

# Chapter 1

## INTRODUCTION

### 1.1 Carbon di oxide Levels

It is generally believed that the global warming that is generally felt in the atmospheric temperature in recent times is due to carbon di oxide emission from the use of fossil fuels. Even though in terms of the value of the heat capacity, carbon dioxide may not be as high value as that of nitrogen oxides or chlorofluoro carbons but still it is considered as the source for the changes in the temperature of the climate the so called greenhouse effect due to the magnitude (amount of) of carbon dioxide emission. The carbon dioxide level in the atmosphere has been increasing over the years and especially after 1950 the increase has been considerable as seen from the data presented in Fig.1 which is reproduced from the data of National Oceanic and Atmospheric Administration (NOAA). Carbon dioxide has thus taken a center stage in the environmental arena in recent years. One of the most alarming global environmental problems of today can be greenhouse effect. This problem is mainly caused by the increased atmospheric CO<sub>2</sub> concentration due to the burning of fossil fuels for power generation and other transport requirements. A response strategy, to reduce the problem of a further increasing greenhouse effect, is to decrease anthropogenic CO<sub>2</sub> emissions, from flue and fuel gases produced in combustion and gasification processes in power plants, by efficiency improvement or CO<sub>2</sub> removal. The removal of CO<sub>2</sub> from these gases is not a major technological problem any more, because many technologies have been developed for this purpose. The real problem in the near future is thus not in which way CO<sub>2</sub> can be removed, but “What to do with the enormous quantity of CO<sub>2</sub>?” This monograph

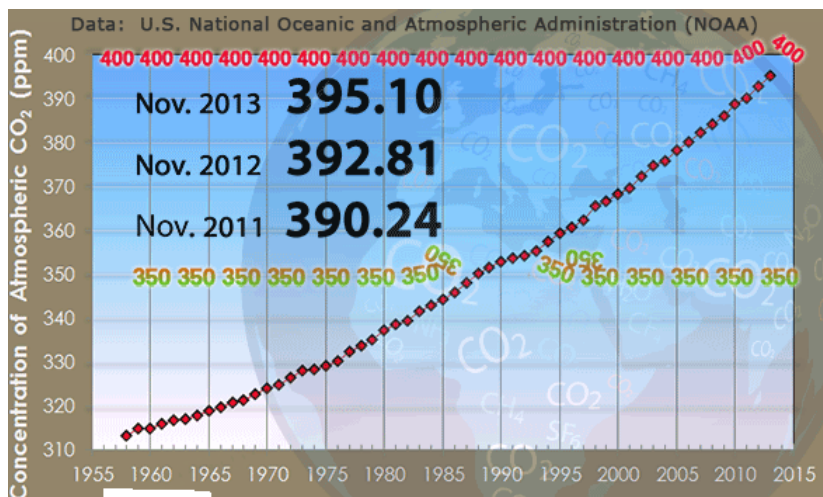


Figure 1.1: The CO<sub>2</sub> level in the atmosphere for the period 1950 to 2013 The figure and data are reproduced from the source data of National Oceanic and Atmospheric Administration (NOAA)

Table 1.1: Main characteristics of CO<sub>2</sub> in relation to other C<sub>1</sub> compounds Reproduced from M.A.Scibioh and B.Viswanathan, Proc.Indn.Natl.Acad.Sci., 70A,(2004)

Factors	CO	COCl <sub>2</sub>	CO <sub>2</sub>
MAK Value	30 ppm	0.1ppm	5000 ppm
Toxicology	affinity for Hemoglobin 210 times that of O <sub>2</sub>	war gas	danger of asphyssiation at 10 vol% in air
Environmental Hazard	Yes	High	Negative
Flammability	12-74 vol%	No	No
Boiling point	81 K	291K	195 K (sublime)
Storage	only atless than 3.5 MPa	difficult	No problem
Transport	Gas bottles or tanks kg quantities	possible	gas bottles or tanks

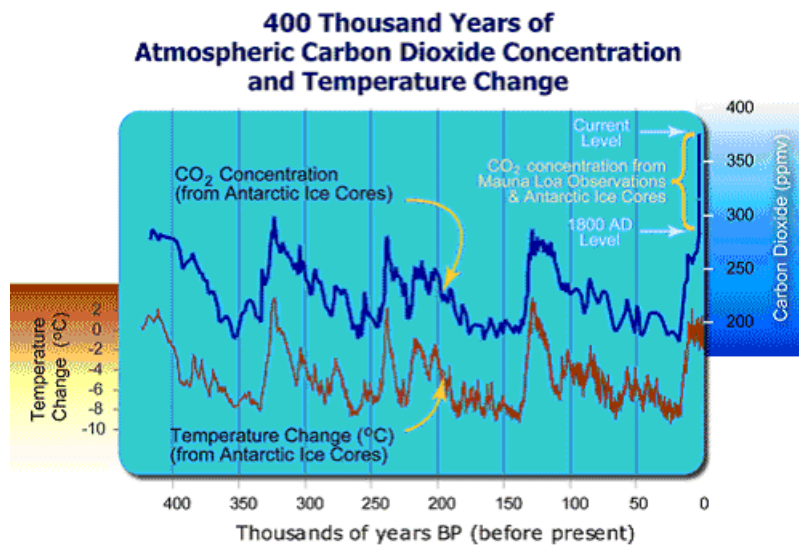


Figure 1.2: Global warming and atmospheric CO<sub>2</sub> concentration

is an attempt to examine some of the possible strategies for fuel and chemical production from CO<sub>2</sub>. While CO<sub>2</sub> is certainly not a panacea any longer, it possesses a number of characteristics that suggest the use of CO<sub>2</sub> could provide both environmental and economic benefit. It is now known and fairly established that so called 'global warming' may become a serious threat to the global environment and human society in this period of the century. Although there exists a lot of unknown factors in the scientific mechanism of warming of the earth and its surroundings and its ultimate and direct consequences (as has been often discussed at various scientific and political fora), the main cause of it is considered to be the anthropogenic emissions of carbon dioxide through combustion of large amount of fossil fuels either for industrial heating purposes or for transportation. Atmospheric CO<sub>2</sub> concentration is now higher than it was at any time in the past 26 million years and is expected to nearly double during this century. Fig.2 depicts the raising levels of atmospheric carbon dioxide and its direct consequence on earths temperature over many centuries. It is clear that in the last 60 years the increase in CO<sub>2</sub> level has been significant and possibly rapid as seen from the expanded graph shown in Fig.1.1. for the period 1950 to 2013. In order to cope with global warming problem, a variety of measures have been proposed and/ or

