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CO_2 activation over catalytic surfaces

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Abstract: This article describes the main strategies to activate and convert carbon dioxide (CO_2) into valuable chemicals over catalytic surfaces. Coherent elements such as common intermediates are identified in the different strategies and concisely discussed based on the reactivity of CO_2 with the aim to understand the decisive factors for selective and efficient CO_2 conversion.

Carbon dioxide and reactivity

Management of carbon resource on Earth has become one of the central themes in science, society and politics owing to continuous relocation of carbon from the underground to the atmosphere in the form of carbon dioxide (CO_2). This is a consequence of the modern life of mankind largely relying on burning or utilising carbon-based fossil fuels, which also causes their depletion. Recently, global warming and consequent climate change have been ascribed to the increasing concentration of atmospheric green-house gases, most represented by CO_2, and the world is joining forces to reduce the amount of CO_2 emission to the atmosphere and convert the "waste" CO_2 into valuable chemicals like polymers and fuels.

CO_2 is a thermodynamically stable molecule with the standard formation enthalpy of -393.5 kJ mol^{-1}.[1] However, CO_2 can be transformed with notable reactivity depending on the chemical environment. Among them *catalysis* offers specific sites to activate CO_2 for its chemical transformation. While CO_2 to polymers is generally enabled by efficient homogeneous catalysts (i.e. reactants and catalyst are in the same liquid phase), large-scale production of useful chemicals like fuels necessitates the use of continuous operation using heterogeneous catalyst to activate CO_2 over catalyst surface. There are several activation methods over catalyst surface reported to date and each method generally leads characteristic reactivity of CO_2 and products due to the unique form of activated CO_2 during transformation. This article aims at concisely describing the reactivity of CO_2 in general, summarising the state-of-the-art activation methods and also highlighting similarities in different modes of CO_2 activation and correlations to product selectivity to evaluate coherent views on CO_2 transformation over catalytic surfaces.

The general properties of CO_2 molecule associated with its reactivity are summarised to the following four points.

1. **Bending of CO_2.** For the uncharged state, the bending of the molecule from its linear equilibrium geometry induces the changes in the shape and energy level of the molecular orbitals. Notably, the more bent the geometry, the lower the energy level of the in-plane (i.e. to the plane of bending) contribution of $2\pi_u$ orbital (the lowest unoccupied molecular orbital, LUMO) as shown in Figure 1. Changing the OCO bond angle from 180° to 157°, the proportion of the LUMO on the carbon is increased from 61% to 78%, while the distance between carbon and oxygen (<0.01 Å) and the energy (ΔE <0.5 eV) remain almost constant.[2] Importantly, this lowering of energy level of the in-plane $2\pi_u$ orbital (LUMO) upon bending makes the carbon atom electrophilic.
2. **Repartition of the charges.** When isolated, positive charge can be found on the carbon atom (the Mulliken's population is +0.368 e) and negative charges on the two oxygen atoms (with a population of -0.184 e).[3] A polarized medium like water can increase the charge on the carbon to 0.407 e (obtained by DFT using a polarizable continuum model with a linear geometry).[3] This environmental effect together with the first point of LUMO lowering can make the carbon atom of CO_2 more reactive.
3. **Electron transfer to CO_2.** When an electron is transferred to CO_2, it becomes a radical anion. Obviously, this electron transfer process is facilitated when CO_2 is bent as the LUMO level is lower (see point 1). Its equilibrium geometry is highly bent (ca. 135°) with the singly occupied molecular orbital (SOMO) at a very high energy level (i.e. nucleophilic) very close to the LUMO of the neutral CO_2 at 135° OCO angle with almost the same orbital character (Figure 1). The bond length is elongated by ca. 0.08 Å compared to the neutral linear state, clearly indicating the weakening of the C-O bond. This specific state has been identified as the key intermediate state in many CO_2 transformation reactions as discussed later. The radical CO_2^- is metastable in vacuum (0.5 eV higher in energy than the linear neutral CO_2[5]) but it can be stabilised on surfaces as detected by infrared and X-ray photoelectron spectroscopy.[6] In this state, the carbon atom bears a negative charge (-0.133 e[3]) which leads to an "Umpolung" of the CO_2 reactivity and the carbon atom becomes nucleophile. Also, the elongation of C-O bond can lead dissociation and formation of surface adsorbed CO and O atom.

