

## Reflections on the electrochemical reduction of carbon dioxide on metallic surfaces

B Viswanathan

National Centre for Catalysis Research, Indian Institute of Technology Madras,  
Chennai 600 036, India

Email: [bvnathan@iitm.ac.in](mailto:bvnathan@iitm.ac.in)

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It is known that carbon dioxide undergoes electrochemical reduction to a variety of products like CO, hydrocarbons and alcohols on metallic surfaces and that the nature of the metal has a role to play in the observed selectivity of products. Rationalization of the results obtained on different metallic surfaces and accounting for the selectivity have been the points of contention in literature. This presentation examines these aspects from the point of view of surface activation of carbon dioxide and proposes a site specific and geometry constrained adsorption of carbon dioxide as the possible reason for the variation in the results reported in literature.

**Keywords:** Electrochemical reduction, Reduction, Carbon dioxide, Selectivity, Surface activation, Adsorption

The activation and conversion to value added chemicals of molecules like carbon dioxide, carbon monoxide and dinitrogen have been challenging<sup>1-3</sup>. The most striking common feature among these molecules is the fact that the frontier orbitals of these molecules are not of bonding character<sup>4</sup>. It is therefore necessary to adopt alternate methods of activation of these molecules to convert them into other useful energetic molecules<sup>5</sup>. However, if one were to succeed in activating these molecules, it would provide a means for energy storage, a concept which is fascinating and also rewarding. The scope of this presentation is to examine the electrochemical activation of carbon dioxide into useful low carbon number fuels and molecules<sup>6</sup>.

Scibioh and Viswanathan<sup>7</sup> have examined the question 'Is carbon dioxide a matter of pollution or profit?' According to them, the question is not how to remove or reduce this emission, but how to make use of this enormous emission for environmental and economic benefit. There are several motivations for producing chemicals from carbon dioxide whenever possible, viz., (1) carbon dioxide is a cheap, non-toxic feedstock that can frequently replace toxic chemicals like phosgene or isocyanates, (2) carbon dioxide is a nearly renewable feedstock, (3) new chemicals like polymers can be produced from carbon dioxide, (4) alternate routes for the existing processes may become efficient and economical if this feed stock is

employed, and, (5) chemicals from carbon source could have some positive impact on carbon balance<sup>8</sup>.

A variety of reactions including some industrial processes like urea and cyclic carbonates and polycarbonates are possible with carbon dioxide<sup>9</sup>. A simple pictorial reaction scheme for possible conversion processes of carbon dioxide is given in Fig. 1. It is seen that alcohols, hydrocarbons, fuel precursor (CO) and a variety of value added chemicals like urea, carbonates and bicarbonates can be produced by the transformation of carbon dioxide and hence it is no longer to be considered as a means of pollution and should rather be taken as a valuable feedstock. The most predominant reaction is carbon dioxide insertion, though a variety of other reactions are also indicated in the reaction scheme given in Fig. 1.

### Electrochemical Reduction of Carbon dioxide

Unlike chemicals that derive value from their intrinsic chemical and physical properties, the value of fuels is in their energy content and the ease with which they are stored and transported. Currently no fuel is produced by the reduction of CO<sub>2</sub> because returning CO<sub>2</sub> to useful state on the same scale as its current production rates is possibly beyond our current scientific and technical ability. However, electrochemical reduction of carbon dioxide in conjunction with the decomposition of water is an attractive proposition, since the electrochemical