implemented world wide for preventing, alleviating, or for adapting to warming. Although the effective and economic measures will differ among countries depending on their specific conditions, the reduction of further emissions by decreasing the fossil fuel consumption seems most important as a common policy or one has to devise methods of converting carbon di oxide to fuels and/or useful chemicals. Energy conservation will continue to be an essential way of reducing the consumption of fossil fuels. Considering the possible high growth rate of developing economies, however, this would not be sufficient. We need abundant non-fossil energy sources also to cope with the energy demand and supply problem. Weaning ourselves away from the carbon-based energy economy towards a greater reliance on renewable energy sources holds out some hope for reducing CO<sub>2</sub> emissions. As fossil fuels are depleted and/or global warming becomes severe, renewable energy (solar electric, wind, hydroelectric, geothermal, solar thermal, and biomass) and nuclear energy may become the primary energy sources. Of these future energy sources, only biomass produces fuels directly. Although biomass derived fuels will doubtless contribute to meeting the future fuel requirements, they will not be able to meet a large fraction of future fuel needs. The reduction of CO<sub>2</sub> to methanol, methane, and other carbon-based fuels using renewable energy sources or nuclear energy would provide a future energy distribution system based on high-energy density liquid and gaseous fuels and without any net increase in atmospheric CO<sub>2</sub>. This could have a significant impact on future CO<sub>2</sub> emissions, especially from the transportation sector. Under the looming threat of global climate change and our hunger for cost-effective and environmentally-friendly energy sources, carbon sequestration will allow us to continue the growth of our current fossil fuel-based economy, while facilitating the transition to sustainable energy sources. Carbon sequestration technologies include the capture, storage and long term utilization of carbon dioxide (CO<sub>2</sub>), that dominates the greenhouse emissions associated with global warming. Turning carbon dioxide into a useful feed stock chemical could help to reduce levels of this greenhouse gas in the atmosphere, as well as providing a cheap source of carbon. The transformation of CO<sub>2</sub> into organic substances can be a promising long term objective. It could allow the preparation of fuels or chemicals from a cheap and abundant carbon source. Three strategies are essentially available to us.

1. Prevention. Avoiding the formation of CO<sub>2</sub> by higher efficiency in electricity generation, transmission and use.

Table 1.2: Sectorwise contribution of CO<sub>2</sub> emissions

sector	percent contribution
Land use and forestry	17
Industry	19
Residential and commercial buildings	8
Transportation	13
Power	26
waste and waste water	3

2. Commercial use of CO<sub>2</sub> that is, utilization and conversion
3. Disposal of CO<sub>2</sub>

## 1.2 Man - made CO<sub>2</sub> Emissions

In the global carbon dioxide cycle of nature, generation and absorption of large amounts of carbon dioxide are in perfect equilibrium: 200 Gt C are generated each year by plant and soil respiration and decomposition and the ocean, and they are matched by an equal amount of CO<sub>2</sub> absorbed by plant photosynthesis and by the oceans. Man is disturbing this equilibrium by generating yearly 8 Gt of CO<sub>2</sub>, of which only 4.5 Gt are reabsorbed by nature. 6 of the 8 Gt are caused by electricity generation (1.8 Gt C/yr) and by transportation and industry and domestic use (4.2 Gt C/yr). The data on CO<sub>2</sub> emission levels by sector wise are given in Table.1. The carbon dioxide emission has been from various sources and it is realized that the emission levels of carbon dioxide have been increasing since the beginning of industrial revolution in the middle of the 19th century and an alarming levels of carbon dioxide emission has been predicted in the coming decades. These steep rising levels of carbon dioxide can be correlated with increasing energy consumption from various sources.

Electricity demand is projected to grow at a rate of 1.8% per year. Rapid growth in computers, office equipment, and electrical appliances is partially offset by improved efficiency. Projected natural gas demand grows at a rate of 1.4 % per year, with the most rapid growth for electricity generation and industrial applications.

Projected coal demand grows by 1.7 % annually (based on tonnage)

with over 90 % used for electricity generation. Projected primary energy demand grows at a rate of 1.5 % per year through 2025. Improved equipments and building efficiency moderates energy demand growth. The transportation sector is expected to grow the most rapidly, due to increased personal and freight travel, slow stock turnover, and consumer.

Though, nuclear power and hydro-power do not emit CO<sub>2</sub>, there are other environmental concerns that have to be considered for these technologies. Fossil fuels are often the only available resource in many countries, and the choice of fuel very often depends on the availability and the economics of exploitation and transportation. CO<sub>2</sub> can be reduced by fuel switching: a pulverized coal-fired power plant produces 0.83 kg CO<sub>2</sub> per kWh of electricity generated, whereas this number drops to 0.41 in a natural gas fired combined cycle plant. In the following section, we set to discuss that much more can be done now by using best available technologies, and more by using technologies in the future to prevent the formation of CO<sub>2</sub>, by more efficient utilization of fossil fuels, be it in the combustion process itself, or be it in the transmission and end use of electric energy.