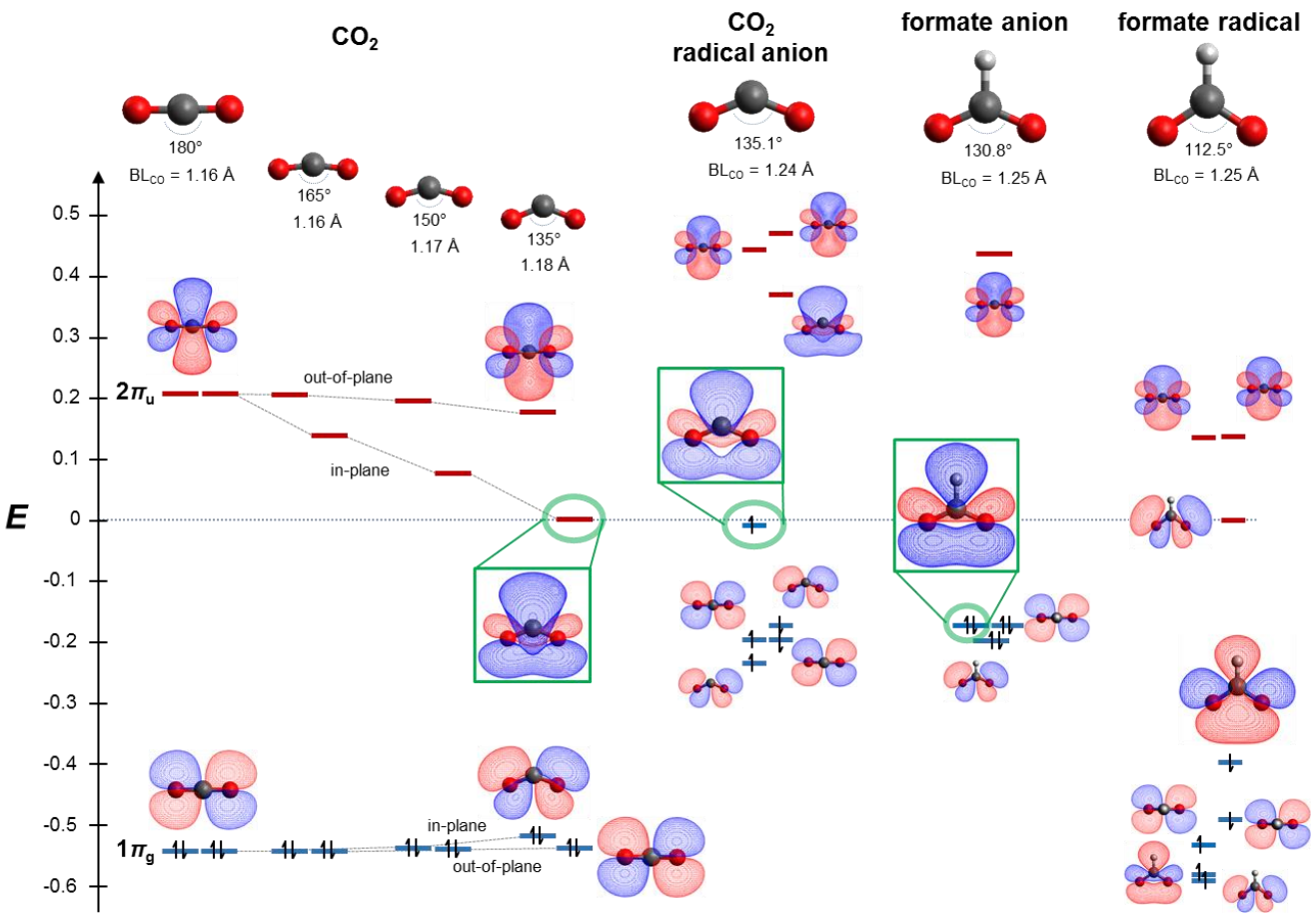

Figure 1. Orbital energy diagrams with characteristic OCO angle CO bond length of CO_2 in the linear and bent forms, radical CO_2^-, formate ion and formate radical. The calculations were performed with (U)CCSD/cc-pVTZ.[4] The energy scale is shown in Hartree.

4. **Hydrogen (hydride) transfer to CO_2**. In both heterogeneous and homogeneous catalytic transformations, one of the most common intermediates is formate. Formate anion and formate (radical) are often reported to be the intermediate prior to further transformation when hydride or hydrogen atom, respectively, reacts with the carbon of CO_2.[7] Although not well documented, interestingly, the CO-bond length, the OCO bond angle and orbital characters of formate anion are very similar to those of the radical CO_2^- (Figure 1). This similarity can be understood as if the hydrogen atom is weakly attached to the radical CO_2^- without altering the chemical character. The highest occupied molecular orbital (HOMO) of formate anion is stabilized compared to that (in this case, SOMO) of the radical CO_2^- as expected. Still the high energy level of the HOMO indicates the strong nucleophilic character of formate anion with similar reactive properties to that of radical CO_2^-. On the other hand, formate radical shows totally different orbital characters and thus reactivity judging from the LUMO and the SOMO at very low energy levels. This would result in highly electrophilic character of formate radical (Figure 1).

These four characteristics of CO_2 reactivity are highly linked and the charge/electron transfer induces and is induced by geometric transformation of CO_2.

