

On the current status of the mechanistic aspects of photocatalytic reduction of carbon dioxide

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Photocatalytic reduction of carbon dioxide, one of the pathways involved in the carbon dioxide conversion process, has been receiving significant attention from the scientific community in the last four decades. Nevertheless, the mechanism of carbon dioxide reduction is still unclear and the information available is not sufficient for developing it into large scale applications, possibly because of the invariable hurdles associated with the reduction process. The reductive photocatalytic conversion of CO₂ involves all the redox reactions occurring at the interface of the semiconductor such as water splitting, hydrogen evolution, oxygen evolution, photo-oxidation reactions and reactions of radical intermediates. The overall product yield is highly dependent on the extent of these competing reactions. Herein, we discuss our perceptions and current status of the interface reactions and their involvement in the fundamental mechanistic aspects of the photocatalytic conversion of CO₂.

Keywords: Carbon dioxide activation, Carbon dioxide reduction, Carbon dioxide anion radical, Anion radicals, Reaction mechanism, Photocatalysis, Sacrificial reagents, Reactive oxygen species, Solar energy conversion

Carbon dioxide conversion into useful chemicals and fuels has been one of the fast progressing research avenues in the last four decades¹⁻¹⁰. Currently, no economically viable technology or processes have evolved that offer direct conversion of carbon dioxide into fuels or fuel precursors. The intense research on these possibilities has not yet reached the desired goal because of the significant overpotential associated with the conversion process. This frustration can be clearly visible in the DOE status report¹¹, wherein the difficulties related to the CO₂ conversion processes are specifically pointed out. One of the major barriers obstructing the efficient conversion of carbon dioxide is the lack of catalysts that can readily convert the abundant solar energy into chemical bonds with inexpensive reducing agents to achieve rapid and selective cleavage of C-O bonds and produce C-H bonds in the fuel products.

The photocatalytic reduction of carbon dioxide is proposed to occur through two pathways. (1) Formation and subsequent hydrogenation of CO₂^{•-}, and, (2) Proton-coupled electron transfer reactions. Direct addition of an electron to CO₂(g) to yield CO₂^{•-} requires large overpotential. Therefore proton assisted electron addition, which offers a lower barrier

to the formation of CO₂ hydrogenation products, is usually preferred¹². In this context, it is more useful to revisit the Latimer-Frost diagram¹³, which correlates the number electrons transferred to the net free energy change associated with the CO₂ reduction process. Figure 1 shows the energy requirement for the electrochemical reduction of various products (Latimer-Frost diagram). In the L-F diagram, a

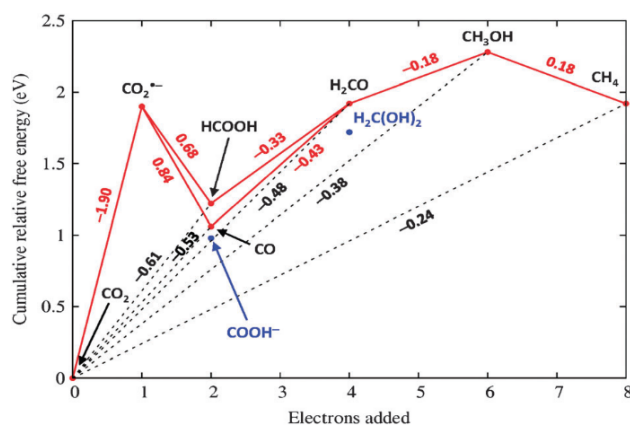


Fig. 1—Latimer-Frost diagram of CO₂ reduction at pH 7. The dashed lines correspond to the potential required for PCET of CO₂. [Reproduced from Ref. 13].

thermodynamically unstable species lying above the line connecting two other correlated species is converted into these two species. For instance, in the case of formaldehyde, which rests just above the line linking carbon monoxide and methanol, is unstable and converts into the latter two.

The mysterious phenomenon, natural photosynthesis, may not be the path to reach Ciamician's vision of artificial photosynthesis. In photosynthesis, the reduction of CO_2 to glucose involves a complex aqueous organic biochemical route which is hard to adapt to an industrial set up¹⁴⁻¹⁶. Thus, the realisation of CO_2 reduction technology is far beyond the reach of the current technology and will only be achieved through a deep understanding of the fundamental precepts of the CO_2 reduction process.

Photo-assisted reduction requires only the initiation from the photon source and there is no need to convert it to electricity. Also, adsorption of the substrate on the photocatalyst surface substantially reduces the overpotential required for the reduction. The carbon footprint associated with the photocatalytic process is comparatively low as compared to other solar fuel production routes¹⁷. Therefore, of the all solar energy conversion processes, the photocatalytic or photochemical pathway is preferred to reach the Ciamician's vision¹⁸. It utilises the point source of carbon dioxide and water as precursors for the reduction and conversion to products at ambient atmosphere. In aqueous medium,

hydrogen evolution is more favourable than CO_2 reduction and the presence of oxygen increases the chance of oxidation of the fuel product. Therefore, various attempts were made to find an alternative proton source for the reduction. The goal of any CO_2 conversion technology is to stabilise the carbon dioxide concentration in the atmosphere and utilise it for the production of energy-rich chemicals to combat current energy¹⁹⁻²³ and environmental issues^{24,25}. These kinds of technologies will not solve the problems due to the atmospheric CO_2 accumulation, and will contribute to reducing the volume of CO_2 produced from the point source; this enables us to achieve a carbon neutral use of chemicals²⁶. These targets were difficult to achieve, and this would be the primary reason, why research is revolving around the CO_2 conversion process (Fig. 2).

The photocatalytic conversion of carbon dioxide involves two approaches:

(1) Gaseous phase reduction: Direct treatment of $\text{CO}_{2(g)}$ with the photocatalyst surface with a hydrogen source usually water vapour.

(2) Liquid phase reduction: Reduction of $\text{CO}_{2(aq)}$ in aqueous solution or any other solvent medium in the presence of a dispersed photocatalyst.

Figure 3(a) represents the conventional picture for depicting the gaseous phase CO_2 reduction mechanism. Such types of representation are typically used to interpret the reaction mechanisms of other photocatalytic reactions. All these reactions are associated with single or multiple electrons or hole

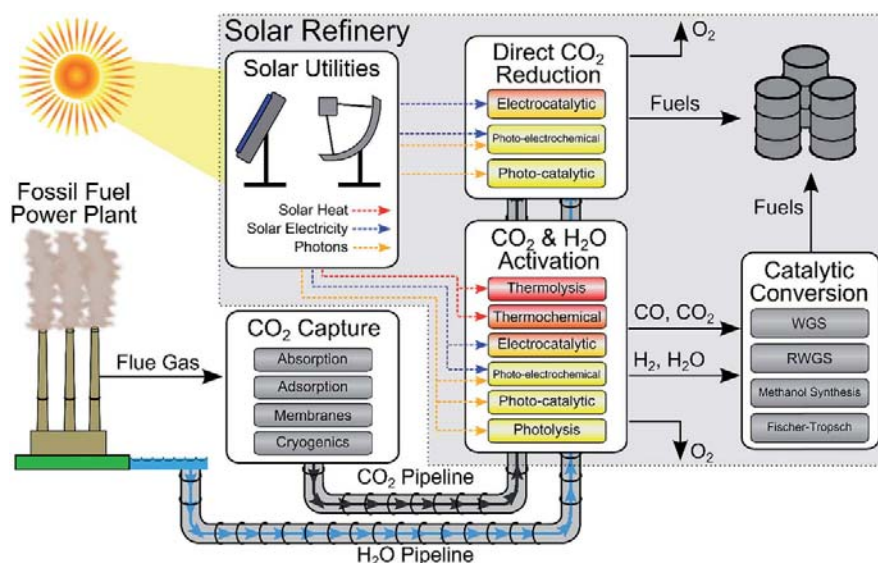


Fig. 2—Schematic representation of a futuristic solar refinery for the transformation and utilisation of carbon dioxide using sunlight and water. [Reproduced from Ref. 17].

transfer reactions. Therefore, such representations convey a basic idea of the reaction mechanism. However, in CO₂ reduction, the process is affected by the competing and different radical reactions involved in the reaction system. Hence, necessary corrections should be made to convey the kind of interface reactions involved in the CO₂ reduction process. The photocatalytic CO₂ reduction involves all processes occurring at the semiconductor surface interface, imposing huge competition and ultimately making the process as less efficient (Fig. 3(b)). Most of the literature does not consider the exact role of competitive reactions on the CO₂ reduction process.

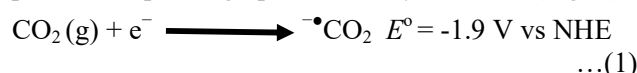
Extensive reviews are available in the literature on the issues associated with CO₂ reduction photocatalysis²⁷⁻⁴⁰. Mechanistic aspects related to carbon dioxide reduction are still unknown, and existing theories are not capable of explaining most of the facts in the CO₂ photo-reduction. Hence, there is an urgent demand to revisit the existing theories on CO₂ activation, and the subsequent conversion to fuel or fuel precursors exclusively. This article primarily aims to revisit the current knowledge on the mechanism of semiconductor mediated photocatalytic reduction of CO₂.

