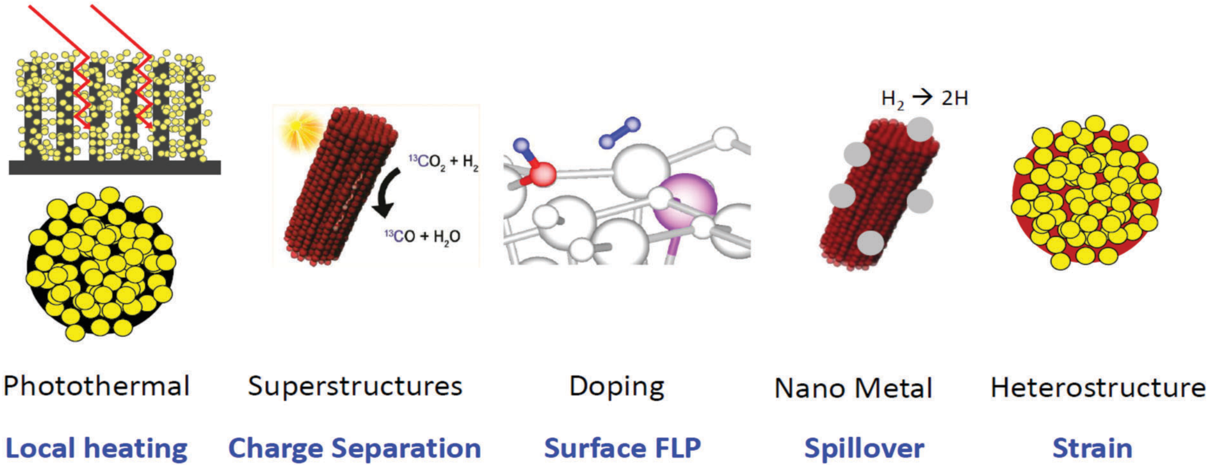

Fig. 6 Five different materials chemistry approaches for tailoring the activity of $In_2O_{3-x}OH_y[O]_z$ for the reverse water gas shift reaction, $CO_2 + H_2 \rightarrow CO + H_2O$.

Surface chemistry tailoring by doping

Surface chemistry properties of catalysts play key roles in the catalytic reactions at active sites. Taking $In_2O_{3-x}OH_y[O]_z$ as an example, since the rate determining step involves the heterolytic dissociation of H_2 on the surface frustrated Lewis pair, tuning the surface acidity and basicity of the surface frustrated Lewis pair could influence the activation energy for hydrogenation of CO_2.

Isomorphous substitution (doping) has been explored as a surface chemistry tailoring approach in the case of $Bi_zIn_{2-z}O_{3-x}OH_y[O]_z$.[41] By varying the concentration of Bi(III) in the lattice, a Sabatier principle 'volcano' type plot was observed for the hydrogenation of CO_2 to CO. A peaking of the rate has been traced to the larger size of Bi(III) and its stereo-chemically active lone pair, which enhance the Lewis basicity of the InOH site comprising the surface active InOH···In frustrated Lewis pair. By arranging the concentration of Bi(III) to be 'just right', it enables the adsorption, heterolytic splitting of H_2, capture of CO_2, conversion of $CO_2 + H_2 \rightarrow CO + H_2O$, and desorption of product H_2O, and thereupon a means of optimising the rate of the reaction at the peak of the Sabatier type 'volcano', illustrated in the middle of Fig. 6.

Hydrogen spillover by nanometal decoration

Hydrogen spillover originates from the dissociation of hydrogen on nanometals decorated on the surface of metal oxides. The adsorbed reactants could react with H spilled over from the nanometals to form intermediates and products more efficiently.

The nanometal advantage is seen in a three orders of magnitude amplification in the conversion rate of $CO_2 + H_2 \rightarrow CO + H_2O$ using $Pd@In_2O_{3-x}(OH)_y[O]_z$. The enhancement is attributed to the combined contributions of the hydrogen spillover and photothermal effects of the nanopalladium co-catalyst attached to the $In_2O_{3-x}(OH)_y[O]_z$ photocatalyst, illustrated second right in Fig. 6.[32] The mechanism involves H_2 dissociation on Pd nanocrystals and subsequent spillover of H to $In_2O_{3-x}(OH)_y[O]_z$. The Pd nanocrystals behave as ''nano-heaters'', generating high local temperatures on $In_2O_{3-x}(OH)_y[O]_z$ whereupon adsorbed CO_2 is hydrogenated to CO.

