# On the Selectivity of Photo-catalytic Reduction of Carbon dioxide

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## 1 Abstract

The main issues in the photo-catalytic reduction of carbon dioxide can be listed as follows:
(i) Why this process has not reached the commercial level in spite of intense research?
(ii) Why the desired selectivity in the photo-catalytic reduction of carbon dioxide cannot be achieved?
(iii) What is the mode of activation of carbon dioxide is favourable for the production of value added chemicals?
These issues are addressed in this article.

## 2 Introduction

Carbon dioxide mainly formed from the combustion of fossil fuels have been considered as a greenhouse gas and hence its release has become a topic of concern for environmental issues. For over a decade now, there are concerted attempts to either limit the emission of carbon dioxide or converting atmospheric carbon dioxide into useful products. This is evident from the number of publicatioos dealing with carbon dioxide conversion to useful products of hydrocarbons.[1-8] It obvious that this field is most fertile and intense research is being pursued all over the world. It is therefore, necessary a periodical review of the field is available.

Under this title there are a number of publications [9-12]. The debate in scientific circle is intense on this topic. This aspect was raised by us under the title "Carbon dioxide: Matter of Pollution or Profit?" in the year 2007 itself.[13].

The field of conversion of carbon dioxide is nascent and fertile. The main issues is to get selective reduction products and establishing conditions for optimum catalytic activity. Second issue is selection of appropriate activation mode, like thermal, photocatalytic mode, electrochemical mode or others. In all these aspects, there is intense research is going on but making the process commercially viable is another challenging issue.

The motivation for compiling this article is to bring the attention of practicing scientist to the issues involved in converting the waste carbon dioxide into a wealth.In order to make this exercise more meaningful, we would like to list out the issues involved in this exercise, and also to attempt to point out the challenges involved.

Various methods of carbon dioxide removal (CDR) are being pursued in response to the climate crisis, but they are mostly not proven at scale. Climate experts are divided over whether CDR is a necessary requirement or a dangerous distraction from limiting emissions.[14]. In spite of these controversies, the efforts to value add to this so called waste product is going on. However, the limited success, leads to frustrations and doubts on achieving success in this endeavour. One of the conversion technologies for the carbon dioxide into worthwhile chemicals through photo-catalysis has been a matter of attraction for the

last four decades among the scientific community. However, the conversion rate has not yet been achieved to the desired efficiency due to the inevitable barriers associated with the process making it as a Holy Grail. Major problem associated is finding the appropriate material, hence efficient material should be engineered to overcome the high energy barrier associated with the reduction process. Product analysis as well as efficiency determination are highly susceptible to errors. Because of these serious limitations, these efforts have been looked upon suspicion and the initial enthusiasm is slowly fading away.[15]. .

# 3 Adsorption Modes of carbon dioxide

The molecule has two centres namely C and O atoms in the molecule. The adsorption can take place either in one of these atoms in the molecule or both. Even on metallic surfaces the surface adsorbed oxygen is known to function as the adsorption centre for carbon dioxide. In short the possible adsorption modes can be generalized and are shown in Fig,1, There can be many other possible modes other than these but however, these can be grouped in these models. The commonn modes of adsorption modes are shown in Fig.1.

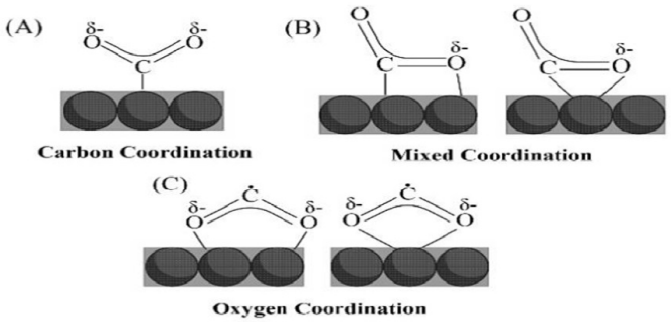


Figure 1: Adsorption modes of carbon dioxide on surfaces

Depending on the mode of adsorption of carbon dioxide and the centres involved, the subsequent reduction of the molecule will take place. Essentially, the $CO^{v}sO^{a}ndCO^{v}sH^{+}$ binding states govern the reduction product obtained. In the gas phase, the main products are methane, methanol and also Fischer Tropsh process products while in aqueous phase, the main products CO, HCOOH and other variety of products as shown in Figure.2. .

