REVIEW ARTICLE

CO_2 Utilization Through its Reduction to Methanol: Design of Catalysts Using Quantum Mechanics and Machine Learning

Meghna A. Manae[1] · Lakshay Dheer[1] · Umesh V. Waghmare[1]

Abstract

Reducing levels of CO_2, a greenhouse gas, in the earth's atmosphere is crucial to addressing the problem of climate change. An effective strategy to achieve this without compromising the scale of industrial activity involves use of renewable energy and waste heat in conversion of CO_2 to useful products. In this perspective, we present quantum mechanical and machine learning approaches to tackle various aspects of thermocatalytic reduction of CO_2 to methanol, using H_2 as a reducing agent. Waste heat can be utilized effectively in the thermocatalytic process, and H_2 can be generated using solar energy in electrolytic, photocatalytic and photoelectrocatalytic processes. Methanol being a readily usable fuel in automobiles, this technology achieves (a) carbon recycling process, (b) use of renewable energy, and (c) portable storage of H_2 for applications in automobiles, alleviating the problem of rising CO_2 emissions and levels in atmosphere.

Keywords CO_2 utilization · Methanol · Hydrogen evolution reaction · CO_2 reduction reaction · Hydrogen storage · Density functional theory · Quantum mechanics · Machine learning · Catalysis · Green technology

Introduction

A dire predicament faced globally today is that of increased CO_2 emissions, which contribute significantly to global warming. While CO_2 occurs naturally in the earth's atmosphere originating from sources such as volcanoes, forest fires, hot springs and geysers, its concentration has increased from pre-industrial levels of 280 ppm to 412 ppm in 2020 (Blunden and Arndt 2020; Eggleton and Eggleton 2013). Such rise in CO_2 levels over the course of the industrial revolution is primarily anthropogenic and can be attributed largely to the increased use of fossil fuels.

While there is an overall increase in fossil fuel based CO_2 emissions over the years, there have been some occasional dips correlating with slumps in industrial activity. For instance, the dip recorded in 2007–2008 corresponded to the global financial crisis (GFC). More recently, due to the COVID-19 pandemic, a sharp reduction in CO_2 emissions has been estimated (Le Quéré et al. 2020). Interestingly however, each such a drop is followed by a steep rise indicating the revival of the economy and industrial activity. Sustained economic growth thus necessitates technologies to stall rising CO_2 emissions.

To combat CO_2 emissions, drastic scaling down of industrial activity is both impractical and futile. Rather, a more effective strategy for sustainability is to convert the emitted CO_2 to potentially useful, value-added chemicals. In this regard, the CO_2 reduction reaction (CO2RR) is especially relevant, and involves reduction of CO_2 to form compounds such as carbon monoxide, methane, methanol (MeOH) and dimethyl ether, among others. In this perspective, our focus is on MeOH as a product of CO2RR and how computer simulations can be a powerful tool in development of efficient catalytic materials to achieve high performance technology.

Hydrogen as a Green Fuel: Importance and Challenges

Dihydrogen (H_2) is critical in its role as a reducing agent in hydrogenation of CO_2. Also, H_2, by itself, is a zero-emission fuel with a high combustion energy, and can be used to power liquid-propellant rockets, automobiles, and fuel cells. H_2 is rarely found in its pure form in the atmosphere because of its molecular weight being significantly lower than air.

✉ Umesh V. Waghmare
  waghmare@jncasr.ac.in

1 Theoretical Sciences Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur, Bengaluru 560064, India

Also, production of H_2 at an industrial scale comes at an energy cost. As of 2020, most usable H_2 is being produced through steam reforming of fossil fuels (Collodi 2010; Liu et al. 2010). Undesirably, this ties back to the problem of CO_2 emissions and the advantage of H_2 being a clean fuel is compromised.

A major technological challenge in the use of H_2 as a fuel in automobiles is its safe storage that is mass and volume efficient. Its qualities of having low ignition energy and high combustion energy make it an excellent fuel but also dangerous to store, transport, and handle. Current techniques to store H_2 include tuning external conditions, i.e., high pressures and low temperatures. Car manufactures such as Honda and Nissan have been developing the former approach with compressed H_2 in tanks at pressures as high as 350–700 bar (Eberle et al. 2012), while the BMW Hydrogen 7 (a limited edition car) uses the latter technique by using liquid H_2 in its fuel tanks by lowering temperatures to -253 °C (Wallner et al. 2008). As of 2019, commercially available fuel cell vehicles (FCV) powered by H_2 include Toyota Mirai, Hyundai Nexo, and Honda Clarity.

Despite the established technologies, H_2 at high pressures requires strong materials for storage and achieving low temperatures requires significant energy, resulting in greater costs. Solid state or chemical storage circumvent these disadvantages and also offers high storage densities. Metal hydrides, which fall in this category, are in development for use in automobiles (Lototskyy et al. 2017). Alternatives for solid state and chemical storage of H_2 are active areas of research, and the technology described here amounts to chemical storage of H_2 in the form of MeOH.

Methanol as an Alternative Fuel

MeOH is used as a precursor in production of several commodity chemicals, such as formaldehyde, acetic acid, methyl tert-butyl ether, among others. In 2005, Nobel laureate George A. Olah, proposed the idea of methanol economy, to replace fossil fuels as the primary source of energy (Olah 2003, 2005; Olah et al. 2009). Methanol can be used readily as an alternative fuel in internal combustion engines, in addition to being used as a cooking fuel (Saraswat and Bansal 2017; Shih et al. 2018). Use of MeOH in internal combustion engines, in lieu of fossil fuel derived petroleum, offers several advantages. It is significantly cheaper, and can also be derived from organic waste. It is harder to ignite than gasoline, making MeOH fires unlikely. In case of accidents, it does not produce opaque smoke clouds, and fires due to MeOH can be easily extinguished with water. These factors add to the promise of a methanol economy, and the global demand of MeOH, which was ~ 70 million metric tons in 2015, is expected to go up significantly (Roy et al. 2018a, b).

Currently, MeOH is produced industrially by passing syngas (a mixture of H_2 and CO) over $Cu/ZnO/Al_2O_3$, at 50–100 bar and 473–573 K (Bart and Sneeden 1987; Behrens et al. 2012). Production of syngas is predominantly through gasification of coal and steam reformation (Liu et al. 2010). We note that the same process is used in the generation of H_2, and ties back to the problem of additional CO_2 emissions. Generating MeOH through CO2RR does not suffer from this disadvantage. As mentioned earlier, MeOH, generated from the addition of H_2 to CO_2, also amounts to chemical storage of H_2 and innovative portable use of H_2 as a fuel.

Sustainable Production of Methanol Using Renewable Energy

CO_2 capture is the first step towards utilization of CO_2. Of the various sources of CO_2 emissions (Davis et al. 2018) (Fig. 1), not all qualify as emission streams which can be used readily as inputs in a CO_2 capture process. Sources which can be used as emission streams include the flue gas from thermal power stations, emissions from oil refineries, blast furnace gas, and cement kiln off-gas (Rubin and De Coninck 2005). In addition to being some of the strongest sources of CO_2 emissions, these sources also generate considerable amounts of waste heat.