It should be mentioned here that the size of Pd nanocrystals can have a deciding influence over product selectivity. It has been observed that the small sizes around 5 nm favour CO while the larger ones around 20 nm make CH_4. The preference originates in the strength of binding and residence time of CO on the Pd nanocrystals, smaller nanocrystals favouring desorption of CO, and larger nanocrystals favouring hydrogenation to CH_4.

This difference in selectivity can be traced to three effects involving the σ-bonding and pi-antibonding contributions to the strength of the Pd–CO surface bond: (i) a higher Pd_nCO coordination number on larger Pd nanocrystals and hence stronger Pd–CO bonding, (ii) greater charge transfer from $In_2O_{3-x}(OH)_y[O]_z$ to larger Pd nanocrystals and therefore stronger Pd–CO bonding, (iii) larger concentration of conduction electrons in larger Pd nanocrystals and therefore stronger Pd–CO bonding.

This nanometal strategy,[42,43] which can be expanded to other nanometals, such as Cu,[44] with much lower materials cost, represents a promising route to scaling up heterogeneous catalytic hydrogenation processes of carbon dioxide.

Strain effect by the heterostructure

The catalytic activity of heterogeneous catalysts can be tuned by applying strain.[45] An enhancement of the hydrogenation rate of carbon dioxide has been observed by synthesizing $In_2O_{3-x}(OH)_y[O]_z$ on the surface of nanocrystalline Ta_3N_5.[46] Detailed diffraction and microscopy studies show that the rate increase likely originates from the lattice strain induced in $In_2O_{3-x}(OH)_y[O]_z$ caused by the lattice mismatch with the underlying Ta_3N_5 support, which itself was catalytically inactive. This strain induced change in the lattice dimensions of $In_2O_{3-x}(OH)_y[O]_z$ must alter the distance between the surface active Lewis base Lewis acid InOH···In sites, thereby improving the activity, illustrated to the right of Fig. 6.

Computational studies of strained lattice systems, based on Density Functional Theory (DFT), may offer a detailed understanding of their electronic properties, like band structure and charge localization. A theory-based approach can provide insight into the effect of strain on the reactivity of the surface frustrated Lewis pair site, and ultimately on the reaction mechanism ensuing on the catalyst surface. The resulting chemical reaction kinetics can also be studied through investigation of the underlying minimum energy reaction pathways, rates of reaction and activation energy barriers, *via* transition state searches and *ab initio* molecular dynamics techniques.[37]

The strain inducing support can be expanded to include other semiconductors, such as ZnO, which can reduce materials cost and improve the potential for the development of large scale CO_2 conversion processes – high throughput screening of materials databases to search for optimally strained pairs offers a route to rational design of these systems.

The aforementioned case histories are but five distinct materials chemistry ways of tailoring the activity of carbon dioxide metal oxide heterogeneous hydrogenation catalysts using both the heat and/or light from the Sun. There are also some other approaches for controlling the defect to enhance the catalytic performance:

Thermal treatment in a reducing atmosphere or under vacuum

It is well known that thermal treatment of metal oxides under vacuum or in a reducing atmosphere is a simple and straightforward approach to create defects in metal oxides. With the formation of defects, a shift in the onset of absorption, accompanied by a dramatic color change and substantial enhancement of solar-driven photocatalytic activity, is usually observed.[47]

Chemical reduction or oxidation

Metal oxides with defects can be obtained by thermally treating metal oxides using some reductants under vacuum, including aluminum, magnesium and zinc reduction, $NaBH_4$ and imidazole. By contrast, defect tailoring can also be realized by chemical oxidation. For example, TiO_{2-x} can be prepared by oxidizing TiO, Ti_2O_3 or TiH_2 powder.[47]

Defect formation caused by electrochemical reduction

Examples have been reported regarding defect formation by electrochemical reduction. Black TiO_{2-x} nanotubes have been prepared by electrochemical reduction through a two-step process.[47] The pristine TiO_2 nanotubes were fabricated first by anodizing Ti foil. An electrochemical reductive doping process was then performed.