The aforementioned chemical nature of CO_2 and its activated forms imply that catalytic transformation over surfaces should create unique environment and space accelerating and facilitating charge separation, CO_2 bending and electron/hydrogen transfer to CO_2. Indeed, CO_2 transformation reactions are reported with activation methods creating such environment for charge repartition (e.g. acid-base catalysis) and facilitating and forcing electron transfer (e.g. photo- and electro-catalysis). We can categorize them into five types, namely thermal activation (which includes (i) metal activation and (ii) acid-base activation), (iii) photo activation, (iv) electro activation and (v) plasma activation (Figure 2), and the general characteristics of CO_2 reactivity and widely found key intermediates and products for each activation methods are briefly summarised in the following sections.

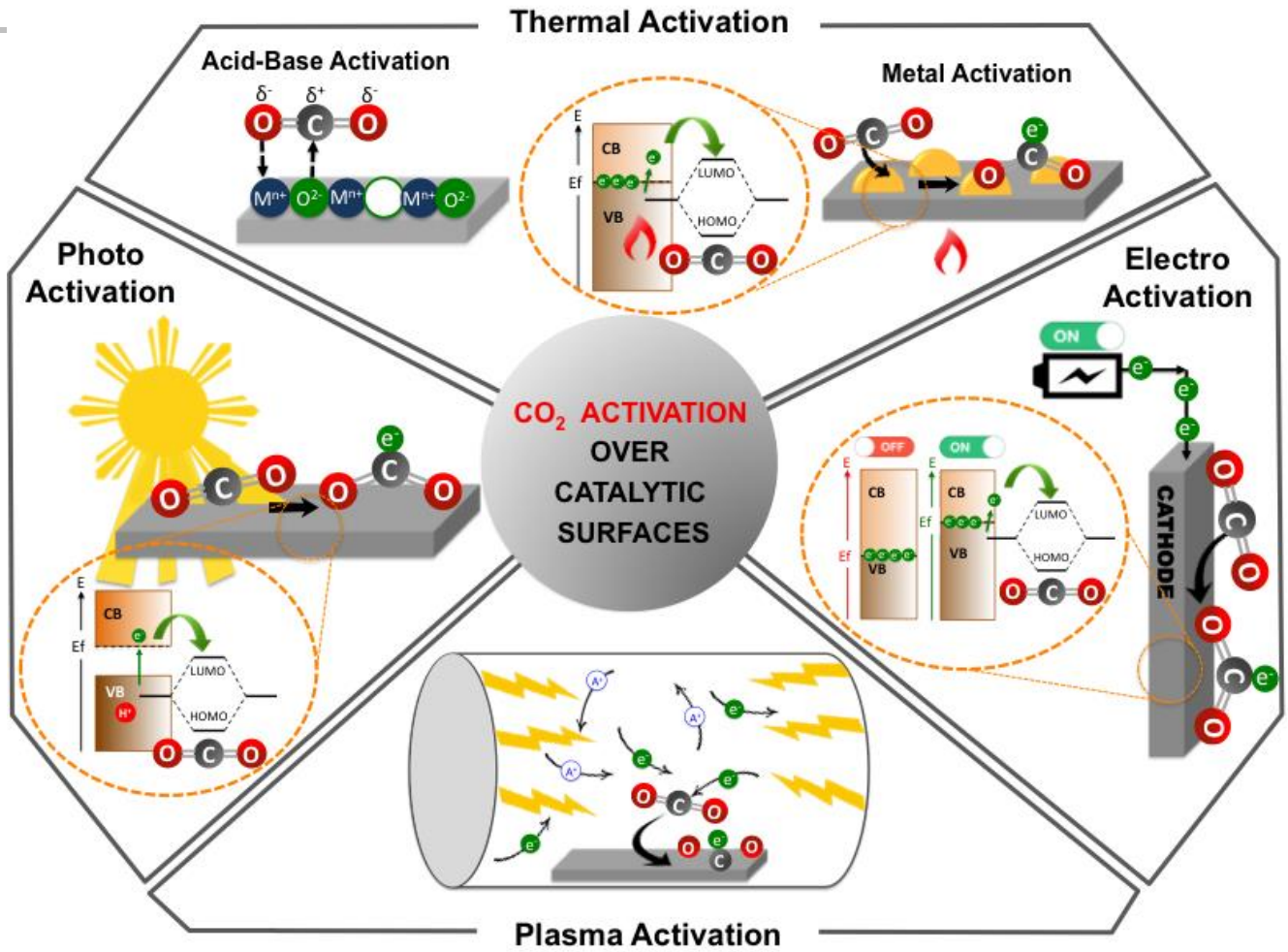

Figure 2. Common methods of CO_2 activation over catalytic surfaces.