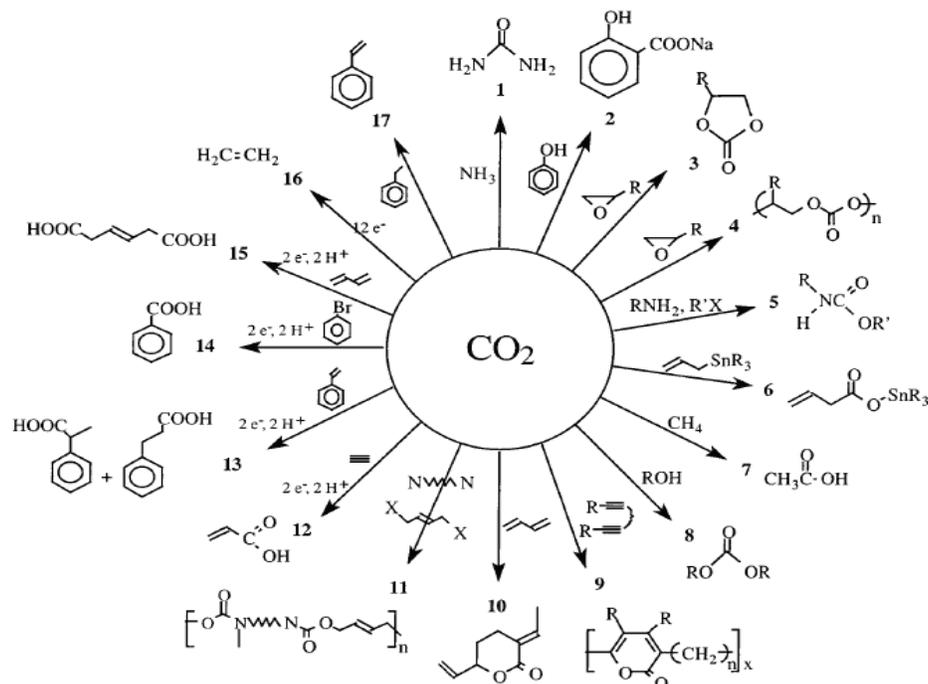


Fig. 1—Some possible chemical transformations of carbon dioxide. [Reproduced from Ref. 7 with permission from Consultancy Development Centre, New Delhi].

reduction may be considered as the sum of the corresponding hydrogenation reactions and the water splitting reaction. Typical representative list of such reactions is given in Table 1.

Even though activation of carbon dioxide and its subsequent conversion to fuels and chemicals can be achieved by radiochemical, photochemical, photo-electrochemical, biochemical, bio-photo-electrochemical and thermo-chemical methods, electrochemical routes have been examined extensively in literature<sup>10-12</sup>. The electrochemical reduction process utilizes only gaseous carbon dioxide and possibly hydrogen from aqueous electrolytes and yields a variety of hydrocarbon products as stated earlier with oxygen as the gaseous non-polluting product. The high Faradaic efficiency that can be achieved and the possibility of carrying out the reaction at around room temperature are the two factors in favour of this route. The possibility of *in situ* production of fuels, like methane and methanol, and also the utilization of the greenhouse gas for production of profitable chemicals make the electrochemical reduction of carbon dioxide promising and attractive<sup>13</sup>.

### Reactions of Relevance for the Electrochemical Reduction of Carbon dioxide

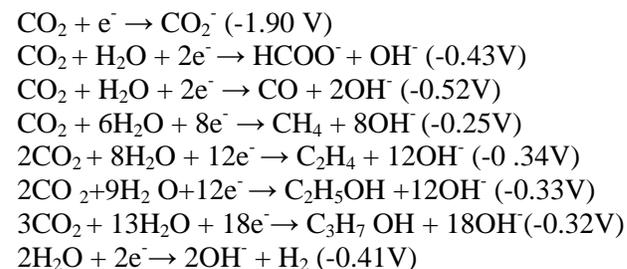
The reactions of relevance are listed below in combination with the water decomposition reaction at

Table 1—Typical electrochemical carbon dioxide reduction in conjunction with water decomposition reaction<sup>a</sup>

Reaction	$\Delta E^\circ$ (V)	$\Delta G^\circ$ (kcal/mol)
$\text{H}_2\text{O} \rightarrow \text{H}_2 + 0.5\text{O}_2$	1.23	56.7
$\text{CO}_2 + \text{H}_2 \rightarrow \text{HCOOH}$		5.1
$\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{HCOOH} + 0.5\text{O}_2$	1.34	61.8
$\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$		4.6
$\text{CO}_2 \rightarrow \text{CO} + 0.5\text{O}_2$	1.33	61.3
$\text{CO}_2 + 3\text{H}_2 \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$		-4.1
$\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_3\text{OH} + 2\text{H}_2\text{O}$		-31.3
$\text{CO}_2 + 2\text{H}_2\text{O} \rightarrow \text{CH}_3\text{OH} + 1.5\text{O}_2$	1.20	166
$\text{CO}_2 + 2\text{H}_2\text{O} \rightarrow \text{CH}_4 + 2\text{O}_2$	1.06	195

<sup>a</sup> Data taken from Ref. 7

$\text{pH} = 7$ , since hydrogen evolution is the predominant reaction in acid medium and in alkaline medium carbon dioxide does not exist. Direct one electron reduction of carbon dioxide requires high negative potential due to large reorganization energy between linear molecule and bent radical anion<sup>4</sup>.