It is necessary to list the product pattern that has been reported by the photocatalytic reduction of carbon dioxide. Typical data assembled from literature are given in Table 1. together with values of reduction potential and also the main uses of each of the product.

Table 1 Common products of photocatalytic CO2 reduction

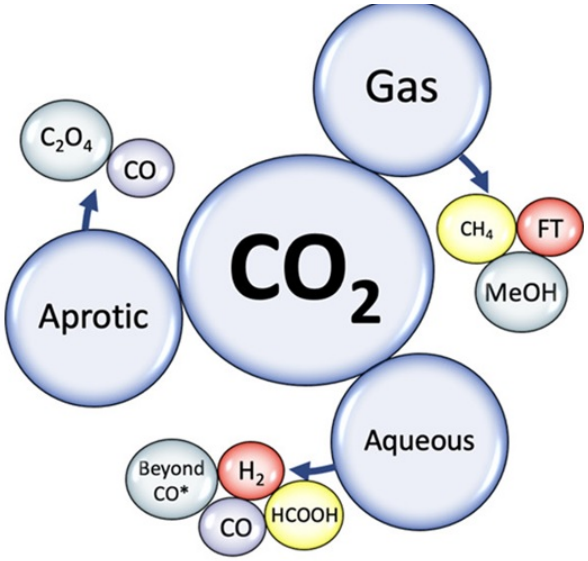


Figure 2: Various products from the reduction of carbon ddioxide in different phases - reproduced from ref.16

| Product | Half reaction of $CO_2$ | Redoxx Potential (V) | main uses |
|---|---|---|---|
| CO | $CO_2 + 2e + 2H^+ \rightarrow CO + H_2$ | 0.52 | Fischer Tropsch synthesis, carbonylation of alkenes, |
| $HCOO^-$ | $CO_2 + 2e + 2H^+ \rightarrow HCOO-$ | 0.41 | Preservative and antibacterial agent leather and textile industry in livestock feed, |
| HCHO | $CO_2 + 4r + H^+ \rightarrow HCHO + H_2O$ | -0.48 | Production of resins and polyfunctional alcohols |
| $CH_3OH$ | $CO_2 + 6e + 6H^+ \rightarrow$ $CH_3OH + H_2O$ | 0.38 | gasoline additive, fuel production of HCHO, acetic acid and methyle tert butyl ester |
| CH | $CO_2 + 8e + 6H^+ \rightarrow$ $CH_4 + 2H_2O$ | 0.24 | reforming to syngas, fuel |
| $C_@O_4^-$ | $2CO_2 + 2e \rightarrow C_2O_4^{2-}$ | 1.00 | cleaning ,Bleaching |
| $CH_3COO-$ | 2CO2+8e+7H+→CH3COO +2H2O | 0.29 | solvent, production of ethyl acetate, acetic anhydride and ester |
| $CH_3CHO$ | $2CO_2 + 10e + 10H^+ \rightarrow$ $CH_3CHO + 3H_2O$ | 0.36 | Production of 2-ethyl-1-octanol and pentaerythritol |
| $C_2H_5OH$ | $2CO_2 + 12e + 12H^+ \rightarrow$ $C_2H_5OH + 3H_2O$ | 0.33 | fuel, solvent , alcoholic beverage antisecptic |
| $C_2H_4$ | $2CO_2 + 12e + !@H^+ \rightarrow$ $C_2H_4 + H_2O$ | 0.35 | production of ethylene oxide ethylne dichloride ethylbenzene and polyethylene |
| $C_2H_6$ | $2CO_2 + 14e + 14H^+ \rightarrow$ $C_@H_6 + 4H_2O$ | 0.27 | production of ethylene power generation cryogenic referigeration |

Values of standard redox potentials are relative to standard hydrogen electrode (SHE) at pH=7. Data given in table are from refererece [17].

# 4 Photo-catalytic Reduction of Carbon dioxide

Photocatalytic reduction of carbon dioxide has several advantages like mild operation condition, small energy consumption and ready availability when solar radiation is employed as the source. Therefore, photocatalytic $CO_2$ reduction has received enormous research interests since the pioneering work to drive $CO_2$ reduction into HCHO and $CH_3OH$17 by illuminating the aqueous suspensions of various semiconductor powders including TiO2, ZnO, CdS, GaP and SiC.

