CHAPTER

11

Electro-Catalytic Reduction of Carbon Dioxide

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11.1 INTRODUCTION

p0005 The conversion of carbon dioxide to useful chemicals is one of the possible ways of utilizing the so-called waste. It is considered that at present, there is no **commercially** viable process for converting carbon dioxide into fuels. However, there are a variety of ways in which carbon dioxide can be converted to useful chemicals, fuels, and fuel precursor, namely CO. Some of the possible carbon dioxide conversion routes are given in Table 11 1. In this table and subsequent tables the species are considered. AQ1

p0010 In spite of these possibilities, intense research in carbon dioxide conversion over the past 30 years has consistently shown low conversion efficiencies possibly because of the high over potentials (~>1 V) required. In spite of the persistent efforts for reducing the overvoltage and also improving the electrochemical cell components, no commercially viable process for converting carbon dioxide into fuels has evolved till date. This frustration is reflected in the following statement of the DOE report by Bell [2] "*The major obstacle preventing efficient conversion of carbon dioxide into energy bearing products is the lack of (suitable and appropriate) catalysts…..Only intermittent research has been conducted into the electrochemical reduction of carbon dioxide over the last 20 years, despite the fact that electrochemical generation of chemical products is a mature technology and already practiced on enormous scales…..Electron conversion efficiencies of greater than 50% can be obtained but at the expense of very high overpotentials (ca.1.5 V).*"

p0015 The scope of electrochemical reduction of carbon dioxide to fuel precursors such as CO, ethylene, methanol, or formic acid at low over potentials has been examined [3] and surfaces that can activate carbon dioxide with reduction of the bond angle from 180° may fulfill this criterion and this type of electrodes may require geometrically constrained sites for CO_2 activation. One of the pictorial representation of this geometry as conceived is shown in Figure 11.1.

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TABLE 11.1 Some of the possible carbon dioxide conversion routes [1]. The gaseous state carbon dioxide is considered for the reactions shown.

Name of the process	Examples
Radio-chemical	$CO_2 \xrightarrow{\text{gamma rays}} HCOOH, HCHO$
Chemical reduction	$2Mg + CO_2 \rightarrow 2MgO + C$ $Sn + 2CO_2 \rightarrow SnO_2 + 2CO$ $2Na + CO_2 \rightarrow Na_2C_2O_4$
Thermo-chemical	$CO_2 \xrightarrow{Ce4+, T>1173\ K} CO + 1/2O_2$
Photo-chemical	$CO_2 \xrightarrow{hv} CO, HCHO, HCOOH$
Electrochemical	$CO_2 + xe^- + xH^+ \xrightarrow{eV} CO, HCOOH, (COOH)_2$
Bio-chemical	$CO_2 + 4H_2 \xrightarrow{\text{Bacterial}} CH_4 + 2H_2O$
Bio-photochemical	CO_2 + oxoglutaric acid $\xrightarrow{hv}$ Isocitric acid
Photo-electrochemical	$CO_2 + 2e^- + 2H^+ \xrightarrow{hv, eV, \text{Semicondctor}} CO + H_2O$
Bioelectrochemical	CO_2 + Oxoglutaric acid $\xrightarrow{\text{enzyme}, eV, \text{Methyl viologen}}$ Isocitric acid
Biophotoelectrochemical	$CO_2 \xrightarrow{hv, \text{enzyme, p-InP}, eV, \text{methyl viologen}} HCOOH$

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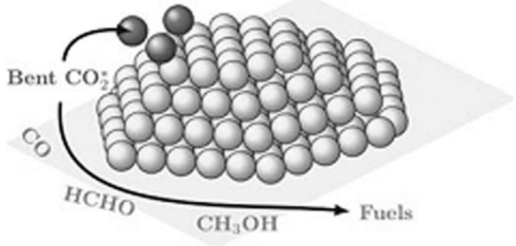

f0005 **FIGURE 11.1** The constrined geometry of activation of carbon dioxide on metallic surfaces. [Reproduced from Reference 3].

p0020 Essentially, there are a variety of questions that can be raised with respect to the direct electrochemical conversion of CO_2 to chemicals and fuels. In the following some of these questions are explicitly stated.

o0005 **1.** What are the factors one has to consider, for selecting the appropriate electrode for carbon dioxide reduction?

o0010 **2.** Which is most important for consideration—Is it the reduction potential or the activation of the molecular carbon dioxide?

o0015 **3.** In selecting the metallic system, should one consider the mode of activation of carbon dioxide in the associated form or in the dissociated form?

o0020 **4.** Does the nature of wave functions of the frontier wave functions of the electrode material and that of CO_2 have to be considered for symmetry and energy compatibility?

o0025 **5.** It is argued in the literature that copper and copper-zinc systems are most appropriate. How does this evolve? What are the governing principles?

o0030 **6.** It is usually stated in the literature that the formation of anion radical is important and essential step in the electrochemical reduction of CO_2. Can any light be thrown on this aspect?
o0035 **7.** It is also argued that the bond angle must be reduced from 180° in the activated state. Does the formation of anion radical favor this postulate?
o0040 **8.** The reduction reaction is capable of forming a variety of products and how does one control the required selectivity?
o0045 **9.** One of the intriguing questions in the study of this reaction is the product analysis. This can be achieved either analyzing the gas phase or the liquid phase and which one is most appropriate and why? Is there any reasoning for this choice?
o0050 **10.** The literature often argues in terms of the relative adsorptive or evolution capacity for hydrogen from water or CO poisoning. How to make a judgment on the relative importance of these steps?

p0025 Ideally. It would have been desirable, if answers to these questions are available *a priori* so that the selection of electrode materials can be made on a rational basis. In the absence of such information, the postulate on the choice of electrode material has to be based on the experimental data already available. The motivation for this presentation is to assemble available information so as to obtain at least partial answers to these questions.