Thermal activation - metal sites

This activation consists in an electron transfer from the metal to CO_2 forming adsorbed radical CO_2^-. Although the required energy for this process is very high due to the large work function of these metal surfaces, higher reaction temperatures can result in a larger number of electrons with sufficient energy to take part in CO_2 activation (Figure 2). The addition of electron donors such as alkali metals can enhance this activation. For instance, a metal promoted with potassium enhances the formation of strongly bound radical CO_2^-.[8] The configuration of this anion on metal surface is determined by the type of metal and its surface plane since the atomic orbitals of metals differ from each other. According to the DFT calculations performed for different metals such as Fe, Co, Ni and Cu, the bonding of radical CO_2^- on metal surface was found stronger for earlier transition metals with lower energy barriers for CO_2 activation.[9]

On clean metal surfaces, radical CO_2^- can be dissociated to adsorbed CO and O or form surface CO_3^{2-} and CO via its disproportionation, depending on the nature of metal. When atomic oxygen or hydrogen is pre-adsorbed on a metal, surface species such as carbonates or formates can be formed, respectively. On Ni for example, a small precoverage of atomic hydrogen induces the formation of formates while too high coverage is known to suppress CO_2 adsorption.[10]

In literature, most of the metal catalysed reactions involving CO_2 are performed in the presence of hydrogen. However, the roles of hydrogen in such reactions catalysed by metal are widely debated. It has been reported that CO_2 can be continuously activated due to the hydrogen constantly reducing the metal which gets oxidised during CO_2 activation. Contrarily, the main role of hydrogen is also claimed to be a direct involvement in the formation of formates to yield products such as CO and other oxygenates. This latter role dominates the major part in literature comparing to the former one.[11] The mechanism of formate formation, Langmuir-Hinshelwood (i.e. reaction of hydrogen and CO_2, both adsorbed on surface) or Eley-Rideal mechanisms (i.e. reaction of gas phase CO_2 with surface adsorbed H), has not been systematically discussed in CO_2 hydrogenation reactions. A study about kinetics of CO_2 methanation on Pt and Co nanoparticles revealed that the diffusion of surface atomic hydrogen was closely related to the reaction rate,[12] implying that the reaction of hydrogen and CO_2 on the metal surface follows Langmuir-Hinshelwood mechanism. However, this mechanism may change, depending on the type of metal.

Some surface species are reported as the key intermediates formed prior to the production of different important chemicals like CO, CH_4 and CH_3OH. CO_2 may undergo through one or several intermediate steps to yield the targeted final product and side-products. The main reported surface intermediates in thermally activated metal catalysed reactions are CO, formate (HCOO) and carboxyl (COOH) species. For example, both surface CO and HCOO have been reported as intermediates for different reactions using Cu-based catalysts. Selective production of CO or methanol can be achieved by changing reaction parameters such as temperature and pressure. When metal is supported on metal oxide, the main role of metal is to dissociate H_2 while CO_2 can be trapped or even activated on metal oxide due to acid-base interaction and other reactions paths may become active, as discussed in the following section.

Thermal activation - acid-base sites

CO_2 is acknowledged as a mildly acidic molecule and it is attracted by the basic sites of solid surfaces, as evidenced by the intensive use of CO_2 to probe the number and strength of basic sites by temperature programmed desorption of CO_2 from a surface. Nevertheless, due to the polarised character of the molecule (point 2), the nature of the molecule is regarded amphoteric because of the more electron-deficient C atom and the more electron-rich O atom, prone to be attacked by either electron rich or electron deficient site/atom, respectively.

The most common referrals to the notion of acidity and basicity of solid materials are Brønsted (acid: proton donor, base: proton acceptor) and Lewis (acid: electron acceptor, base: electron donor) sites. Generally acid-base materials are metal oxides and they are categorised into basic (e.g. MgO), acidic (e.g. γ-Al_2O_3), amphoteric (e.g. CeO_2 and ZrO_2) and neutral (SiO_2) materials. A metal oxide surface is regarded as Lewis acid when the oxygen atom of CO_2 chemically interacts with the surface through the metal cation (M^{n+}) and as Lewis base when the carbon atom of CO_2 interacts through O^{2-} site (Figure 2), creating surface spots inducing charge repartitioning (point 2).

CO_2 is adsorbed or reacts over acid-base materials, resulting in three common forms (i) carbonate (CO_3^{2-}) formed through reaction with O site, (ii) bicarbonate (HCO_3^-) formed through reaction with surface OH and (iii) linear adsorption (parallel or perpendicular to the surface). Increased degree of surface acidity can promote the linear configuration, whereas more basic metal oxides promote the formation of a bent and reactive CO_2^- on the surface due to the electron-donating character of the surface (points 1 and 3).[13] The forms (i) and (ii) can be considered as the products through such activation over basic sites mainly consisting of surface oxygen atoms.

The CO_2 transformation into valuable chemicals over acid-base catalysts is known as the non-reductive route since no formal redox of C or O takes place. As discussed earlier, the presence of an active metal together with acid-base sites of metal oxide material is a common approach to induce reductive reactions in the presence of, for example, hydrogen.[14]

From the first adsorbed species, the widely reported chemicals produced via the non-reductive CO_2 transformation are cyclic and linear organic carbonates, carbamates, carboxylic acids, polymers or urea. In all cases, the presence of Lewis acid – Lewis base pairs in close vicinity with specific acidity/basicity strength is advantageous or likely required. Besides, there are more indications that CO_2 is activated over surface oxygen defect sites, followed by its subsequent dissociation into CO and O or its attack from more reactive species leading to the formation of reaction intermediates.[15] This implies that in such activation mechanisms acid-base sites may involve and induce the surface redox process of reducible metal oxides (e.g. for oxygen storage materials).