In the following sections let us consider only the heterogeneous process though it ca also be applicable to homogeneous process.. Heterogeneous processes are typically based on semiconductor or plasmonic metal solid photocatalysts.The Photocatalytic $CO_2$ reduction over a semiconductor photocatalyst undergoes at least three mechanistic steps5,18. First, light with photon energy equal to or greater than the semiconductor energy band gap is absorbed, exciting the electrons from the Valence band maximum (VBM) to the conduction band minimum (CBM), while leaving holes at the VBM. Next, the photo-generated electrons and holes transfer to the catalyst surface (through cocatalyst if applicable). Finally, adsorbed $CO_2$ is reduced by photo-generated electrons and the adsorbed reductant is oxidized by photo-generated holes. Ideally, $CO_2$ reduction is accompanied by water oxidation or some other value-added oxidations. Moreover, such a process must satisfy two thermodynamic requirements. The redox potential of reduction half-reaction must be more positive than the CBM, and the redox potential of oxidation half-reaction must be more negative than the VBM. In addition, from the perspective of reaction kinetics, there must be catalytic sites in which CO2 activation takes place.

There are a variety of configurations in which this reaction has been attempted to perform. when semiconducting combinations are used there are various Z or s schemes, various modifications like doping , co-catalyst and other agents have been attempted. Still there appears to be a large barrier in pushing this reaction to commercial level. These studies show that the difficulty faced in making this reaction commercially viable does not depend on the catalyst selection but the real reason is still not known. Another aspect is the dissocution of carbon dioxide in the medium in which the photocatalytic reaction is carried out. This is controlled by the solubility limit and in most often used solvent, its solubility is small (for example 0,145 g per 100 ml at 273 K Other than these, let us list other barriers that have to be crossed in realizing the reaction at the level of commercially viable. .

[1] The capture of carbon dioxide: This is an intensively pursued field since gas phase carbon dioxide is dispersed. Various solvent media are proposed and being examined. this will continue to a exercise which will receive attention for some period now.

[2]Among the various options available for the conversion of carbon dioxide to value added chemicals, photocatalytic or electrocatalytic methods seem to be promising as of today. However, achieving the required selectivity is an issue. there can be various reasons for this aspect. but the main parameters is the surface activation of carbon dioxide and the closeness of the redox potential values for the various products.

[3] Photo-catalytic reaction for studying carbon dioxide reaction on commercial scale requires an appropriate reactor configuration. Even, the laboratory scale reactor is not standard so that the reproducibility could be established unequivocally.

. [4] The selectivity issue has been considered. It appears that in this photo-catalytic reduction of carbon dioxide the selectivity should not be considered as the primary condition. value addition alone should be emphasized. secondly, the utilisation of the waste product to some useful chemical must be considered at face value.

[5] Optimum catalytic activity should not also be the criterion. among the available catalyst systems, one must make use and get some value addition and also should be satisfied with the environmental benefits derived

The main issue in the utilization of carbon dioxide is the activation of this substrate. The term activation in this context means how the reactivity of the molecule is altered by an external source probe like photolysis, thermolysis, molecular interaction. In the use of these probes the molecular structure is altered, but in photocatalysis the energy state of the molecule is altered and LUMO levels is occupied by photoexcitation. In this process of photoexcitation, the bonding scheme of the molecule is only altered and possibly the bonding scheme is altered. The bonding state within the molecule is altered as a result of photo-excitation. In this sense, this activation is preferred since it retains all the possibilities of transformation even after activation even though there may be some preference. .That is one of the reasons the importance of selectivity is important in the conversion of carbon dioxide. Therefore photo-catalytic reduction of carbon dioxide is however, yet is useful and the product obtained is value added substrate. in this sense, photo-catalytic reduction of carbon dioxide is one of the ways to make carbon dioxide as a useful molecule and does not contribute to waste or environmental degradation. Another advantage in photo-catalytic reduction is the process simplicity and less energy consumption. In photo-excitation the molecular geometry can be retained but in other modes of activation the molecular geometry may or may not be retained. When the molecular geometry is retained, the transformation can be manipulated while when the molecular geometry is altered the transformation is directional and selective. Bond order decrease is better way of activation rather than band breaking by other probes.In this sense, photo-catalytic reduction of carbon dioxide may have to be preferred route for the utilization of carbon dioxide and also to contribute to environmental concerns.