Underlying Theories of CO₂ Reduction Photocatalysis

The underlying principles of photocatalytic carbon dioxide reduction are mostly based on the electrochemical point of view. Most of the electrochemical reactions are carried out under pure reaction conditions. Consequently, how it would apply to the photocatalytic reaction condition is a debatable issue and discussed in many perspectives appeared elsewhere⁴¹⁻⁴⁸. The major goal of

photocatalytic or electrocatalytic reduction is to avoid the initial activation step of CO₂ by forming intermediates with lower potential energy, thus rendering it more thermodynamically favourable.

The initial step of the direct reduction of CO₂ is believed to be the formation of carbon dioxide anion radical (^{-•}CO₂). The subsequent hydrogenation of ^{-•}CO₂ radicals gives rise to a variety of reduction products depending upon the catalyst surface (Fig. 4).



The E° for the process is considerably higher or more negative than any of the individual hydrogenation reactions of carbon dioxide and requires an enormous amount of energy. This reaction is applicable in the case non-protic solvents. Regarding protic solvents, the measurement of the thermodynamic potential highly depends on the kind of electrode used, which is due to the participation of the adsorbed hydrogen (H^\bullet) in the reduction process.

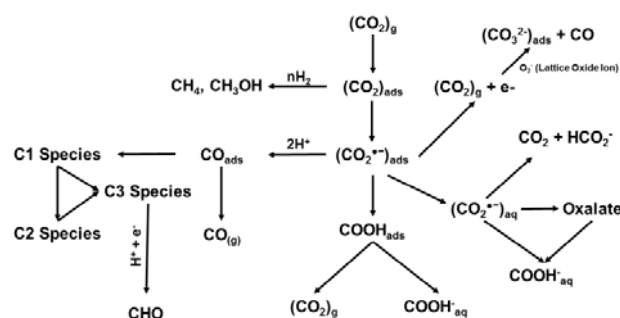


Fig. 4-Formation and subsequent conversion of ^{-•}CO₂. [Reproduced from Ref. 12].

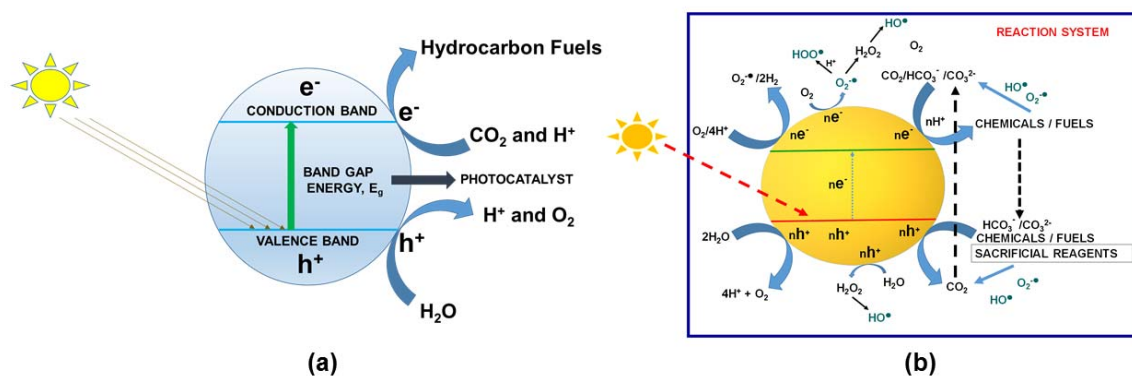


Fig. 3 - (a) Mechanism of gaseous phase CO₂ reduction photocatalysis. [Reproduced from Ref. 104], and, (b) Possible reactions involved in the CO₂ reduction process.

Any of the CO₂ utilisation techniques involving this initiation step would require the application of a high negative potential to the cathode. If the anode reaction were to be water oxidation, then a total potential of 3.129 V across the cell would be needed to drive the complete reaction! In the photocatalytic reduction of CO₂, oxidation and reduction reactions are carried out by the charge carriers produced as a result of the light-induced initiation of the photocatalyst. The energy required for the photocatalytic conversion of CO₂ is lower than the corresponding electrocatalytic reduction¹⁷.

Every semiconductor possesses certain kinds of reduction and oxidation potentials, and the value depends on the position of the conduction and valence band with respects to the standard hydrogen electrode, or vacuum (Fig. 5). Among the currently known semiconductors, no one has sufficient reduction potential for the reduction of carbon dioxide into corresponding carbon dioxide radical anion. While approaching carbon dioxide onto the surface of the photocatalyst, the interaction changes the geometry from linear to bent, which in turn decreases the energy of the LUMO level⁴⁹. The energy required for the activation of CO_{2(ads)} will be less compared to the CO_{2(g)}. The addition of electrons into the CO₂ molecule depends on the interaction with the surface catalytic species⁵⁰. Modification of the surface properties of photocatalysts helps to produce particular reduction products.

Carbon dioxide can attach to the photocatalyst surface through either carbon or oxygen⁵¹ (Fig. 6). The interaction depends on the nature of active sites present on the photocatalytic surfaces. Each photocatalytic material possesses its adsorption

mechanism, and the kind of electron transfer would be different. The adsorption of carbon dioxide on various metal oxide surfaces thoroughly explained in the book "Surface Science of Metal Oxide" by Victor E. Henrich⁵². In aqueous phase reduction, especially in alkaline pH, carbonate or bicarbonate ion is the predominant species. The surface interaction of carbonate or bicarbonate structures with the photocatalytic material is different from CO₂ in the gaseous state. Since carbonate and bicarbonate exist as ions, the interaction of these ions with the photocatalytic surface is mainly either through hydrogen or oxygen. Herein, one cannot expect the first electron addition to the LUMO level of carbon dioxide in aqueous phase photocatalytic reduction. Therefore, the reaction mechanism associated with the aqueous phase should be different from that of gaseous phase CO₂ reduction. To the best of our's knowledge, detailed studies are not available on the interaction of carbonate and bicarbonate structures

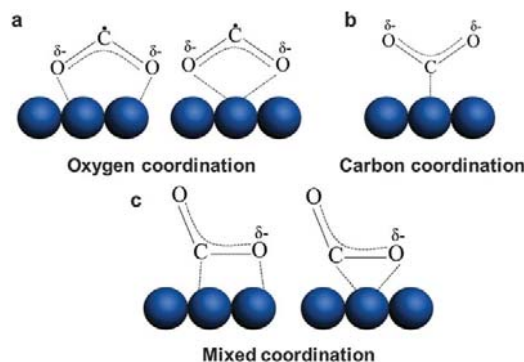


Fig. 6–Possible binding modes of CO₂ on the surface. [Reproduced from Ref. 51].

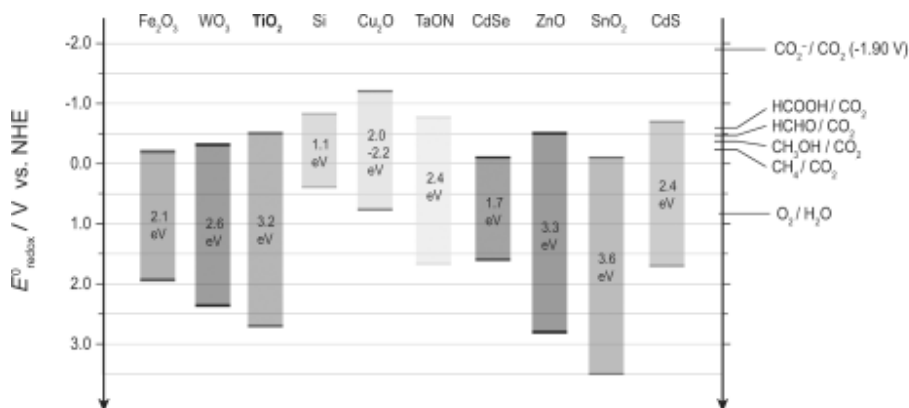
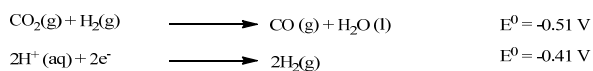


Fig. 5–The standard potential of semiconductors w.r.t. CO₂ reduction. [Reproduced from Ref. 39].

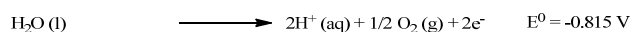
with the metal oxide or any other photocatalyst^{53,54}. Detailed studies are needed to resolve the mechanism of aqueous phase photocatalytic reduction of carbon dioxide. In water splitting and photo-oxidation reactions, carbonate and bicarbonate are the typically used hole scavengers. Therefore, carbon dioxide radical ion observed in the aqueous medium may be because of the direct oxidation of carbonate or bicarbonate with holes!

The primary goal of photocatalytic, electrocatalytic or any other alternative conversion reactions is to avoid the initial activation of CO₂ and to produce intermediates with lower potential energy and drive the reaction in a favourable pathway. The intermediate formation depends on the interaction of CO₂ with catalyst surfaces or electron rich entities. The difficulty in executing multiple proton-coupled electron transfers creates an additional thermodynamic barrier to the photocatalytic or electrocatalytic reduction of CO₂. The equations (Eqs A to M) given are the most common proton-coupled electron transfer reactions of CO₂(g) at pH seven⁵⁵.

A. Carbon Monoxide

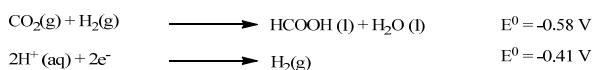


The potential required for water oxidation must be added to the above to elucidate the overall potential associated with the complete reduction reaction.

