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CO$_2$: Challenges and Opportunities

As CO$_2$ is one of the most important greenhouse gases, the uncontrollable rise of its concentration in the atmosphere, which in part arises from the burning of fossil fuels including coal, oil, and gas, significantly contributes to global warming [1]. The ensuing climate change represents an urgent environmental issue for sustainable developments of industrialized societies [2], because the increase in the Earth's temperature has already caused an array of catastrophes, for instance, melting glaciers and ice caps, rising sea levels, more frequent and severe heat waves, and changes in weather patterns. The Intergovernmental Panel on Climate Change predicted that if the emission of greenhouse gases like CO$_2$ were maintained at the present level, even, more severe influences would come in the near future, such as more frequent and intense extreme weather events, water shortages, and food insecurity. A key to mitigating the impacts of climate change is to reduce CO$_2$ emissions and the transition to a low-carbon economy.

To meet these challenges, a range of state-of-the-art technologies have been developed, such as the use of renewable energy resources, the improvement of energy utilization efficiencies, the development of sustainable agriculture and forestry, and so on. Among them, carbon sequestration and storage, which captures CO$_2$ from power plants and industrial processes and stores it underground, gains particular interest and has been widely employed. On the other hand, given its high abundance and low cost [3], the use of CO$_2$ as a feedstock to manufacture value-added fine chemicals in place of increasingly scarce fossil fuel resources is perhaps an even more promising alternative solution [4]. However, CO$_2$, a typical end-product produced by a plethora of chemical and biological oxidation processes, is not only thermodynamically stable but also kinetically inert; therefore, CO$_2$ utilization has long posed a great challenge to chemists [5].

In the ground state of CO$_2$, the central C atom adopts *sp* hybridization and forms a σ- and a π-bond with each terminal O atom. Therefore, CO$_2$ is a stable linear non-polar molecule that features a short C–O bond length of 1.17 Å and a high C-O bond dissociation energy of 127 kcal/mol. In light of the varying electronegativities of C and O atoms, the C atom of CO$_2$ possesses

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a partial positive charge that is balanced by a little negative charge on the two O atoms. Hence, CO$_2$ activation merely has two routes, i.e., nucleophilic attack on C and electrophilic attack on O. To date, the vast majority of reported CO$_2$ functionalization processes can be interpreted as CO$_2$ reduction, whereas reactions following the other route are rather rare. Notably, direct reduction of CO$_2$ is economically unviable, because its one-electron reduction potential was measured to be as low as –1.9 V. To circumvent the generation of highly reactive CO$_2$$^{\bullet-}$ species, CO$_2$ transformations are typically initiated by the interaction of reducing agents with the C atom followed by immediate C–O bond rupture or C–X (X = H, C) bond formation.

The lowest-energy unoccupied molecular orbitals (LUMOs) of CO$_2$, which serve as the electron-accepting orbitals, are two three-center π* orbitals with a predominant parentage of the C 2p atomic orbital (Figure 1). Populating electrons into the CO$_2$ doubly degenerate LUMOs causes the bending of the linear O-C-O arrangement and lengthening of the C–O bonds. Such large geometric adjustments, added by the high energy of the CO$_2$ LUMO as evidenced by its highly negative reduction potential, render CO$_2$ rather inert, and its activation thereby necessarily suffers from high activation barriers. On the other hand, despite raising the energy of the entire molecule, CO$_2$ bending lowers its in-plane π* LUMO and increases the C 2p contribution in this orbital, both of which ought to facilitate the bonding with the incoming reductant. Consequently, the electron-accepting ability of CO$_2$ gets enhanced.
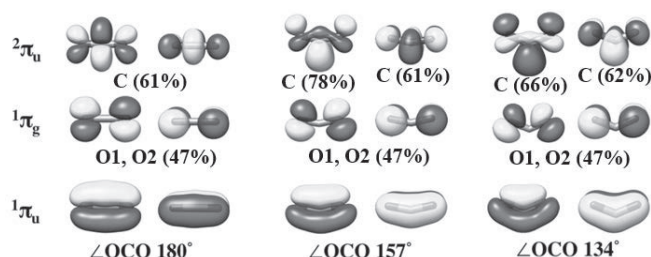

Fig. 1: Molecular orbitals of CO$_2$ at different OCO angles.