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11.2 ELECTROCHEMICAL REDUCTION OF CARBON DIOXIDE ON METALS IN AQUEOUS AND NON-AQUEOUS MEDIA

p0030 The investigations reported in the literature have identified that the large over potential is due to the fact that the first step in CO_2 reduction is the formation of the high energy intermediate $(^{*}CO_2)^{-}$ namely, carbon dioxide anion radical. It is therefore necessary that one examines all the possible carbon dioxide reduction reactions in conjunction with water decomposition reaction as most of the electrochemical reactions have been carried out in aqueous medium with suitable supporting electrolyte namely $KHCO_3$. Solubility of carbon dioxide in water is very small ($\sim$0.08 M) and hence, one may have to resort to study this reaction in non-aqueous medium or in ionic liquids [4].

p0035 However most of the studies reported in the literature are in aqueous medium. Hence, it is necessary to generate a compilation of the possible reactions with the information of feasibility and this is attempted by the data given in Table 11.2. It may be true that the data given in Table 11.2 may not include all of the possible or reported reactions in carbon dioxide reduction, these aspects will be taken up in a subsequent section and only data relevant to most of the reports available in the literature alone are considered for compilation of this table. In fact, in a recent communication, Kuhl et al. [5] have reported the identification of 16 different products by the reduction of carbon dioxide on metallic copper surfaces, among which the following products have been identified in previous studies, namely methane, methanol, ethylene, CO, formate, ethanol, *n*-propanol, allyl alcohol, acetaldehyde, and propionaldehyde. The five new reduction products identified by them include ethylene glycol, glycolaldehyde, hydroxyacetone, acetone, and glyoxal and these are the oxygenated C_2 and C_3 products. The analysis of the results of this investigation will be taken up subsequently.

TABLE 11.2 Typical electrochemical reactions for CO_2 reduction in conjunction with water decomposition. The reactant species considered are in gaseous state.

Reaction	ΔE^0 (V)	ΔG^0 (kcal/mol)
$H_2O \rightarrow H_2 + 1/2O_2$	1.229	56.7
$CO_2 + H_2 \rightarrow HCOOH$		5.1
$CO_2 + H_2O \rightarrow HCOOH + 1/2O_2$	1.34	61.8
$CO_2 + H_2 \rightarrow CO + H_2O$		4.6
$CO_2 \rightarrow CO + 1/2O_2$	1.33	61.3
$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$		−4.1
$CO_2 + 4H_2 \rightarrow CH_3OH + 2H_2O$		−31.3
$CO_2 + 2H_2O \rightarrow CH_3OH + 1.5O_2$	1.20	166
$CO_2 + 2H_2O \rightarrow CH_4 + 2O_2$	1.06	195

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TABLE 11.3 Possible carbon dioxide (gaseous state) reduction reactions in conjunction with water decomposition reaction at pH = 7.

Reaction	Potential (V)
$CO_2 + e^- \rightarrow (CO_2)^-$	−1.90
$CO_2 + H_2O + 2e^- \rightarrow HCOO^- + OH^-$	−0.43
$CO_2 + H_2O + 2e^- \rightarrow CO + 2OH^-$	−0.52
$CO_2 + 6H_2O + 8e^- \rightarrow CH_4 + 8OH-$	−0.25
$2CO_2 + 8H_2O + 12e^- \rightarrow C_2H_4 + 12OH^-$	−0.34
$2CO_2 + 9H_2O + 12e^- \rightarrow C_2H_5OH + 12OH^-$	−0.33
$2CO_2 + 13H_2O + 18e^- \rightarrow C_3H_7OH + 18OH^-$	−0.32
$2H_2O + 2e^- \rightarrow 2OH^- + H_2$	−0.41

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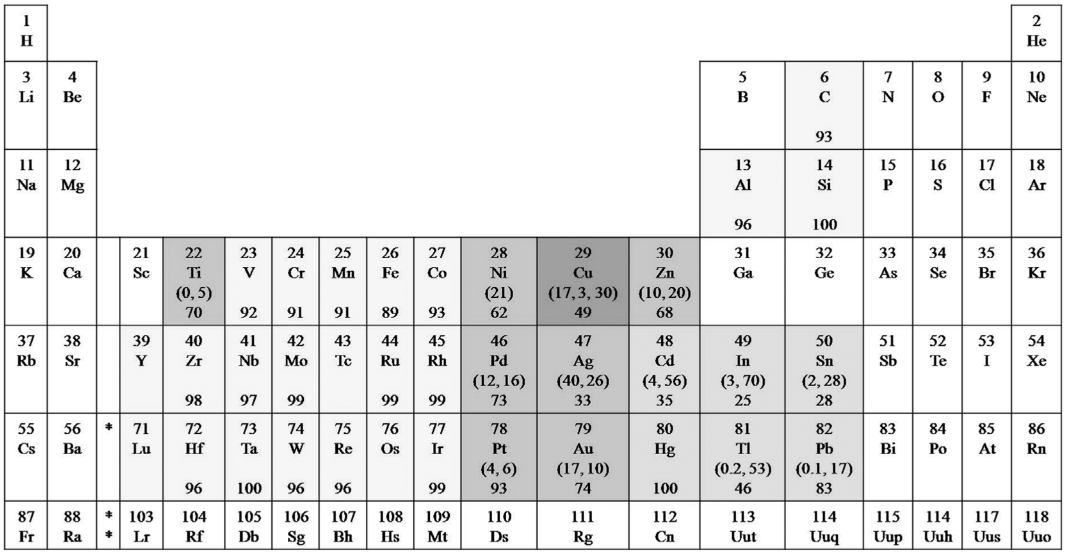
p0040 The possible and relevant electrochemical reduction of carbon dioxide reactions in combination with water decomposition are listed in Table 11.3 at pH = 7 since in acid medium the hydrogen evolution is the predomiant reaction and in alkaline medium carbon dioxide does not exist. Direct one electron reduction of carbon dioxide requires high negative potential due to large reorganization energy between the linear molecule and bent radical anion. The Hydrogen Evolution Reaction (HER) potential is pH dependent while the reduction of carbon dioxide, though generates hydroxide anion is less dependent on pH and in slightly acid conditions or neutral medium the HER is thermodynamically more favorable.

p0045 Since hydroxide anions are generated in the reduction of carbon dioxide, the pH at the electrode surface will be higher than that of the bulk solution and hence the reduction of carbon dioxide is adversely impacted by the basic layer on the electrode. It is therefore necessary to study the reduction of carbon dioxide in electrolytes like $KHCO_3$ or K_3HPO_4 and the anions of these electrolytes have the appropriate buffering capacity. Electrochemical reduction of carbon dioxide in aqueous medium (−0.43 vs. SHE at pH 7) is competitive with hydrogen evolution reaction (−0.41 V vs. SHE at pH 7) and in acid medium the latter will be the predominant reaction. Hence most of the carbon dioxide reduction reaction is carried out in neutral medium or slightly acidic medium only (around pH 6.8 or so). Only electrodes which have high hydrogen over potential will favor CO_2 reduction. In Figure 11.2 the classification of metal electrodes for CO_2 reduction is shown in the conventional periodic table