One of the major advantages of acid-base materials is the fine-tunability. One can tune the density and strength of acid and base sites based on material types (single/mixed metal oxides, zeolites, MOF, etc.), composition, nano-structure and dispersion. At present, true understanding of the roles of acid-base sites and of their geometrical and electronic structures for efficient CO_2 activation needs to be advanced for bottom-up catalyst design.

Photocatalytic activation

Artificial photosynthesis represents a promising alternative route to convert atmospheric and anthropogenic CO_2 into useful carbon-containing chemicals. The utilisation of sunlight as an abundant and economic energy source has triggered numerous studies on the photocatalytic transformation of CO_2 into valuable chemicals. Particularly, converting the energy contained in sunlight into storable chemical energy carriers such as methanol is an attractive mean to efficiently utilise the fluctuating and discontinuously available natural energy.

The reaction is mediated by a photocatalyst that harvests light and transforms the energy into a reactive form activating CO_2 and other reactant(s). Generally, H^+ source is required for photocatalytic CO_2 conversion and water (possibly H_2) is commonly used because of its abundance on Earth. The chemical reaction during artificial photosynthesis is as follows.

$$aCO_2 + bH_2O \xrightarrow{h\upsilon,\ \text{photocatalyst}} C_xH_yO_z\ (+\ O_2)$$

Photocatalysts are usually semiconductor materials which absorb a characteristic wide range of light spectrum with sufficient energy to produce an internal charge separation upon light absorption. Photoexcited electron is promoted from the valence band (VB) of the semiconductor material to the empty conduction band (CB), leading to the formation of a positively charged hole in the VB (Figures 2

and 3). The generation of electron-hole pairs is only initiated if the light energy is equal to or larger than the band gap (E_g) of the semiconductor material ($h\nu \geq E_g$).[16]

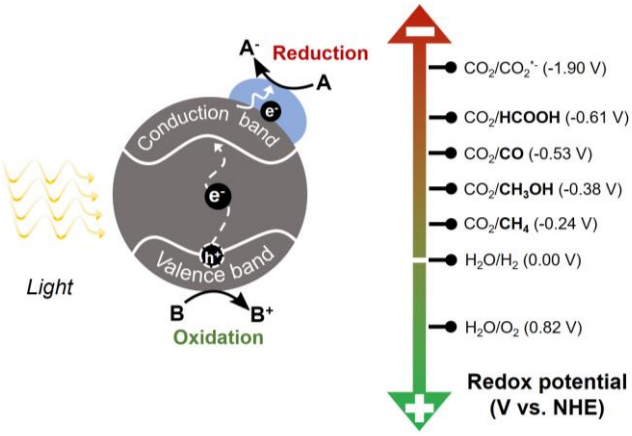

Figure 3. Photoexcited electron formation and its involvement in the reduction reaction in a typical photocatalytic system. Redox potentials of the main products obtained from CO_2 are listed against the normal hydrogen electrode (NHE) as the standard for zero potential.

When CO_2 is at the catalyst surface (e.g. adsorption), it can be activated via electron transfer (point 3), forming more reactive radical CO_2^-, which can be further reacted with proton and other chemical species in vicinity.[17] For these reactions to take place, the reduction potentials of the possible products should be less negative than the conduction band of the catalyst (Figure 3). The surface properties and the number of electrons and protons that can be transferred will determine the product selectivity. For example, eight electrons and eight protons are required to generate methane, which is obviously not facile. In reality, the existence of both protons and electrons often leads to the production of H_2, thus competing with the CO_2 reduction.[18]

The vast majority of the mechanistic studies have been performed on TiO_2 with various co-catalysts, and several pathways have been proposed for the formation of CO, methanol and methane[19]. However, the detection and identification of involved radical intermediates is very challenging due to their short lifetime and subsequent transformation. General understanding on how the reaction is driven towards a desired product is still in its infancy.
Regardless of all the knowledge gained over the last years, CO_2 photoconversion efficiency remains low. A suitable photocatalyst design is required to maximise light utilisation, retard electron-hole recombination, and facilitate charge separation and migration.[20] Furthermore, engineering photoreaction system is essential to enhance CO_2 activation rate and may lead to breakthrough because properly making use of CO_2 phase (in a dissolved or gaseous form) and reactor engineering have indeed led to enhanced CO_2 reactivity.