Therefore, a thermocatalytic approach to the CO2RR is attractive because it would reduce CO_2 emissions while making use of the already generated waste heat. When the required intake of H_2 is generated using solar energy through photocatalytic and photoelectrocatalytic approaches, this further reduces the overall CO_2 emission in the process.

Despite generating H_2 using clean energy sources, and carrying out CO2RR using waste heat, use of the produced MeOH as a fuel will add to CO_2 emissions. In principle, CO_2 generated from burning of MeOH as a fuel can be recycled
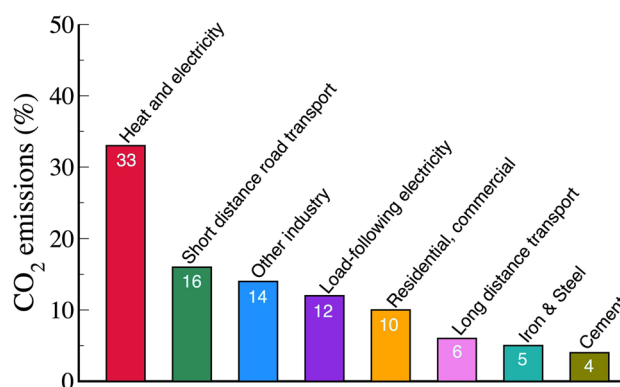

Fig. 1 Share of CO_2 emissions due to various human activities for the year 2014, with the percentages indicated inside the bars. The overall annual CO_2 emissions amounts to 33.9 gigatons (Davis et al. 2018)

back to generate more MeOH, making the process carbon neutral (Fig. 2). In the overall process, renewable energy conversion, hydrogen generation and storage, and reduced CO_2 emissions can be achieved.

In this perspective, we discuss various aspects of realizing this goal (Fig. 2), with an emphasis on how computer simulations can be cost-effective and efficient tools in development of such technology. In the next section, we discuss two main theoretical approaches to this problem. This is followed by sections on H_2 generation and CO2RR. Finally, the challenges and opportunities for simulation techniques are presented along with conclusions.

Uncovering Overall Operation of Catalysis: Computer Simulations

Catalysts play key role in most industrial reactions in terms of their efficiency of conversion as well as selectivity of products. A catalyst is a material on the surface of which reactants find an energetically easy pathway to form products in selective manner. In the past 2–3 decades, remarkable progress has been achieved experimentally in the field of reduction of CO_2 (Álvarez et al. 2017; Roy et al. 2018a, b; Wang

et al. 2015). However, experimental identification and isolation of reaction intermediates forming on the catalyst surface is still a challenge owing to their short lifetimes. Computer simulations are powerful tools in complementing experiments in this task. Despite having short lifetimes, intermediates are minima in the energy landscape of the reaction, and are accessible to first-principles quantum mechanical density functional theory (DFT) calculations. These calculations determine interatomic interaction potential through simulation of quantum motion of electrons, giving access to interactions between various reacting species with the catalyst surface and each other (Weijing et al. 2018). Transition states, in comparison to reaction intermediates, have even shorter lifetimes. Experimentally, this is the characteristic difference between the two. Both intermediates and transition states are stationary points in the energy landscape: intermediates are local minima while transition states are typically first-order saddle points, and this topological difference helps in the optimization and analysis of these entities.

Revealing Mechanism of Catalysis Using Quantum Mechanics: Density Functional Theory

First-principles DFT calculations give an estimate of the electronic structure (energy and density) of the ground state for a given nuclear geometry. Among computational quantum mechanical methods, DFT is one of the most popular, efficient and versatile methods, and used extensively in materials science. In DFT, exact form of the exchange–correlation (XC) energy functional is not known, and many flavors of its approximations have been developed. Primary among these are the local-density (LDA) (Becke 1986) and generalized gradient (GGA) (Perdew et al. 1996) approximations. LDA is based on XC energy of uniform electron gas and tends to give an overbinding description, leading to high chemisorption energies and barriers (Becke 1986, 2014). Overbinding of LDA is partially corrected in GGA (Beck 1993; Becke 2014), which is a commonly used functional approximation in computational heterogeneous catalysis. Although functionals more accurate than GGA (hybrid XC functionals such as B3LYP, PBE0, M05-2X) have been developed, their high computational cost for large systems typically restrict the level of theory to GGA.

Results obtained within DFT depend on the XC functional used, and therefore, the functionals need to be selected carefully to estimate energies which are accurate and physically meaningful (Christensen et al. 2015). A reliable way to support the selection of an optimal XC functional is through comparison of the calculated values (structural parameters and band gaps of reactants and products) with experiment. However, experimental values of adsorption energies, activation barriers, and structures of intermediates may not be available. Several studies have benchmarked
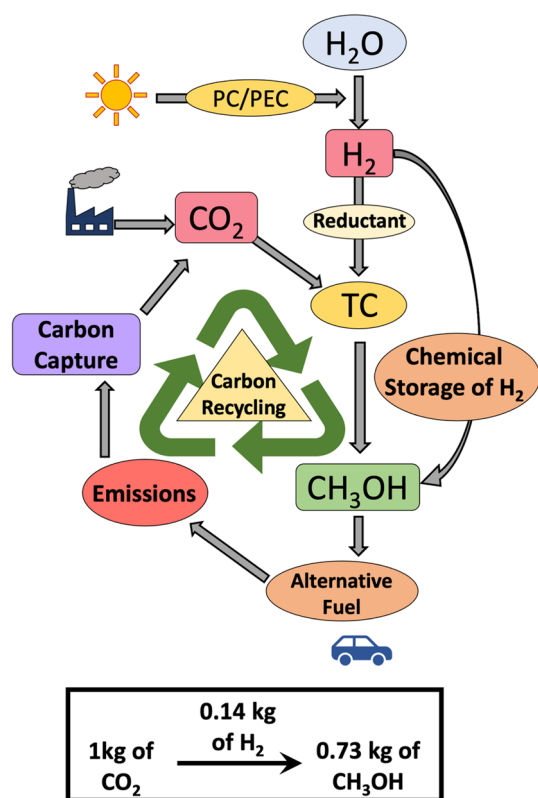

Fig. 2 Schematic of a sustainable process where MeOH is generated. PC, PEC and TC denote photocatalytic, photoelectrocatalytic, and thermocatalytic, respectively

the performance of various XC functionals in the context of catalysis. For instance, the RPBE (Hammer et al. 1999) and BEEF-vdW (Wellendorff et al. 2012) XC functionals have been specifically developed to study catalytic reactions and are shown to be ideal for estimation of chemisorption energies (Teng et al. 2014; Wellendorff and Silbaugh 2015). Both GGA and LDA do not capture the van der Waals interactions, and a parametrized form of the Grimme D2 scheme (Grimme 2006) of van der Waals correction improves the description of interactions greatly. PBE–Grimme D2 (Perdew et al. 1996), a popular and frequently used GGA-XC functional in heterogeneous catalysis, is known to be reliable in reproducing experimental enthalpies relevant to CO_2 reduction reactions fairly accurately (Christensen et al. 2015; Perdew et al. 1996).