Significantly, the heterogeneously catalysed reverse water gas shift reaction $CO_2 + H_2 \rightarrow CO + H_2O$ is a key step for the large volume production of hydrocarbons and methanol by known industrial processes. Notably, methanol can be catalytically dehydrated to dimethyl ether, a favored fuel replacement in cars, trucks and ships for the environmentally unfriendly diesel fuel.

This carbon dioxide utilization strategy has been identified as a techno-economically relevant approach for making chemicals and fuels from carbon dioxide, which if practiced at a globally significant scale will provide the added benefit of being able to reduce greenhouse gas emissions in our atmosphere and hopefully ameliorate climate change.[48]

Metal oxide heterojunctions – strong metal support effect

In heterogeneous catalysis, metal oxides are often employed as supports for nanostructured metal oxide and metal catalysts. They serve a number of useful purposes, which include the prevention of sintering of supported catalysts thereby maintaining their surface area and activity; provision of porosity thus preserving access of reactants to surface active sites of the catalyst; as well as enabling unrestricted mass transport of reactants and products through the catalyst bed, without creating prohibitively high pressure gradients.

Traditional supports chosen for these purposes, such as MgO (basic), Al_2O_3 (acidic), SiO_2 (neutral), are often viewed as ''innocent bystanders'', meaning the effect on the electronic and structural properties of the support on the attached catalyst is minimal. Nevertheless, in the annals of heterogeneous catalysis there are many well-documented examples, where the activity and selectivity of the catalyst are altered in either positive or negative ways by the underlying support.

It was dubbed the ''strong metal-support effect'', the origin of which was attributed to charge transfer and structural effects involving the catalyst and the support.[49] The changes in activity and selectivity could be related to the direction and extent of charge transfer between the catalyst and support and the effect this shift of charge would have on the electronic and structural properties of the catalyst and support. Also lattice mismatch at the interface between the catalyst and support, as mentioned earlier, could create lattice strain and defects with accompanying electronic and steric effects. As mentioned previously, these induced defects at the interface could increase carrier lifetimes and enhance the Lewis acidity and Lewis basicity of these defect centres, which are key factors in determining the reactivity of the CO_2 hydrogenation reaction; therefore, lattice mismatch at the interface between the catalyst and support could lead to a rate enhancement.

In the language of solid state physics, the process of charge transfer between a metal oxide catalyst and metal oxide support will depend on whether they are both semiconductors (SC–SC, Type I, II heterojunction), a metal and semiconductor (M–SC, SC–M, Schottky junction) or both metals (M–M). Semiconducting and metallic metal oxides abound in the periodic table and the metallic ones may display temperature dependent metal–nonmetal Peierls or Mott transitions. Details of the electronic band structures of metal oxide supported metal oxide catalysts, projected onto an absolute energy scale, with respect to vacuum, will determine the direction and extent of charge transfer across the junction.

To describe charge-transfer effects on the activity and selectivity of a heterogeneous catalytic reaction, at the outset one has to know the relative distribution of valence and conduction bands and Fermi energies of the metal oxide catalyst and metal oxide support on either side of the heterojunction. In this exercise, due cognizance must be observed for the change in electronic band and defect state energy levels as the Fermi energies equilibrate across the heterojunction, keeping in mind that most metal oxides are slightly deficient in lattice oxygen endowing them with n-type dopant properties.

Within this framework and in the language of chemistry, the catalyst can clearly function as a donor or an acceptor of charge, respectively to or from the support. This will affect the structure and bonding of adsorbed surface species, as mentioned for CO above. In the context of heterogeneous catalytic hydrogenation of carbon dioxide by metal oxides containing different kinds of surface active defects, one can appreciate that charge transfer from the catalyst to the support will likely make Brønsted and Lewis acidity stronger and Brønsted and Lewis basicity weaker. As mentioned earlier, the enhanced Lewis acidity and Lewis basicity of the defect centres could result in a decrease in the activation energy for the rate determining carbon dioxide hydrogenation step; thus, the conversion rate will increase. This direction of charge transfer should also make surface active hydrides less hydridic. The opposite case will prevail for these examples if the charge transfer is in the reverse direction.