Electrocatalytic activation

The reduction of CO_2 in aqueous solutions by electrocatalytic activation was first reported in around 1870 when formic acid was synthesized from an aqueous bicarbonate solution using Zn and carbon electrodes (Bunsen Cell).[21] Since then, there has been steadily increasing interests in the field of electrochemical reduction of CO_2 to valuable chemicals.
The working principle is analogous to and the basis of photocatalysis. Surface-catalysed electro-activation makes use of charge transfer across the interface between the surface (often metallic) and adsorbed CO_2 (Figure 2). This charge transfer occurs from the metal's Fermi level with the formation of radical CO_2^- and this process is energy intensive (-1.90 V, Figure 3). As discussed previously, multiple electron transfers or coupled protonation, or proton-coupled electron transfer reactions are required to produce highly reduced chemicals such as formic acid, methane or methanol (Figure 3).
In reality, however, even if the reduction (or redox) potentials are not that high (Figure 3), CO_2 reduction does not take place easily and actual electrical potentials for CO_2 reduction are much more negative in most cases than the theoretical ones, resulting in so-called overpotential. Various parameters such as the type of electrode, electrolyte, pH, CO_2 concentration, pressure and temperature cause the overpotential.
The metal type used as cathode (the electrode where reduction reaction takes place) has been known to define the specific path where CO_2 reduction is driven (Figure 4). Three main products from CO_2, namely CO, formic acid and hydrocarbons, are often reported besides H_2 arising from the reduction of H^+.[22] In addition, surface structure and surface architecture (roughness, defects and porosity) are also known to impact product selectivity.[23]

Most setups employed for CO_2 electrocatalytic reduction are electrolytic cells where a cathode and an anode are immersed in aqueous electrolyte and gaseous CO_2 is continuously bubbled through the solution. Although the use of aqueous solutions is

advantageous because it serves as proton source, the competition between CO_2 reduction and hydrogen production can become a major issue, as is the case for photocatalysis. Also, CO_2 reduction rate can be limited due to its low solubility in water at standard temperature and pressure. Pressuring the aqueous solution with higher CO_2 pressure and the use of non-aqueous solvent can improve the local CO_2 concentration near the cathode surface.[22b] With the latter approach using N,N-dimethylformamide, propylene carbonate and methanol, CO_2 solubility can be increased by 20, 8 and 5 folds, respectively. Also the use of non-aqueous electrolyte is known to open transformation paths to oxalates and derivatives.[24]
Similar to photocatalytic activation, reaction engineering plays key roles in electrocatalytic CO_2 conversion to improve the contacts between CO_2 and the cathode with optimised mass transport properties and with a proper amount of proton source like H_2O. Making use of CO_2 phase adequately (in a dissolved or gaseous form) and reactor engineering could indeed afford outstanding CO_2 reactivity even in continuous operation.[25]

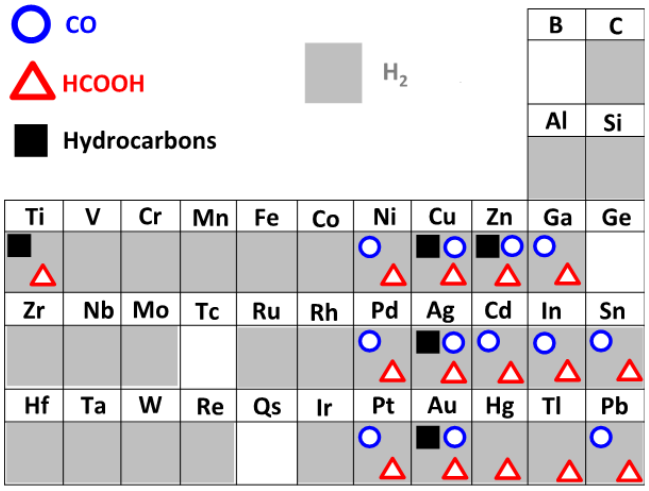

Figure 4. General selectivity trends defined by the metal type for CO_2 reduction when used as cathode.[22]

Plasma-activation

Besides thermal, photo and electro activation of CO_2, plasma activation is another approach rapidly gaining popularity as a more sustainable mean to drive CO_2 conversion with high productivity and selectivity at lower energy inputs. Plasma is the state where electron is not bound to an atom or molecule, thus existing as (partially) ionised gas.[26] Molecules and atoms in this state show very interesting reactivity. For example, while a very high temperature (1600-2000 K) is necessary to dissociate CO_2 into CO and O_2 in the gas phase, in the plasma state the thermodynamically unfavourable reaction proceeds at even ambient conditions by giving 5.5 eV to the molecule through breaking the C=O bond via stepwise vibrational excitation.[27] Most recent applications of plasma in CO_2 conversion make use of non-thermal plasma whose bulk (ion) temperature can be as low as room temperature, while electrons are hot (high kinetic energy).
Although plasma-activated CO_2 dissociation can take place without a catalyst, its presence is known to greatly improve conversion efficiency at lower energy consumption.[27] Often dielectric barrier discharge (DBD) plasma is used for catalytic reactors. Reported plasma-catalyst synergetic effects on the catalyst surfaces are morphological changes of catalyst, chemical/electronic structure changes, altering reaction paths (thus product selectivity) and lower activation barrier and higher reaction rates.[28] All of these effects are induced by the enhanced electric field created by the presence of negatively charged surface due to higher mobility of electrons than that of ions. In addition, catalyst shape and nanostructures are known to affect the strength of electric field and, consequently, the chemical and electronic structure (i.e. reactivity) of catalyst in the presence of plasma.[28]
One of the most successful examples of plasma-catalyst synergy for CO_2 conversion has been reported for dry reforming of methane where two major greenhouse gases react to yield syngas.[26-27]