Investigating Reaction Pathways and Mechanisms

The energies of intermediates, reactants and products, constitute parameters in the thermodynamic analysis of the reaction. The relative energy of products in comparison to reactants, the enthalpy, is the amount of heat generated or consumed in a reaction (see Fig. 3). Energies of the transition states, on the other hand, provide activation energies (Fig. 3) which are inversely related to the rate of the reactions. They are a measure of energy to activate an intermediate through stretching or breaking of bonds.

The structures and energies of the reactants, products, all intervening intermediates and transition states constitute the complete pathway, or mechanism, of a reaction (Fig. 3). Often, more than one mechanism is proposed experimentally based on identification of some intermediates. In such a situation, theory is in a position to narrow down the most likely pathway or the mechanism by comparing intermediate energies and associated activation barriers (Cherevotan et al. 2021). Structures of the catalyst-reacting species complex
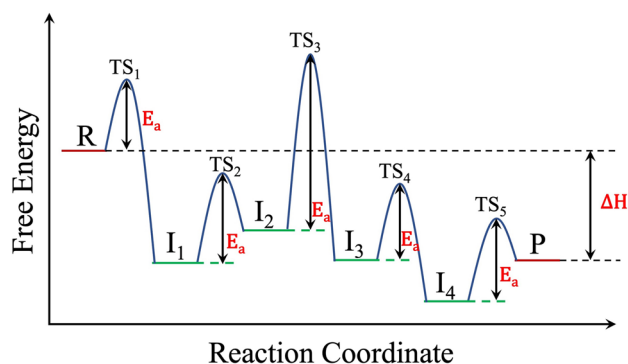

Fig. 3 Schematic of a reaction mechanism, where, R, P, I, TS, represent the reactant, product, intermediates, transition states, respectively, and E_a, ΔH represent activation energies, and enthalpy of the reaction, respectively

are useful to identify active sites on catalysts along with spectroscopic information. This is especially important for multistep reactions, where different active sites on a catalyst assist in different steps of the reaction. Identification of active sites also helps in the design of more efficient and cheaper catalysts.

In the forthcoming sections ("Mechanistic Insights into HER from Computer Simulations" and "Mechanistic Insights into CO2RR from Computer Simulations"), the mechanisms and catalysts for Hydrogen Evolution Reaction and CO2RR are discussed, with emphasis on how computer simulations have helped in mechanistic understanding, and hence in the design of new materials to increase the efficiency of these chemical processes.

Descriptors for High-Throughput Screening: Machine Learning

Understanding the mechanism of a reaction is tremendously useful in intuitive approaches for improving the catalyst. However, using purely mechanistic approaches to predict new materials as catalysts is enormously computationally expensive. This is further complicated by the exceedingly large number of candidate materials which can potentially serve as catalysts, and first-principles calculations of detailed mechanistic pathways on each of these materials and their various surfaces is simply impractical. Therefore, there is a need for an efficient simulation tool to screen through a large library of materials, possibly through an algorithm which can analyze the data on structural, chemical, and electronic properties of materials to provide insightful predictions. These paradigms already exist in areas such as drug design and protein structure prediction, and while their translation to material science has been limited by the available data and computational costs, the recent advances in computational throughput and access to data have increased its feasibility. Databases of information on materials, such as the Materials Genome Initiative (de Pablo 2014), Materials Project (Jain et al. 2013), and MatWeb (MatWeb 2013), among others, are the examples of these initiatives.

In general, descriptors are a set of physically meaningful parameters or properties of materials, and material databases comprise typically a large number of descriptors, for a large set of materials (Ghiringhelli et al. 2015). Artificial neural networks (ANN) are useful in modelling the relationship between all the descriptors and the target property [the key performance index (KPI)] (Bhadeshia 2009, 1999). In contrast, machine learning (ML) schemes such as least absolute shrinkage and selection operation (LASSO) and bootstrapped projected gradient descent (BoPGD) are the feature selection schemes that can be effectively used in determination of the minimal set of fingerprint descriptors starting from a large pool of descriptors or their combinations
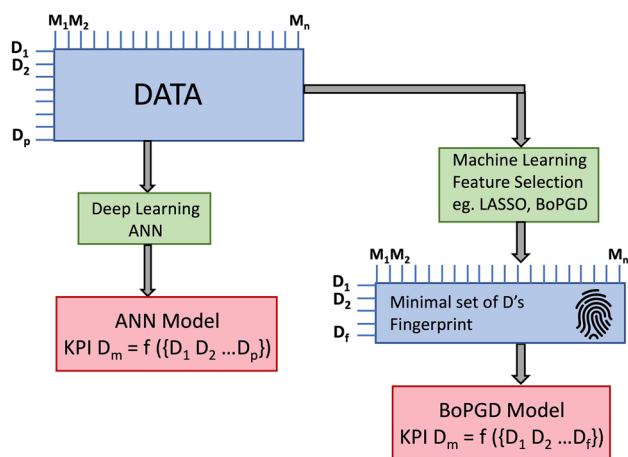
Fig. 4 Representation of machine learning schemes to map a set of descriptors D_i for a set of n materials M_j to obtain a model which can predict the Key Performance Index (KPI) for a new material

(Kumar et al. 2018; Pankajakshan et al. 2017). Descriptors should ideally (a) be easy to calculate, (b) be able to uniquely characterize the material property (i.e. be distinctive for different materials), and (c) the set of such descriptors should be as small as possible. These can be used to develop a simple model (M) which relates the fingerprint descriptors (D) (corresponding to a set of materials (C)), with a KPI or key performance indicator (Fig. 4). Recently, dimensional analysis and scaling laws were combined with BoPGD ML approach to derive models that learn from data as well as wisdom (Kumar et al. 2018; Pankajakshan et al. 2017). Such models are often more generalizable than ANNs because their construction involves determination and use of physically meaningful descriptors. This model, M, can then be applied to new materials, to predict their KPI. In the forthcoming sections ("Descriptors for HER" and "Descriptors for CO2RR"), descriptors for H_2 generation and CO2RR, and the role they play in greater understanding of the respective processes are discussed.

Hydrogen Evolution Reaction

H_2, as a fuel, possesses the highest energy per unit mass. It has the added benefit of being a clean fuel since the only by-product of its combustion is H_2O. It is also used extensively as a reducing agent. A clean and efficient method of producing H_2 has thus been studied extensively for the past few decades. One of the most elementary processes to produce H_2 is water splitting, i.e., the chemical splitting of H_2O into oxygen and hydrogen, which was first reported in 1789 (De Levie 1999; van Troostwijk and Deiman 1789). Electrochemical splitting of water is a redox reaction consisting of an oxidation (oxygen evolution reaction, OER)

and a reduction (hydrogen evolution reaction, HER) half-cell reactions:

$$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^- \,(OER)$$
$$2H^+(aq) + 2e^- \rightarrow H_2(g) \,(HER)$$
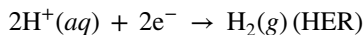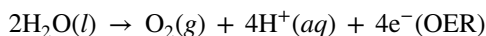
An ideal water splitting photocatalyst should have electronic conduction band minima (CBM) just above the hydrogen reduction potential and valence band maxima (VBM) just below the oxygen evolution potential on the standard hydrogen electrode (SHE) scale (Fig. 5). CBM is the lowest energy unoccupied electronic state, while VBM is the highest energy occupied state. The gap between the CBM and VBM is called the band gap, and this gap determines whether a material is a conductor, insulator, or a semi-conductor. Optical excitation of an electron (e^-) from VBM to CBM, creates a hole (h^+) in the VBM (Fig. 5), and resulting pair of electron and hole can be used to catalyse both the half-cell reactions (HER and OER, respectively) and thus efficiently split water molecules to yield H_2 (g) and O_2 (g).