### 3. Prevention: Lower CO<sub>2</sub> Emissions through better technology- CO<sub>2</sub> Prevention in Electricity Generation

Coal has been the most widely used fuel since the beginning of the industrial revolution. Even today 40 % of all electricity is generated from coal, however very often with a very low thermal efficiency around 30 %. It might appear logical to apply the easy solution and to simply switch all coal plants to natural gas. For some countries this is a valid option. But others will have to rely on coal simply because coal is so available, for such a long time yet, and it is so evenly distributed all over the world, and coal is so important for the national economies and foreign exchange balance of giant countries such as China and India, but also Russia and the USA.

Coal, therefore, will remain the most important fuel for electricity generation. Several coal-fired technologies are available today (Pulverized Coal-fired Power Plants, Pressurized Fluidized-bed Combustion), which reach thermal efficiency of 42 - 47 %, and these values has climbed to 50-52% by the year 2010. Best available technologies by then will be steam temperatures of 973 K, and requiring advanced high temperature materials (super alloys) currently only used in gas turbines. The cycle efficiency can be further increased with a working medium other than water (waterammonia mixture).The overall

fuel-to-bus bar efficiency of power plants can be increased by further increasing the top cycle temperature and by raising the cycle efficiency with reheat and/or regenerative features or by using heat exchangers with small temperature differentials and/or high specific heat transfer coefficients. The largest potential and the largest achievements towards high efficiency are offered by natural gas fired combined cycle plants. Since the first introduction of industrial gas turbines in 1939 the inlet temperature has steadily climbed from 823 K to around 1523 K today. There is no reason why this trend should not continue. If the gas turbine gets coupled with a heat recovery steam generator and a steam turbine, then today thermal efficiency of 55 to 58.5% are possible. This number could well have reached values from 62-65% by 2010. By using the reheat concept higher efficiency can be reached without going to higher turbine inlet temperatures. To reach the goal of 65% efficiency by 2010, a combination of the following technologies had been necessary. reheat gas turbine

higher gas temperatures

further advanced high temperature materials and advanced cooling

To sum it up, best available technology will be able to raise the plant efficiency from 30 to 65%.

CO<sub>2</sub> Prevention in Transmission and Distribution

High voltage and medium voltage systems transmit electric energy with losses of about 15% today. Best available technologies in 2010 will have reduced these losses to 10%.

- making more use of transformerless HVDC transmission systems which reduce AC losses by 40-50% - power systems control avoiding losses from local overloads.

CO<sub>2</sub> Prevention in Electricity Consumption

This presents by far the biggest savings potential. Three quarters of electricity load in industry is typically motor-driven. Two thirds of this load is connected with pumps, with ventilation fans, and with compressors for cooling and heating, ventilation and air conditioning. Much of the distributed electrical energy is today simply lost in the electro-mechanical conversion, in mechanical throttling valves and in gear boxes. Power electronics and variable speed drives (VSDs) are key technologies to avoid such energy consuming throttling devices. Many industry categories, e.g. pulp and paper, have already converted from constant-speed 50 or 60 Hz motor systems to variable speed systems based on lowest operating costs. Often the available power can thus be doubled compared with throttled systems, provided the whole system

is optimized and not the motor alone.

#### CO<sub>2</sub> Prevention Potential in Optimized System

Let us assume we combine optimized end use systems making more intelligent use of electric energy, with highest efficient transmission of power, which in itself is generated in the most efficient fossil-fired power plant. If the inefficiently utilized application using inefficiently generated electric power is associated with an amount of 100% CO<sub>2</sub>, then this amount can be brought down to a mere 35% by optimized end use of electricity and use of highest efficient power generation and distribution technology.

We have to move towards a new paradigm which considers whole systems of energy conversion and end use. Traditional electric utilities have to be optimized to generate large amounts of electric energy in the most efficient way. Large industrial users of electric power and independent power producers need to apply this systems approach. Where could all these new technologies bring us to if they were not only available but also applied? Assuming the same energy mix as in 1990 the CO<sub>2</sub> emissions would increase from 1.8 to 3 GtC/year. Applying best available technologies this number can be reduced to 1.47 GtC/year. The best available new technologies can reduce CO<sub>2</sub> emissions from electricity generation and use by 30 to 50 %. 4. Utilization of Carbon Dioxide There are several motivations for producing chemicals from CO<sub>2</sub> whenever possible.

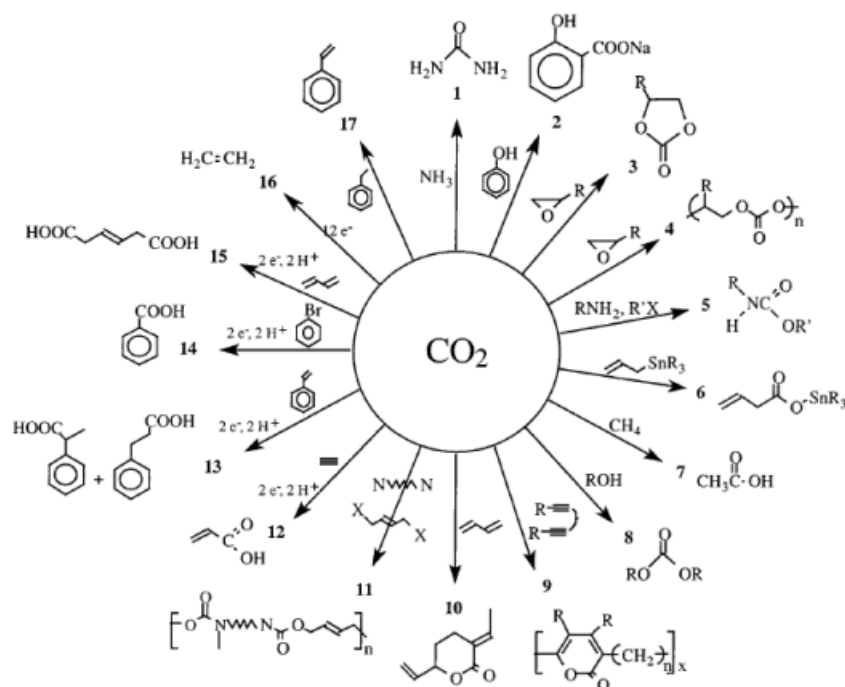
- (1) CO<sub>2</sub> is a cheap, nontoxic feed stock that can frequently replace toxic chemicals such as phosgene or isocyanates.
- (2) CO<sub>2</sub> is a totally renewable feed stock compared to oil or coal.
- (3) The production of chemicals from CO<sub>2</sub> can lead to totally new materials such as polymers.
- (4) New routes to existing chemical intermediates and products could be more efficient and economical than current methods.
- (5) The production of chemicals from CO<sub>2</sub> could have a small but significant positive impact on the global carbon balance.