It is inferred that compared to direct reduction of carbon dioxide, the reduction of carbon dioxide in the presence of water decomposition appears to be favourable for the formation of small molecule fuels or fuel precursor like carbon monoxide. If one were to operate in this mode, this will be the reverse reaction of the anode reaction of the fuel cell operating with that fuel, or, it can also be conceived as the electrical energy being converted into the chemical energy. This is similar to electrochemical water decomposition being considered as the reverse of hydrogen-oxygen fuel cell reaction. Since the Gibbs free energy is always positive for most of the reactions in this sequence involving carbon dioxide with the added overvoltage which is of the order of 1 volt, the water decomposition reaction becomes a competing reaction. Therefore, the type of product formed on metallic electrodes for carbon dioxide reduction depends on the overvoltage for hydrogen evolution on the metallic surface. For example, on mercury surfaces where the hydrogen evolution overvoltage is high, formate is the most preferred product in carbon dioxide reduction.

The metallic electrodes can be grouped into four groups as follows for carbon dioxide reduction<sup>14</sup>:

1. metals like Pb, Hg, In, Sn, Cd, Tl and Bi with high hydrogen evolution overvoltage, promote the formation of formate;
2. metals like Au, Ag, Pd, Ga and Zn with medium HER (Hydrogen Evolution Reaction) overvoltage with simultaneous weak adsorption of CO promote the formation of fuel precursor CO from the reduction of CO<sub>2</sub>;
3. metals like Ni, Fe, Pt, Ti Co, Rh and Ir which have low hydrogen overvoltage but exhibit strong CO adsorption, give the major product as hydrogen;
4. other metals like Cu, where the major product of reduction of CO<sub>2</sub> is hydrocarbons (CH<sub>4</sub>) and alcohols.

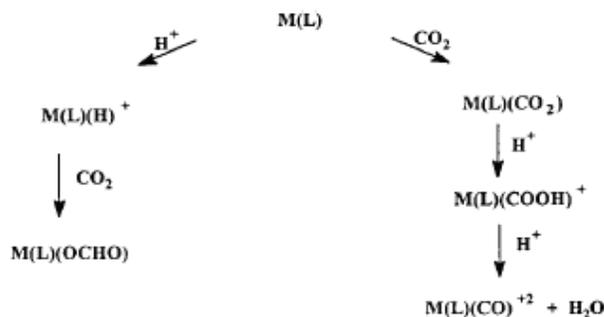
#### Activation of Carbon Dioxide on Metallic Surfaces

In essence, the activation of carbon dioxide on metallic surfaces can be by coordination through the carbon or oxygen centres or by involving mixed coordination on single or multiple sites. Electrochemical reduction of carbon dioxide on a variety of metal surfaces has been studied. Among the various metals studied, copper electrodes have been shown to catalyze the reduction of CO<sub>2</sub> to methane in bicarbonate solutions<sup>7</sup> with current efficiency of nearly 65%. In spite of the fact that the overpotentials

are large, of the order of 1.5 V, this is a remarkable transformation in which eight electrons are transferred to CO<sub>2</sub> with cleavage of two C-O bonds and formation of four C-H bonds. The reaction is believed to involve coordinated CO as an intermediate and to overcome poisoning of the electrode under catalytic conditions. Under slightly different conditions, CO<sub>2</sub> can also be reduced to ethylene at Cu electrodes<sup>15</sup>.

Homogeneous electrocatalysts typically catalyze CO<sub>2</sub> reduction by two electrons to either formate or CO along with H<sub>2</sub> formation. However, for some catalysts, CO<sub>2</sub> reduction occurs with current efficiencies close to 100% even in acidic solutions. This indicates high selectivity for CO<sub>2</sub> reduction over the more thermodynamically favored reduction of protons to H<sub>2</sub>. For example, the reduction of CO<sub>2</sub> to CO by nickel cyclam catalysts occurs with nearly 100% current efficiency in water at pH 4.1. CO<sub>2</sub> is reduced to CO in 0.02 M HBF<sub>4</sub> in dimethylformamide solutions<sup>7</sup> with current efficiencies greater than 95%. In addition, some of these catalysts operate at low overpotentials so that the conversion of electrical to chemical energy is highly efficient. The selectivity in these cases appears to arise from the preferential reaction of 17-electron intermediates with CO<sub>2</sub> rather than protons.