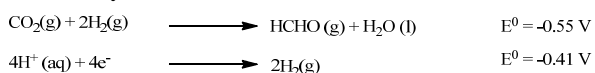


Hence, a potential of -1.735 V required for converting CO₂ (g) into CH₄ (g) at pH 7.

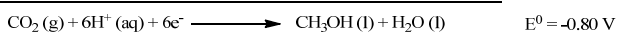
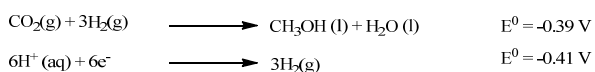
B. Formic Acid



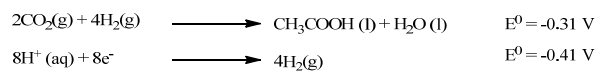
C. Formaldehyde



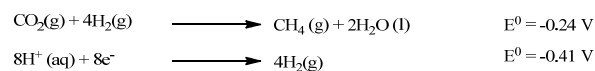
D. Methanol



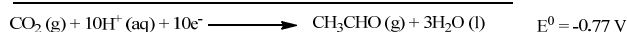
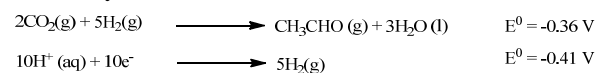
E. Acetic Acid



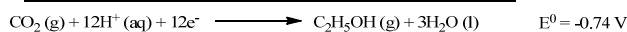
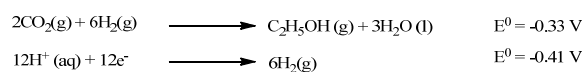
F. Methane



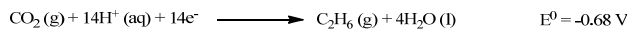
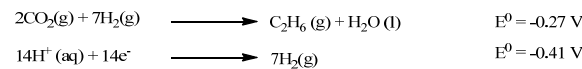
G. Acetaldehyde



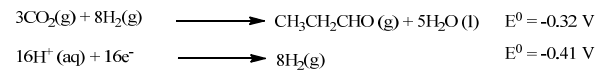
H. Ethanol



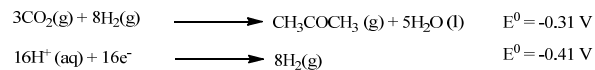
I. Ethane



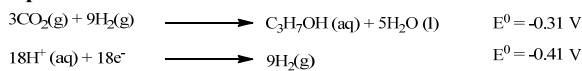
J. Propanal



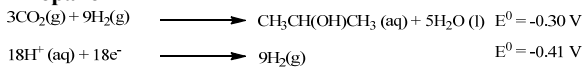
K. Acetone



L. Propanol



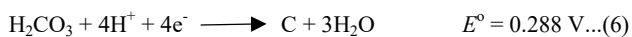
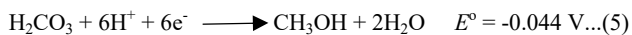
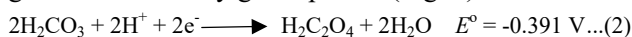
M. 2-Propanol



For photocatalytic conversion reactions, the potential required must be less because of the adsorptive interaction between CO₂/water with the photocatalyst surface. The reactions (A-M) give an

idea of the reduction potential corresponding to the formation of fuel products w.r.t NHE at pH 7. These kinds of data cannot apply to the reactions that are carried out under other pH conditions (Table 1). At different pH and temperatures, the value of standard reduction potential changes significantly (Table 2). According to the recent developments, the conduction band becomes more negative up to 1mv in a unit change in the pH⁵⁶⁻⁵⁸. Therefore, necessary pH correction should be made to the reduction potential while using it for result interpretations.

The above-mentioned potentials are for CO₂ in the gaseous state. Many reports mistakenly used this gaseous phase data to interpret the reactions in the liquid phase reduction. In liquid phase CO₂ reduction, CO₂ molecule exists in the form of H₂CO₃, HCO₃⁻ or CO₃²⁻ according to the pH of the reaction medium. The reduction potential required for the reduction of H₂CO₃, HCO₃⁻ or CO₃²⁻ is different from that for gaseous CO₂ at any given pH⁵⁹⁻⁶³ (Fig. 7).



The corresponding reactions with respect to carbonates are:

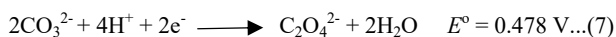
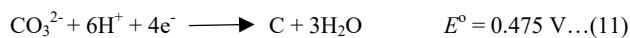


Table 1 – Reduction potential required for CO₂ reduction at various pH

Reaction	E ⁰ (V vs. NHE)		
	pH 0	pH 7	pH 14
CO ₂ (g) + 8H ⁺ (aq) + 8e ⁻ → CH ₄ (g) + 2H ₂ O (l)	+0.169	-0.24	-0.65
CO ₂ (g) + 6H ⁺ (aq) + 6e ⁻ → CH ₃ OH (l) + H ₂ O (l)	+0.030	-0.39	-0.79
CO ₂ (g) + 4H ⁺ (aq) + 4e ⁻ → HCHO (g) + H ₂ O (l)	-0.071	-0.55	-0.89
CO ₂ (g) + 2H ⁺ (aq) + 2e ⁻ → CO (g) + H ₂ O (l)	-0.103	-0.51	-0.93
CO ₂ (g) + 2H ⁺ (aq) + 2e ⁻ → HCOOH (g) + H ₂ O (l)	-0.199	-0.58	-1.02
2CO ₂ (g) + 2H ⁺ (aq) + 2e ⁻ → H ₂ C ₂ O ₄	-0.425	-0.888	-1.29
H ⁺ (aq) + e ⁻ → H ₂ (g)	-0.103	-0.41	-0.93



All reduction reactions of carbon dioxide or H₂CO₃, HCO₃⁻ or CO₃²⁻ associated with a thermodynamic potential near to zero. However, due to the large overpotentials associated with each of the reactions, these kinds of reaction were not normally observed in aqueous solutions under normal conditions. More visible details and examples related to these aspects explained in the famous book, *Standard Potential in Aqueous Solution* by Allen J Bard and co-workers⁶³.

Identity Crisis of Carbon Dioxide Radical Anion

The most prominent theory for the gaseous phase CO₂ reduction mechanism is the formation of carbon dioxide anion radical intermediates, which is considered to be the rate-limiting step in the step-down procedure. Electron spin resonance studies^{64,65} identified the presence of radical anion in the CO₂ reduction system and found that CO₂ radical anion has a bent structure with a bond angle⁶⁶ of about 134°. However, the controversy lies with the source at which carbon dioxide anion radical is produced; whether it is formed directly from carbon dioxide or from any other sources. In aqueous solution, the CO₂ molecule does not exist. Hence, the anion radical detected may be originating from bicarbonate or any other source. The CO₂ anion radicals can also be formed as a result of some intermediate reactions⁶⁷. Surprisingly, these intermediates are

Table 2 – Variation of reduction potential at different temperatures for the reaction,

CO ₂ + H ₂ O + 2e ⁻ → COO ⁻ + OH ⁻ . [Reproduced from Ref. [63]						
T (°C)	2	10	25	40	50	60
E ⁰ (V)	-0.699	-0.708	-0.723	-0.739	-0.750	-0.760

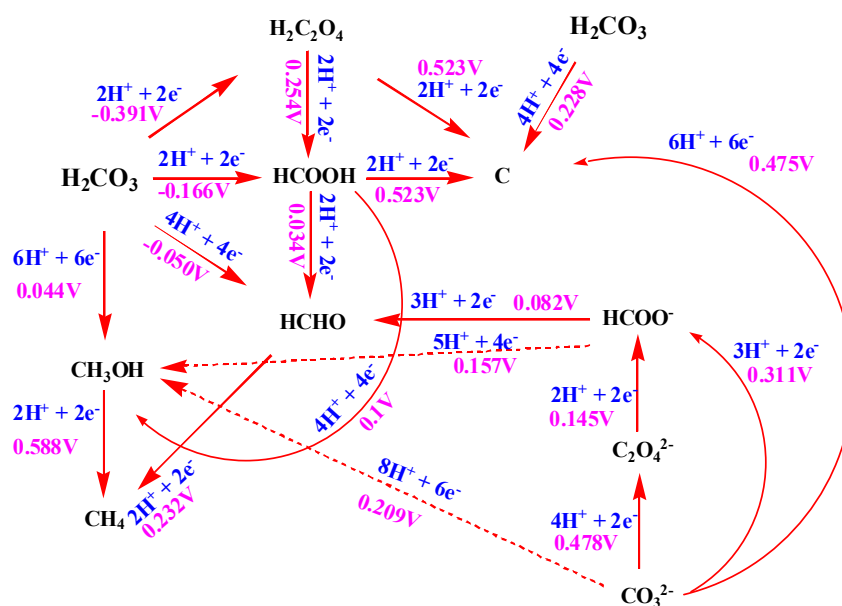
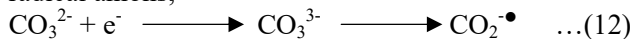


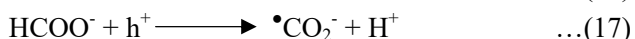
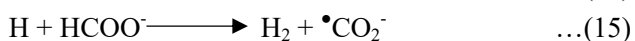
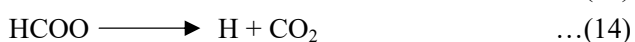
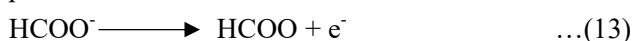
Fig. 7–Reactions of carbon dioxide in aqueous solution.

the core chemicals produced in the CO_2 reduction process.