Carbon dioxide is generally considered to be a green, or environmentally benign, solvent in that it is relatively nontoxic, is nonflammable, and is naturally abundant. As such, CO<sub>2</sub> has been suggested as a sustainable replacement for organic solvents in a number of chemical processes.

#### Production of Chemicals

Approximately 110 MT (megatons) of CO<sub>2</sub> are currently used for chemical synthesis annually. The chemicals synthesized include urea



Figure 1.3: Scheme.1.Chemical Transformations of CO<sub>2</sub>

(1), salicylic acid (2), cyclic carbonates (3), polycarbonates (4) and CO, CH<sub>4</sub> and other C<sub>n</sub> compounds. The largest of these uses is in urea production, which reached approximately 90 million metric tons per year in 1997. In addition to these commercial processes using CO<sub>2</sub> (compounds 1-4 in Scheme 1), there are a number of reactions currently under study in various laboratories that hold promise (remaining reactions in Scheme 1). These reactions differ in the extent to which CO<sub>2</sub> is reduced during the chemical transformation. The simplest reactions of CO<sub>2</sub> are those in which it is simply inserted into an X-H bond. Examples are the insertion of CO<sub>2</sub> into organic amines to afford carbamic acids which may be converted into organic carbamates. More recent examples include the insertion of CO<sub>2</sub> in P-N bonds of P(NR<sub>2</sub>)<sub>3</sub> compounds to form P(NR<sub>2</sub>)(OCONR<sub>2</sub>)<sub>2</sub> compounds and the reaction of ammonium carbamates (derived from CO<sub>2</sub>) with alkyl halides in the presence of crown ethers to form useful urethane intermediates (5). This is an example of using CO<sub>2</sub> to replace phosgene, a highly toxic intermediate in chemical synthesis. Reactions are known in which CO<sub>2</sub> undergoes insertion into Sn-C bonds

of allyl tin compounds to form carboxylated allyl derivatives (6) and which are catalyzed by Pd complexes; these are shown in Scheme 1. Another interesting reaction is the insertion of CO<sub>2</sub> into alkanes such as methane to form acetic acid (7). Although the turnover numbers for this catalytic process are low, the simultaneous activation of a C-H bond and CO<sub>2</sub> insertion is intriguing. The thermodynamics of this reaction are marginal; however, adjusting the reaction conditions and coupling this reaction with energetically favorable product processes could improve conversion efficiency. Carbonates, (RO)<sub>2</sub>CO (8), can also be prepared by inserting CO<sub>2</sub> into O-H bonds followed by dehydration or by oxidative carboxylation of olefins. This synthetic approach has the possibility of providing a new route to compounds that have very large potential markets. Related reactions in which CO<sub>2</sub> is incorporated into product molecules without reduction have been used in the synthesis of polymers. A number of new catalysts have been developed for copolymerization of CO<sub>2</sub> and oxiranes to form polycarbonates (4); These studies have increased the productivity of this reaction by 10<sup>2</sup> times and have also expanded the range of applicable monomers (oxiranes). Another potentially interesting new class of polymers, polypyrones (9, Scheme 1), has been prepared from diacetylenes and CO<sub>2</sub> in the presence of Ni catalysts. A related reaction is the telomerization of butadiene and CO<sub>2</sub> to produce lactones (10), which can be important chemical intermediates. Polyurethanes (11) have also been prepared by the reactions of dicarbamate ions formed by insertion of CO<sub>2</sub> into diamines, followed by Pd-catalyzed coupling to 1,4-dichloro-2-butene. Reductive carboxylations in which the CO<sub>2</sub> unit is incorporated into the product are also known. In the case of alkynes and olefins, electrochemical reductive carboxylations result in effective addition of the formic acid C-H bond to C-C double or triple bonds. For example, Ni bipyridine complexes and sacrificial Mg anodes have been employed to reductively couple acetylene and CO<sub>2</sub> to form propenic acid (12). Similarly, the reductive coupling of CO<sub>2</sub> with styrene (13) is catalyzed by benzonitrile. Bromoarenes can also be reductively carboxylated to form the corresponding carboxylic acid (14) using Ni diphosphine catalysts. More recently, the sequential reductive coupling of two molecules of CO<sub>2</sub> to butadiene to form 3-hexen-1,6-dioic acid has been reported (15). This approach provides a new route to a Nylon precursor. Another important monomer, ethylene (16), can be prepared by electrochemical reduction of CO<sub>2</sub> in aqueous solutions with current efficiencies as high as 48%. The production of

this monomer by this remarkable 12-electron reduction offers a potential route to polyethylene from CO<sub>2</sub>. The preceding results indicate that it may be possible to produce a large variety of polymers in the future using materials derived from CO<sub>2</sub>. Under oxidative conditions, CO<sub>2</sub> may react with olefins to afford cyclic carbonates that find wide industrial applications. Heterogeneous catalysts are currently more promising than homogeneous ones in these transformations. Another potentially useful reaction of CO<sub>2</sub> is the dehydrogenation of hydrocarbons. Examples are the dehydrogenation of ethylbenzene and propane over metal oxides to form styrene (17) and propene, respectively. In these reactions, no part of the CO<sub>2</sub> molecule is incorporated into the organic product, rather the oxygen of CO<sub>2</sub> serves to remove two H atoms of the hydrocarbon. This reaction is at the opposite extreme of the simple insertion reactions discussed.