1 **H**																		**2** **He**
3 **Li**	**4** **Be**												**5** **B**	**6** **C** **93**	**7** **N**	**8** **O**	**9** **F**	**10** **Ne**
11 **Na**	**12** **Mg**												**13** **Al** **96**	**14** **Si** **100**	**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**	*	**71** **Lu**	**72** **Hf** **96**	**73** **Ta** **100**	**74** **W** **96**	**75** **Re** **96**	**76** **Os**	**77** **Ir** **99**	**78** **Pt** **(4, 6)** **93**	**79** **Au** **(17, 10)** **74**	**80** **Hg** **100**	**81** **Tl** **(0.2, 53)** **46**	**82** **Pb** **(0.1, 17)** **83**	**83** **Bi**	**84** **Po**	**85** **At**	**86** **Rn**
87 **Fr**	**88** **Ra**	* *	**103** **Lr**	**104** **Rf**	**105** **Db**	**106** **Sg**	**107** **Bh**	**108** **Hs**	**109** **Mt**	**110** **Ds**	**111** **Rg**	**112** **Cn**	**113** **Uut**	**114** **Uuq**	**115** **Uup**	**114** **Uuh**	**117** **Uus**	**118** **Uuo**

1. The numerical figures in without bracket denotes hydrogen evolution efficiencies
2. The Numerical figures in bracket denotes CO, HCOOH and HC formation efficiencies in that order.

f0010 **FIGURE 11.2** Possible metal electrodes promoting either water decomposition or CO_2 reduction. It is seen that the metals fall into distinct four groups namely only hydrogen evolving systems, CO, HCOOH or HC forming systems respectively.

form with color code distinguishing the products formed. The legend to this figure indicates the metals that will electrocatalytically reduce CO_2 to various products. Alternate classification has also been resorted to in the literature based on the electronic configuration of the metal (like sp or d) and the electrolyte type (aqueous or non-aqueous) [6]. According to this classification, the status of carbon dioxide reduction in terms of the product formed on various metals is summarized in Table 11.4. The data given in this table can at best be used as a guiding tool and more considerations may have to be resorted to for complete understanding of the product patterns that are obtained on many of the metallic electrodes.

p0050 The stumbling block in achieving CO_2 reduction depends upon how effectively one can decrease the high over potential. The energetic efficiency of most of the metallic surfaces is limited by the large over potential required for the CO_2 reduction. Yet another limitation of electro-catalytic reduction of carbon dioxide for scalable chemical synthesis is that the materials should be capable of promoting the reaction without any perceptible deactivation for longer duration. This kind of stability in the case of metallic electrodes under the experimental conditions required for carbon dioxide reduction appears to be difficult.

p0055 The rate-limiting step for the CO_2 reduction process is the formation of a high energy CO_2^- radical anion intermediate by the reaction

$$CO_2 + e_{aq}^- \rightarrow CO_2^- (E^0 = -2.21\text{V vs. SCE in DMF}).$$

A reaction network for carbon dioxide reduction in aqueous medium is shown in Figure 11.3. This reaction network shows how the high energy intermediate $[CO_2^-]$ anion radical plays a

TABLE 11.4 Classification of metals in terms of sp or d and the typical products that will be formed in the reduction of carbon dioxide.

Metals	Products	
	Aqueous medium	Non-aqueous medium
	sp group metals	
Cu, Zn, Sn	HCOOH	–
Cd, In,Sn,Hg, Pb,Bi	HCOOH, CO, Hydrocarbon	–
Cu, Zn, Cd, In, Sn, Pb,	–	Hydrocarbon, CO, CO_3^{2-}
In,Sn,Au, Hg	–	CO
Zn,Pd,In,Sn,Hg, Tl,Sn	–	Oxalic acid
	"d" group metals	
Ni, Pt	–	CO, CO_3^{2-}
Ni, Rh,Pd, Ir	HCOOH,CO	–
Fe, No, Ru, Pd, Pt	Hydrocarbon	–
Ti,Cr,Fe,Nb,Mo,Pd	–	Oxalic acid
Mo,Ru,Pd,W, Os, Pt	Methanol	–
Cr, Mn, Fe, Co,Zr, Rh, Ir	CO	–

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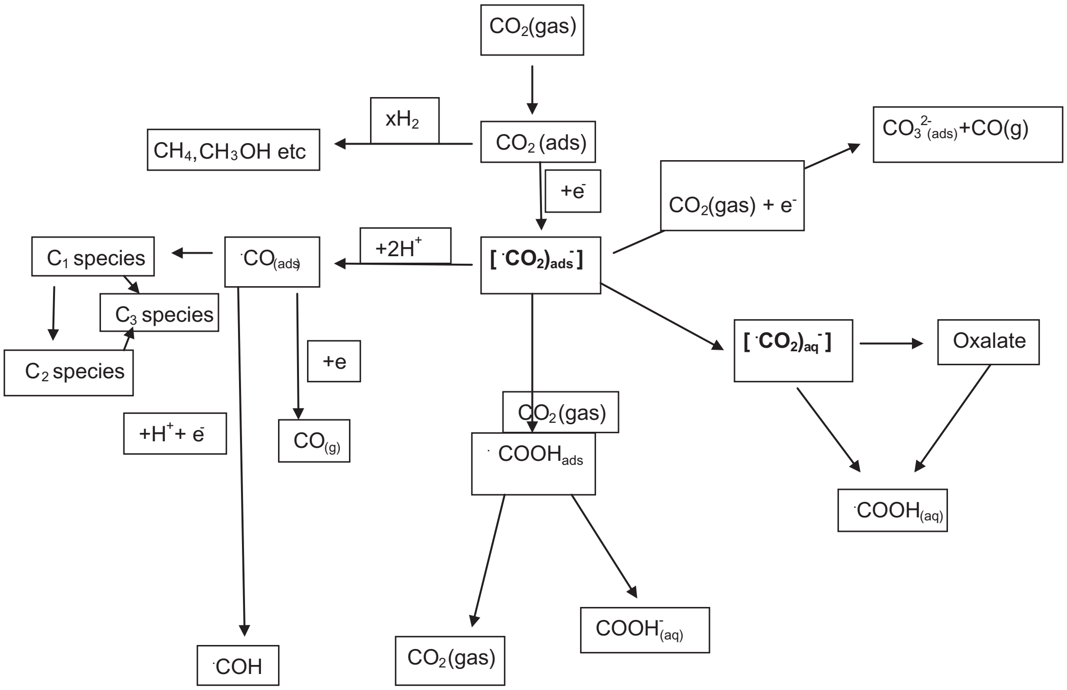