It is important to note that these ideas will also apply when the metal oxide support is itself a catalyst, where charge transfer induced cooperative effects may have synergistic or antagonistic effects on the resulting activity and selectivity pattern of the heterogeneous catalytic heterostructure.

Promoters and inhibitors

There is a long history in heterogeneous catalysis, especially for a number of large-scale industrial chemical processes, such as steam reforming, water gas shift, Fischer–Tropsch and methanol synthesis, of an additive being somehow able to promote the activity, selectivity and stability performance metrics of the chemical reaction.[50–53] The opposite effect can also occur, thereby inhibiting the chemical reaction. These modification effects, well documented in the annals of heterogeneous catalysis, have been under active scrutiny recently, both experimentally and theoretically, and generally traced to be structural or electronic in origin. The former can include changes in the surface structure and area, accessibility to active sites and sintering of the catalyst.[51] The latter includes alterations in the electronic band structure through charge transfer and re-hybridization, changes in adsorption energies of reactants, intermediates and products, and modifications of the free energy reaction profile.

Depending on the catalyst and catalytic reaction, the promotion and inhibition effects will be different and each case will need to be studied as a distinct system. This will certainly be the case for the use of promoters to enhance the performance of heterogeneous catalytic hydrogenation reactions of CO_2 to chemicals and fuels. Examples have been reported regarding the improvements of water gas shift by adding alkali to Pt/CeO_2, Pt/TiO_2, Pt/ZrO_2, and Pt/Al_2O_3, as well as in the case of Fischer–Tropsch processes catalysed by iron and ruthenium based materials. These findings are significant since the promoters bring these reactions to a lower temperature region. There are also reports showing that with alkali additives, the CO_2 conversion can be done in the absence of a noble metal.[54] Most of the cases witnessed a higher selectivity for methane production. In the context of CO_2 heterogeneous catalysis, promoters for the reverse water gas shift reaction have been reported.[55] In some cases the promoters are not only limited to alkali or alkaline earth metal oxides or hydroxides as additives, but also extended to some transition metal versions such as iron and lanthanum.[55]

CO_2 utilization road-map

On a final note we would like to explore the idea of establishing a testing and certification facility for the standardization of the performance of heterogeneous catalysts that convert CO_2 to value-added chemicals and fuels.

As mentioned earlier, catalysis has proven to be indispensable for the large volume manufacture of chemicals and fuels from fossil resources. In the context of climate changes, the growth of the CO_2 industry to the chemical and fuel industry will require the discovery of highly active, selective and stable catalysts that can efficiently and economically enable these CO_2 conversions on a massive scale. To truly impact climate changes, the envisioned CO_2 refineries will have to operate at the hundred megaton per year scale. Developing and commercializing industrial heterogeneous catalysts that can operate efficiently and stably at this scale will require standardization and certification of their performance, reliability, durability and safety.

Chemicals and fuels produced in a CO_2 refinery can be cost competitive with fossil feedstocks in a global marketplace only if catalysts can perform to warranted specifications for at least the length of their guarantee, which is typically 10–15 years for heterogeneous catalysts and reactors. It is however challenging to identify which catalysts will meet desired industry performance metrics, upon which envisioned business models will be founded, because currently there exist no standards to enable comparison of figures-of-merit between laboratories working on catalyst research and development for CO_2 utilization.

In this context, qualification tests are pivotal for defining, achieving, improving and maintaining CO_2 catalyst performance standards. Furthermore, it is desirable for the CO_2 catalysis community to be able to routinely obtain standardised test results in order to undertake a meaningful techno-economic life cycle analysis of energy and economic flows of an envisioned CO_2 refinery process.

While basic science in the field of heterogeneous CO_2 catalysis is burgeoning and patents are proliferating at an enormous rate, there is currently no standardization practice of the performance metrics for any of the reported catalysts.

This will be the bottleneck to technology transfer and will impede the development of CO_2 conversion demonstrators, pilot plants and ultimately CO_2 refineries.