#### Production of Fuels

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 fuels are currently made by the reduction of CO<sub>2</sub>. This is because the electricity and hydrogen produced today are largely derived from fossil fuels which produce large amounts of CO<sub>2</sub>. Renewable energy sources and nuclear energy do not produce CO<sub>2</sub>, and therefore, production of fuels from these sources would provide fuels but not contribute to net CO<sub>2</sub> emissions. The following reactions show CO<sub>2</sub> reduction reactions in which energy in the form of electricity or hydrogen, derived from nuclear or renewable resources, is stored as either liquid or gaseous carbon based fuels ( $\Delta E^0$  and  $\Delta G^0$  values are for 298 K). The high energy density of these fuels and their transportability makes them desirable; however, the energy required to produce these fuels must be minimized to ensure efficient use of renewable and nuclear energy sources. In general, entropy considerations suggest that these energy storage reactions are best carried out at low temperatures to reduce the free energy required. Both hydrogenation reactions and corresponding electrochemical reactions are shown in equations below. In the electrochemical reactions, CO<sub>2</sub> is reduced at the cathode and O<sub>2</sub> is produced at the anode. These electrochemical reactions may be considered as the sum of the corresponding hydrogenation reactions and the water splitting reaction.

	$\Delta E^0$	$\Delta G^0$ (Kcal/mol)
$\text{H}_2\text{O} \rightarrow \text{H}_2(\text{g}) + 0.5\text{O}_2(\text{g})$	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

### 1.3 Hydrogenation Reactions

$\text{CO}_2$  is currently used as an additive in the synthesis of methanol from CO and  $\text{H}_2$ , and it is believed that reduced forms of  $\text{CO}_2$  are kinetically important intermediates in this process. The thermodynamics for methanol production from  $\text{H}_2$  and  $\text{CO}_2$  are not as favorable as that for production of methanol from  $\text{H}_2$  and CO. For instance, at 473 K the equilibrium yield of methanol from  $\text{CO}_2$  is slightly less than 40 % while the yield from CO is greater than 80%. The reduction of  $\text{CO}_2$  is rendered favorable by the use of hybrid catalysts that dehydrate methanol to form dimethyl ether. Ethanol has also been produced by the hydrogenation of  $\text{CO}_2$ . This fuel is attractive because it has a slightly higher energy density than methanol and it is not as toxic. However, the selectivity for ethanol production is generally low (less than 40%). The hydrogenation of  $\text{CO}_2$  to methane and higher hydrocarbons is also known. For  $\text{C}_2$  and higher hydrocarbons, hybrid catalysts such as Cu-ZnO- $\text{Cr}_2\text{O}_3$  and H-Y zeolite are generally used. Catalytic synthesis of formic acid derivatives by  $\text{CO}_2$  hydrogenation, together with other substrates, in supercritical  $\text{CO}_2$  is also known.

### 1.4 Electrochemical Reduction of $\text{CO}_2$

Carbon dioxide reduction at a number of metal electrodes has been investigated, and Cu electrodes were found to catalyze  $\text{CO}_2$  reduction to methane in bicarbonate solutions with current efficiencies as high as 65%. Although over potentials are large (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. Cu electrodes have been studied extensively to gain insight into the mechanism, which is thought 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. Copper oxides on gas diffusion electrodes at large negative potentials have also been reported to reduce CO<sub>2</sub> to ethanol. Homogeneous electro-catalysts typically catalyze CO<sub>2</sub> reduction by two electrons to either formate or CO together with H<sub>2</sub> formation. However, for some catalysts, CO<sub>2</sub> reduction occurs with current efficiency 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, and CO<sub>2</sub> is reduced to CO in 0.02M HBF<sub>4</sub> in dimethylformamide solutions with current efficiencies greater than 95%. In addition, some of these catalysts operate at low over potentials 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 metallocarboxylic 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 2. It is unusual for homogeneous catalysts to form reduction products that require more than two electrons. However, it has been reported that 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). Although turnover numbers were not given for these highly reduced species, their formation raises the exciting possibility that a single-site catalyst can result in multielectron reductions of CO<sub>2</sub> and even C-C bond formation. The relatively mild conditions and low over po-

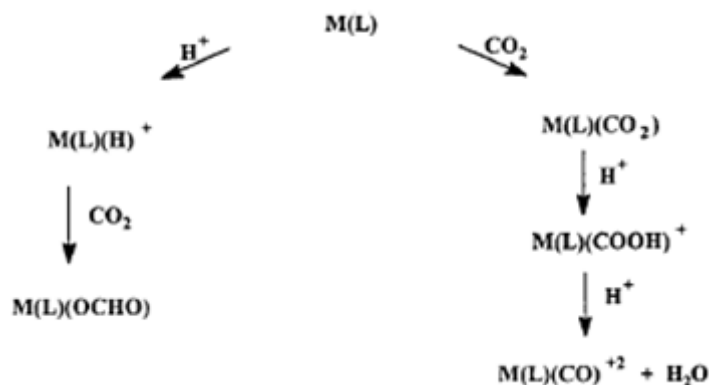


Figure 1.4: Scheme 2: Possible Pathways for the Competing Interaction of Low-Valent Catalysts with Protons or  $\text{CO}_2$

tentials required for some of the homogeneous catalysts make them attractive for future studies; however, a number of barriers must be overcome before useful catalysts are available for fuel production.