In the case of electrocatalysis, OER and HER are carried out on specifically designed catalysts which reduce the electrochemical overpotential, thus making the reactions feasible. Overpotential is the voltage difference between the thermodynamic reduction potential and the potential at which the reaction occurs experimentally (Morales-Guio et al. 2014). Efficient catalysts are those materials that facilitate the reaction at lower overpotentials. Currently, the best catalysts for HER are platinum-group metals, which include ruthenium, rhodium, palladium, osmium, iridium,
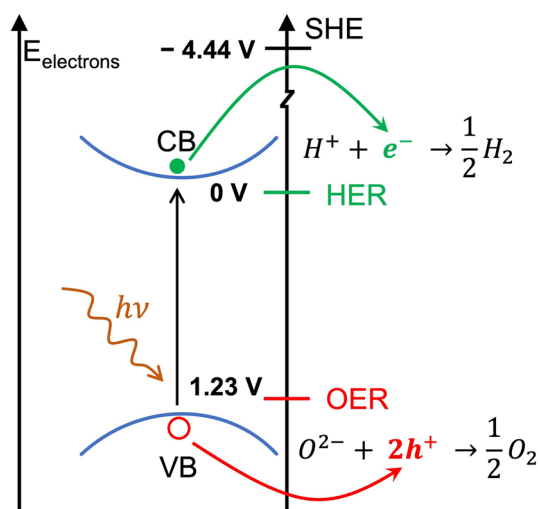

Fig. 5 Conduction band maximum (CB) and valence band minimum (VB) of an ideal water splitting photocatalyst aligned with the standard hydrogen electrode (SHE) scale. HER and OER mean hydrogen evolution reaction, and oxygen evolution reaction, respectively. Electron (filled green circle) and hole (unfilled red circle) are indicated e^-, and h^+, respectively (colour figure online)

and platinum. However, the dearth and high cost of these elements hinders their use as catalysts on an industrial scale (Bockris 1970; Trasatti 1972).

Mechanisms and Conditions for HER

HER can proceed via two reaction pathways (Fig. 6), Volmer-Heyrovsky and Volmer-Tafel pathways, both consisting of two elementary steps, each involving the transfer of one electron from the cathode to H^+, evolving H_2 (Morales-Guio et al. 2014). The first step (Volmer) is common to both pathways and corresponds to the adsorption of the first proton on an available active site of the catalyst. An electron transfers from the catalyst to the proton to yield an adsorbed H atom (Fig. 6). Following this step, the formation and subsequent evolution of H_2 can occur via two dissimilar routes. The first is the Heyrovsky step, where, a proton from the solution reacts with the adsorbed H-atom to form H_2. This happens simultaneously with transfer of another electron from the electrode evolving H_2. This step is also referred to as the *ion + atom* reaction (Morales-Guio et al. 2014). The second pathway involves the Tafel step, where, another proton attaches to the electrode surface in the vicinity of the first H-atom. The two adsorbed H-atoms coalesce to give H_2, and thus this is a *combination* reaction.

HER is generally carried out in acidic media where hydronium ions (H_3O^+) serve as the source of protons. Previously, it has been shown that some of the most effective materials for acidic HER are sulfides, carbides and phosphides (Attanayake et al. 2020; Chhetri et al. 2016; Dheer et al. 2020; Kouser et al. 2015; Roy et al. 2018a, b; Sarkar et al. 2020; Vesborg et al. 2015; Zou and Zhang 2015). However, for industrial scaling of HER, OER, the oxidation half of the reaction, should also be efficient in the same medium (Attanayake et al. 2020; Gong et al. 2016; Montoya et al. 2017; Thenuwara et al. 2016a, b; Thenuwara et al. 2016a, b). Since many inexpensive OER catalysts fail in acidic medium, it is preferable to choose an alkaline medium to split water and generate hydrogen (Thenuwara et al. 2018). Additionally, alkaline medium is known to reduce corrosion of non-noble metal catalysts and keep them functional for longer cycles. HER follows the same mechanisms in both acidic and alkaline media but there is an additional

step involved in the latter. The catalyst also has to break the stronger covalent H–O–H bonds to produce H^+ for the reaction, instead of the dative covalent bond in H_3O^+ ion, which is a weaker interaction. Computer simulations of the H_2O adsorption and splitting gives insight into the activity of a catalyst in alkaline medium based on the activation of the H–O–H bond (Kou et al. 2018; Mahmood et al. 2018; Maslovara et al. 2019; Mohammed-Ibrahim and Sun 2019; Narasimman et al. 2021).

## Mechanistic Insights into HER from Computer Simulations

A catalytic process involves interaction of reactants, intermediates, and products on the electrode surface. Quantifying the strength of interaction of these molecular moieties gives insights into the possible mechanism and helps identify the rate-determining step along the reaction. It is possible to obtain the relative potential energy cost associated with each elementary reaction along a pathway and determine the activity of the material as a catalyst. Identifying active sites and tuning the catalytic activity of a material is also possible using computational analysis.

As mentioned above, for a catalyst to carry out HER in an alkaline medium, it should be able to activate the H–O–H bond and cleave it within reasonable energy cost (Thenuwara et al. 2016a, b). Once the protons are generated, the H-atom intermediate should adhere to the catalyst neither exceedingly strongly, nor very weakly. This is because of the Sabatier principle which states that if the intermediate (H* in this case) attaches strongly to the material, the formation of product from the intermediate will be hindered. On the other hand, if the catalyst interacts with an intermediate weakly, it will quickly desorb from the surface before forming the product, rendering the reaction unfeasible.