Just like the design qualification test protocols for photovoltaics pioneered at the National Renewable Energy Laboratory (NREL), there is a desperate need for similar standardization of catalysts that enable conversion of gaseous CO_2 into chemicals and fuels. This will be crucial to ensure the overall performance, reliability, durability and safety of gas-phase heterogeneous catalysts that can generate chemicals and fuels with efficiencies and costs that make them commercially attractive compared to their fossil fuel competition.

In the war against climate change, this is an opportune moment in time to begin to develop test methods and implement standards in the field of CO_2 catalysis. The goal is to create a CO_2 utilization roadmap for guiding the development of high performance catalysts that will drive the production of a global network of CO_2 refineries.

This will require the establishment of a laboratory that specializes in the design and development of catalyst reactors and analytical instrumentation, specifically for the purpose of evaluating the efficacy, durability and reliability of catalytic materials able to convert gaseous CO_2 into chemicals and fuels, using electrical, solar and thermal forms of energy, under a standard set of reaction conditions. These CO_2 catalysts will emanate from university, government and industrial research and development laboratories and the goal is to place their performance on a CO_2 roadmap.

Champion catalysts for the gas-phase, heterogeneous catalytic hydrogenation of carbon dioxide

To discover, evaluate and optimize a high performance gas-phase carbon dioxide heterogeneous hydrogenation catalyst with all the desired attributes of activity, selectivity and stability will necessitate creative nanomaterial synthesis coupled with state-of-the-art structure–property characterization, operando spectroscopic investigations in conjunction with kinetic studies, ^2H and ^{13}C isotope labelling, and kinetic isotope investigations to probe surface transition states and mechanisms.

These are the bare minimum requirements to identify surface reaction intermediates, establish the rates and extent of conversion of reactants to desired products, determine turnover frequencies, ascertain reaction rate determining steps, obtain transition state information, define mechanistic details and elucidate deactivation pathways and how to circumvent them. Studies of this type can be profitably enhanced and enriched by computational materials simulations driven by ever increasing computational power and the proliferation of high-quality calculated materials data.

There is still much research to be done in the continuing quest for champion heterogeneous catalysts that can selectivity hydrogenate carbon dioxide to desired energy carriers. These conversions must be practiced at a large enough scale and through a global network of CO_2 refineries, such that they can begin to meaningfully impact climate change by converting greenhouse gas emissions into value-added chemicals and fuels.

It's a big vision with huge challenges and there is much work to be done but we have taken the first steps towards the conversion of our global energy system from one that is endangering the future health and well-being of humanity to one that can sustain it forever!

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References

1 R. J. D. Tilley, *Defects in Solids*, John Wiley & Sons, Inc., 2008.

2 A. M. Stoneham, *Theory of Defects in Solids: Electronic Structure of Defects in Insulators and Semiconductors*, Oxford University Press, 2001.

3 A. Wold and K. Dwight, *Solid State Chemistry: Synthesis, Structure, and Properties of Selected Oxides and Sulfides*, Springer Science & Business Media, 1993.

4 D. M. Smyth, *The Defect Chemistry of Metal Oxides*, Oxford University Press, 2000.

5 J. Jupille and G. Thornton, *Defects at Oxide Surfaces*, Springer Series in Surface Sciences, 2015.

6 C. Freysoldt, B. Grabowski, T. Hickel, J. Neugebauer, G. Kresse, A. Janotti and C. G. Van de Walle, *Rev. Mod. Phys.*, 2014, **86**, 253–305.

7 A. Alkauskas, P. Deak, J. Neugebauer, A. Pasquarello and C. G. V. d. Walle, *Advanced Calculations for Defects in Materials*, Wiley, 2011.

8 P. A. Cox, *Transition Metal Oxides*, Oxford University Press, 1992.

9 A. Walsh and K. T. Butler, *Acc. Chem. Res.*, 2014, **47**, 364–372.

10 C. A. Downing, A. A. Sokol and C. R. A. Catlow, *Phys. Chem. Chem. Phys.*, 2014, **16**, 21153–21156.

11 V. E. Henrich and P. A. Cox, *The Surface Science of Metal Oxides*, Cambridge University Press, 1994.

12 D. A. Drabold and S. Estreicher, *Theory of Defects in Semiconductors*, Springer, 2007.

13 M. V. Ganduglia-Pirovano, A. Hofmann and J. Sauer, *Surf. Sci. Rep.*, 2007, **62**, 219–270.

14 S. Kattel, P. J. Ramírez, J. G. Chen, J. A. Rodriguez and P. Liu, *Science*, 2017, **355**, 1296–1299.

15 A. A. Sokol, S. A. French, S. T. Bromley, C. R. A. Catlow, H. J. J. van Dam and P. Sherwood, *Faraday Discuss.*, 2007, **134**, 267–282.