## 1.5 Photochemical Reduction of $\text{CO}_2$

Many of the reactions described rely on energy input either in the form of reactive bonds (alkenes, alkynes,), hydrogen, or electricity. Photochemical systems, been studied in an effort to develop systems capable of directly reducing  $\text{CO}_2$  to fuels or chemicals using solar energy. Transition-metal complexes have been used as both catalysts and solar energy converters, since they can absorb a significant portion of the solar spectrum, have long-lived excited states, are able to promote the activation of small molecules, and are robust. Carbon dioxide utilization by artificial photo-conversion presents a challenging alternative to thermal hydrogenation reactions which require  $\text{H}_2$ . The systems studied for photochemical  $\text{CO}_2$  reduction studies can be divided into several groups:  $\text{Ru}(\text{bpy})_3^{2+}$  both as a photosensitizer and a catalyst;  $\text{Ru}(\text{bpy})_3^{2+}$  as a photosensitizer and another metal complex as a catalyst;  $\text{ReX}(\text{CO})_3(\text{bpy})$  or a similar complex as a photosensitizer;  $\text{Ru}(\text{bpy})_3^{2+}$  and  $\text{Ru}(\text{bpy})_3^{2+}$ -type complexes as photosensitizers in microheterogeneous systems; metalloporphyrins both as a photosensitizers and catalysts; and organic photosensitizers and transition-metal complexes as catalysts. Photochemical  $\text{CO}_2$  reduction is normally car-

ried out under 1.0 atm CO<sub>2</sub> at room temperature. Therefore, the concentration of dissolved CO<sub>2</sub> in the solution is low (e.g., 0.28 M in CH<sub>3</sub>CN, 0.03 M in water). These systems produce formate and CO as products. In the most efficient systems, the total quantum yield for all reduced products reaches 40%. In some cases with Ru or Os colloids, CH<sub>4</sub> is produced with a low quantum yield. Under photochemical conditions, the turnover number and the turnover frequency are dependent on irradiation wavelength, light intensity, irradiation time, and catalyst concentration, and they have not been optimized in most of the photochemical experiments described. Typical turnover frequencies for CO or HCOO<sup>-</sup> are between 1 and 10 h<sup>-1</sup>, and turnover numbers are generally 100 or less. The aforementioned molecular sensitizers can be replaced with semiconductor electrodes or particles to achieve light harvesting. These systems may use enzymes or catalysts to promote electron transfer from the semiconductor-solution interface to CO<sub>2</sub> or reduce CO<sub>2</sub> directly. Typically these reduction requires a potential bias in addition to solar energy input to achieve CO<sub>2</sub> reduction and electrode corrosion is a major concern. This corrosion can sometimes be overcome using high CO<sub>2</sub> pressures.

## 1.6 Chemistry in Super-critical CO<sub>2</sub>

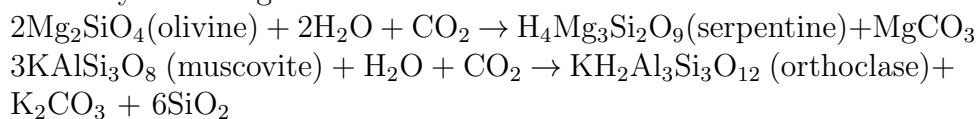
In this section we shall deal with super-critical CO<sub>2</sub> as a reaction medium and Green CO<sub>2</sub> Chemistry.

As noted above, CO<sub>2</sub> is generally considered to be a green or environmentally benign solvent and is naturally abundant. CO<sub>2</sub> has been suggested as a sustainable replacement for organic solvents in a number of chemical processes and is currently used in the extraction of caffeine, in dry cleaning, and in parts degreasing. The nontoxic nature of CO<sub>2</sub> has a number of advantages. For example, in food and pharmaceutical applications, use of CO<sub>2</sub> greatly reduces future liability costs and can also facilitate regulatory approval of certain processes. An example is the conversion of pharmaceuticals into nanometer-size particles for injectable uses. Another instance in which supercritical carbon dioxide could be advantageous is in situations involving contact between hydrophilic and hydrophobic solvents. In this case, the mutual solubility of the two phases is designed to be small. However, some cross-contamination is inevitable, typically leading to a costly remediation. The use of CO<sub>2</sub> as the hydrophobic phase produces con-

tamination that is both benign and readily reversible. Examples include liquid-liquid extraction between organic and aqueous phases as well as emulsion polymerization of water-soluble monomers. In applications where emissions are unavoidable, CO<sub>2</sub> is relatively benign to the environment. Examples range from use of CO<sub>2</sub> in enhanced oil recovery to use as a foaming agent or as the solvent in dry cleaning. Using supercritical CO<sub>2</sub> as a solvent also has advantages that arise from chemical and/or physical properties. In reactions involving gaseous reactants in liquid phases, the use of supercritical CO<sub>2</sub> with its ability to dissolve large amounts of most gases could allow kinetic control of reactions as opposed to limiting of reaction rates by the transport of the gaseous reactant across the gas-liquid interface. In reactions where CO<sub>2</sub> is a reagent, its use as a solvent would also favor the reaction. Carbon dioxide may also offer advantages in reactions such as free-radical polymerization and oxidation where a chemically inert solvent is required.

## 1.7 Carbon Dioxide Fixation by Inorganic Materials

The reaction of CaCO<sub>3</sub> and CO<sub>2</sub> in water to form Ca(HCO<sub>3</sub>)<sub>2</sub> is responsible for the fixation of large quantities of CO<sub>2</sub> in the oceans. However, it is kinetically slow. Similarly, CO<sub>2</sub> can also be fixed by naturally occurring minerals as shown below.



Although the reactions are thermodynamically favorable, they are slow and would need to be enhanced kinetically before they could contribute significantly to adjusting the carbon balance. Furthermore, this would generally require mining and processing large amounts of materials to store relatively little CO<sub>2</sub>. Currently, large quantities of CaCO<sub>3</sub> are converted into CaO and CO<sub>2</sub> (which is released into the atmosphere) in cement manufacture. If a natural ore could be substituted for CaO, a significant release of CO<sub>2</sub> into the atmosphere could, in principle, be avoided.