Descriptors for HER

Gibbs free energy of adsorption of H, ΔG_{H*}, is a widely used parameter to probe the catalytic activity of any material for HER and a value close to 0 eV is desirable (Choi et al. 2013; Greeley et al. 2006; Hinnemann et al. 2005; Nørskov et al. 2005). Pt is known for stabilising the H*

Fig. 6 The mechanism of hydrogen evolution on the surface of a cathode
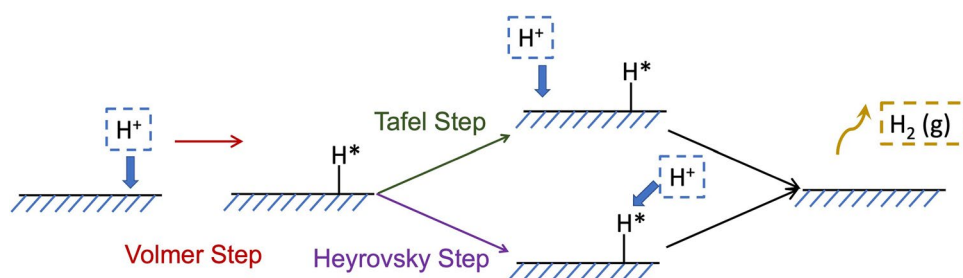
intermediate with a ΔG_{H*} of approximately -0.1 eV. By computing ΔG_{H*} within first-principles DFT for various metallic surfaces, Nørskov et al. showed a volcano shape relationship between ΔG_{H*} and exchange current density (Nørskov et al. 2005). However, this approach does not consider the effects of an electrode–electrolyte interface, and a passivation layer on measuring the properties of metals. Work function of a metal, φ, is another parameter that was recently demonstrated as a descriptor for HER by Zeradjanin et al. (Zeradjanin et al. 2017). Work function is the minimum thermodynamic work, or energy, required to remove an electron from the surface of a material. They showed that there exists a similar volcano type relation between the exchange current density and the difference in work functions ($\Delta\varphi$) of hydrogenated and non-hydrogenated metals in the presence of an interfacial layer of water molecules. $\Delta\varphi$ as a descriptor only explains the ability of hydrogen to adhere to potential catalysts without considering important factors like changes in the electrolyte, interfacial interactions, to name a few, which play a key role in determining the kinetics of the reaction. While there are not many other descriptors of HER, it is worth noting that they depend invariably on how H binds to the surface.

Reduction of CO_2 to MeOH

### Established Mechanisms of CO_2 Reduction to MeOH

CO_2 is a significantly stable molecule and hence the activation of the C=O bond is a challenge. Here, activation of a bond refers to cleavage or elongation of the bond. Also, CO_2 is a Lewis acid, implying that a catalyst should have the ability to donate electrons to (the anti-bonding orbitals of) CO_2 for successful thermocatalytic conversion of CO_2. The overall reaction ($CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$) is exothermic with an enthalpy of -49.3 kJ mol^{-1} at 298.15 K, meaning, high temperatures would hinder the reaction. Currently, a metal that can successfully reduce CO_2 to MeOH on an industrial scale is Cu (Liu et al. 2003; Wang et al. 2011).

Mechanism of a catalytic reaction naturally depends on the catalyst being used, and three established mechanisms of CO2RR to MeOH on Cu as the catalyst are discussed below, since it is currently the most widely used (Li et al. 2015; Tang et al. 2017). These established mechanisms form the standard with which reaction mechanisms on new catalytic materials can be compared with, to assess their catalytic performance. The three mechanisms are the formate (orange and purple pathways in Fig. 7), RWGS (CO hydrogenation) (red pathway in Fig. 7), and carboxylic acid (green and blue pathways in Fig. 7) mechanisms, differentiated by first intermediates, which are formate (HCOO*), carbon monoxide (CO), and *trans*–COOH, respectively. These intermediates effectively control the rate of the reaction, and their formation is the rate-determining step in the respective mechanism. It should be noted that the aforementioned intermediates have been experimentally obtained. Therefore, they act as starting points of computational research to decipher the subsequent intermediates and map the entire mechanism (Fig. 7). These identify the intermediates which crucially affect reaction rates, which are hard to isolate experimentally. This is an illustration of how experiment and computer simulations work synergistically to obtain mechanisms.

Despite significant overlapping parts of these pathways (Fig. 7), the mechanism appears complex. Further, the formate pathway additionally branches into formate-1,

Fig. 7 Reaction pathways of CO_2 hydrogenation to MeOH on Cu as the catalyst. Pathways coloured green, orange, purple, red, and blue indicate the *cis*–COOH, formate (1 and 2), formate-3, RWGS and *trans*–COOH pathways. The various pathways are differentiated based on the intermediate formed after the addition of the first H$^+$ atom
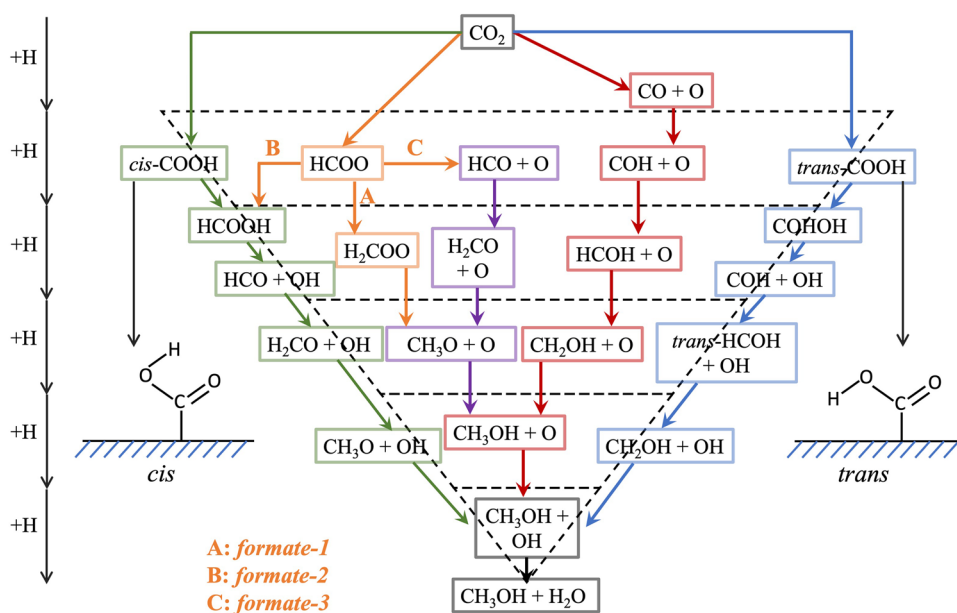
formate-2, and formate-3 pathways. In the forthcoming subsection, the mechanism is clarified with the aid of first-principles computer simulations. Further, catalysts apart from Cu, and the accompanying mechanism are also discussed.

Mechanistic Insights into CO2RR from Computer Simulations

Computer simulations have found the formate-2 pathway to be kinetically favourable over the formate-1 pathway (Fig. 7) in the case of Cu(111) (Grabow and Mavrikakis 2011; Tang et al. 2017). Kinetically favourable implies that the barriers between intermediates (E_a in Fig. 3) are reasonably low. The HCOO* intermediate can bind to the surface either in a monodentate or a bidentate fashion, depending on the catalyst, meaning that it can form one (monodentate) or two (bidentate) bonds with the surface. If HCOO* were to bind to the surface in a bidentate manner, then the incoming H* can only attack the C atom of HCOO*, thus reducing the possibility of the formate-2 pathway. This has been observed in the case of Cu (111) (Grabow and Mavrikakis 2011; Zhao et al. 2011) and Ni-doped Cu (111) (Yang et al. 2012). This example illustrates how computer simulations probe these reactions at an atomistic level, providing insight which is not possible through experiments.