$$CH_4 + CO_2 \longrightarrow 2CO + 2H_2$$

Without a catalyst this reaction takes place but with poor selectivity (higher hydrocarbons and oxygenates are observed).[28] In the presence of a catalyst, both conversion and selectivity can be improved.
Plasma-activated CO_2 conversion is still in its infancy, much younger than other methods described in this article and requires greater efforts for its full exploitation. That said, this approach can be more effective than other methods because of the highly energetic electrons on the catalyst surface which can activate neutral CO_2 into radical CO_2^- among other reaction intermediates. Low temperature activation is particularly beneficial when a reaction is exothermic (e.g. methanol synthesis from CO_2 hydrogenation) since one can expect higher equilibrium CO_2 conversion and higher methanol selectivity at lower temperature.[29]

Concluding remarks

Despite its high thermodynamic stability, CO_2 can be transformed into valuable chemicals, mainly carbon monoxide, hydrocarbons, methanol and formic acid, over catalytic surfaces through various means of activation. Aided by external energy sources such as temperature, light or electricity, a unique environment can be created to activate this rather inert molecule by facilitating charge transfer (mainly electron injection) processes to the molecule. Going through the different activation methods and reaction intermediates and products, commonly observed reaction paths can be summarised (Figure 5).

By far the most important intermediates are radical CO_2^- and formate according to literatures and these intermediate species are considered to show analogous reactivity based on the electronic structures (Figure 1). Gaining electronic and mechanistic insights into how CO_2 becomes reactive and undergoes through one or several intermediate steps is of great importance to enhance CO_2 conversion towards targeted products. This has been demonstrated for a Ni-catalyst system where selectivity to formate or CO can be defined by how the CO_2 coordinates to Ni, i.e. via C or O.[2] With the theoretical and experimental tools available nowadays, such rational approaches should be maximally used to design new generation catalysts in conjunction with appropriate activation methods in conjunction with reactor engineering, aiming at creation of tailored surface sites favouring CO_2 activation and subsequent selective conversion.

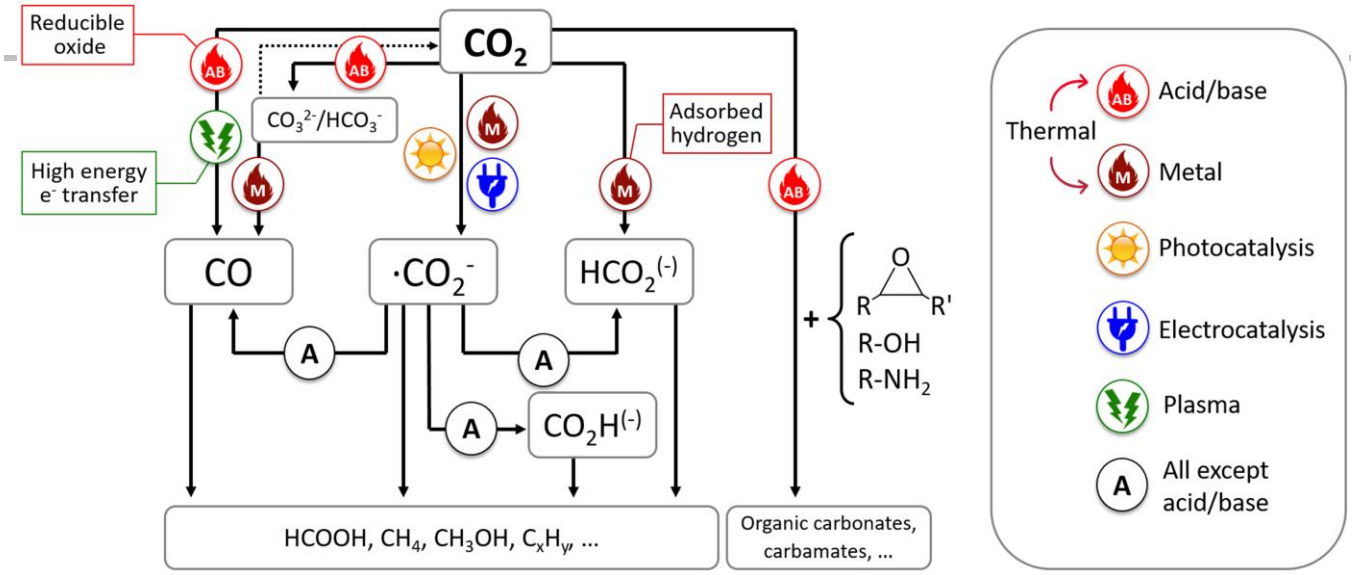

Figure 5. Key intermediates and products highlighting the similarities among the different activation methods.