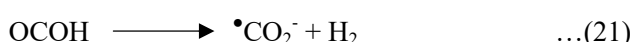
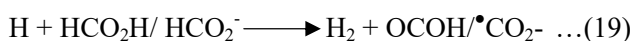
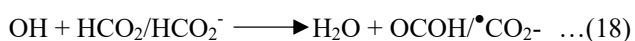
Carbonate ions act as one of the precursors for CO_2 radical anions,



It also forms from formate ions via the following path:



Alternatively, it may be formed from the reaction of hydroxyl radicals



While considering these possibilities, the detected CO_2 anion radical could be produced as a result of the reactions mentioned above (Eq. 14-23) rather than the one electron addition to the $\text{CO}_2(\text{g})$. Carbon dioxide anion radicals are short-lived and readily transform to oxalate in neutral and alkaline medium or CO_2 in an acidic solution of formic acid. In the former case, oxalate is formed by the

head-to-head recombination of CO_2 radical while in the latter it is by the disproportionation reaction of two OCOH radicals.



The bimolecular decay constant of CO_2 anion radicals was found to be around $1.4 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and independent of pH in the range 3-8 at a constant ionic strength⁶⁸. The radical traps or solvents stabilise the anion radical. More than 90% of the carbon dioxide anions undergo head to tail recombination via a hetero O-C coupling. It forms carbanion (A) as intermediate (Fig. 8) which further rearranges into oxalate ion (which can be a source CO and carbonate) or undergo proton catalysed disproportionation reaction which gives either CO_2 and HCO_2^- or CO and HCO_3^- as a final product. Similarly, the homo C-C coupling of two $\bullet\text{CO}_2^-$ with antiparallel spin results in the formation of oxalate anion (B). The $\bullet\text{CO}_2^-$ undergoes reactions with ions present in the solution and readily convert into CO_2 molecule^{69,70}. The nature of $\bullet\text{CO}_2^-$ in water is discussed in detail elsewhere⁷¹. More intense research is needed in this area to prove the identity of the carbon dioxide radical anion in the CO_2 reduction system.

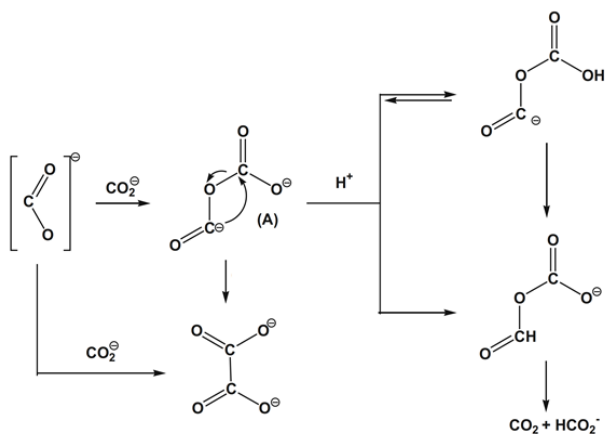


Fig. 8—The bimolecular decay of carbon dioxide radical anion. [Reproduced from Ref. 66].

Role of Photocatalyst Modifications

The design of efficient material for photocatalytic reduction of carbon dioxide is an urgent need. So far, a wide range of materials has been investigated, including oxides, sulphides, chalcogenides, oxynitrides, perovskites, carbon and carbon nitride based materials, graphene analogues, as well as traditional semiconductors (III-V and, more recently, III-V nitrides)^{32,72}. Currently, no material is available which satisfies all the necessary conditions for the activation and conversion of carbon dioxide. The champion material must have an appropriate bandgap to absorb visible light and band edge positions to provide energetic electrons to the reduction reaction. The material must have the ability to execute the proton-coupled electron transfer in an easy manner. Also, the material must have good charge transport properties, stability and comprise cheap, inexpensive and non-toxic earth abundant elements. Various efforts have been made to engineer a better material for solar fuel production to address the challenges mentioned above effectively. We refer the concerned readers to the corresponding reviews.

- The design of surface sites for the successive CO₂ adsorption and subsequent activation
 - The design of step sites on the surface^{73,74}
 - The design of porous structure with large surface area⁷⁵
 - Design of high-energy facet^{76,77}
 - Surface Modifications^{78,79}
 - Inducing surface oxygen vacancies⁸⁰
- Design of visible light active photocatalyst
 - Heteroatom doping⁸¹

- Solid solutions modified with nanoparticles⁸²
- Sensitization⁸³
- Design of photocatalyst with better charge separation and transportation
 - Addition of co-catalysts^{84,85}
 - Construction of Heterojunctions⁸⁶⁻⁸⁸
 - Use of one-dimensional nanomaterials⁸⁹⁻⁹¹
 - Incorporation of the Z-scheme system^{92,93}

The activation of CO₂ has been a bottleneck, and therefore the design strategies yield marginal increase in the product yield. Therefore, if we were to discovered a photocatalyst with high visible light harnessing capacity, it may not be suitable for the CO₂ reduction unless and otherwise, it possesses an appropriate band edge position to provide energetic electrons for the activation of the CO₂. Extensive reviews on the design of catalyst for CO₂ reduction are available in the literature⁹⁴⁻¹⁰¹. Herein, we put forth some insights into the development of efficient materials for CO₂ reduction.

It is a well-known fact that incorporating heteroatoms do not change the reduction potential of the semiconductor, and it creates some intermediate states above the valence band¹⁰²⁻¹⁰⁵. The presence of heteroatom increases the rate of adsorption of CO₂ adsorption on the photocatalytic surface and thereby facilitates the electron transfer. Any catalyst modification increases the rate of competing reactions involved in the CO₂ reduction and restricts the increased product yield in a marginal level. Many of the published reports do not consider the interaction of CO₂ with the heteroatom and irrespectively reporting that the increase in product yield is due to the increased visible light activity of the photocatalyst alone.

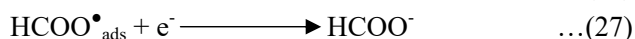
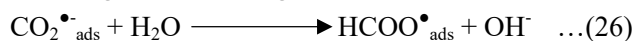
Surface metal deposition facilitates the electron transfer from the *d* state of the metal orbital to pi* orbital of the carbon dioxide molecule, which will ultimately restructure CO₂ from linear to bend. Normally, the deposited metal could act as a reduction site. The presence of a co-catalyst promotes separation and migration of photo-generated charge carriers by forming an internal electric field between semiconductor and co-catalyst¹⁰⁶. The particle size, shape, surface characteristics of deposited metal atoms and its affinity towards CO₂ plays a crucial role in the final product yield. A metal particle with smaller particle size possesses higher Fermi level energy and prevents the semiconductor-to-metal electron transfer, while metals with high particle size act as an electron-hole recombination centre¹⁰⁷.

The deposited metal must have a strong affinity towards CO₂ adsorption then only it will facilitate the electron transfer to the adsorbed carbon precursors. It does not modify the reduction potential of the photocatalyst, while it brings down the barrier associated with the CO₂ activation. The increased photo-response is because of the surface plasmon resonance¹⁰⁸, and better separation of the charge carriers contributes to the increase in the photocatalytic activity and concurrently increases the rate of competing reactions. While the metal implementation does not change the energy of electrons present in the conduction band (reduction potential) or it helps to utilise the available electrons more efficiently. These modifications will play a pivotal role with the ‘undiscovered champion material’ for CO₂ reduction, where effective utilisation of the energetic electrons is necessary.

While selecting a metal for catalyst modification for CO₂ reduction, one wants to follow certain selection criteria’s. The metal selected for catalyst modification must have high hydrogen evolution overpotential. Otherwise, hydrogen evolution will be the predominant reaction. The type of reduction product formed depends on the overpotential of the deposited metal surface towards hydrogen evolution. The metals can be classified into four groups, according to the hydrogen evolution overpotential^{109,110} (Fig. 9).

1. Pb, Hg, In, Sn, Cd, Tl, and Bi show high hydrogen evolution overvoltage and negligible CO adsorption strength. Due to this, the adsorbed

carbon precursors undergo proton-coupled electron transfer and facilitate the formation of formates through the following reactions.

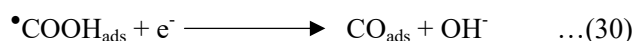


The formate ion also is produced as a result of reaction with adsorbed hydrogen.

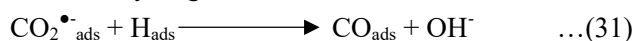


Except for Hg, which activates the CO₂ molecule at 1.6V vs. NHE, all other metals have higher overvoltage for CO₂ reduction.

2. Au, Ag, Pd, Ga and Zn associated with medium hydrogen evolution overvoltage and weak CO adsorption promote the formation fuel precursor CO from the reduction of CO₂. Herein, the carbon atom of the CO₂ molecule coordinates with the metal surface and facilitates the formation of [•]COOH instead of HCOO[•]. It is clear that CO will be the predominant product on metals, which stabilise the CO₂^{•-} more efficiently and possess weak CO adsorption.



The CO_{ads} is also formed by the direct reaction with adsorbed hydrogen.