The *trans*–COOH pathway is named so because in the –COOH group, attached to the surface, the H and carbonyl O are in a *trans* configuration or arrangement. While a *cis* configuration is also possible (see insets in Fig. 7 for *cis* and *trans* configurations), it cannot be formed directly from hydrogenation of CO_2. In the *trans*–COOH configuration, the H atom is closer to the surface of the catalyst (Fig. 7). They are distinguishable only by the direction of the OH group. Computer simulations indicate that the *cis* and *trans* configurations are interconvertible because of similar stabilities (Tang et al. 2017). Therefore, the formation of the *cis* and *trans* configurations does not necessarily decide which pathway is chosen (green or blue in Fig. 7), since the *cis* and *trans* configurations can switch easily.

Descriptors for CO2RR

A catalyst's ability to bind with an adsorbate strongly depends on the electronic structure of the surface. In the context of CO2RR, the catalyst's ability to activate the O=C=O bond depends on its capacity to donate electrons from its filled *d*-orbitals to the anti-bonding (π^*) orbitals of CO_2. The *d*-band model suggests that the extent of coupling between the *d* and π^* orbitals can be correlated with location of the *d*-band centre, which can be experimentally determined as well. Therefore, the energy location of the *d*-band

centre is an excellent descriptor for pure materials (Hammer and Norskov 1995).

Ma et al. (2015) used artificial neural networks (ANN) to develop a model to capture adsorbate–substrate interactions to propose better catalysts for CO2RR. They showed that along with the location of the *d*-band centre, higher moments of the *d*-band such as its occupation, centre, width, skewness, and kurtosis, and local Pauling electronegativity are efficient descriptors for alloys and mixtures. They found this to be especially true in the case of coinage metals (Cu, Ag, Au) as compared to Group 10 transition metals (Ni, Pd, Pt).

A more recent study used Bootstrapped Projected Gradient Descent (BoPGD) to build a model which can predict the KPI (binding energy of the adsorbed CO on the catalyst surface) from a large number of descriptors (Pankajakshan et al. 2017). From the large number of descriptors, a smaller set of fingerprinted descriptors are chosen, making the model efficient and chemically intuitive. This study found that the inclusion of work function as an additional descriptor, greatly improves the *d*-band model. The BoPGD, a feature selection scheme, offers several advantages over ANN and other ML tools: it uses fingerprinted descriptors, employs a clustering algorithm which makes it scale more efficiently, it does not have instability issues that methods like LASSO face, and most importantly, chemical insights can be gleaned from the analysis.

Summary and Outlook

Challenges and Opportunities for Computer Simulations

First-principles based computer simulations are useful in determination of relevant structures like the reactants, products, intermediates and transition states, which govern the mechanism of the catalytic reaction. Determining these stationary points does not provide dynamical insights into the reaction. However, performing dynamical simulations on catalytic reactions, which typically have a large system size, is computationally intractable. Further, the reaction pathway mapped by calculations usually involves one reactant molecule which gets converted to one product molecule. In reality, however, several molecules are constantly being adsorbed and desorbed from the given unit of surface, which will naturally affect the mechanism and rate of reaction. Computationally, this can be accounted for by performing coverage studies, however, these are very demanding calculations. A reaction typically will have multiple available pathways. In the interest of computational cost, few likely pathways are selected for thorough study, and the most feasible pathway is decided upon. However, when dynamical aspects and a finite concentration of the reactants (i.e. more

than one molecule of the reactant) are considered, this determined pathway may not be the most feasible. Further, zero point energy, Gibbs free energy and entropy contributions to the energy are not included because of high computational costs. When a molecule is adsorbed on a surface, it can do so in various orientations with respect to the surface, and the possibilities increase with the size of the adsorbate. However, to conserve computational cost, only select orientations are intuitively chosen in analysis.

In principle, all of the deficiencies mentioned above can be overcome if computational resources are not a bottleneck. Conversely, these deficiencies present an opportunity for a method which can rapidly scan through a large number of materials at reduced computational cost. While quantum mechanics is able to relate properties using atomic structure, machine learning can be effective in achieving an integrated framework to capture processing-structure–property-performance relationships in material science. The use of descriptors along with machine learning helps in efficiently scanning a large number of materials and even propose new ones. Further, the scalable synthesis of materials continues to be an experimental challenge, limiting use of predicted materials for practical applications.

Conclusions

We presented how development of thermocatalytic reduction of CO_2 to MeOH can be facilitated through microscopic understanding and computational design with simulations. Overall, a scheme for sustainable generation of MeOH involves use of renewable sources of energy for generation of H_2 and using it as a reducing agent in thermochemical CO2RR at sources where the amount of CO_2 emissions is particularly high and is accompanied by generation of waste heat. Examples of such sources include flue gas from thermal power stations, cement and steel factories, and oil refineries. The product, MeOH, is an alternative fuel that also serves as a solution for chemical storage of H_2. Further, the CO_2 emissions upon use of MeOH as a fuel, can be recycled back to the CO2RR step, in principle, making the process carbon neutral and effectively achieving carbon recycling.

First-principles simulations capture the catalyst-reactant interaction accurately, and have been remarkably effective in predicting energetics, rates, mechanisms of reactions, and importantly, proposing new materials as catalysts. With a two pronged approach of (a) first-principles mechanistic analysis, which aids understanding, and (b) machine learning to identify fingerprint descriptors for predictive models, which facilitate high-throughput screening of a large number of materials, much can be achieved towards development of new, efficient and cost-effective materials. Currently, only 5% of commercial H_2 production comes from renewable sources and CO_2 emissions are on the rise. The technologies discussed here address the energy and environmental problems of current importance, and highlight the role played by computer simulations in design of materials needed in their accelerated development.

References

Álvarez A, Bansode A, Urakawa A, Bavykina AV, Wezendonk TA, Makkee M, Gascon J, Kapteijn F (2017) Challenges in the greener production of formates/formic acid, methanol, and DME by heterogeneously catalyzed CO_2 hydrogenation processes. Chem Rev 117(14):9804–9838

Attanayake NH, Dheer L, Thenuwara AC, Abeyweera SC, Collins C, Waghmare UV, Strongin DR (2020) Cover feature: Ni-and Co-substituted metallic MoS2 for the alkaline hydrogen evolution reaction (ChemElectroChem 17/2020). ChemElectroChem 7(17):3541

Bart JCJ, Sneeden RPA (1987) Copper–zinc oxide–alumina methanol catalysts revisited. Catal Today 2(1):1–124

Beck AD (1993) Density-functional thermochemistry. III. The role of exact exchange. J Chem Phys 98(7):5646–5648

Becke AD (1986) Completely numerical calculations on diatomic molecules in the local-density approximation. Phys Rev A 33(4):2786

Becke AD (2014) Perspective: fifty years of density-functional theory in chemical physics. J Chem Phys 140(18):18A301

Behrens M, Studt F, Kasatkin I, Kühl S, Hävecker M, Abild-Pedersen F, Zander S, Girgsdies F, Kurr P, Kniep B-L (2012) The active site of methanol synthesis over Cu/ZnO/Al2O3 industrial catalysts. Science 336(6083):893–897

Bhadeshia HKDH (1999) Neural networks in materials science. ISIJ Int 39(10):966–979

Bhadeshia HKDH (2009) Neural networks and information in materials science. Stat Anal Data Min ASA Data Sci J 1(5):296–305. https://doi.org/10.1002/sam.10018