## 1.8 Barriers for Further Progress

In spite of tremendous research efforts in capture, conversion and utilization of carbon dioxide, why then we have not accomplished sufficient outputs or what are the areas that set barriers? At the outset, social, economic, and technical barriers all exist to utilizing CO<sub>2</sub> as a feed stock to produce fuels and chemicals. To make decisions on potential ways to address this issue, information is needed concerning

- (1) the magnitude of environmental consequences,
  - (2) the economic costs of these consequences,
  - (3) options available that could help avoid or diminish the damage to our environment and the economy
  - (4) the environmental and economic consequences for each of these options
  - (5) an estimate of cost for developing the technology to implement these options
- and (6) a complete energy balance which accounts for energy demanding steps and their costs.

These are to state on broad basis but a few. Economic barriers to CO<sub>2</sub> utilization can be associated with introduction of new products, the properties of which are unknown, introduction of new processes for existing products, and lack of complete life-cycle analyses for production of many chemicals. Polycarbonate polymers produced by copolymerization of epoxides and CO<sub>2</sub> are examples of new products. As catalysts for these reactions improve, focus is shifting from the technical obstacles associated with production to potential markets for these new materials. The situation is not unlike that encountered with the first production of polymers that are currently used on large scales. Similarly, if alternative processes to produce existing products are found, introduction may be slow due to the large capital investments already made in current processes. For example, direct hydrocarboxylation of butadiene to adipic acid or production of polyurethanes from carbamates (both derived from CO<sub>2</sub>) could be economically and environmentally attractive. However, these processes may not be commercialized because of competition with existing processes which have incurred large capital investments. Finally, methods must be developed that allow complete life-cycle analyses of competing synthetic strategies. Analyses must include economic and environmental costs as well as the conservation of materials. It is possible that a process using CO<sub>2</sub> as a feed stock could actually produce more CO<sub>2</sub> than

one not using CO<sub>2</sub>. Full life cycle analyses should permit quantitative evaluation of how much CO<sub>2</sub> is avoided by one process versus another. These analyses must also include the possibility of replacing fossil energy sources with non-fossil sources. For fuels production, the availability of electrical energy or a source of H<sub>2</sub> is critical. Electricity can be produced from either nuclear or renewable energy sources, and the electrolysis of water using this electrical energy could produce H<sub>2</sub> from a non-fossil source. For the purpose of illustrating the potential of renewable energy sources, it is estimated that a 10% conversion efficiency of solar energy to methanol could produce one giga ton of methanol using a vast area. The theoretical efficiency of a single band-gap solar cell is 33%, and higher efficiency is possible with stacked cells having different band gaps. For example, solar energy conversion efficiency of 30% have been obtained with dual band gap cells, and single band-gap devices have been reported with 25% conversion efficiency. If CO<sub>2</sub> could be reduced to fuels such as methanol and methane with 75% energy conversion efficiency, ultimate solar energy conversion efficiency in the 15-25% range are not unrealistic. The crucial question lies in identifying materials, catalysts, and processing conditions that will afford these high conversion efficiency economically since there are no fundamental thermodynamic barriers. However, there are significant issues involving how to account for the cost of H<sub>2</sub>, the energy required to produce H<sub>2</sub>, and the acceptance of nuclear energy. Significant barriers exist in every area of CO<sub>2</sub> utilization. For the synthesis of fuels and chemicals, many barriers are common and progress will require a better understanding of reaction mechanisms, thermodynamics of reaction intermediates, and structure-reactivity relationships. Reactions of CO<sub>2</sub> that must be better understood include C-C, C-H, and C-X bond formation and C-O bond cleavage reactions. For example, formation of C-C bonds between olefins + CO<sub>2</sub> and alkynes + CO<sub>2</sub> appears to involve initial alkene or alkyne coordination followed by CO<sub>2</sub> attack at an activated carbon atom. These reactions are effective for a variety of applications. However, for HOCH<sub>2</sub>COOH formation, CO<sub>2</sub> coordination and reduction to a hydroxyl methyl ligand (CH<sub>2</sub>OH) is proposed to precede C-C bond formation. The coordination site requirements in various CO<sub>2</sub> transformations are also poorly understood, and systematic studies of this important mechanistic aspect are needed. Insertion of CO<sub>2</sub> into M-H bonds occurs via an associative pathway in which hydride directly attacks the CO<sub>2</sub> carbon atom as an M-O bond forms and the M-H bond is cleaved. This reaction may

be accelerated by a vacant coordination site as in olefin insertion reactions; however, data are not available on this point. During many catalytic cycles, M-H or M-C bonds are formed; however, thermodynamic data for their homolytic or heterolytic cleavage are generally not available. Such data would be useful in designing new catalytic processes. The cleavage of C-O bonds as  $\text{CO}_2$  is reduced is also not well understood. During  $\text{CO}_2$  electrochemical reduction to CO mediated by Pd catalysts, a vacant coordination site facilitates the C-O bond cleavage. This cleavage occurs via migration of a water molecule or hydroxide ion from a metal carboxylate carbon atom to a vacant coordination site on the metal. In other C-O bond cleavage reactions, formation of  $\text{MC(O)OM}$  linkages or one electron M-COOH reduction appears to facilitate C-O bond cleavage. The energetic differences between possible pathways are not understood and could be clarified by theoretical calculations. In many instances,  $\text{CO}_2$  binding occurs via bonds to both the  $\text{CO}_2$  carbon and oxygen atoms. The role of such cooperative interactions is not well understood, and systematic studies should be informative. Factors controlling regio- and stereoselectivity of metal-centered  $\text{CO}_2$  transformations are also ill defined. These may be important in polymer synthesis using propylene oxide and related monomers in analogy to propene polymerization. Likewise, chain transfer reagents to control polymer molecular weights are also needed. Catalysts with higher turnover frequencies than currently available are needed. Finally, extension of successes in polycarbonate synthesis to polyesters from olefins and  $\text{CO}_2$  is an attractive goal. Regarding heterogeneous  $\text{CO}_2$  hydrogenation catalysis, the principal barriers are poor product selectivity and unacceptably high reaction temperatures. Thus, in ethanol production by  $\text{CO}_2$  hydrogenation, ethanol is generally one component of a mixture of alcohols and hydrocarbons, and more selective catalysts are needed. Catalysts capable of operating at lower reaction temperatures for hydrogenating  $\text{CO}_2$  to methanol are also needed. Current catalysts operate at around 523 K and the thermodynamics for  $\text{CO}_2$  to methanol conversion are entropically unfavorable (and enthalpically favorable). At lower temperatures, the equilibrium concentration of methanol is higher, which would lead to higher conversion per pass and more efficient operation. Homogeneous hydrogenation catalysts typically catalyze the reduction of  $\text{CO}_2$  to formate-based products. Catalysts capable of reductions beyond the formate level are desirable for more useful products. Electrocatalysts for  $\text{CO}_2$  reduction would permit the conversion of electrical