Due to its high stability and inertness, CO$_2$ functionalization inevitably requires sufficient energy input and, more critically, appropriate catalysts that direct the reaction to proceed along energetically favorable pathways. In this connection, understanding mechanistic intricacies at the atomic level is helpful to achieve the rational design of more efficient catalysts [6].

Homogeneous catalytic hydrogenation of CO$_2$ to formic acid/formate or to methanol is an important strategy to produce C1 building blocks for value-added fine chemicals and fuels. This is primarily because formic acid is touted as a chemical

hydrogen storage. Also, methanol has garnered much attention as a sustainable alternative fuel used in direct methanol fuel cells. The thermodynamic coupling of CO_2 to H_2 to furnish HCOOH entails $\Delta G = 7.8$ kcal.mol^{-1}. However, utilizing a base such as NH_3 to produce HCO_2^- and NH_4^+ lowers the thermodynamic requirement to $\Delta G = -2.3$ kcal.mol^{-1}. This emphasizes the crucial role of a base to enhance the driving force of CO_2 hydrogenation. Importantly, hydrogenation of gaseous CO_2 often involves high reaction barriers that can be overcome by the use of transition metal complexes. A series of noble-metal complexes reported to date is capable of catalyzing CO_2 hydrogenation with fast kinetics and high turnover numbers (TONs). For instance, an Ir(III) trihydride PNP complex can yield formic acid with the highest TON of 3 500 000 and turnover frequency (TOF) of 150 000 h^{-1} at 200°C and 80 bar [7]. Another related Ru(II) pincer complex is reported to carry out CO_2 activation at a TOF of 21 500 h^{-1} [8]. Inexpensive transition metal catalysts, such as the iron trans dihydride pincer complex, were able to perform at a low pressure of 6-10 bar with a turnover frequency of 156 h^{-1} [9].

Controlled experiments and computational studies have led to a better understanding of the elementary steps involved during CO_2 hydrogenation by a metal-hydride (M-H) complex. As shown in Figure 2, the reaction of CO_2 hydrogenation typically consists of three crucial steps: (a) base-assisted H_2 splitting that leads to the generation of a new metal-hydride bond; (b) hydride transfer from M-H to the central C atom of CO_2 via an outer sphere mechanism by which CO_2 does not directly bind to the metal center. Here, weak non-covalent interactions induced by externally added protons or Lewis acids (LA) play an important role in stabilizing the bent conformation of CO_2 poised for the hydride nucleophilic attack on CO_2; (c) product dissociation via the formation of acid-base complexes, HCOOH•B. Notably, either of the two steps: H_2 splitting or hydride transfer has been identified as the rate-determining step (RDS) for the overall process.

As a matter of fact, the electronic structure requirement of these two steps is inversely correlated. While the strength of the base (p$K_{a(BH+)}$) determines the ease of heterolytic dihydrogen cleavage, strong σ donor ability and strong trans influence of ligand opposite to the hydride is found to affect CO_2 insertion into M–H. Obviously, a strong M–H bond in the hydride intermediate (Figure 2)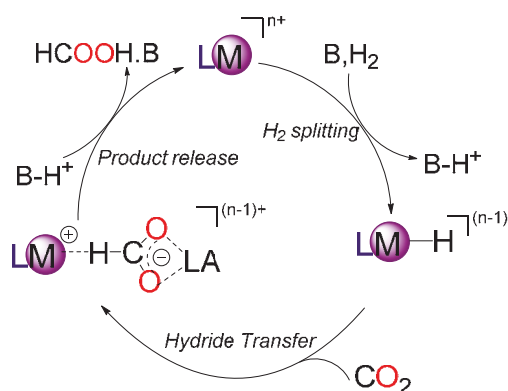 would favor rapid H_2 splitting, while at the same time disfavoring the possibility of hydride transfer. Contrarily, a labile M–H bond would be ideal to activate an inert substrate such as CO_2 but would have a limited driving force for *in situ* generation. Hence, an exquisite balance between these two steps is needed to achieve catalytic conversion of CO_2, which is primarily controlled by the bond dissociation free energy of the M–H bond in the metal-hydride intermediate. Thermodynamically, this bond strength is quantified by a physical property, known as the hydricity, ΔG_H^O–(M–H) of the metal-hydride complex [10]. Importantly, H_2 splitting and hydride transfer have completely opposite hydricity requirements. A low hydricity determines a greater degree of hydride donating possibility, while a high hydricity is helpful for faster H_2 splitting kinetics. Correlating hydricity with the kinetic barriers for these two steps reveals that a calculated hydricity of 59.7 kcal mol^{-1} should be optimum for homogeneous CO_2 hydrogenation catalyzed by metal-phosphine complexes when NEt$_3$ is used as a base [6]. This thermodynamic quantity can be utilized to design novel CO_2 hydrogenation catalysts based on earth-abundant metals like Fe and Co to provide a greener channel towards CO_2 utilization, expanding its opportunities in value-added transformations.