This selectivity of reduced forms of the catalyst for H<sup>+</sup> versus CO<sub>2</sub> also appears to determine the nature of the CO<sub>2</sub> reduction product observed. If the reduced form of the catalyst reacts with CO<sub>2</sub> to form an M-CO<sub>2</sub> complex, protonation yields a metalcarboxylic acid; further reaction can then produce CO by C-O bond cleavage to form hydroxide or water. Thus, reaction of a reduced form of the catalyst with CO<sub>2</sub>, as opposed to protons, leads to CO formation. If the reduced form of the catalyst reacts with protons to form a hydride complex, subsequent reaction of the hydride with CO<sub>2</sub> leads to formate production; these two possibilities are illustrated in Scheme 1.



Pathways for the competing interaction of low-valent catalysts with protons or CO<sub>2</sub>

Scheme 1

It is unusual for homogeneous catalysts to form reduction products that require more than two electrons. However, the formation of glycolate (HOCH<sub>2</sub>COO<sup>-</sup>), glyoxylate (OCHCOO<sup>-</sup>), formic acid, formaldehyde, and methanol as CO<sub>2</sub> reduction products using [Ru(tpy)(bpy)-(CO)]<sup>2+</sup> complexes as electrocatalysts (bpy = 2,2'-bipyridine, and tpy = 2,2':6',2''-terpyridine)<sup>16</sup> has been reported. Although turnover numbers were not known for these reduced species, their formation raises the possibility of a single-site catalyst resulting in multi-electron reductions of CO<sub>2</sub> and even C-C bond formation. The relatively mild conditions and low overpotentials required for some of the homogeneous catalysts make them attractive; however, a number of barriers must be overcome before useful catalysts are made available for fuel production.

At this stage, it is necessary to discuss the activation of carbon dioxide on metallic surfaces. Even though one can visualize associative adsorption of CO<sub>2</sub> with either carbon, oxygen or mixed centres on single or multiple sites, the most probable mode of adsorption would be a dissociative adsorption involving a CO<sub>ads</sub> type species. This species, if it desorbed as such, gives the fuel precursor, and if it undergoes further hydrogenation with the hydrogen evolved from water, it accounts for the other observed products like hydrocarbons and alcohols. Therefore, the essential concept of activation of CO<sub>2</sub> has to be clearly formulated. This requires a description of the molecular orbitals of CO<sub>2</sub>. The essential orbitals contributing to the molecular orbitals are the 2s and 2p orbitals of carbon and oxygen. The three 1s orbitals of carbon and two oxygen atoms remain basically unchanged in the molecule and are designated as 1σ<sub>g</sub>, 2σ<sub>g</sub> and 1σ<sub>u</sub>. The 2s and 2p<sub>x</sub> orbitals of carbon and oxygen directed along the molecular axis give rise to 3σ<sub>g</sub>, 4σ<sub>g</sub>, 5σ<sub>g</sub> and 2σ<sub>u</sub>, 3σ<sub>u</sub>, and 4σ<sub>u</sub>. The 2p<sub>y</sub> and 2p<sub>z</sub> give rise to three doubly degenerate π orbitals designated as 1π<sub>g</sub>, 1π<sub>u</sub> and 2π<sub>u</sub>. The 22 electrons in CO<sub>2</sub> are distributed as follows: 6 in core σ orbitals arising from 1s levels and the remaining 16 in four σ orbitals and two doubly degenerate π orbitals. The highest occupied molecular orbital is 1π<sub>g</sub> and the lowest unoccupied molecular orbital is 2π<sub>u</sub> orbital. The energetic positions of the sigma orbitals do not change considerably as the molecule undergoes distortion from linear geometry to bent geometry. However, the energies of π-orbitals show pronounced alterations on going from linear geometry to bent geometry and also the degeneracies of these orbitals

are lifted. This is usual since the charge density in the π orbitals is concentrated between the two bonding centres in a lateral disposition. The bending of the molecule from linear geometry though affects the degeneracy of 1π<sub>u</sub> and 1π<sub>g</sub>, the energy difference between the two split orbitals is not high. However, the degeneracy of 2π<sub>u</sub> is lost and the two resulting orbitals are designated as 2b<sub>1</sub> with almost the same energy as in the linear molecule in the bent configuration. The other component is designated as 6a<sub>1</sub> the energy of which falls sharply as compared to that in the linear molecule. Electron occupancy in this molecular orbital can give rise to a bent configuration. The relative energy positions of the orbitals of carbon dioxide at two geometries, namely the bond angle, is either 180° or 90° as shown in Fig. 2.