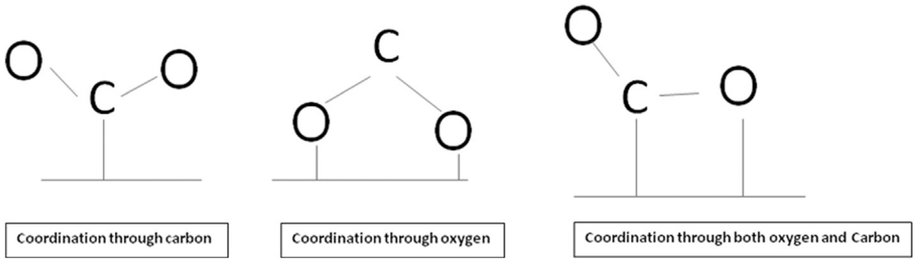
f0015 **FIGURE 11.3** A reaction net-work is shown for the reduction of CO_2 in aqueous medium. *CO_2 anion radical formation* is considered to be the central point of this network.

pivotal role in the formation of oxygenated reduction products. Alternate route based on single carbon enol-type intermediates has also been proposed [5]. Carbon dioxide reduction in aqueous medium is often vitiated by the possible simultaneous evolution of hydrogen from the decomposition of water. This reaction can also be carried out in non-aqueous medium, for example in Propylene carbonate (PC), acetonitrile (AcN), dimethyl formamide (DMF), dimethyl sulfoxide (DMSO), and methanol (MeOH)[preferred solvent], since the CO_2 solubility can be increased and the competing hydrogen evolution reaction can be suppressed. This reaction network is different from the one proposed by Jaramillo et al. [5] since they have visualized a number of one carbon surface species which are responsible for the oxygenated C_2 and C_3 products. In Table 11.4, the data [limited data] on the electro-catalytic reduction of CO_2 on different metal electrodes in methanol medium are assembled which indicate that the product distribution is different in non-aqueous medium. In non-aqueous medium the Faradaic efficiency for hydrogen evolution decreased and that for other products increased. Many metals in methanol medium with TBAP or LiCl as electrolyte produced fuel precursor CO while in aqueous medium only Zn, Ag, and Au favored the formation of CO. In non-aqueous medium the metals can be grouped as follows:

p0055 **1.** Oxalate producing metals namely Pb, Hg, Tl, and Pb.
o0060 **2.** Fuel precursor CO producing metals, Ni, Cu, In, Sn, AgPt, and Au.
o0065 **3.** Metals that produce both CO and oxalate, Cr, Fe, Mo, Pd, and Cd.

p0065 In non-aqueous medium, the supporting electrolyte also has a crucial role in deciding the type of products formed [7,8]. In non-aqueous medium too, the central point is the formation of CO_2^{-*} anion radical and subsequent steps involve addition of other radicals, CO_2 or primary reduction products which give rise to other further reduced products [7,9,10]. The formation of anion radical as the central species has been established either in free state in solution or in adsorbed state or in bonding with hydrogen or other cations in ionic liquids [11–13].

p0070 The activation of CO_2 on metallic surfaces can be conceived as adsorption through oxygen, carbon, or mixed coordination. These different modes of adsorption can give rise to changes both in bond angle and bond distances. One such pictorial representation is given in Figure 11.4.



f0020 **FIGURE 11.4** The simple possible adsorption states of CO_2 through carbon, oxygen and also mixed coordination [15].

p0075 Mixed coordination involving carbon and one of the oxygens can be favorable for reduction and this mode of activation can also involve the bond angle reduction from 180°. Single crystal surfaces with specific planes or possessing stepped surfaces may be favorable for this kind of activation of CO_2. Electro-catalytic reduction of CO_2 on Pt (210), Pt (310), and Pt (510) (with order of activity in the same sequence) surfaces has been studied and it has been shown that open structures of Pt will be favorable for CO_2 reduction [15]. On single crystal surfaces, the activity order for CO_2 reduction is reported to be Pt(110) > Pt(100) > Pt(111) [16]. A recent study reports that Bi or Te adsorbed on Pt(111) or Sb adsorbed on Pt(100) showed increased CO_2 reduction activity [17]. Similar observations have also been recorded for the formic acid oxidation which can be considered to be the reverse of CO_2 reduction [18]. The structure sensitivity of CO_2 reduction and the electro-catalytic reduction of CO_2 and the selectivity observed are enhanced by the presence of steps and kinks to atomically flat surfaces of noble metals and of copper have been established by a number of studies [5,19–27]. In spite of this molecular level elucidation of the electrode surface and even the process taking place on the electrode, the net Faradaic efficiency ($\sim$40%) observed is still low and the realized over potential ($\geq$1 V) is high. There is a claim that the efficiency of the process can be increased to about 70% and the over potential can be reduced to about $\sim$0.2 V if the electro-chemical reduction is carried out in ionic liquids [4]. However, aqueous phase electro-catalytic reduction of carbon dioxide still has to face additional hurdles as follows [1,28]:

o0070 **1.** As stated, the CO_2 reduction and hydrogen production are competing processes and hence the desired selectivity could not be achieved.
o0075 **2.** Since different products can be formed, their separation and recovery are not that easy.
o0080 **3.** The solubility of CO_2 in aqueous medium is limited ($\sim$0.08 M) and hence high pressures are normally required.
o0085 **4.** Since the products formed (especially CO) can be adsorbed on the electrode surface preferentially, the initial activity and selectivity cannot be sustained.
o0090 **5.** The electrochemical reaction has to be carried out under extreme pure conditions as the impurities can adversely affect the electrode reaction.
o0095 **6.** Fundamental understanding has to evolve how the potential and the site geometry in tandem activate the adsorbed CO_2 molecule and facilitate the reduction reaction.

s0015 11.3 ELECTRO-REDUCTION OF CARBON DIOXIDE ON METALLIC ELECTRODES

p0080 Even though a number of state-of-art documents have been made available in the literature [1,29,30] on this scientific topic, it appears still that the electro-catalytic process of carbon dioxide reduction has not yet matured to be an available commercial process. The amount of water in the medium possibly accounts for the low Faradaic efficiency observed for the carbon dioxide reduction at high water content the preferred reaction is hydrogen evolution and at very low water content, possibly only CO and oxidized products alone are formed.