3. The metals, Pt, Fe, Ni and Ti, have low hydrogen evolution overpotential. It adsorbs CO molecule more efficiently on the surface. Hence, hydrogen

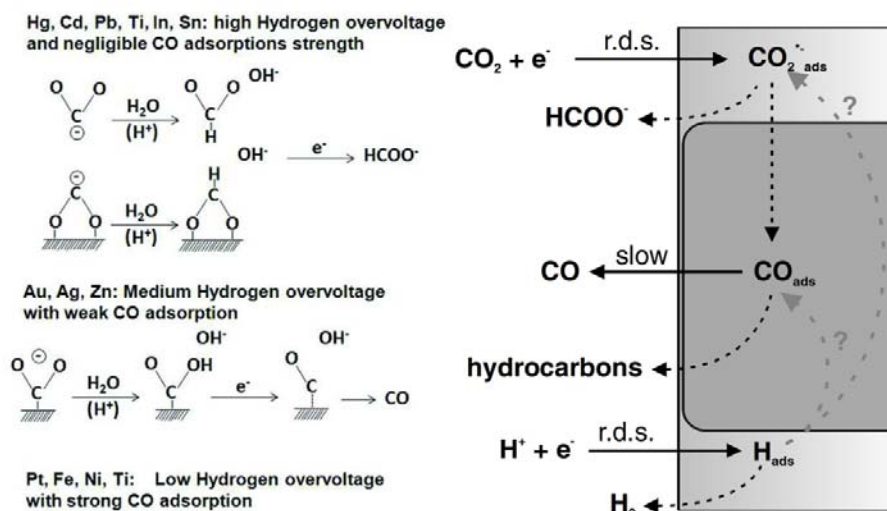


Fig. 9–Reaction pathways of CO₂ reduction on different metal surfaces. [Reproduced from Refs 7 & 51].

production will be the predominant reaction which decreases the availability of electrons to the adsorbed CO_2 molecule. In this case, the adsorption of CO_2 on the metal surface is fragile.

4. The metals, Cu, La, Ce, and Mg, adsorb the CO_2 molecule effectively, and lower hydrocarbons will be the main products. CO will be the main reaction intermediate in this case, and surface adsorption of CO ceases the hydrogen evolution reaction. Because of the medium interaction of between CO and the metal surface, subsequent reduction of CO takes place simultaneously, which contributes to the formation of hydrocarbons and alcohol.

The effective catalyst for CO_2 reduction must be capable of catalysing the protonation of adsorbed CO to produce either $-\text{COH}$ or $-\text{CHO}$ surface species. Furthermore, it must have poor activity towards the competing hydrogen evolution reaction. Peterson and Norskov¹¹¹ theoretically proposed the strategies for the discovery of champion catalysts for CO_2 reduction with reduced overpotential (Fig. 10). These strategies are also applicable to the photocatalyst surface.

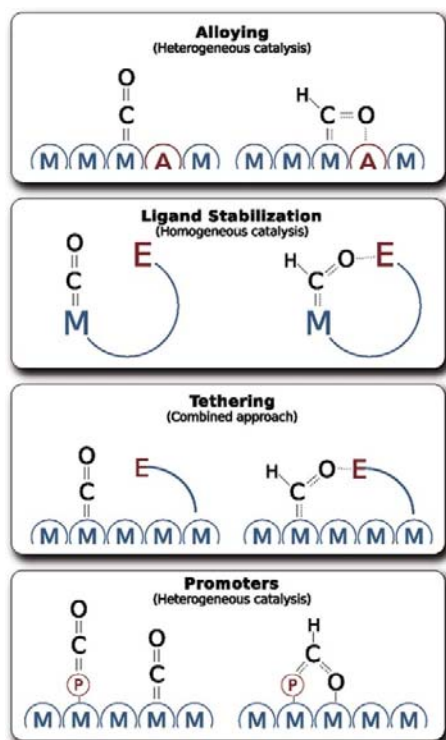


Fig. 10—Proposed strategies for the design of champion catalyst for CO_2 reduction. [Reproduced from Ref. 111].

- *Alloying*: CO and CHO tend to bind to the surface through carbon and form an upright and planar geometry on the carbon atom. The catalyst material has different affinities towards carbon and oxygen. Alloying an element to the catalyst matrix may allow the CHO^* to bind to the surface through both carbon and oxygen atoms and therefore attain the stability without being disturbed the CO^* . A balance should have to be maintained for the introduction of an element with high oxygen affinity, else it may change the potential determining step.
- *Ligand stabilisation*: In a concept similar to alloying, with the imposition of more electrophilic ligands which are geometrically capable of interacting selectively with the CHO^* lowers the energy. The partial bond between ligand- CHO^* stabilises the planar complex without disturbing the CO^* .
- *Tethering*: Hitching of a ligand to the surface and it interacts either with adsorbed CHO^* or CO^* .
- *Addition of promoters*: The addition of promoters can modify the relative binding strength of adsorbates. Here, added promoter helps to stabilise the adsorbate complex in a bidentate manner. It also acts as an adsorbed promoter for CO.
- *Hydrogen bond stabilisation*: The hydrogen bond donors near the surface may interact with the adsorbed CO^* and CHO^* in different styles due to the difference in the binding geometries. Due to the presence of the strong hydrogen bonding group, COH^* preferentially stabilises on the surface than CO^* .

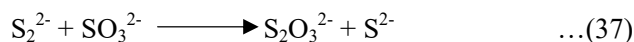
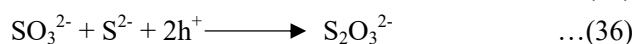
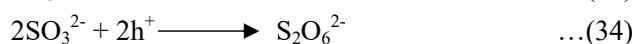
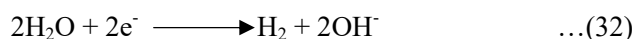
Since CO_2 reduction is highly site specific, a small difference in the property of the material affects the complete reaction. The introduction of heteroatom or deposition of metal blocks the active sites present on the surface of the catalyst. New metal free materials like carbon nitride¹¹²⁻¹¹⁵ offer an alternative material for CO_2 transformation, only the lack of in-depth studies pulls back its substantial potency. This time what we need is a comprehensive study of the fundamental mechanistic aspects of CO_2 reduction, which will throw the lights on the design of the active material.

Role of Sacrificial Reagents and Reactive Oxygen Species

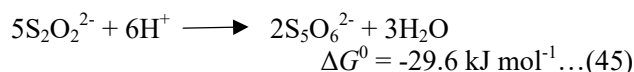
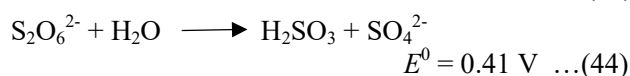
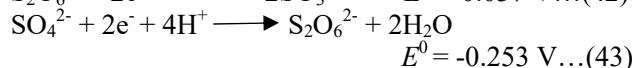
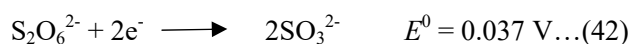
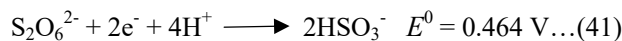
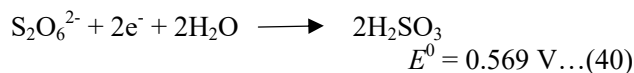
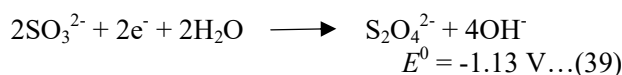
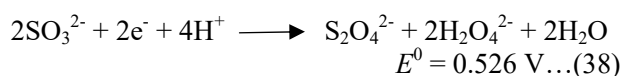
The main advantage of the photocatalyst is that the redox sites were available on the same surface. This

benefit acts as a disadvantage in many cases, described in detail in the following sections. Excellent reviews are available in the literature on the role of sacrificial reagents in the photocatalytic reactions¹¹⁶⁻¹²². The addition of sacrificial reagents into the reaction system complicates the overall reduction process and also absorbs a portion of the irradiated light. The production of a chemical by sacrificing a chemical moiety is uneconomical. The sacrificial reagents initially increase the product yield and then disintegrate into various products. Typically used sacrificial reagents are organic electron donors such as methanol, organic acids, and hydrocarbons, which are the main reduction products of CO₂ reduction. Hence, the utilisation of such sacrificial agents is not possible in the CO₂ reduction process.

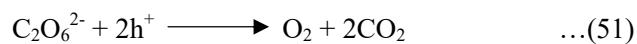
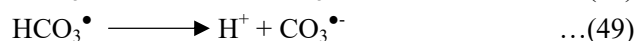
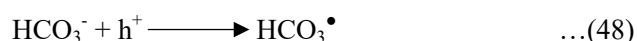
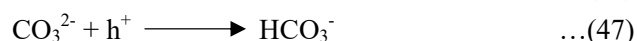
Another set of sacrificial reagents is the inorganic electron donors like sulphide (S²⁻) and sulphite (SO₃²⁻) which mainly trap the hole from valence band and transform into corresponding ions.



Many of the current literature have considered the direct hole oxidation reactions whereas inorganic electron donors can be undergoing a series of electron-coupled proton transfer reactions within the potential range of CO₂ reduction.