#### Orbital Ordering As a Function of Bond Angle in Carbon Dioxide

The essential point in the activation of carbon monoxide and dinitrogen is the population of the anti-bonding π orbitals which facilitates the dissociation of the molecule. In the case of carbon dioxide, this population of anti-bonding states leads to the change in the bonding angle and hence the adsorption site has to have specific geometry. Though this is not similar to the bidentate binding of CO it shows that the sites activating these molecules must have specific geometry and orientation. In the case of carbon dioxide activation, the carbon and one of the oxygen

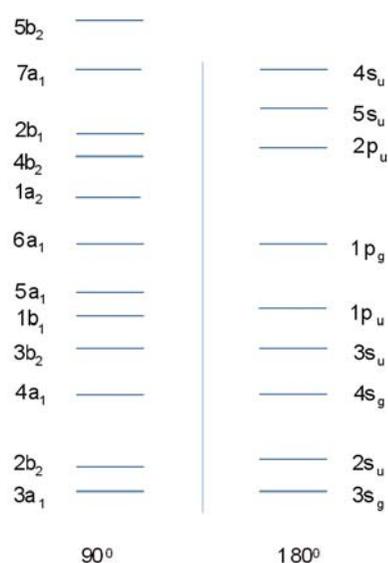


Fig. 2—The relative positions of the energy levels of orbitals of carbon dioxide at 180° and 90°. The point to note is that some orbitals have lost their degeneracy when the bond angle is decreasing from 180°. [Data plotted from Ref. 4].

centres of this molecule has to be activated with the bond angle being not  $180^\circ$ . This imposes some geometrical restrictions on the site on which carbon dioxide molecule can be activated.

Though it is known that the reaction  $\text{CO}_2 + e^- \rightarrow \text{CO}_2^-$  (-1.90 V) is not thermodynamically favourable, it may become probable in the adsorbed configuration wherein the  $\text{CO}_2$  is adsorbed on the metallic surfaces by multipoint adsorption. Among the various multipoint adsorption configurations for  $\text{CO}_2$ , the one involving the carbon and one of the oxygen appears to be the most probable based on a variety of spectroscopic experimental IR<sup>17</sup>, HREELS and XPS<sup>4,12</sup> data which show that this adsorbed species mostly manifest somewhat like adsorbed CO (not in the conventional carbonyl type) species and adsorbed oxygen.

### On the Adsorption Geometry of $\text{CO}_2$

The activation of carbon dioxide on metallic surfaces has been studied extensively in the past. In general, either mixed carbon-oxygen or pure oxygen coordination have been recognized as the probable mode of adsorption rather than pure carbon coordination. In all these theoretical studies the consistent result is that the carbon dioxide molecule is bent on adsorption and the bond angle is less than  $180^\circ$ .

It is interesting to refer to the DFT study of carbon dioxide reduction to hydrocarbons on copper surfaces<sup>18</sup>. This report identifies the reaction path on the basis of the construction of potential energy profiles and has shown that stripping of the oxygen and also insertion of hydrogen are the steps controlling the reaction. The oxygen containing species like CHO prefers to dissociate to form CH rather than to form  $\text{CH}_2\text{O}$ . This study also favours the postulate that was made in this study that  $\text{CO}_2$  activation has to take place through carbon and one of the oxygen atoms of carbon dioxide on a site of suitable geometry for the bent configuration. If this were to be true, the subsequent hydrogen addition will take place with the elimination of oxygen in the bent geometry accounting for the formation of hydrocarbons from carbon dioxide. This aspect may be the essential difference between hydrogenation of carbon monoxide and carbon dioxide.

In Fig. 3 some of the possible multi-point interactions of carbon dioxide on metallic surfaces are given. It was shown that direct carbon metal interaction alone is not energetically favourable.

On this basis and also from the projections of the molecular orbitals, one of the possible modes of activation of carbon dioxide is shown in Fig. 4. Since direct coordination through carbon is repulsive in nature, activation through carbon and oxygen is envisaged. In this mode of activation it may be possible that the carbon-oxygen bond may be activated and thus the  $\text{CO}_2$  molecule may undergo reduction.