Breaking the C–O bond in CO_2 to furnish carbon monoxide (CO) is another attractive strategy for CO_2 reduction, as CO is a fuel precursor to methane. In this direction, homogeneous electrochemical CO_2 reduction to CO using earth-abundant catalysts has been intensively explored over the years [11]. Transition metal complexes featuring low-valent metal centers (e.g., Ni(I), Co(I), Fe(II), etc.) and macrocyclic ligands, such as cyclam, tetraphenylporphyrin (TPP) have served as electrocatalysts as they are efficient one-electron reductant with low overpotentials. Pioneering works by Savéant [12] and Robert [13] have made extensive use of iron complexes of porphyrin derivatives for electro- and photo-electro catalytic reduction of CO_2 to CO via 2e$^-$/2H$^+$ pathways. Kubiak and coworkers reported homogeneous electrocatalytic CO_2 reduction to CO by Ni(cyclam) complexes on inert glassy carbon electrodes at a low overpotential (−1.21 V vs. NHE) in water [14].

Experimental kinetic studies and density functional theory (DFT)-based computational investigations have revealed that the first electron transfer to CO_2 from the metal complex is generally followed by a subsequent electron uptake from the electrode or reduced metal during the electrochemical reduction to CO. The C–O bond cleavage process is known to be assisted through polarization by weak Brønsted acid (e.g., water) or Lewis acid (e.g., metal center, cation). Metal-catalyzed electrochemical CO_2 reduction to CO traverses a common mechanism (Figure 3) involving the formation of the metal-CO_2 complex (M-CO_2) followed by a proton-coupled electron transfer (PCET) and C–O cleavage to yield a metal-bound CO complex (M–CO). The final CO release regenerates the active catalyst. The redox non-innocence behavior of ligands, such as TPP is known to assist the electron transfer events, as observed in a highly synchronized metal-to-CO_2 and ligand-to-metal electron transfer in the Fe-TPP-mediated CO_2 reduction to CO [15]. Particularly, the binding of CO_2 to the Fe-center is facilitated by the donation of an electron from the Fe-d$_{z2}$ to the in-plane O–C–O π* orbital of CO_2, resulting in a partial electron transfer to CO_2. A similar electron-transfer event was also recorded in the Ni-cy-

Fig. 2: Mechanistic steps for transition metal catalyzed hydrogenation of CO_2.
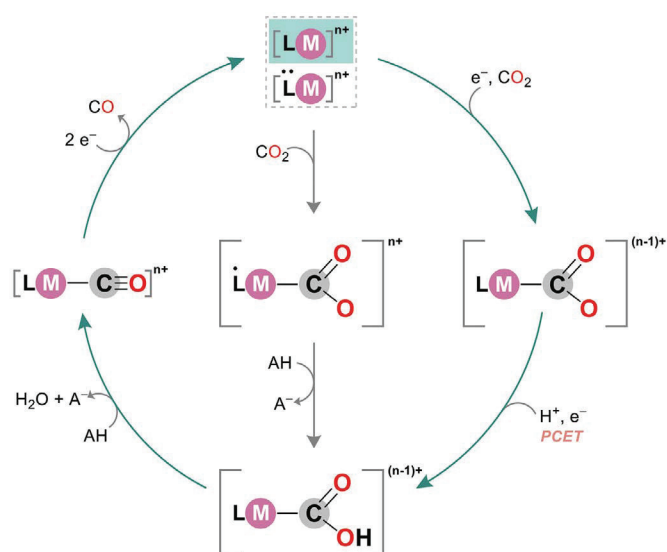
Fig. 3: Common reaction mechanism for electrocatalytic CO$_2$ reduction to CO, showing both redox-active and inactive ligands.

clam-catalyzed CO$_2$-to-CO reduction [16]. In the Fe-TPP case, the redox-active nature of the ligand plays a crucial role in stabilizing the reactive M-CO$_2$ intermediate. The attachment of a proton to the metal-bound partially reduced CO$_2$ enhances its electron-accepting ability and results in the metal-carboxylate complex. Finally, this complex undergoes C–O bond cleavage in presence of another proton and forms the metal-bound CO complex with the release of water. Thus, homogeneous electrochemical CO$_2$-to-CO reduction mediated by transition metal complexes serves as a very effective strategy of CO$_2$ reduction, where an optimal combination of metal and ligand can promote a highly synchronous electron transfer process.