energy to fuels in a single step, but many barriers exist. Heterogeneous electrocatalysts are needed that operate at lower over potentials with higher selectivity. Although Cu electrodes catalyze  $\text{CO}_2$  reduction to methane, comparable catalysts for producing methanol are unknown. Methanol production has been reported at Mo electrodes but selectivity and current densities are very low, typically less than 40% and 1 ma/cm<sup>2</sup>, respectively. Similarly, homogeneous catalysts possessing all of the desired properties for  $\text{CO}_2$  reduction are not known. Fast, selective, and energy-efficient homogeneous electrocatalysts are known for reducing  $\text{CO}_2$  to CO but are unstable. Other catalysts operate at unacceptably large over potentials, require Hg electrodes, or have low catalytic rates. Additionally, rapid and efficient homogeneous catalysts for catalyzing  $\text{CO}_2$  reduction by more than two electrons are not known. Better understanding is needed of the requirements for reducing  $\text{CO}_2$  beyond formate and CO in either a single or sequential steps. Photochemical processes offer an attractive approach to  $\text{CO}_2$  reduction using sunlight. However, significant obstacles exist such as the requirement of expensive sacrificial reagents, rather than water, to quench the sensitizer and to provide the thermodynamic driving force for  $\text{CO}_2$  reduction. Also, sensitizers more completely using the solar spectrum are desired. Direct photochemical reactions of  $\text{CO}_2$  complexes are rare and offer the possibility of coupling  $\text{CO}_2$  reduction to O atom transfer; such reactions have yet to be demonstrated. Regarding supercritical  $\text{CO}_2$  utilization, understanding the binary and ternary phase behavior of  $\text{CO}_2$ -substrate-reactant systems is needed to conduct reactions under the most favorable temperature and pressure conditions (i.e., to generate the number of phases and phase compositions desired). Most catalytic reactions studied to date have not utilized catalysts specifically designed to operate in supercritical  $\text{CO}_2$ . This led to solubility problems and use of catalysts not capitalizing on the properties of supercritical  $\text{CO}_2$ .

### 6. Promising Research Directions

Future research objectives should be to overcome the knowledge barriers identified above and to provide a better understanding of  $\text{CO}_2$  chemistry and fundamental reaction processes.

1. The production of chemicals and fuels from  $\text{CO}_2$  would be significantly enhanced by fundamental studies of the kinetics and thermodynamics of catalytically relevant C-H, C-X, M-H, M-X, and M-C bond-forming and cleavage reactions.
2. Increased use of  $\text{CO}_2$  as a replacement for phosgene is another attractive goal.

3. Catalysts that facilitate carboxylation of saturated and unsaturated hydrocarbons are another important objective.
4. Biomimetic studies of CO and formate dehydrogenase and methanogenic enzymes are relatively unexplored areas.
5. New catalysts for epoxide and olefin + CO<sub>2</sub> copolymerization are needed that are less sensitive to water and oxygen, more active, and more stereoselective.
6. Chain transfer reagents for such reactions are also needed.
7. Catalysts for formation of polyurethanes and polyesters using CO<sub>2</sub> as a monomer would also be desirable.
8. Heterogeneous catalysts that are more selective and active must be developed.
9. In situ techniques that lead to better structural characterization of catalytic intermediates are also needed. Specifically modified surfaces to improve selectivity and surfaces modified with single-site catalysts are important areas for future development.
10. In photochemical and electrochemical CO<sub>2</sub> reduction, protons are the ultimate source of product H atoms. A better understanding of features promoting selective reactions with either CO<sub>2</sub> or protons is needed. Similarly, a better understanding of factors controlling formate versus CO production is needed as well as how they relate to ultimate methanol or methane production.
11. New approaches to reduce CO<sub>2</sub> by six or eight electrons with high selectivity and low over potentials are required.
12. Better understanding of C-C bond-forming reactions is necessary to design catalysts that selectively produce ethanol or ethylene. First-row transition-metal catalysts and water soluble catalysts will be important in reducing costs and in lowering resistive losses, respectively.
13. Flash photolysis and pulsed radiolysis experiments coupled with time-resolved spectroscopy offers fundamental information on transient intermediates. CO<sub>2</sub> complex photo-activation represents a possible route to C-O bond cleavage coupled with O-atom transfer.
14. Supercritical CO<sub>2</sub> is a relatively inert solvent for hydrogenations, oxidations, carbonylations, polymerizations, electrophilic reactions, and activation of small molecules. The study of catalysts designed specifically for use in supercritical CO<sub>2</sub> is important for understanding reactions in this medium and factors influencing regio- and enantioselectivity. The ability to predict ternary and quaternary phase behavior would also significantly enhance development of this field.

15. Heterogeneous catalysis in supercritical CO<sub>2</sub> has received relatively little attention, although initial results using surfactants, micelles, and emulsions are promising. While CO<sub>2</sub> is certainly not a panacea, it possesses a number of characteristics that suggest the use of CO<sub>2</sub> could provide both environmental and economic benefit!

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