It appears today that this effort is not yielding the desired outcome, but it is hoped that in course of time this process may become economically viable and it will contribute to decrease the environmental concerns. It is suggested that photo-catalytic reduction of carbon dioxide may be a preferred route.

# 5 MO Diagram of Carbon dioxide

The 2s and 2p orbitals of carbon and th 2p orbitals of oxygen combine to form the molecular orbitals of carbon dioxide. one such a diagram is shown in Fig.3. The HOMO orbitals of the lone pair electrons from the 2p orbitals of oxygen and the LUMO orbitals are the Pi* orbitals combined from 2p orbitals of carbon and the two oxygen atoms. The activation of arbon dioxide means occupying the pi* orbital by excitation from the occupied molecular orbital of carbon dioxide.

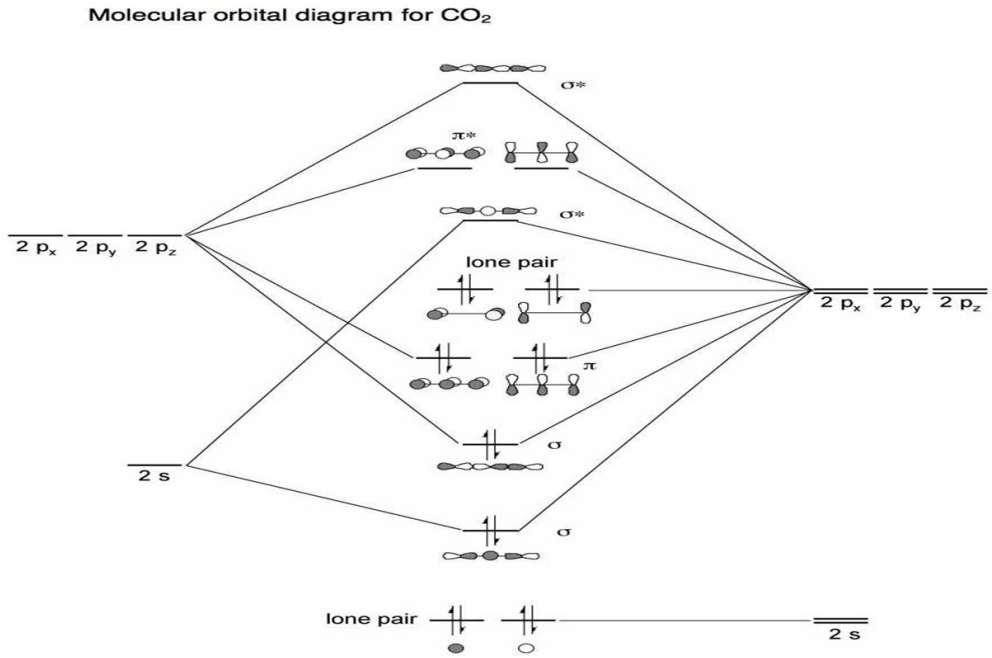


Figure 3: Molecular orbital diagram of carbon dioxide

# 6 Reduction Potentials of Carbon dioxide

It is essential to compile the values of reduction potential (versus Standard Hydrogen Electrode (SHE) and implication of these values has to be realized. In Table 2. these values are tabulated for ready reference. It is necessary to note that the values of reduction potential values are dependent on the pH of the medium. Therefore, the reduction reaction of carbon dioxide under acid or alkaline medium will be different and the reaction course will be dependent on the acidity or alkalinity of the medium. This effect has to be kept in mind.