p0085 AQ2 In the case of demanding reactions like CO_2 reduction, it is necessary that one has to design catalyst surface (as stated the sites should have constrained geometry) and retain them under the influence of electrode potential. The possible reconstructions and adsorption from the electrolyte medium can vitiate the CO_2 reduction reaction. The main electro-reduction products that are obtained on various metals in aqueous and non-aqueous media with appropriate electrolytes are given in Tables 11.5A and 11.5B. The selection of data for this table is arbitrary and many such data sets are available in the literature. It is seen from this table that in most of the cases the product is either fuel precursor (CO) or oxygenated compounds though rarely hydrogenated hydrocarbons are obtained. This may account for the C_2 and C_3 oxygenated products observed in the literature [5]. In essence, the attempt to reduce CO_2 using water can also be considered as the reverse of methanol fuel cell reaction. Our understanding of the methanol or hydrocarbon fuel cell reactions is not complete, and hence our efforts to carry out CO_2 reduction using similar metallic electrodes appear to be lacking behind.

p0090 It is necessary that one gets a comprehension of the basic properties of carbon dioxide molecule and a compilation of this information is given in Table 11.6 and the corresponding molecular orbital picture for free carbon dioxide molecule is given in Figure 11.5.

p0095 The frontier molecular wave functions of carbon dioxide are of π character (both HOMO and LUMO) and hence direct activation of this molecule appears to be difficult. Secondly, it is necessary that the C–O bond has to be activated instead of activating through the two oxygen ends of the molecule. These limitations provide clue that the molecule can be activated by charge transfer to the molecule and only those metals whose Fermi level is

TABLE 11.5A Data on the reduction of CO_2 on different metal electrodes in aqueous medium with 0.1 M $KHCO_3$ electrolyte.

Metal electrode	Potential vs. SHE (V)	Current efficiency (%)				Electrolyte	Reference
		Hydrogen	Methane	CO	Formic acid		
Ti	−1.60	99.7	0.0	Trace	0.0	0.1 M $KHCO_3$	59
V	−1.40	86.0	0.1	1.1	0.0	0.1 M $KHCO_3$	4
Fe	−0.91	94.8	0.0	0.0	0.0	0.1 M $KHCO_3$	59
Co	−1.40	102.0	0.3	0.0	0.0	0.1 M $KHCO_3$	4
Ni	−1.48	88.9	18	0.0	1.2	0.1 M $KHCO_3$	59
Cu(100)	−1.39	10.3	19.8	1.9	11.7	0.1 M $KHCO_3$	4
Cu(111)	−1.52	13.1	15.5	4.9	16.6	0.1 M $KHCO_3$	4
Cu	−1.44	20.5	33.3	1.3	9.4	0.1 M $KHCO_3$	4
Zn	−1.54	9.9	–	79.4	6.1	0.1 M $KHCO_3$	59
Ga	−1.24	79.0	0.0	28.3	2.8	0.1 M $KHCO_3$	59
Mo	−1.40	103.0	0.0	0.0	0.0	0.1 M $KHCO_3$	4
Ru	−1.40	111.0	0.0	0.0	0.0	0.1 M $KHCO_3$	4
Pd	−1.20	26.2	0.0	28.3	2.8	0.1 M $KHCO_3$	59
Ag	−1.37	12.4	0.0	81.5	0.8	0.1 M $KHCO_3$	59
Cd	−1.40	39.0	0.1	14.4	39.0	0.1 M $KHCO_3$	4
In	−1.55	3.3	–	2.1	94.9	0.1 M $KHCO_3$	59
Sn	−1.48	4.6	–	7.1	88.4	0.1 M $KHCO_3$	59
Ta	−1.40	90.0	0.1	0.9	0.0	0.1 M $KHCO_3$	4
W	−1.40	102.0	0.1	1.9	0.0	0.1 M $KHCO_3$	4
Ir	−1.40	99.0	0.1	0.0	0.0	0.1 M $KHCO_3$	4
Pt	−1.07	95.7	0.0	0.0	0.0	0.1 M $KHCO_3$	59
Au	−1.14	10.2	0.0	87.1	0.7	0.1 M $KHCO_3$	4
Pb	−1.63	5.0	0.0	0.0	97.4	0.1 M $KHCO_3$	59

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TABLE 11.5B Data on the reduction of CO_2 on different metal electrodes in methanol medium with various electrolytes.

Metal electrode	Potential vs. SHE (V)	Current efficiency (%)				Electrolyte	Reference
		Hydrogen	Methane	CO	Formic acid		
Fe	−2.60	22.2	n.a	15.6	1.4	10 mMLiCl/100mMTBAP	4
Ni	−2.60	44.0	n.a	45.7	8.3	10 mMLiCl/100mMTBAP	4
Cu	−2.80	5.8	68.4	15.7	6.8	500 mM LiCl	66
Cu	−2.80	3.6	6.4	35.0	17.2	50 mMKBr	66
Cu	−2.80	3.5	15.8	15.2	n.a	50 mMKI	66
Cu	−2.80	6.2	1.0	40.0	4.8	30 mMCsI	66
Zn	−2.60	0.0	n.a	89.7	n.a	10 mMLiCl/100mMTBAP	4
Pd	−2.60	0.0	n.a	51.9	1.5	10mMLiCl/100mMTBAP	4
Ag	−2.60	1.9	n.1	77.4	2.1	10 mMLiCl/100mMTBAP	4
Cd	−2.60	0.0	n.a	77.4	2.1	10 mMLiCl/100mMTBAP	4
In	−2.60	0.0	n.a	89.2	2.3	10 mMLiCl/100mMTBAP	4
Sn	−2.60	0.0	n.a	81.8	3.5	10 mMLiCl/100mMTBAP	4
Pt	−2.60	17.4	n.a	66.6	7.7	10 mMLiCl/100mMTBAP	4
Au	−2.60	13.9	n.a	83.2	3.7	10 mMLiCl/100mMTBAP	4
Pb	−2.30	5.0	0.0	2.0	75.0	10 mMLiCl/100mMTBAP	4