In summary, on one hand, the increase in CO$_2$ concentration causes severe environmental impacts on the human being. On the other hand, the utilization of CO$_2$ to make value-added chemicals is the ideal way to confront these crises, which warrants more systematic research on CO$_2$ activation.

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ZITATE ZUM KLIMAWANDEL

„Climate change is a global issue - from the point of view of the Earth's climate, a molecule of CO$_2$ emitted in Bejing is the same as a molecule emitted in Sydney."

Jeff Goodell

Quelle: https://www.englischezitate.de/zitat/jeff-goodell/14601/

PhD Bhaskar Mondal

Bhaskar Mondal graduated from the University of Calcutta, India in 2007 and received his Ph.D. degree in 2011 from the Indian Association for the Cultivation of Science, Kolkata, India. Then he moved to the United Kingdom, where he worked as a postdoctoral research associate at the University of Strathclyde. In 2013, he started working at the Max Planck Institute for Chemical Energy Conversion, Germany as a postdoctoral researcher in the group of Prof. Frank Neese and Dr. Shengfa Ye. After a couple of years of a postdoctoral stint at the RWTH Aachen University, Germany with Prof. Franziska Schoenebeck, he joined the Indian Institute of Technology (IIT) Mandi, Himachal Pradesh, India in 2019 as an Assistant Professor. His broad research area is computational chemistry and transition metal catalysis with specific interests in electronic structure, reactivity, and spectroscopy of homogeneous transition metal catalysts relevant to small-molecule activation, C–H oxidation, and selective organic transformations.

Prof. Dr. Shengfa Ye

Shengfa Ye graduated from Peking University and received his doctorate in inorganic chemistry at the University of Stuttgart under the supervision of Prof. W. Kaim (2005). After working as a postdoctoral fellow at Max-Planck Institute for Bioinorganic Chemistry and University of Bonn, in 2011, he was appointed as a group leader (staff scientist) at Max-Planck Institute for Chemical Energy Conversion and Max-Planck Institute for Coal Research. In 2020, he became a professor at State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences. His present research work focuses on elucidating the mechanisms of small-molecule activation by metalloenzymes and transition-metal complexes using a combined spectroscopic and theoretical approach.

PhD Lisa Roy

Lisa Roy received her B.Sc. and M.Sc. degrees in chemistry from the University of Calcutta, India in 2007 and 2009 respectively. Thereafter, she joined the group of Prof. Ankan Paul at the Indian Association for the Cultivation of Science, where she obtained her PhD degree in 2015. Subsequently, she worked as a postdoctoral researcher in the Molecular Theory and Spectroscopy research-group led by Prof. Frank Neese, under the guidance of Prof. Shengfa Ye, at the Max Planck Institute for Chemical Energy Conversion, Germany. She received the Department of Science and Technology, India, Inspire Faculty Award in 2017 and worked as an independent scientist at CSIR Central Mechanical Engineering Research Institute from 2017-18. Presently, she is working as an Assistant Professor at Institute of Chemical Technology - IOC Bhubaneswar campus. Her current research interests include bio-inspired homogeneous catalytic reactions, small molecule activations and utilization of non-covalent interactions for sustainable energy and resources.

ZITATBOX

Prof. Dr. Udo E. Simonis

„Seen from the historical point of view the urge for growth has (almost) always outweighed the striving for justice, growth was in fact a substitute for justice. However, if climate change were to be viewed as an existential problem of stability and justice – and therefore as a climate disaster, then the thinking on economic growth might start to change and its limitations might become clearer. There might then be an ecological "greening" of the global economy – a "Global Green New Deal", so to speak."

Senator John Kerry (Dec 2009)

„I've often said that global climate change is an issue where no one has the luxury of being "half-pregnant." You either are or you aren't. And so it is with climate change. You either understand and accept the science – or you don't. Folks this isn't a cafeteria where you can pick and choose and accept the science that tells us what is happening, but then reject the science that warns us what will happen.

Quelle: http://www.die-klimaschutz-baustelle.de/climate_change_quotations.html