Blunden J, Arndt DS (2020) State of the climate in 2019. Bull Am Meteor Soc 101(8):S1–S429

Bockris JO (1970) O'M. Reddy, AKN modern electrochemistry, vol 2. Plenum Press, New York

Cherevotan A, Raj J, Dheer L, Roy S, Sarkar S, Das R, Vinod CP, Xu S, Wells P, Waghmare UV (2021) Operando generated ordered heterogeneous catalyst for the selective conversion of CO_2 to methanol. ACS Energy Lett 6(2):509–516

Chhetri M, Maitra S, Chakraborty H, Waghmare UV, Rao CNR (2016) Superior performance of borocarbonitrides, $B_xC_yN_z$, as stable, low-cost metal-free electrocatalysts for the hydrogen evolution reaction. Energy Environ Sci 9(1):95–101

Choi WI, Wood BC, Schwegler E, Ogitsu T (2013) Site-dependent free energy barrier for proton reduction on MoS2 edges. J Phys Chem C 117(42):21772–21777

Christensen R, Hansen HA, Vegge T (2015) Identifying systematic DFT errors in catalytic reactions. Catal Sci Technol 5(11):4946–4949

Collodi G (2010) Hydrogen production via steam reforming with CO_2 capture. Chem Eng Trans 19:37–42

Davis SJ, Lewis NS, Shaner M, Aggarwal S, Arent D, Azevedo IL, Benson SM, Bradley T, Brouwer J, Chiang Y-M et al (2018) Net-zero emissions energy systems. Science 360(6396):eaas9793

De Levie R (1999) The electrolysis of water. J Electroanal Chem 476(1):92–93

Dheer L, Bhattacharjee S, Lee SC, Waghmare UV (2020) Van der Waals hetero-structures of 1H-MoS$_2$ and N-substituted graphene for catalysis of hydrogen evolution reaction. Mater Res Express 6(12):124006

Eberle U, Müller B, Von Helmolt R (2012) Fuel cell electric vehicles and hydrogen infrastructure: status 2012. Energy Environ Sci 5(10):8780–8798

Eggleton T, Eggleton RA (2013) A short introduction to climate change. Cambridge University Press

Ghiringhelli LM, Vybiral J, Levchenko SV, Draxl C, Scheffler M (2015) Big data of materials science: critical role of the descriptor. Phys Rev Lett 114(10):105503

Gong M, Wang D-Y, Chen C-C, Hwang B-J, Dai H (2016) A mini review on nickel-based electrocatalysts for alkaline hydrogen evolution reaction. Nano Res 9(1):28–46

Grabow LC, Mavrikakis M (2011) Mechanism of methanol synthesis on Cu through CO$_2$ and CO hydrogenation. ACS Catal 1(4):365–384

Greeley J, Jaramillo TF, Bonde J, Chorkendorff IB, Nørskov JK (2006) Computational high-throughput screening of electrocatalytic materials for hydrogen evolution. Nat Mater 5(11):909–913

Grimme S (2006) Semiempirical GGA-type density functional constructed with a long-range dispersion correction. J Comput Chem 27(15):1787–1799

Hammer B, Norskov JK (1995) Why gold is the noblest of all the metals. Nature 376(6537):238–240

Hammer BHLB, Hansen LB, Nørskov JK (1999) Improved adsorption energetics within density-functional theory using revised Perdew–Burke–Ernzerhof functionals. Phys Rev B 59(11):7413

Hinnemann B, Moses PG, Bonde J, Jørgensen KP, Nielsen JH, Horch S, Chorkendorff I, Nørskov JK (2005) Biomimetic hydrogen evolution: MoS2 nanoparticles as catalyst for hydrogen evolution. J Am Chem Soc 127(15):5308–5309

Jain A, Ong SP, Hautier G, Chen W, Richards WD, Dacek S, Cholia S, Gunter D, Skinner D, Ceder G (2013) Commentary: the materials project: a materials genome approach to accelerating materials innovation. APL Mater 1(1):11002

Kou T, Smart T, Yao B, Chen I, Thota D, Ping Y, Li Y (2018) Theoretical and experimental insight into the effect of nitrogen doping on hydrogen evolution activity of Ni3S2 in alkaline medium. Adv Energy Mater 8(19):1703538

Kouser S, Thannikoth A, Gupta U, Waghmare UV, Rao CNR (2015) 2D-gas as a photocatalyst for water splitting to produce H2. Small 11(36):4723–4730

Kumar N, Rajagopalan P, Pankajakshan P, Bhattacharyya A, Sanyal S, Balachandran J, Waghmare UV (2018) Machine learning constrained with dimensional analysis and scaling laws: simple, transferable, and interpretable models of materials from small datasets. Chem Mater 31(2):314–321

Le Quéré C, Jackson RB, Jones MW, Smith AJP, Abernethy S, Andrew RM, De-Gol AJ, Willis DR, Shan Y, Canadell JG et al (2020) Temporary reduction in daily global CO$_2$ emissions during the COVID-19 forced confinement. Nat Clim Change 10:647–653

Li Y, Chan SH, Sun Q (2015) Heterogeneous catalytic conversion of CO$_2$: a comprehensive theoretical review. Nanoscale 7(19):8663–8683

Liu X-M, Lu GQ, Yan Z-F, Beltramini J (2003) Recent advances in catalysts for methanol synthesis via hydrogenation of CO and CO$_2$. Ind Eng Chem Res 42(25):6518–6530

Liu K, Song C, Subramani V (2010) Hydrogen and syngas production and purification technologies. Wiley

Lototskyy MV, Tolj I, Pickering L, Sita C, Barbir F, Yartys V (2017) The use of metal hydrides in fuel cell applications. Prog Nat Sci Mater Int 27(1):3–20

Ma X, Li Z, Achenie LEK, Xin H (2015) Machine-learning-augmented chemisorption model for CO$_2$ electroreduction catalyst screening. J Phys Chem Lett 6(18):3528–3533

Mahmood N, Yao Y, Zhang J, Pan L, Zhang X, Zou J (2018) Electrocatalysts for hydrogen evolution in alkaline electrolytes: mechanisms, challenges, and prospective solutions. Adv Sci 5(2):1700464

Maslovara S, Aničijević DV, Brković S, Georgijević J, Tasić G, Kaninski MM (2019) Experimental and DFT study of CoCuMo ternary ionic activator for alkaline HER on Ni cathode. J Electroanal Chem 839:224–230

MatWeb, L. L. C. (2013). MatWeb—material property data. Tra-Con Tra-Bond, p 2115

Mohammed-Ibrahim J, Sun X (2019) Recent progress on earth abundant electrocatalysts for hydrogen evolution reaction (HER) in alkaline medium to achieve efficient water splitting—a review. J Energy Chem 34:111–160

Montoya JH, Seitz LC, Chakthranont P, Vojvodic A, Jaramillo TF, Nørskov JK (2017) Materials for solar fuels and chemicals. Nat Mater 16(1):70–81

Morales-Guio CG, Stern L-A, Hu X (2014) Nanostructured hydrotreating catalysts for electrochemical hydrogen evolution. Chem Soc Rev 43(18):6555–6569