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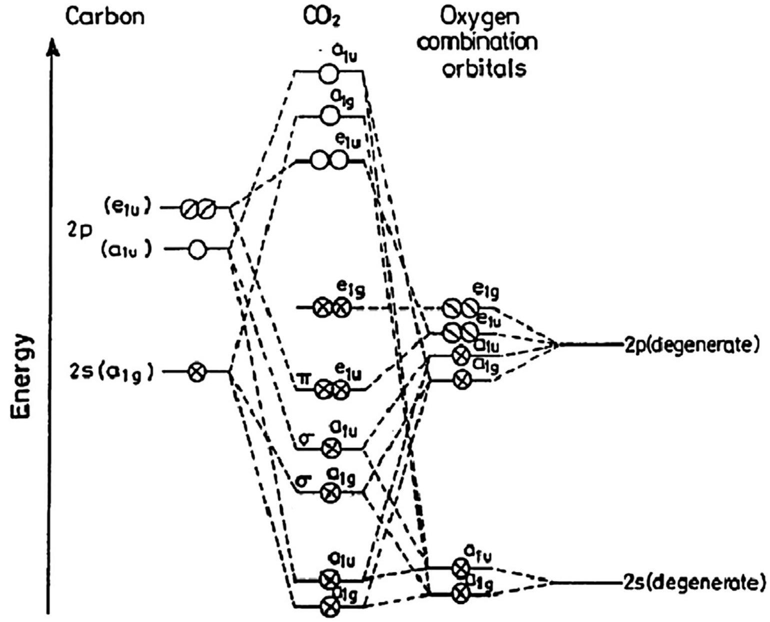
TABLE 11.6 Selected relevant properties of carbon dioxide.

Property considered	Value
Point group	Dαh
Ground state	${}^1\Sigma_g$
Boiling point (ºC)	−78.5
LUMO	$2\boldsymbol{\pi}_u$
HOMO	$1\boldsymbol{\pi}_g$
Bond length (Å)	1.16 (C–O)
Bond energy (eV)	5.453
Ionization potential (eV)	13.78
Electron affinity (eV)	−0.6
IR absorption data (cm^{-1})	1320, 668, 235

t0035

appropriately placed with respect to the LUMO of CO_2 with proper symmetry considerations can activate this molecule. This could also explain why only certain metals and only certain metal planes are capable of promoting carbon dioxide reduction. This situation may provide answer why such high over potentials are required for the reduction of CO_2 on certain other metals. In a recent communication, Li and Kanan argue [31] that direct electrochemical reduction of metal oxides provides a possible route for generating appropriate active sites with non-native configurations. Their argument in support of this hypothesis is that copper electrodes are either prepared by potential cycling or anodic pulses gave altered product selectivity at high over potential in CO_2 reduction electrolysis [31–34]. The possible reason could be appropriate sites which can not only activate the C–O bond but also bring down the bond angle are possibly generated only when the oxide layer is thick enough and the kinetics of



f0025 **FIGURE 11.5** Schematic molecular orbital diagram for carbon dioxide.

reduction process is such that there is not much annealing so that surface roughness is retained. The so-called reduction in over potential is feasible only with a particular type of activation of the reactant molecule since mostly activation over voltage is a major component of over potential. It is at this stage still a postulate and further experiments alone will show the exact reason for the reduction in over potentials for surfaces generated from electrochemical reduction of thick oxide layers.

p0100 At this stage, it is necessary that one deals with the activation of carbon dioxide on metallic surfaces. Even though one can visualize associative adsorption of CO_2 with either carbon, oxygen or mixed centers on single or multiple sites, the most probable mode of adsorption would be a dissociative adsorption involving a CO_{ads} type species. This species if desorbed as such gives the fuel precursor and if this species undergoes further hydrogenation with the hydrogen evolved from water then accounts for the other observed products like hydrocarbons and alcohols. Therefore, the essential concept of activation of CO_2 has to be formulated. This requires a description of the molecular orbitals of CO_2. The essential orbitals contributing to the molecular orbitals are the 2s and 2p orbitals of carbon and oxygen. The three 1s obitals of carbon and two oxygen atoms remain basically unchanged in the molecule and are designated as $1\sigma_g$, $2\sigma_g$, and $1\sigma_{u.}$ The 2s and $2p_x$ orbitals of carbon and oxygen directed along the molecular axis give rise to $3\sigma_g$, $4\sigma_g$, $5\sigma_g$, and $2\sigma_u$, $3\sigma_u$, and $4\sigma_{u.}$ The $2p_y$ and $2p_z$ give rise to three doubly degenerate π orbitals designated as $1\pi_g$, $1\pi_u$, and $2\pi_u$. The 22 electrons in CO_2 are distributed, 6 in core σ orbitals arising from 1s levels and the remaining 16 are distributed in 4 sigma orbitals and 2 doubly degenerate Pi orbitals. The highest occupied molecular orbital is $1\pi_g$ and the lowest unoccupied molecular orbital is $2\pi_u$ 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 the degeneracies of these orbitals are lifted. This is normal since the charge density in the π orbitals is concentrated between the two bonding centers in a lateral disposition. The bending of the molecule from linear geometry though affects the degeneracy of $1\pi_u$ and $1\pi_g$, the energy difference between the two split orbitals is not high. However, the degeneracy of $2\pi_u$ is lost and the two resulting orbitals are designated as $2b_1$ which has almost the same energy as in the linear molecule in the bent configuration and the other component is designated as $6a_1$ whose energy falls sharply as compared to that in the linear molecule. Electron occupancy in this molecular orbital can give rise to a bent configuration.

p0105 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, the sites activating these molecules should have a specific geometry and orientation. In the case of carbon dioxide activation, the carbon and one of the oxygen centers of this molecule has to be activated with the bond being not 180^o. This imposes some geometrical restrictions on the site on which carbon dioxide molecule can be activated.

p0110 Though, the reaction $CO_2 + e^- \rightarrow CO_2^- (-1.90\ V)$ is not thermodynamically favorable, the reaction may become probable in the adsorbed configuration wherein the CO_2 is adsorbed on the metallic surfaces by multi-point adsorption. Among the various multipoint adsorption configurations for CO_2, the one involving the carbon and one of the oxygen appears to be probable based on a variety of spectroscopic experimental IR [35], HREELS and XPS [36,37] data which show that this adsorbed species mostly manifest somewhat like adsorbed CO (not in the conventional carbonyl type) species and adsorbed oxygen.

p0115 Several studies have been reported on the activation of carbon dioxide on metallic surfaces. In general, either mixed carbon-oxygen or pure oxygen coordination have been recognized as the probable modes of adsorption 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°.

p0120 It is interesting to refer to the DFT study of carbon dioxide reduction to hydrocarbons on copper surfaces [38]. 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 CH_2O. This study also favors the postulate that CO_2 activation has to take place through carbon and one of the oxygen atoms of carbon dioxide on a site of suitable geometry. 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.