The activation of carbon dioxide can be achieved as stated earlier by a variety of methods. Even though it is not our intention to outline all the possible methods of activation of carbon dioxide, it is essential

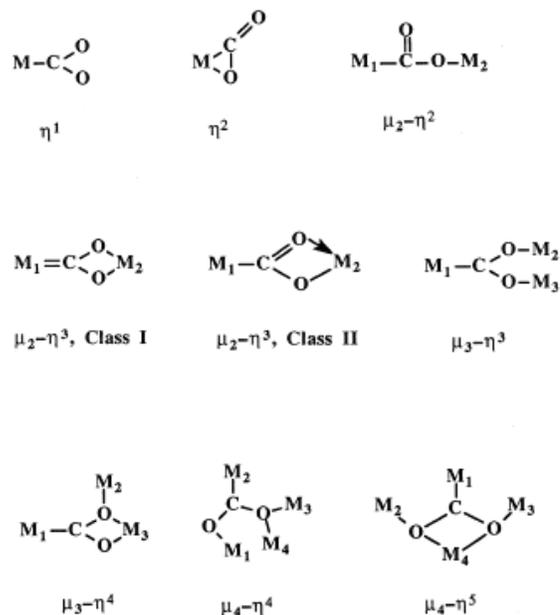


Fig. 3—Some of the possible modes of activation of carbon dioxide involving multi-point of adsorption on metallic surfaces. [Reproduced from Ref. 8 with permission from INSA, New Delhi].

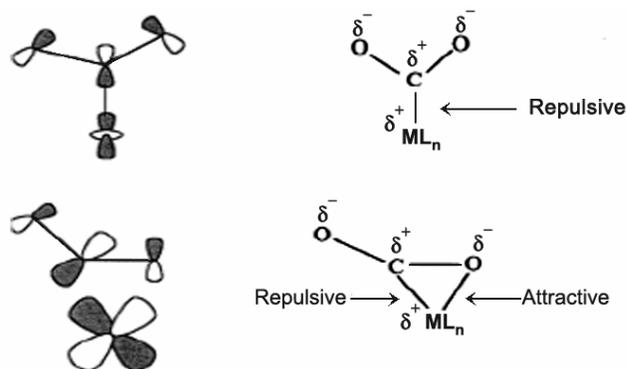
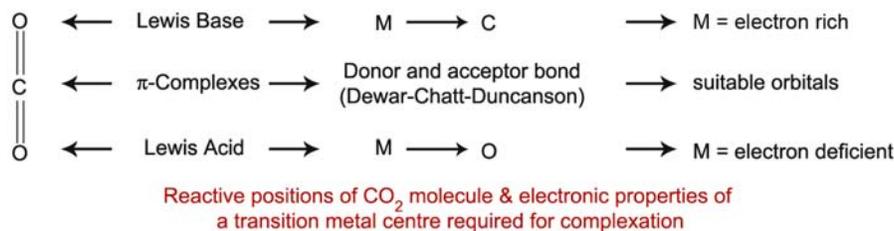
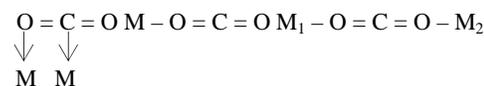


Fig. 4—The possible interaction of the molecular orbital of carbon dioxide with metal orbitals.

**Scheme 2**

to know some basic concepts of this process. The direct thermal decomposition of carbon dioxide to carbon monoxide is an endothermic process with the net free energy change ( $\Delta G^\circ$ ) of 257 kJ/mol. For 100 % conversion, a temperature of 3348 K may be required, since only at this temperature the  $\Delta G^\circ$  becomes zero. There are other possibilities like thermochemical routes etc., but these are not within the scope of this article. From the electrochemical point of view, the conversion of carbon dioxide can be achieved in combination with the electrolysis of water. As stated, a wide range of products starting from CO to more complex, pure and oxygenated hydrocarbons of high energy content can be directly formed. However, the voltage to be applied for the simple carbon dioxide splitting is 1.33 V at 298 K. The thermoneutral voltage is 1.47 V, which is nearly the same as that for water electrolysis. However for effective splitting, one has to add electrode overvoltage and ohmic losses, and a voltage of nearly 2 V or more is required to promote this reaction in aqueous electrolytes. This will possibly account for the selectivity observed with different metals and also why only certain metallic surfaces could promote electrochemical reduction of carbon dioxide.