Table 2 Typical carbon dioxide reaction and the standard Reduction potential in volts $2CO_2 + 2H^+ + 2e \rightarrow H_2C_2O_4$ -0.913

| |
|---|
| $CO_2 + 4H* + 4e \rightarrow HCHO + H_2O$ -0.480 |
| $CO_2 + 6H^+ + 6e \rightarrow CH_3OH + CH_3OH + H_2O$ -0.380 |
| $CO_2 + 8h^+ + 8e \rightarrow CH_4 + H2O$ - 0.240 |
| $2CO_2 + 12H^+ + 12e \rightarrow C_2H_4 + 4H_2O$ - 0.349 |
| $2CO_2 + 12H^+ + 12e \rightarrow C_2H_5OH + 3H_2O$ -).329 |
| $2CO_2 + 14H^+ + 14e \rightarrow C_2H_6 + 4H_2O$ -0.270 |
| $3CO_2 + 18H^+ + 18e \rightarrow C_3H_7OH + 5H_2O$ -0.310 |

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It is seen from the values of reduction potentials given in Table 2 that the reduction potentials values are close to each other and hence selective formation of product is difficult. Exclusive formation of one carbon product can therefore difficult. A schematic representation of the reduction potentials for various products from carbon dioxide is shown in Fig.4.

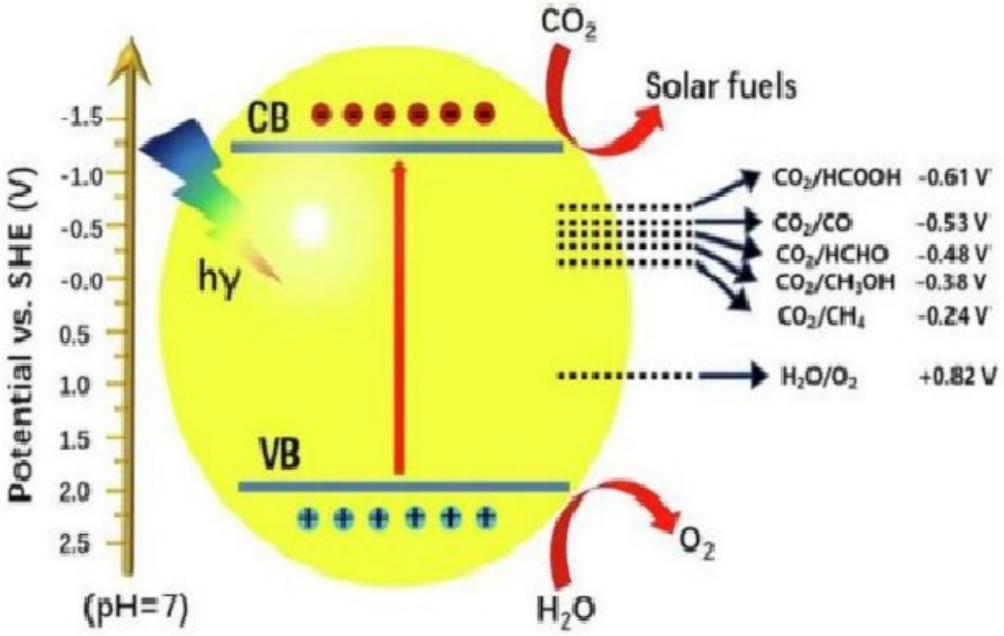


Figure 4: Selected values of reduction potentials for carbon dioxide

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# 7 Thermodynamic Parameters of the Reduction of Carbon dioxide

. The standard enthalpies (H○ 298K(kJ/ mol) and Gibbs free energies (G○ 298K (kJ/mol)) for different products formed in the reduction of carbon dioxide.Thermodynamics data adapted from the authors of [18].
(1) $2CO_2 \rightarrow 2CO + O_2$; 293.0 257.2
(2) $CO_2 + H_2 \rightarrow CO + O_2$; 41.2 28.6
(3) $CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$; 49.5 3.5
(4) $2CO_2 + 6H_2 \rightarrow 2C_2H_5OH + 3H_2O$; 86.7 32.4
(5) $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$; 165.0 113.5
(6) $2CO_2 + 7H_2 \rightarrow C_2H_6 + 4H_2O$; 132.1 78.7
(7) $3CO_2 + 10H_2 \rightarrow C_3H_8 + 6H_2O$; 125.0 70.9
(8) $4CO_2 + 13H_2 \rightarrow n - C_4H_(10) + 8H_2O$; 121.6 66.9
(9) $2CO_2 + 6H_2 \rightarrow C_2H_4 + 4H_2O$; 64.0 28.7
(10) $3CO_2 + 9H_2 \rightarrow C_3H_6 + 6H_2O$; 83.6 42.1
(11) $4CO_2 + 13H_2 \rightarrow n - C_4H_8 + 8H_2O$; 90.3 45.2

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