CO₂ Utilization Through its Reduction to Methanol: Design of Catalysts Using Quantum Mechanics and Machine Learning

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Abstract
Reducing levels of CO₂, 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 CO₂ to useful products. In this perspective, we present quantum mechanical and machine learning approaches to tackle various aspects of thermocatalytic reduction of CO₂ to methanol, using H₂ as a reducing agent. Waste heat can be utilized effectively in the thermocatalytic process, and H₂ can be generated using solar energy in electrolytic, photocatalytic and photoelectrochemical 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 H₂ for applications in automobiles, alleviating the problem of rising CO₂ emissions and levels in atmosphere.

Keywords CO₂ utilization · Methanol · Hydrogen evolution reaction · CO₂ 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 CO₂ emissions, which contribute significantly to global warming. While CO₂ 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 CO₂ 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 CO₂ 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 CO₂ 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 CO₂ emissions.

To combat CO₂ emissions, drastic scaling down of industrial activity is both impractical and futile. Rather, a more effective strategy for sustainability is to convert the emitted CO₂ to potentially useful, value-added chemicals. In this regard, the CO₂ reduction reaction (CO₂RR) is especially relevant, and involves reduction of CO₂ 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 (H₂) is critical in its role as a reducing agent in hydrogenation of CO₂. Also, H₂, 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. H₂ is rarely found in its pure form in the atmosphere because of its molecular weight being significantly lower than air.
Also, production of H\textsubscript{2} at an industrial scale comes at an energy cost. As of 2020, most usable H\textsubscript{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\textsubscript{2} emissions and the advantage of H\textsubscript{2} being a clean fuel is compromised.

A major technological challenge in the use of H\textsubscript{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\textsubscript{2} include tuning external conditions, i.e., high pressures and low temperatures. Car manufacturers such as Honda and Nissan have been developing the former approach with compressed H\textsubscript{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\textsubscript{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\textsubscript{2} include Toyota Mirai, Hyundai Nexo, and Honda Clarity.

Despite the established technologies, H\textsubscript{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\textsubscript{2} are active areas of research, and the technology described here amounts to chemical storage of H\textsubscript{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 \( \sim 70 \) 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\textsubscript{2} and CO) over Cu/ZnO/Al\textsubscript{2}O\textsubscript{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\textsubscript{2}, and ties back to the problem of additional CO\textsubscript{2} emissions. Generating MeOH through CO2RR does not suffer from this disadvantage. As mentioned earlier, MeOH, generated from the addition of H\textsubscript{2} to CO\textsubscript{2}, also amounts to chemical storage of H\textsubscript{2} and innovative portable use of H\textsubscript{2} as a fuel.

**Sustainable Production of Methanol Using Renewable Energy**

CO\textsubscript{2} capture is the first step towards utilization of CO\textsubscript{2}. Of the various sources of CO\textsubscript{2} emissions (Davis et al. 2018) (Fig. 1), not all qualify as emission streams which can be used readily as inputs in a CO\textsubscript{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\textsubscript{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\textsubscript{2} emissions while making use of the already generated waste heat. When the required intake of H\textsubscript{2} is generated using solar energy through photocatalytic and photoelectrocatalytic approaches, this further reduces the overall CO\textsubscript{2} emission in the process.

Despite generating H\textsubscript{2} using clean energy sources, and carrying out CO2RR using waste heat, use of the produced MeOH as a fuel will add to CO\textsubscript{2} emissions. In principle, CO\textsubscript{2} generated from burning of MeOH as a fuel can be recycled...
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 CO₂ 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 H₂ 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 CO₂ (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
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 CO₂ 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 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.

![Fig. 3 Schematic of a reaction mechanism, where, R, P, I, TS, represent the reactant, product, intermediates, transition states, respectively, and Eₐ, ΔH represent activation energies, and enthalpy of the reaction, respectively](image)

**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)] (Bhandesia 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.
(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$_2$O. 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$_2$O 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:

$$\begin{align*}
2\text{H}_2\text{O}(l) &\rightarrow \text{O}_2(g) + 4\text{H}^+(aq) + 4e^- \text{(OER)} \\
2\text{H}^+(aq) + 2e^- &\rightarrow \text{H}_2(g) \text{(HER)}
\end{align*}$$

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,
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 H₂ (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 H₂ 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 H₂. This happens simultaneously with transfer of another electron from the electrode evolving H₂. 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 H₂, and thus this is a combination reaction.

HER is generally carried out in acidic media where hydronium ions (H₃O⁺) 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). 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 H₂O⁺ ion, which is a weaker interaction. Computer simulations of the H₂O 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*
intermediate with a $\Delta G_{H^*}$ of approximately $-0.1$ eV. By computing $\Delta G_{H^*}$ within first-principles DFT for various metallic surfaces, Nørskov et al. showed a volcano shape relationship between $\Delta G_{H^*}$ 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, $\phi$, 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 ($\Delta \phi$) of hydrogenated and non-hydrogenated metals in the presence of an interfacial layer of water molecules. $\Delta \phi$ 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$_2$ → CH$_3$OH + H$_2$O) 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,
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 ($E_d$ 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 (x*) orbitals of CO$_2$. The d-band model suggests that the extent of coupling between the d and x* 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 Nørskov 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 CO₂ 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 H₂ and using it as a reducing agent in thermochemical CO₂RR at sources where the amount of CO₂ 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 H₂. Further, the CO₂ 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 H₂ production comes from renewable sources and CO₂ 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.

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