16 K. Larmier, W.-C. Liao, S. Tada, E. Lam, R. Verel, A. Bansode, A. Urakawa, A. Comas-Vives and C. Copéret, *Angew. Chem., Int. Ed.*, 2017, **129**, 2358–2363.

17 G. Dutta, A. A. Sokol, C. R. A. Catlow, T. W. Keal and P. Sherwood, *ChemPhysChem*, 2012, **13**, 3453–3456.

18 H. Yaghoubi, Z. Li, Y. Chen, H. T. Ngo, V. R. Bhethanabotla, B. Joseph, S. Ma, R. Schlaf and A. Takshi, *ACS Catal.*, 2015, **5**, 327–335.

19 L. Liu, Y. Jiang, H. Zhao, J. Chen, J. Cheng, K. Yang and Y. Li, *ACS Catal.*, 2016, **6**, 1097–1108.

20 K. Kosuge, *Chemistry of Non-Stoichiometric Compounds*, Oxford Science Publications, 1994.

21 S. Andersson and A. D. Wadsley, *Nature*, 1966, **211**, 581–583.

22 K. Manthiram and A. P. Alivisatos, *J. Am. Chem. Soc.*, 2012, **134**, 3995–3998.

23 S. D. Lounis, E. L. Runnerstrom, A. Llordés and D. J. Milliron, *J. Phys. Chem. Lett.*, 2014, **5**, 1564–1574.

24 C. J. Kevane, *Phys. Rev.*, 1964, **133**, A1431–A1436.

25 C. R. A. Catlow and B. E. F. Fender, *J. Phys. C: Solid State Phys.*, 1975, **8**, 3267.

26 C. Noguera, *Physics and Chemistry at Oxide Surfaces*, Cambridge University Press, 1996.

27 K. K. Ghuman, L. B. Hoch, T. E. Wood, C. Mims, C. V. Singh and G. A. Ozin, *ACS Catal.*, 2016, **6**, 5764–5770.

28 K. K. Ghuman, L. B. Hoch, P. Szymanski, J. Y. Y. Loh, N. P. Kherani, M. A. El-Sayed, G. A. Ozin and C. V. Singh, *J. Am. Chem. Soc.*, 2016, **138**, 1206–1214.

29 K. K. Ghuman, T. E. Wood, L. B. Hoch, C. A. Mims, G. A. Ozin and C. V. Singh, *Phys. Chem. Chem. Phys.*, 2015, **17**, 14623–14635.

30 L. B. Hoch, T. E. Wood, P. G. O'Brien, K. Liao, L. M. Reyes, C. A. Mims and G. A. Ozin, *Adv. Sci.*, 2014, **1**, 1400013.

31 L. B. Hoch, P. Szymanski, K. K. Ghuman, L. He, K. Liao, Q. Qiao, L. M. Reyes, Y. Zhu, M. A. El-Sayed, C. V. Singh and G. A. Ozin, *Proc. Natl. Acad. Sci. U. S. A.*, 2016, **113**, E8011–E8020.

32 J. Jia, P. G. O'Brien, L. He, Q. Qiao, T. Fei, L. M. Reyes, T. E. Burrow, Y. Dong, K. Liao, M. Varela, S. J. Pennycook, M. Hmadeh, A. S. Helmy, N. P. Kherani, D. D. Perovic and G. A. Ozin, *Adv. Sci.*, 2016, **3**, 1600189.

33 W. Wang, S. Wang, X. Ma and J. Gong, *Chem. Soc. Rev.*, 2011, **40**, 3703–3727.

34 Z. W. Seh, J. Kibsgaard, C. F. Dickens, I. Chorkendorff, J. K. Nørskov and T. F. Jaramillo, *Science*, 2017, **355**, eaad4998.