p0125 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_2 and intermediates), surface architecture (roughness, stepped surface, porosity, and defects), surface crystallography (dislocations and vacancies), electronic configurations (s, p, or d metals) has been emphasized. Since this is not easily obtained on many metallic surfaces, the water decomposition and hydrogen evolution reaction predominate on most of the metallic surfaces. Possibly, based on the above parameters only, the metals have been grouped into four classes outlined elsewhere in this article, though as stated the hydrogen overvoltage and CO adsorption strength can also be considered as basis for this classification.

p0130 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. Though there are a variety of adsorption modes, those adsorption modes of carbon dioxide where the bond angle deviates from 180° alone will be able to yield useful products. The path for reduction of carbon dioxide most possibly involves activating both the carbon and one of the oxygen atoms of carbon dioxide and at the same time the adsorption strengths are not strong so that subsequent hydrogenation and desorption of the hydrogenated product is feasible. This can impose some geometrical restrictions on the activation center on metallic surfaces either in the form of some certain exposed planes or presence of stepped sites.

p0135 In aqueous medium, the electrochemical reduction of carbon dioxide involves the oxidation of water at the anode, and the electrons released are 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 water reduction, on most surfaces, hydrogen evolution may predominate over CO_2 reduction so that the catalyst chosen should have high over potential for hydrogen reduction allowing H^+ transfer steps selectively for formation of reduction products of $CO_{2.}$ On most of the metals, hydrogen evolution predominates over the CO_2 reduction reaction. Only on a limited number of metallic surfaces, other reduction products like CO, HCOOH, and hydrocarbons (mostly CH_4, and C_2H_4, and C_2H_6) are formed.

p0140 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 [39–41] in a series of investigations have studied carbon dioxide reduction on copper surfaces in different media to produce with high Faradaic efficiencies for a variety of products like formic acid, methane, ethylene, and carbon monoxide. The surface treatment, physical form, and the method of preparation of copper have profound effect on the electro catalytic properties for the reduction of carbon dioxide. 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 yet been established. Even though CO_2 is reduced on typical (100), (110), and (111) planes of copper, Hori et al. [42,43], 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.

p0145 In the recent past, a variety of alternative options have been examined for carbon dioxide sequestration and utilization [44–49]. At this time which one of these [50] or other processes based on photo-chemical [47,51–58], bio-chemical [59–61], or mediated electrochemical using metal complexes [51,62–65] will become a commercially viable is not clearly known though considerable progress has been made in each of these methodologies. The electrochemical reduction of carbon dioxide can give rise to a variety of products and fuels [5], formation of formic acid [66–73], CO [72,73], methane [74,75], ethylene [68,76], and methanol [77] and these have been shown to be the consistent products in a number of investigations.

p0150 Though, the initial step of activation of carbon dioxide is the formation of anion radical [CO_2^-] [refer to Figure 11.3], other postulates have also been invoked for accounting for the various products observed. Jaramillo et al. [5] have invoked various C_1 adsorbed species (like COOH, CO, CHO, $C(OH)_2$, and HCHO to account for the oxygenated C_2 and C_3 products observed by them. Peterson and Norskov [78] in their attempt to universalize their "volcano"-based analysis proposed that the protonation of the adsorbed CO (possibly to give adsorbed CHO species) is the step which probably accounts for the high over potential normally encountered in the electro-catalytic reduction of CO_2. The relevance of this study lies in the fact that they are capable of proposing strategies like alloying, ligand substitution, tethering, and addition of promoters which will be beneficial for formulating electro-catalytic systems for the reduction of CO_2. There are also other proposed modes of surface activation of CO_2 which could account for the major products that are usually postulated in the electro-catalytic reduction of CO_2. Whatever may be the surface transformations that produce the observed fuels and chemicals, the net (overall or product-wise) meaningful Faradaic efficiencies are observed only at high over potentials. The electrochemical reduction of carbon dioxide can become a viable commercial process only when one can obtain high energy efficiency and high reaction rates. This is possible only when one can realize high selectivity (for a given product) at low over potentials. If the intermediate [CO_2^-] radical anion formation (standard potential of -1.9 V vs. SHE) is essential for the electro-reduction of CO_2, then high over potential is unavoidable. This over potential can be decreased if this intermediate can be stabilized on the catalyst surface and this is possible if the catalyst surface can exhibit non-native configurations which can activate the linear molecule in a bent geometry [3]. This way one may possibly compete with the simultaneous preferential hydrogen evolution reaction. Whipple and Kenis in their perspective article [50] have advocated in addition to the conventional variables like electrolyte, temperature, and reactor design [79–83], a more rational combination of catalysts and electrolytes. Our understanding of electrode-electrolyte interface [83–86] has not reached a mature status so that one will be able to define and reason out the electron transfer at the interface taking into precisely the solvent coordination of the depolarizer. This will be particularly relevant when the electro-reduction of CO_2 is carried out in electrolytes (mostly bicarbonate) where the solubility is limited. Whipple and Kenis [50] have naively pointed out this in terms of limitation of mass transport to the electrode. Hudson [87] has attempted to show a better method of the reduction of CO_2 to methane and methanol at low temperature, high pressures, in mixed supercritical fluid with various electrolytes with modified nanotube Pt surfaces. Though these studies have relevance to the Mars mission, this study may add quality to the life and industry on earth.

p0155 Bocarsly and his coworkers [88–90] have come up with an alternate way of reducing the over potential. The strategy they adopted is pyridinium species catalyzed electro-reduction of CO_2 on Pt and Pd cathodes. The reaction sequence has been proposed to be the inner sphere reaction of pyridinium radical and carbon dioxide to generate surface bound hydroxyl/formyl radical. Their main contention is this mediated reduction can considerably reduce the over potential normally encountered in the electro-reduction of carbon dioxide. The mediated electro-reduction can take place at a potential of -0.72 V which transforms into an over potential of 0.20 V only. One of the results that is worth noting is the bonding interaction of nitrogen of pyridine and carbon dioxide which resulted in a O–C–O bond angle reduction to 124° with the sp hybridized carbon turning to sp^2 hybridized state. This proposal is in conformity with the proposal referred earlier [90]. Another important aspect of this study is the cost estimate of producing methanol by the reduction of CO_2 which indicates a combination of electrochemical and thermal routes may become economical. The team at the University of Gothenburg [91] has claimed that the role of the surface morphology and orientation was important for the reduction of carbon dioxide on copper surfaces. The electrolyte anion determines the orientation of the surface between (111) and (100) orientations, the former being more selective for methane formation, while the later is responsible for the formation of C=C bonds.