In aqueous electrolytes (sodium or potassium bicarbonate), the reduction process for water decomposition and reduction of carbon dioxide require almost the same voltage (-0.41 V for H<sup>+</sup>/H<sub>2</sub>O while for CO<sub>2</sub>/CO the value is -0.52 V at pH = 7) and hence compete with each other. As a result, the normal Faradaic efficiency for carbon dioxide reduction is lower since the hydrogen evolution reaction is the preferred reaction. Therefore it is clear that the net Faradaic efficiency for carbon dioxide reduction will depend on various factors, essentially the catalytic activity of the electrode, the potentials applied, the pH and nature of electrolyte employed, the effective concentration of carbon dioxide near the electrode surface and the consequences like mass transport, ionic and buffer strength and other associated factors.

Linear bonding scheme of CO<sub>2</sub> without bond angle variation**Scheme 3**

Among all the factors mentioned, the influence of nature of the electrode appears to be overwhelming. In the literature, the relevance of factors like the orientation of the crystal lattices (accounting for the preferential adsorption of substrate CO<sub>2</sub> and intermediates), surface architecture (roughness, stepped surface, porosity and defects), surface crystallography (dislocations and vacancies) and electronic configurations (*s*, *p*, or *d* metals) has also been emphasized. Since this is not easily obtained on many metallic surfaces, the water decomposition and hydrogen evolution reaction predominates on most of the metallic surfaces. Based on only the above parameters the metals have been grouped into four classes outlined elsewhere in this article, though as stated earlier the hydrogen overvoltage and CO adsorption strength can also be considered as basis for this classification.

Though we have classified the metal electrodes on the basis of the thermodynamic control in the form of hydrogen overvoltage and CO adsorption strength, the geometrical factors can also contribute to the observed selectivity of the products formed. The activation of carbon dioxide on metallic sites has been visualized in a number of ways. The possible modes of activation of carbon dioxide are assembled in Fig. 3. The reactive positions of CO<sub>2</sub> molecule and the sites of adsorption are shown in Scheme 2. Adsorption of carbon dioxide in an undistorted, without bond angle variation form (i. e., retaining the 180° bond angle) can give rise to the following adsorption modes (Scheme 3).

Some of the other possible modes of activation of carbon dioxide have been discussed earlier in this article. Though there are a variety of adsorption modes, it should be noted that those adsorption modes

of carbon dioxide where the bond angle deviates from  $180^\circ$  alone will be able to yield useful products. This means that though carbon dioxide can be adsorbed in a number of ways, the three linear forms shown in Scheme 3 will not yield useful reduced products. This imposes some restrictions on the geometry of the adsorption site. The path for reduction of carbon dioxide most probably involves activating the carbon and one of the oxygen atoms of carbon dioxide. At the same time the adsorption strengths are not very strong and thus that subsequent hydrogenation and desorption of the hydrogenated product are feasible. This can impose some geometrical restrictions on the activation centre on metallic surfaces either in the form of some certain exposed planes or presence of stepped sites.

Till the 1980s studies on electrochemical reduction of  $\text{CO}_2$  have been mainly centered around the amalgamated electrons (Cu, Zn and Pb) for the formation for formic acid. Even though since 1980, various other electrodes including semiconductors have been examined, the current efficiencies were remarkably low. The first reports on highly efficient copper electrodes for hydrocarbon formation from  $\text{CO}_2$  reduction were of Hori *et al.*<sup>19,20</sup> in 1985 and 1986.

In aqueous medium, the electrochemical reduction of carbon dioxide involves the oxidation of water at

the anode, with the released electrons being utilized in the reduction of carbon dioxide at the cathode to generate hydrocarbons and alcohols. Since the reduction potential of carbon dioxide is close to that of water reduction on most surfaces, hydrogen evolution may predominate over  $\text{CO}_2$  reduction and hence the catalyst chosen should have high overpotential for hydrogen reduction, allowing  $\text{H}^+$  transfer steps selectively for formation of reduction products of  $\text{CO}_2$ . In the periodic table (Fig. 5) the approximate values of hydrogen evolution current efficiencies (%) in  $\text{KHCO}_3$  solutions around 273 K at  $-2.2$  V are given. It is seen that on most of the metals hydrogen evolution predominates over the  $\text{CO}_2$  reduction reaction. Only on a limited number of metallic surfaces, other reduction products like CO, HCOOH and hydrocarbons (mostly  $\text{CH}_4$ , and  $\text{C}_2\text{H}_4$ , and  $\text{C}_2\text{H}_6$ ) are formed.