35 J. Sauer and H.-J. Freund, *Catal. Lett.*, 2015, **145**, 109–125.

36 T. W. Keal, P. Sherwood, G. Dutta, A. A. Sokol and C. R. A. Catlow, *Proc. R. Soc. A*, 2011, **467**, 1900.

37 M. Ghoussoub, S. Yadav, K. K. Ghuman, G. A. Ozin and C. V. Singh, *ACS Catal.*, 2016, **6**, 7109–7117.

38 P. G. O'Brien, A. Sandhel, T. E. Wood, A. A. Jelle, L. B. Hoch, D. D. Perovic, C. A. Mims and G. A. Ozin, *Adv. Sci.*, 2014, **1**, 1400001.

39 L. B. Hoch, P. G. O'Brien, A. Jelle, A. Sandhel, D. D. Perovic, C. A. Mims and G. A. Ozin, *ACS Nano*, 2016, **10**, 9017–9025.

40 L. He, T. E. Wood, B. Wu, Y. Dong, L. B. Hoch, L. M. Reyes, D. Wang, C. Kübel, C. Qian, J. Jia, K. Liao, P. G. O'Brien, A. Sandhel, J. Y. Y. Loh, P. Szymanski, N. P. Kherani, T. C. Sum, C. A. Mims and G. A. Ozin, *ACS Nano*, 2016, **10**, 5578–5586.

41 Y. Dong, K. K. Ghuman, W. Zhou, J. Y. Y. Loh, A. Jelle, J. Jia, P. Duchesne, M. Ghoussoub, L. Reyes, D. Wang, R. Popescu, C. Kubel, Q. Wang, L. Wang, Z. Hu and G. A. Ozin, under review.

42 X. Meng, T. Wang, L. Liu, S. Ouyang, P. Li, H. Hu, T. Kako, H. Iwai, A. Tanaka and J. Ye, *Angew. Chem., Int. Ed.*, 2014, **53**, 11478–11482.

43 F. Sastre, A. V. Puga, L. Liu, A. Corma and H. García, *J. Am. Chem. Soc.*, 2014, **136**, 6798–6801.

44 S. Kattel, B. Yan, Y. Yang, J. G. Chen and P. Liu, *J. Am. Chem. Soc.*, 2016, **138**, 12440–12450.

45 H. Wang, S. Xu, C. Tsai, Y. Li, C. Liu, J. Zhao, Y. Liu, H. Yuan, F. Abild-Pedersen, F. B. Prinz, J. K. Nørskov and Y. Cui, *Science*, 2016, **354**, 1031–1036.

46 H. Wang, J. Jia, K. T. Butler, M. Ghoussoub, L. Wang, Z. Zheng, Y. Dong, A. Walsh and G. A. Ozin, under review.

47 X. Chen, L. Liu and F. Huang, *Chem. Soc. Rev.*, 2015, **44**, 1861–1885.

48 G. A. Ozin, *Adv. Mater.*, 2015, **27**, 1957–1963.

49 M. E. Strayer, T. P. Senftle, J. P. Winterstein, N. M. Vargas-Barbosa, R. Sharma, R. M. Rioux, M. J. Janik and T. E. Mallouk, *J. Am. Chem. Soc.*, 2015, **137**, 16216–16224.

50 J. M. Thomas and W. J. Thomas, *Principles and practice of heterogeneous catalysis*, John Wiley & Sons, 2014.

51 K. Jens, F. Studt, F. Abild-Pedersen and T. Bligaard, *Fundamental concepts in heterogeneous catalysis*, John Wiley & Sons, 2014.

52 J. R. Ross, *Heterogeneous catalysis: fundamentals and applications*, Elsevier, 2011.

53 G. Ertl, *Handbook of heterogeneous catalysis: 8 volumes*, 2008.

54 X. G. Meng, S. X. Ouyang, T. Kako, P. Li, Q. Yu, T. Wang and J. H. Ye, *Chem. Commun.*, 2014, **50**, 11517–11519.

55 H.-C. Wu, T.-C. Chen, J. H. Wu, C.-H. Chen, J.-F. Lee and C.-S. Chen, *Catal. Sci. Technol.*, 2016, **6**, 6087–6096.