p0160 Recently, the application of dynamic potential-pH diagrams to selected electro-catalysts for the oxidation of water has been demonstrated which combined the conventional thermodynamic considerations with the possible kinetic constraints [92]. Similar model may be possible for the electrochemical reduction of carbon dioxide and the generation of such diagrams will provide another possibility for selection of electro-catalysts for the reduction of carbon dioxide.

s0020 11.3.1 Perspective Outlook

p0165 It is necessary at this stage some of the perspectives for the electrochemical reduction of carbon dioxide are considered. If one were to consider the possibility, the electrochemical reduction of carbon dioxide can give rise to a variety of hydrocarbon-based chemicals which can have value either from the point of view of fuel or as chemical. If carbonyl compounds with multiple carbon atoms can be generated by the reduction of carbon dioxide (either electrochemically or photo-catalytically), then the value addition could be achieved even if one does not generate fuels. Electrochemical processes are amenable for selectivity optimization in the form of the applied potential at which the process is carried out. This can be exploited only when the data are generated in terms of current densities with respect to each of the products and not the total current density values that are commonly reported. This calls for the evolution of a methodology for a proper way of expressing this quantity.

p0170 Another aspect in which clarity is required is to define the cell volume in relation to the electrode area and this has to be such that the cell volume is small with smaller dead volume compared to the electrode area. This will ensure that the majority of the products are effectively present in the electrolyte and hence quantitative estimates are available for further scale-up operations.

p0175 The C–C coupled products that are formed in the electrochemical reduction of carbon dioxide are generated from some kind of *enol* form of the C_1 surface species. The possible surface C_1 species envisaged are $-C(OH)=O$, $-CH=O$, $-C(OH)_2$, $-C(OH)$, $-CH_2O$, $-CO$ and these mono-carbon species couple to give rise to C_2 or C_3 oxygenated products [5]. This has to be examined in the context of the postulate that we have outlined before that the initial active species is carbon dioxide anion radical namely $[CO_2^-]$. It is necessary that this aspect is clarified in future studies. These envisaged future studies should keep in mind that some of the products reported so far are oxygenates (mostly carbonyl or hydroxyl compounds) and hence it is possible the C–C coupling reaction will precede the breaking of the C–O bond.

p0180 Even though a variety of products have been reported in the electrochemical reduction of carbon dioxide, many of these species have some detection limits as outlined in ref [5]. If this were to be true, then it is possible that more possible products can emerge from the electrochemical reduction of carbon dioxide and one is necessitated to devise appropriate analytical methods for deducting quantitatively these products.

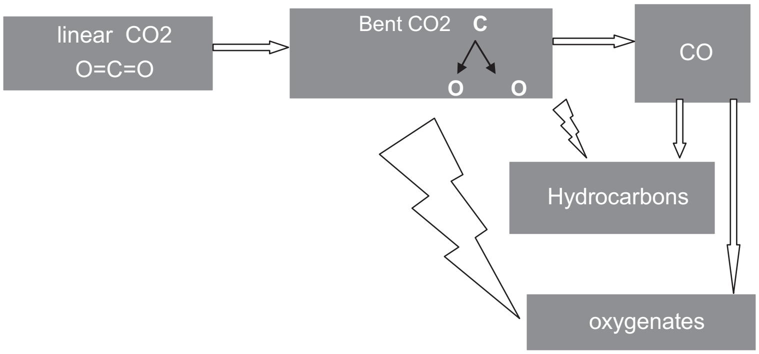
p0185 A recent study [31] has proposed that the copper electrodes prepared from a substrate with limited thickness of oxide layers on reduction resulted in metallic electrodes of considerable roughness and required less over potential than polycrystalline copper electrodes. The cause for the reduction of over potential for the conversion of carbon dioxide has to be established on a scientific basis so that this advantage can be realized on other electrodes as well. It is possible when one possibly generates the required active metallic sites (namely constrained sites so as to activate both oxygen and carbon end of the molecule) from the reduction of certain thickness of the oxide. When bulk oxide is reduced it may not be possible to generate such non-native surface species. This is only a postulate at this stage.

p0190 Peterson and Norskov [78] postulate that effective catalysts must be capable of catalyzing the protonation of adsorbed CO to generate either –CHO or –COH surface species. In addition, they demand for efficient CO_2 reduction catalyst should have poor activity for the simultaneous hydrogen evolution reaction. They have even proposed strategies for the discovery of new catalysts with reduced over potential. Is it possible that this strategy can be subjected to experimental verification?

p0195 The claim that has been repeatedly made [50] in the literature is that the possibility of producing hydrocarbon fuels from CO_2 may alleviate the energy and climate change issues. The veracity of this claim needs to be examined and if this becomes true, what will be the role of electrochemical reduction of CO_2 in the overall picture? In this context, one can refer to the commentary of Maginn [93] that thermodynamics dictates that fuels produced from reduction of CO_2 utilizing renewable energy sources will still be expensive than those produced from fossil fuel sources. If one were to assume that this statement is true, then one will wonder will these efforts in reducing CO_2 are worth the trouble?

p0200 Most of the reports in literature are mainly concerned with the reaction path to account for the production of the various products experimentally observed. It is necessary that the initial activation of carbon dioxide on surfaces has to be considered and this activation step alone may control if the reaction proceeds through the adsorbed CO [78] or the enol intermediates [5] that have been suggested in the literature. The initial step of the activation of carbon dioxide on metallic surfaces under electrochemical conditions possibly has not yet been elucidated. In the classical book by Hayward and Trapnell [94] the ease of formation of adsorbed CO intermediate and the formation of carboxylate type species have been postulated. However, when undissociated CO_2 were to be adsorbed on the surface, then the coverage and the variation of the heat of adsorption with coverage can have significance.

p0205 The postulate that the activation on CO_2 on the surface has to have a particular geometry to be able to undergo subsequent hydrogenation to yield hydrocarbons or oxygenates is pictorially shown in Figure 11.6. The efforts in the future will focus how these processes can be carried out economically and with appropriate selectivity to the desired fuel or chemical. It is possible that one can hope to at least mimic nature in converting carbon dioxide toward value added product. In this connection, Aulice Scibioh and Viswanathan [95] have advocated that carbon dioxide possesses a number of characteristics that suggest that its use can provide both economic and environmental benefits. The electrochemical reduction of carbon dioxide is one such possibility and only time will prove if carbon dioxide is a matter of pollution or profit?



f0030 **FIGURE 11.6** A simplified scheme for the possible routes for the electrochemical reduction of CO_2.

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