Narasimman R, Waldiya M, Jalaja K, Vemuri SK, Mukhopadhyay I, Ray A (2021) Self-standing, hybrid three-dimensional-porous MoS2/Ni3S2 foam electrocatalyst for hydrogen evolution reaction in alkaline medium. Int J Hydrogen Energy 46(11):7759–7771

Nørskov JK, Bligaard T, Logadottir A, Kitchin JR, Chen JG, Pandelov S, Stimming U (2005) Trends in the exchange current for hydrogen evolution. J Electrochem Soc 152(3):J23

Olah GA (2003) The methanol economy. Chem Eng News 81(38):5

Olah GA (2005) Beyond oil and gas: the methanol economy. Angew Chem Int Ed 44(18):2636–2639

Olah GA, Goeppert A, Prakash GKS (2009) Chemical recycling of carbon dioxide to methanol and dimethyl ether: from greenhouse gas to renewable, environmentally carbon neutral fuels and synthetic hydrocarbons. J Org Chem 74(2):487–498

de Pablo JJ, Jones B, Kovacs CL, Ozolins V, Ramirez AP (2014) The materials genome initiative, the interplay of experiment, theory and computation. Curr Opin Solid State Mater Sci 18(2):99–117

Pankajakshan P, Sanyal S, de Noord OE, Bhattacharya I, Bhattacharyya A, Waghmare U (2017) Machine learning and statistical analysis for materials science: stability and transferability of fingerprint descriptors and chemical insights. Chem Mater 29(10):4190–4201

Perdew JP, Burke K, Ernzerhof M (1996) Generalized gradient approximation made simple. Phys Rev Lett 77(18):3865

Roy A, Chhetri M, Prasad S, Waghmare UV, Rao CNR (2018a) Unique features of the photocatalytic reduction of H$_2$O and CO$_2$ by new catalysts based on the analogues of CdS, Cd$_4$P$_2$X$_3$ (X = Cl, Br, I). ACS Appl Mater Interfaces 10(3):2526–2536

Roy S, Cherevotan A, Peter SC (2018b) Thermochemical CO$_2$ hydrogenation to single carbon products: scientific and technological challenges. ACS Energy Lett 3(8):1938–1966

Rubin E, De Coninck H (2005) IPCC special report on carbon dioxide capture and storage. Cambridge University Press. TNO (2004): cost curves for CO$_2$ storage, Part 2:14

Saraswat VK, Bansal R (2017) India's leapfrog to methanol economy. NITI Aayog

Sarkar S, Dheer L, Vinod CP, Thapa R, Waghmare UV, Peter SC (2020) Stress-induced electronic structure modulation of manganese-incorporated Ni$_2$P leading to enhanced activity for water splitting. ACS Appl Energy Mater 3(2):1271–1278

Shih CF, Zhang T, Li J, Bai C (2018) Powering the future with liquid sunshine. Joule 2(10):1925–1949

Tang Q, Shen Z, Huang L, He T, Adidharma H, Russell AG, Fan M (2017) Synthesis of methanol from CO$_2$ hydrogenation promoted

by dissociative adsorption of hydrogen on a Ga_3Ni_5 (221) surface. Phys Chem Chem Phys 19(28):18539–18555

Teng B-T, Wen X-D, Fan M, Wu F-M, Zhang Y (2014) Choosing a proper exchange—correlation functional for the computational catalysis on surface. Phys Chem Chem Phys 16(34):18563–18569

Thenuwara AC, Cerkez EB, Shumlas SL, Attanayake NH, McKendry IG, Frazer L, Borguet E, Kang Q, Remsing RC, Klein ML (2016a) Nickel confined in the interlayer region of birnessite: an active electrocatalyst for water oxidation. Angew Chem 128(35):10537–10541

Thenuwara AC, Shumlas SL, Attanayake NH, Aulin YV, McKendry IG, Qiao Q, Zhu Y, Borguet E, Zdilla MJ, Strongin DR (2016b) Intercalation of cobalt into the interlayer of birnessite improves oxygen evolution catalysis. ACS Catal 6(11):7739–7743

Thenuwara AC, Dheer L, Attanayake NH, Yan Q, Waghmare UV, Strongin DR (2018) Co–Mo–P based electrocatalyst for superior reactivity in the alkaline hydrogen evolution reaction. ChemCatChem 10(21):4832–4837

Trasatti S (1972) Work function, electronegativity, and electrochemical behaviour of metals: III. Electrolytic hydrogen evolution in acid solutions. J Electroanal Chem Interfacial Electrochem 39(1):163–184

Vantroostwijk AP, Deiman JR (1789) Sur une manière de décomposer l'Eau en Air inflammable et en Air vital. Obs Phys 35:369

Vesborg PCK, Seger B, Chorkendorff IB (2015) Recent development in hydrogen evolution reaction catalysts and their practical implementation. J Phys Chem Lett 6(6):951–957

Wallner T, Lohse-Busch H, Gurski S, Duoba M, Thiel W, Martin D, Korn T (2008) Fuel economy and emissions evaluation of BMW hydrogen 7 mono-fuel demonstration vehicles. Int J Hydrogen Energy 33(24):7607–7618

Wang W, Wang S, Ma X, Gong J (2011) Recent advances in catalytic hydrogenation of carbon dioxide. Chem Soc Rev 40(7):3703–3727

Wang W-H, Himeda Y, Muckerman JT, Manbeck GF, Fujita E (2015) CO_2 hydrogenation to formate and methanol as an alternative to photo-and electrochemical CO_2 reduction. Chem Rev 115(23):12936–12973

Weijing D, Weihong Z, Xiaodong Z, Baofeng Z, Lei C, Laizhi S, Shuangxia Y, Haibin G, Guanyi C, Liang Z (2018) The application of DFT in catalysis and adsorption reaction system. Energy Procedia 152:997–1002

Wellendorff TL, Silbaugh D (2015) Garcia-Pintos, JK Nørskov, T. Bligaard, F. Studt, and CT Campbell. Surf Sci 640:36

Wellendorff J, Lundgaard KT, Møgelhøj A, Petzold V, Landis DD, Nørskov JK, Bligaard T, Jacobsen KW (2012) Density functionals for surface science: exchange-correlation model development with Bayesian error estimation. Phys Rev B 85(23):235149

Yang Y, White MG, Liu P (2012) Theoretical study of methanol synthesis from CO_2 hydrogenation on metal-doped Cu (111) surfaces. J Phys Chem C 116(1):248–256

Zeradjanin AR, Vimalanandan A, Polymeros G, Topalov AA, Mayrhofer KJJ, Rohwerder M (2017) Balanced work function as a driver for facile hydrogen evolution reaction–comprehension and experimental assessment of interfacial catalytic descriptor. Phys Chem Chem Phys 19(26):17019–17027

Zhao Y-F, Yang Y, Mims C, Peden CHF, Li J, Mei D (2011) Insight into methanol synthesis from CO_2 hydrogenation on Cu (1 1 1): complex reaction network and the effects of H_2O. J Catal 281(2):199–211

Zou X, Zhang Y (2015) Noble metal-free hydrogen evolution catalysts for water splitting. Chem Soc Rev 44(15):5148–5180