Addition of carbonate or bicarbonate ion increases the stoichiometric hydrogen and oxygen evolution from water¹²³⁻¹²⁹ and it suppresses the backward reaction of H₂ and O₂ to water over the deposited metallic surfaces. Therefore, it promotes the splitting of water into H₂ and O₂. The surprising thing is that many of the current articles do not consider these possibilities in the case of aqueous phase CO₂ reduction even though those facts are well established! The direct hole oxidation of HCO₃⁻/CO₃²⁻ is thermodynamically more feasible than the proton-coupled electron reduction. In aqueous phase reduction, the CO₂ precursors itself enhances the rate of the competing hydrogen and oxygen evolution reactions.



Recent works¹³⁰⁻¹³² have shown that the presence of carbonate ion in the solution increases the water-splitting reaction in many folds on a metal-supported photocatalyst (Fig. 11). In-depth studies on the effect of carbonate on the hydrogen evolution reveal that the effect is more pronounced in TiO₂ than in others. The photocatalysts can be classified into four groups according to the effect of carbonate addition¹³³.

- Pt/TiO₂, RuO₂/TiO₂, NiO_x/TiO₂, Rh/TiO₂, Cu/TiO₂, Pt/ZrO₂, Pt/K₄Nb₆O₇, Pt/K₂Ti₆O₁₃, Pr/Na₂Ti₆O₁₃ – Photocatalysts that can split water only in the presence of carbonates.
- RuO₅/Ta₂O₅, Rh/SrTiO₃, NiO_x/SrTiO₃, RuO₂/Na₂Ti₆O₁₃, RuO₂/K₂Ti₆O₁₃, RuO₂/BaTi₄O₆ – Photocatalyst whose activity is enhanced by the addition of carbonates.
- RuO₂/ZrO₂, Pt/SrTiO₃ – Photocatalyst whose activities remain unchanged with the addition of carbonates.
- NaTaO₃, LiTaO₃, KTaO₃, Ba₂Ta₂O₆, Sr₂Ta₂O₆, Sr₂Ta₂O₇, Sr₂Nb₂O₇ – Photocatalyst whose activities decreased by the addition of carbonate ions.

Reactive oxygen species play a crucial role in the photocatalytic CO₂ reduction process. The *in situ* oxygen generated in the system through water oxidation captures an electron from the conduction

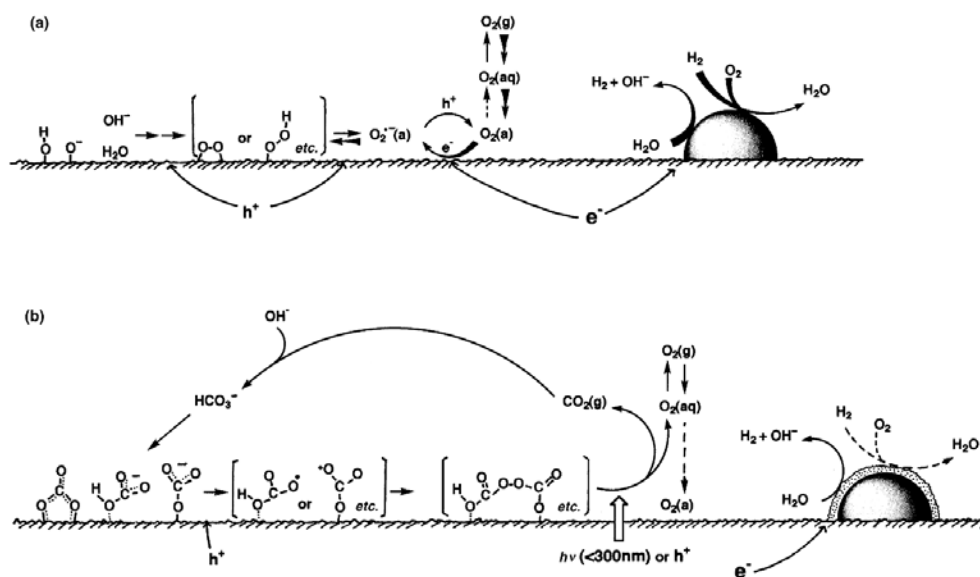


Fig. 11—Stoichiometric water splitting over Pt/TiO₂ (a) in water (b) in carbonate salt solution. [Reproduced from Ref. 128].

band and transform into corresponding superoxide radical with higher oxidation potential. The products formed during the CO₂ reduction processes are highly susceptible to the oxidative attack of ROS. The oxidation of hydrocarbons produces CO₂ back to the reaction system. There will be a chance same to undergo the carbon atom multiple times for reduction reactions in a cyclic manner. Herein, the paramount challenge is the control of the activity of in situ produced oxygen and reactive oxygen species in the reaction system. Detailed information on the production and reactions of reactive oxygen species is available elsewhere¹³⁴ (Table 3).

Hydroxyl radicals produced in the system reacts with the carbonate species and forms carbonate anion radical. Further, it will be undergoing a series of reactions with other inorganic radicals present in the system¹³⁵ (Table 4).

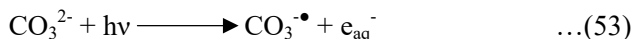
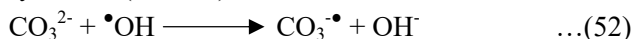


Photo-oxidation of methanol is proposed through two mechanisms: (1) direct hole oxidation, and, (2) oxidation by $\bullet\text{OH}$ radical formed by the oxidation of surface adsorbed water¹³⁶. The hydroxyl radical oxidises the methanol if water is the predominant species at the surface and in all other cases, the direct hole oxidation is preferred.

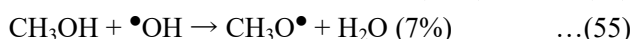
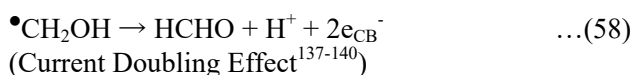
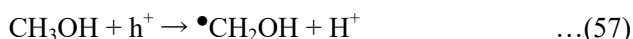
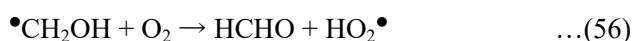


Table 3—Common reactions of reactive oxygen species in aqueous solution. [Extracted from Ref. 134]

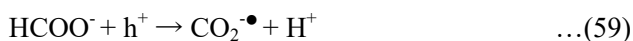
Reactions	Rate constant, k (L mol ⁻¹ s ⁻¹)
$\text{HO}_2^{\bullet}/\text{O}_2^{\bullet-} + \text{H}_2\text{CO}_3/\text{HCO}_3^-/\text{CO}_3^{2-} \rightarrow \text{HO}_2^- + \text{CO}_3^{\bullet-}$	0.04 at pH 10.1
$\text{O}_2^{\bullet-} + \bullet\text{CO}_3^- \rightarrow \text{CO}_3^{2-} + \text{O}_2$	$4 \pm 1 \times 10^8$
$\text{HO}_2^{\bullet} + \text{Cu}^+ \rightarrow \text{Cu}^{2+} + \text{H}_2\text{O}_2$	2.3×10^9
$\text{HO}_2^{\bullet} + \text{Cu}^{2+} \rightarrow \text{H}^+ + \text{Cu}^+ + \text{O}_2$	10^8
$\text{O}_2^{\bullet-} + \text{Cu}^+ \rightarrow \text{Cu}^+ + \text{O}_2$	4.81×10^9
$\text{O}_2^{\bullet-} + \text{Cu}(\text{HCO}_2)^+ \rightarrow \text{O}_2 + \text{Cu}(\text{HCO}_2)$	1.7×10^8
$\text{HO}_2^{\bullet}/\text{O}_2^{\bullet-} + \text{H}_2 \rightarrow \text{H} + \text{H}_2\text{O}_2$	<1
$\text{O}_2^{\bullet-} + \text{H}^+ \rightarrow \text{HO}_2^{\bullet}$	$5 \pm 1 \times 10^{10}$
$\text{HO}_2^{\bullet} + \text{OH}^{\bullet} \rightarrow \text{H}_2\text{O}_3$	0.71×10^{10}
$\text{O}_2^{\bullet-} + \text{OH}^{\bullet} \rightarrow \text{OH}^- + \text{O}_2$	1.1×10^{10}
$\text{HO}_2^{\bullet} + \text{H}_2\text{O}_2 \rightarrow \text{OH}^- + \text{H}_2\text{O} + \text{O}_2$	0.5
$\text{O}_2^{\bullet-} + \text{H}_2\text{O}_2 \rightarrow \text{OH}^- + \text{OH} + \text{O}_2$	0.13
$\text{O}_2^{\bullet-} + \text{HO}_2^- \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	<2
$\text{HO}_2^{\bullet}/\text{O}_2^{\bullet-} + \text{SO}_3^{2-} \rightarrow \text{SO}_3^{\bullet-} + \text{OH}^- + \text{H}_2\text{O}_2$	82
$\text{HO}_2^{\bullet}/\text{O}_2^{\bullet-} + \text{I}_2 \rightarrow \text{I}_2^- + \text{H}^+ + \text{O}_2$	1×10^8
$\text{O}_2^{\bullet-} + \text{I}_2 \rightarrow \text{I}_2^- + \text{O}_2$	5.5×10^9
$\text{O}_2^{\bullet-} + \text{I}_3^- \rightarrow \text{I}_2^- + \text{I}^- + \text{O}_2$	8×10^8

Table 4—Selected reactions of carbonate radical in aqueous solution. [Extracted from Ref. 135]