Since copper appears to have a unique place in carbon dioxide reduction, there have been a number of studies reported on this system. Kaneco and his coworkers<sup>21-23</sup> in a series of investigations have studied carbon dioxide reduction on copper surfaces in different media to produce high Faradaic efficiencies for a variety of products like formic acid, methane, ethylene and carbon monoxide. It has been shown that the surface treatment, physical form and the method of preparation of copper have profound

1 H																	2 He	
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne	
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar	
19 K	20 Ca	21 Sc	22 Ti (0, 5) 70	23 V 92	24 Cr 91	25 Mn 91	26 Fe 89	27 Co 93	28 Ni (21) 62	29 Cu (17, 3, 30) 49	30 Zn (10, 20) 68	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr	
37 Rb	38 Sr	39 Y	40 Zr 98	41 Nb 97	42 Mo 99	43 Tc	44 Ru 99	45 Rh 99	46 Pd (12, 16) 73	47 Ag (40, 26) 33	48 Cd (4, 56) 35	49 In (3, 70) 25	50 Sn (2, 28) 28	51 Sb	52 Te	53 I	54 Xe	
55 Cs	56 Ba	* Lu	71 Hf 96	72 Ta 100	73 W 96	74 Re 96	75 Os	76 Ir 99	77 Pt (4, 6) 93	78 Au (17, 10) 74	79 Hg 100	80 Tl (0.2, 53) 46	81 Pb (0.1, 17) 83	82 Bi	83 Po	84 At	85 Rn	
87 Fr	88 Ra	* Lr	103 Rf	104 Db	105 Sg	106 Bh	107 Hs	108 Mt	109 Ds	110 Rg	111 Cn	112 Uut	113 Uuq	114 Uup	115 Uuh	116 Uus	117 Uuo	118 Uuo

Fig. 5—Periodic table showing the efficiencies of various metals for the electrochemical reduction of  $\text{CO}_2$ .

effects on the electrocatalytic properties for the reduction of carbon dioxide. It has been established in literature that copper is the vital component for the reduction of carbon dioxide, though the actual nature of the active sites and their geometrical orientation are still not established. Even though CO<sub>2</sub> is reduced on typical (100), (110) and (111) planes of copper, Hori *et al.*<sup>19,20</sup> showed that on (100) planes ethylene is the preferred product while on (111) planes the product is predominantly methane. However, on (110) planes both products are formed.

Based on the heat of adsorption measurements, it has also been shown that the presence of Cu(I) species as Cu<sub>2</sub>O may be responsible for methanol formation. In the literature the role of Cu<sup>+</sup> sites on the formation of hydrocarbons has been debated with respect to the adsorption geometry of CO fragment, as well as with the energetics of adsorption intermediate species like HCOO and CH<sub>2</sub> + CH. Copper loaded on ZnO showed higher Faradaic efficiency for the formation of methane and ethylene, this being attributed to the preferential stabilization and dispersion of Cu<sup>+</sup> sites on ZnO. These interface sites may possibly promote the non-linear adsorption of CO<sub>2</sub> in addition to shielding these active sites from poisoning by impurities.

Beck *et al.*<sup>24</sup> in a recent publication have shown the comparative cost of various kinds of energy storage media and demonstrated the utility of electrochemical reduction of carbon dioxide.

### Concluding Remarks

The objective of this report is to provide fundamental understanding of CO<sub>2</sub> reduction at the molecular level so that the catalyst design is possible. There have been persistent statements in the literature which explicitly demonstrate that economic difficulties and physical limitations have to be overcome before CO<sub>2</sub> utilization becomes a viable process.

All these results lend credence to the postulate given in this presentation that only those sites which can activate carbon dioxide in a bent geometry are capable of producing fuels. Such surfaces have to be geometrically and configurationally ascertained to be present on the metallic surface for effecting electrochemical reduction of carbon dioxide. It may be possible that with the modern methods of

architecting surfaces, metallic electrodes of suitable geometry can be made routinely for a viable carbon dioxide-to-fuels process development. Also, the electric field gradients that are possible may be cumulatively adding to the efficiency of the process, though at present this has to be realized.

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