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Keywords: Carbon dioxide • activation • mechanism • surface • heterogeneous catalysis

References

[1] L. A. Curtiss, K. Raghavachari, P. C. Redfern, J. A. Pople, *J. Chem. Phys.* **1997**, *106*, 1063-1079.
[2] B. Mondal, J. Song, F. Neese, S. Ye, *Curr. Opin. Chem. Biol.* **2015**, *25*, 103-109.
[3] S. Nakamura, M. Hatakeyama, Y. Wang, K. Ogata, K. Fujii in *Advances in CO_2 Capture, Sequestration, and Conversion, Vol. 1194*, American Chemical Society, **2015**, pp. 123-134.
[4] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. Montgomery, J. A., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, **2009**.
[5] H. J. Freund, M. W. Roberts, *Surf. Sci. Rep.* **1996**, *25*, 225-273.
[6] W. Taifan, J.-F. Boily, J. Baltrusaitis, *Surf. Sci. Rep.* **2016**, *71*, 595-671.
[7] D. Cheng, F. R. Negreiros, E. Aprà, A. Fortunelli, *ChemSusChem* **2013**, *6*, 944-965.
[8] F. Solymosi, *J Mol. Catal.* **1991**, *65*, 337-358.
[9] C. Liu, T. R. Cundari, A. K. Wilson, *J. Phys. Chem. C* **2012**, *116*, 5681-5688.
[10] J. Wambach, G. Illing, H. J. Freund, *Chem. Phys. Lett.* **1991**, *184*, 239-244.
[11] C.-S. Chen, W.-H. Cheng, S.-S. Lin, *Catal. Lett.* **2000**, *68*, 45-48.
[12] S. K. Beaumont, S. Alayoglu, C. Specht, N. Kruse, G. A. Somorjai, *Nano Lett.* **2014**, *14*, 4792-4796.
[13] K. R. Hahn, M. Iannuzzi, A. P. Seitsonen, J. r. Hutter, *J. Phys. Chem. C* **2013**, *117*, 1701-1711.
[14] T. Hyakutake, W. v. Beek, A. Urakawa, *J. Mater. Chem. A* **2016**, *4*, 6878–6885.
[15] L. Liu, W. Fan, X. Zhao, H. Sun, P. Li, L. Sun, *Langmuir* **2012**, *28*, 10415−10424.
[16] A. Dhakshinamoorthy, S. Navalon, A. Corma, H. Garcia, *Energ. Environ. Sci.* **2012**, *5*, 9217-9233.
[17] X. Chang, T. Wang, J. Gong, *Energ. Environ. Sci.* **2016**, *9*, 2177-2196.
[18] A. Corma, H. Garcia, *J. Catal.* **2013**, *308*, 168-175.
[19] S. N. Habisreutinger, L. Schmidt-Mende, J. K. Stolarczyk, *Angew. Chem. Int. Ed.* **2013**, *52*, 7372-7408.
[20] L. Liu, Y. Li, *Aerosol. Air. Qual. Res* **2014**, *14*, 453-469.
[21] E. Royer, *C.R. Acad. Sci* **1870**, *70*, 731-735.
[22] (a) E. V. Kondratenko, G. Mul, J. Baltrusaitis, G. O. Larrazábal, J. Pérez-Ramírez, *Energ. Environ. Sci.* **2013**, *6*, 3112-3135; (b) Y. Liu, J. Qiao in *Electrochemical Reduction of Carbon Dioxide: Fundamentals and Technologies*, CRC Press, **2016**, pp. 1-46.

[23] B. Viswanathan in *New and Future Developments in Catalysis*, Elsevier, Amsterdam, **2013**, pp. 275-295.
[24] R. P. S. Chaplin, A. A. Wragg, *J. Appl. Electrochem.* **2003**, *33*, 1107-1123.
[25] S. Verma, X. Lu, S. Ma, R. I. Masel, P. J. A. Kenis, *Phys. Chem. Chem. Phys.* **2016**, *18*, 7075-7084.
[26] A. Fridman in *Plasma Chemistry*, Cambridge University Press, Cambridge, **2008**.
[27] B. Ashford, X. Tu, *Curr. Opin. Green. Sus. Chem.* **2017**, *3*, 45-49.
[28] E. C. Neyts, K. Ostrikov, M. K. Sunkara, A. Bogaerts, *Chem. Rev.* **2015**, *115*, 13408-13446.
[29] A. Álvarez, A. Bansode, A. Urakawa, A. V. Bavykina, T. A. Wezendonk, M. Makkee, J. Gascon, F. Kapteijn, *Chem. Rev.* **2017**, DOI:10.1021/acs.chemrev.6b00816.