Reactions	Rate constant, k (M ⁻¹ s ⁻¹)
$\bullet\text{CO}_3^- + \bullet\text{CO}_3^- \rightarrow \text{CO}_2 + \text{CO}_4^{2-}$	$2k = 1.2 \times 10^7$ at pH 8.4-13.5
$\bullet\text{CO}_3^- + \text{O}_2 \rightarrow \text{CO}_3^{2-} + \text{O}_2$	1.5×10^9 at pH 11.6
$\bullet\text{CO}_3^- + \text{H}_2\text{O}_2$	8×10^5 at pH 8-9
$\bullet\text{CO}_3^- + \text{HO}_2^-$	5.6×10^7 at pH 13-14
$\bullet\text{CO}_3^- + \text{CH}_3\text{CH}_2\text{OH} + \text{OH}^- \rightarrow \text{CO}_3^{2-} + \text{CH}_3\text{CHOH} + \text{H}_2\text{O}$	$1.5-1.7 \times 10^4$ at pH 12.5
$\bullet\text{CO}_3^- + \bullet\text{CH}_3 \rightarrow \text{CH}_3\text{OCO}_2^-$	$3 \pm 1 \times 10^9$



The same mechanism applies to all alcohols which contain hydrogen bearing hydroxyl group attached to the alpha carbon atom. Likewise, formate ion also shows a similar kind of mechanism. It produces $\text{CO}_2\bullet^-$ as the reducing intermediate, which is believed to be the main intermediate product of CO_2 reduction. This kind of reaction favours the formate-based CO_2 reduction mechanism. According to the formate-based mechanism, CO_2 is directly hydrogenated by a hydrogen atom produced as a result of a water-splitting process, and forms a HCOO species which may undergo further protonation or C-O bond cleavage. The ESR detected $\text{CO}_2\bullet^-$ on the surface of the photocatalyst may be produced directly from the adsorbed formate rather than from the first electron addition to the CO_2 molecule!



While considering all these facts, the physical separation of oxidation and reduction sites would be more crucial. In a recent publication¹⁴¹, the photosynthetic conversion of CO_2 to hydrocarbons on Pd/TiO₂ in conjunction with the nafion has been reported. The role of the Nafion layer is to enhance the local proton activity within the layer to facilitate PCET reactions and to stabilise intermediates and to inhibit the re-oxidation of the CO_2 reduction products. Nf/Pd-TiO₂ is more active than Pd-TiO₂ for the photoproduction of hydrocarbons. The photosynthetic activity of the Nf/Pd-TiO₂ catalyst was maintained through repeated cycles of photoreaction, which confirms the stability of the Nafion layer. The proposed Nf/Pd-TiO₂ should serve as a model of more efficient catalysts for the artificial photosynthesis. However, the photoconversion efficiency of the process is very low because the activation of the stable CO_2 requires highly energetic electrons. Figure 12 shows the conceptual design of the catalyst system employed in the study.

Based on the above, a conceptual analysis and possible adaptations are presented. Essentially the points of relevance are:

- The use of a direct proton source other than water facilitates the carbon dioxide reduction.

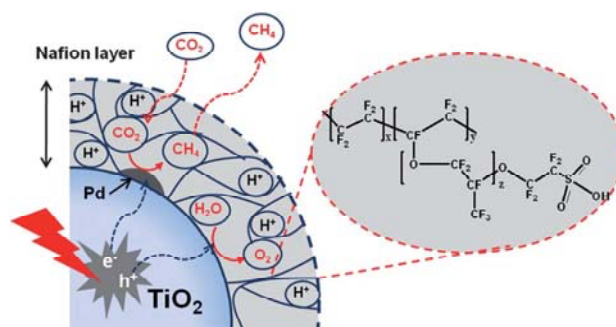


Fig. 12–Pd/TiO₂ on Nafion catalyst system for the photochemical reduction of CO_2 . [Reproduced from Ref. 141].

- The species employed for the proton source should not undergo any electrochemical reaction within the potential range for CO_2 reduction reaction.
- The reactivity of the proton should be as high as that in the nafion, where the proton is in a highly electronegative environment of fluorine atoms.
- The available protons should be capable of reacting with carbon dioxide directly promoted by the light absorbed in TiO₂ and reduction reaction should be carried out on some reactive metal sites.
- To overcome the low solubility of CO_2 the source is any carbonate, which can in situ generate CO_2 and thus can sustain the source.

Considering these aspects and based on argumentative formulations, it is possible that other PCET catalyst support systems which may sustain more acidic protons can be tried, such as heteropoly acids or superacids such as sulphated zirconia.

Proposed Reaction Pathways

There are no proposed reaction pathways for the aqueous phase reduction of carbon dioxide, and most of the articles use the proposed mechanistic pathways of $\text{CO}_{2(\text{g})}$ to interpret the aqueous phase reduction. Based on the binding mode of carbon dioxide anion radical on the surface of the semiconductor, researchers proposed plausible reaction pathways for a CO_2 reduction on TiO₂ surface²⁸, which are (a) formaldehyde pathway (b) carbene pathway, and, (c) glyoxal pathway (Fig. 13).

The final products are (CH_4 or CH_3OH) formed as a result of successive electron coupled protonation reactions of the adsorbed CO_2 . In the first two cases, i.e., (a) and (b), the proposers considered only the reduction path. However, a photocatalytic system consists of reduction and oxidation, hence the more

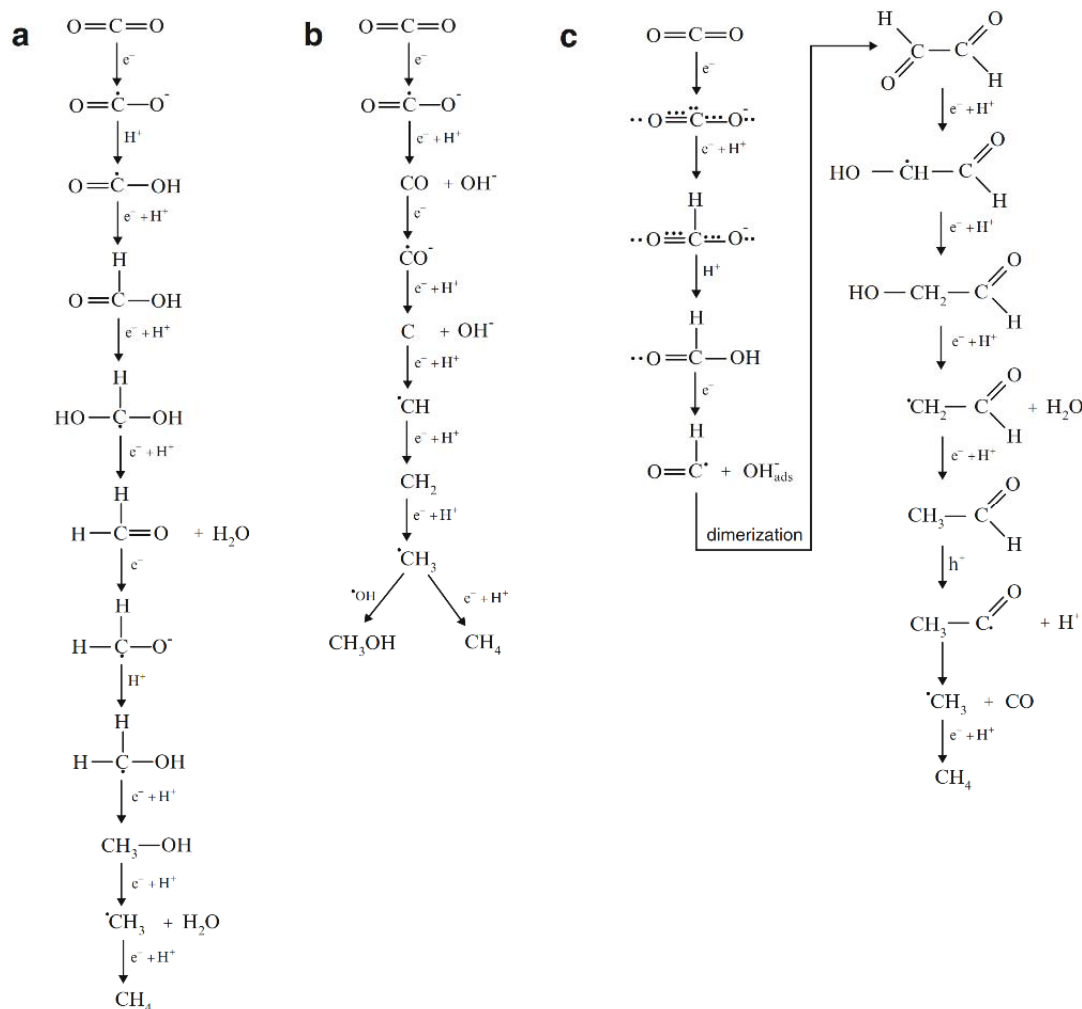


Fig. 13—Proposed reaction pathways for $\text{CO}_{2(\text{g})}$ reduction. [(a) Formaldehyde pathway (b) carbene pathway (c) glyoxal pathway]. [Reproduced from Ref. 28].

accurate proposition will be the third one (c), which considers the role of oxidation in the reaction mechanism. Here the dimerization of formyl radical gives the glyoxal, which is further transformed into acetaldehyde through the reduction of vinoxyl radicals. The produced acetaldehyde is highly susceptible to the hole attack and transforms into an unstable acetyl. The decarbonylation of the acetyl radical yields methyl radical, which would act as a direct precursor for methane. The reaction pathways mainly depend on the surface structure of the semiconductor and the interaction of $\text{CO}_{2(\text{g})}/\text{HCO}_3^{2-}$ structures interact with the surface. Therefore, it will be difficult to propose a general mechanism for CO_2 reduction because the mechanism is highly dependent

on the nature of the catalyst and active sites and varies with the semiconductor surface.

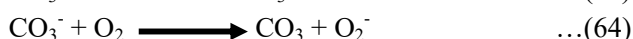
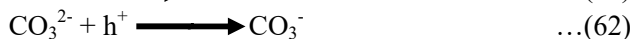
It is interesting to see another perspective of the proposed reaction pathways wherein the hydrogenation of the CO_2 molecule is believed to be significant¹⁴². Three pathways are conceived, viz., (a) redox mechanism via CO intermediate, (b) formate mechanism via formate intermediate [HCOO], and, (c) carboxyl mechanism via carboxylic acid [COOH] intermediate (Fig. 14).

- Redox mechanism: CO is the principal intermediate of this pathway and undergoes continuous hydrogenation to form methane or methanol.
- Formate mechanism: The direct hydrogenation of CO_2 with an H atom produced as a result of water

splitting without undergoing the CO₂ dissociation step. Thus, the formed [HCOO] species can either be protonated or be subjected to a C-O dissociation. Further, hydrogen transfer step yields methanol or methane.

- **Carboxyl mechanism:** As in the case of formate mechanism, the direct hydrogenation of CO₂ occurs without undergoing the dissociation step. The intermediate formed [HCOOH] undergoes further hydrogenation, and followed by dissociation, yields the final products.

In the case of liquid phase CO₂ reduction, the reaction pathways are much more complicated than the gaseous phase reduction. Therefore, a few studies are only available that accounts for the reaction pathway. The valence band hole directly oxidises the carbonate ion present in the aqueous solution to carbonate neutral radical, which further decomposes to yield carbon monoxide and oxygen¹⁴³. The formed CO undergoes further hydrogenation and produces formaldehyde. Flash photolysis¹⁴³ and EPR^{54,144} experiments provide strong evidence for the direct hole oxidation reaction of CO₃²⁻ to CO₃⁻.



In another pathway, the direct reduction of aqueous carbonate with the conduction band electrons produces formate as an intermediate. The subsequent hydrogenation leads to the formation of formaldehyde and methanol^{145,146} (Fig. 15).

Based on these two assumptions, Yang *et al.* conducted their experiments in the presence of carbonates over Cu/TiO₂ and concluded that the reaction mechanism proposed by Chandrasekhar *et al.*¹⁴³

is more favourable pathway under their reaction condition's¹⁴⁷. Recently, Nakanishi and coworkers¹⁴⁸ suggested that the hydrogen carbonate act as a source of molecular carbon dioxide instead of direct reaction with the electrons in an aqueous medium. The experiment conducted with aqueous solutions of Na₂CO₃ and NaHCO₃ under continuous argon bubbling reveals that in the presence of Na₂CO₃, CO₂ evolution was not observed from the aqueous solution while in NaHCO₃ solution, CO₂ was released concurrently with CO. The rate of CO production decreased as the rate of CO₂ evolution from the solution decreased (Fig. 16). Based on these assumptions, the hydrogen carbonate can be transformed into molecular carbon dioxide at the

	Intermediates	Unknown pathways(?)	Products
Carboxylic	COOH*	COH*	H ₂
		HCO*	CO
Formic	HCOO*	HCOH*	CH ₄
		H ₂ COH*	CH ₃ OH
		H ₃ COH*	HCOOH
		C* + O*	HCOO-
Redox	CO*+O*		HCHO

Fig. 14–Proposed mechanistic aspects for CO₂ photocatalytic reduction and plausible intermediates. [Reproduced from Ref. 142].

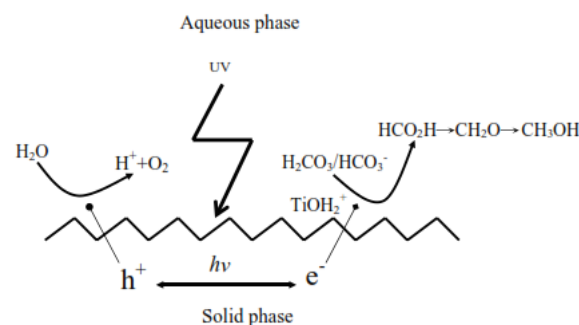


Fig. 15–Reduction of carbonates in aqueous solution. [Reproduced from Ref. 146].

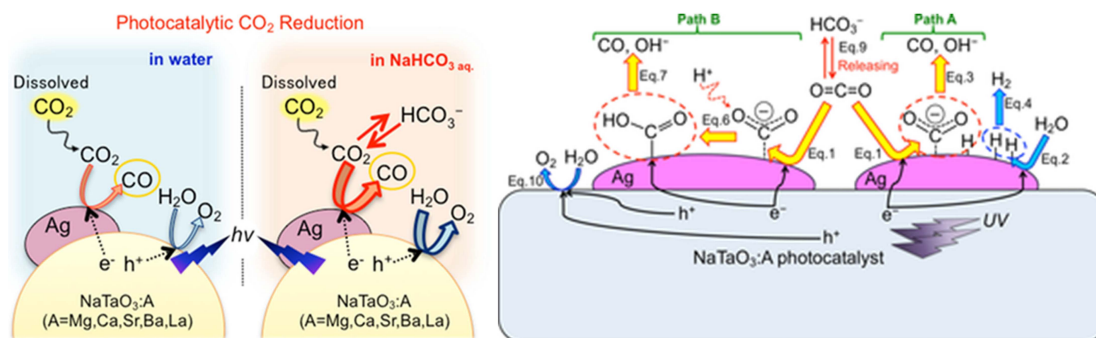


Fig. 16–Proposed mechanism of aqueous phase CO₂ reduction to form CO. [Reproduced from Ref. 148].

interface. Detailed mechanistic studies are not available in this case, and the result from the experiment also need to be proved using state-of-the-art analytical methodologies. Therefore, in-depth studies, both experimental and computational, [149] are required to propose a well-accepted reaction pathway for a CO₂ reduction in an aqueous medium.

Conclusion and Future Perceptions

The future studies in the photocatalytic reduction CO₂ should concentrate on the critical issues related to the mechanistic aspects and experimental methodologies. No detailed studies have been reported on the reactions of CO₂ anion radical and its properties. The scattered research studies make the relevance and participation of this species unclear in the CO₂ reduction process. The product analysis in CO₂ reduction and the established procedures for the analysis of the products have not yet been considered in detail. For example, whether the analysis has to be done in the gas or aqueous phase or both and what sampling techniques have to be observed. Another issue in the experimental studies is the absence of a standardised reactor design to compare the results obtained at several scientific research labs. Since the products formed can be simultaneously present in more than one phase, it is necessary to have a standardised reactor design for the comparison of the results.

The issue of carbon artefacts on the reduction of CO₂ has not yet clearly understood. Even though some studies deal with the carbon impurities, these concern has not been developed sufficiently. ¹³C Labelling is suggested as a remedy for this issue. Nevertheless, not all laboratories are capable of carrying out experiments with labelled isotopic atoms. In this situation, an alternative methodology has to be evolved to resolve this issue.

The exact role of competition reaction on the photocatalytic CO₂ reduction has not been studied in detail. The involvement of reactive oxygen species in the CO₂ reduction reduces the overall efficiency of the system. In a recent work, Liu *et al.*¹⁵⁰, have used an ROS-resistant cobalt phosphorous alloy for controlling the detrimental effects caused by the reactive oxygen species. Hydrogen evolution is another problem faced in CO₂ reduction. Most of the semiconductors are susceptible to hydrogen evolution and are more thermodynamically favourable than CO₂ reduction reactions. Therefore, controlling hydrogen evolution reaction is the major task in CO₂ photocatalytic conversion studies. In-depth studies on competitive

reactions of carbon dioxide reduction are needed urgently.

In search of a new photocatalytic material, one should exit out from the titanium dioxide rut. The reduction capacity of TiO₂ is poor as compared to other semiconductor oxides in the same row. A co-operative effort is required for the search of new materials for CO₂ reduction. The material should have appropriate reduction potential, and at the same time, significant band gap. It will be even better if the material possesses a valence band edge more negative than the oxygen evolution potential.

Detailed studies on metal free photocatalysts such as carbon nitride, boron nitride, boron carbon nitride and their derivatives are also required. In this case, one can selectively control the composition of the material by simple modifications in the preparation method¹⁵¹. The lack of independent studies on these materials has reduced its potential applications. One of the interesting things, in this case, is that carbon nitride can be prepared from carbon dioxide as a raw material (reaction of CO₂ with ammonia yields urea), but 'today' this route is not economical. Detailed studies are required to elucidate the involvement of hydrogen carbonate in the CO₂ aqueous phase reduction.

Last but not least, to quote Micheal Schmidt¹⁵², "*Further improvements in CO₂ catalysis are possible, not only for the elimination of the CO₂^{•-} intermediate, but also for eliminating the more stable formate, CO, and formaldehyde intermediates for the synthesis of useful methanol and methane fuels. It must be remembered, however, that no matter what achievements are made in catalysis, the fundamental thermodynamics of the overall problem will not be changed and a substantial input of energy will be needed for conversion of CO₂ to more reduced carbon products*".

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