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CO_2 as A Fuel and Chemical Feedstock

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Abstract
CO_2 is utilized by nature to produce innumerable substances consumed by living beings. With growing concerns regarding global warming and increase of the temperature at an alarming rate, it is essential to recycle CO_2 present in the atmosphere. CO_2 emission can be minimized both directly and by abridging the use of fossil fuels. Chemical conversion of CO_2 to fuels serves as a captivating technology for converting large quantities of CO_2 into usable chemicals. Conversion of CO_2 into value-added chemical feedstock and intermediates is possible due to electrochemical conversion.

Keywords: CO_2, Chemical Feedstock, Global Warming, Electrochemical Conversion

1. Introduction
Carbon dioxide can be used or recycled as a fuel or chemical feedstock. CO_2 being an inert molecule must be made reactive by supplying energy externally. Renewable energy should be used as it employs environmentally friendly possibilities for storing energy, producing methane, methanol and liquid fuels etc. Atmospheric carbon dioxide is an abundant (750 billion tons of carbon in the atmosphere) but dilute source of carbon (only 0.036% by volume) which can be sequestrated and utilized. The net emancipation of 36.1 billion metric tons of carbon dioxide added to the atmosphere annually is massive as compared to 110 million tons of CO_2 used to produce chemicals like urea, salicylic acid, cyclic carbonates, and polycarbonates. There would be an increase in the utilization of CO_2 as a starting material as it is an inexpensive, nontoxic starting material. Creation of new materials and markets for them will increase this utilization, producing an increasingly positive, albeit relatively small, impact on global CO_2 levels. Phosgene as a starting material for manufacturing of “Urea” is replaced by CO_2.

2. Current Uses of Carbon Dioxide
Synthesis of urea involves the maximum use of carbon dioxide in organic synthesis. Urea, CO $(NH_2)_2$, is an important nitrogen fertilizer. Also it is an intermediate in organic synthesis melamine and urea resins, which are used as adhesives and bonding agents. Ethylene and propylene carbonates are used widely in various chemical synthesis. They react with ammonia and amines to form carbamates and subsequently reactions with diamines to yield di-hydroxyethyl carbamates, which may react further with urea to form polyurethanes.

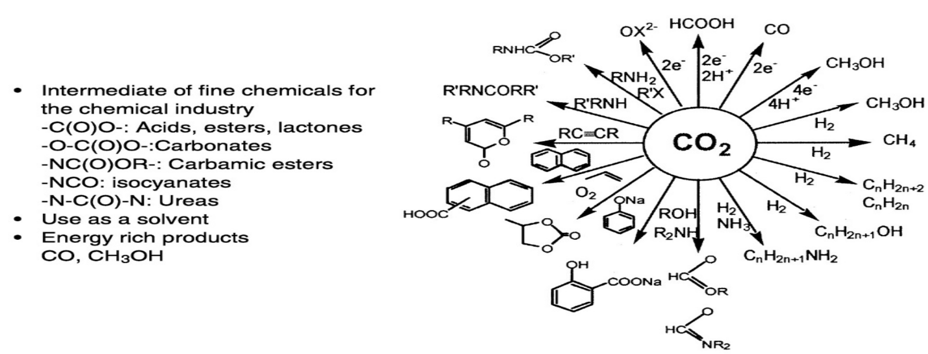

Fig 1: Utilization of CO_2 in synthetic chemistry. [Aresta].

3. Carbon Dioxide as a Solvent

Supercritical carbon dioxide is a hydrophobic solvent which replaces organic solvents. Its critical temperature is 31 °C. It has very low viscosity. Carbon dioxide when substituted for an organic solvent, solvent costs and emission of toxic organics are minimized. By changing the carbon dioxide pressure separation of the products and catalyst can be controlled easily. Currently, supercritical carbon dioxide is used in manufacture of dimethyl carbonate, caffeine extraction, dry cleaning, and parts degreasing.

4. Reactivity of Carbon Dioxide

Carbon dioxide is a linear molecule in which the oxygen atoms are weak Lewis bases and the carbon atom is an electrophile. Reactions of carbon dioxide are dominated by nucleophilic attacks at the carbon atom, which result in bending of the O—C—O angle to about 120°. Figure 2 illustrates three different nucleophilic reactions: hydroxide attack on CO_2 to form bicarbonate; addition of ammonia to CO_2 to give urea, the addition of an electron to CO_2 to yield the carbon dioxide radical ion.

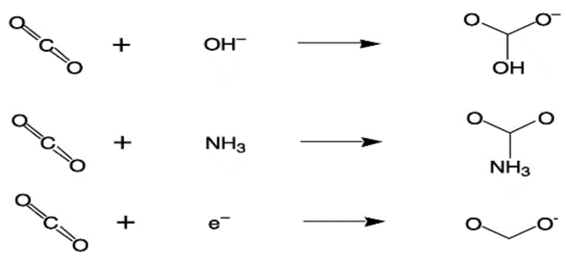

Fig 2: Reactions of carbon dioxide are dominated by nucleophilic attacks at the carbon atom.

5. Thermodynamic Barriers To Co₂ Utilization

Carbon dioxide is a very stable molecule, hence energy must be supplied to make it unstable (reactive). High temperatures, reactive reagents, electricity or the energy from photons may be exploited to carry out carbon dioxide reactions. Methane is produced from CO_2 by electrochemical reduction. Reduction may also be accomplished photochemically by utilizing a dye to absorb visible light, since CO_2 itself does not. Table 1 represents the values of Enthalpy, Entropy & Gibbs free energy for various compounds formed using CO_2 at a 298 K (25 °C).

Table 1: Thermodynamic feasibility of compounds from CO_2

Compound	Reaction Temperature (K)	ΔH° (kJ/mol)	ΔS° (kJ/mol-K)	ΔG° (kJ/mol)
Methane	616	-253.0	-0.410	-130.7
Methanol	320	-131.0	-0.409	-9.1
Urea	315	-133.6	-0.424	-7.2
Dimethyl Carbonate	573	22.59	0.077539	-0.52

6. Conversion of Carbon Dioxide to Fuels

6.1 Hydrogenation

Carbon dioxide can be converted to fuels by reduction to methanol or methane. Energy required for it can be supplied from renewable sources. Fossil fuels have a dominant position globally due to the high energy density of carbon-based fuels and their availability as either gases, liquids, or solids. The value of a fuel is based on its energy content and its ease of transport and storage. Thus, methane is less desirable than methanol because of its low fuel density and high cost of transport. Carbon dioxide is a by-product of fuel use, not a feedstock for fuel production. Conversion of CO_2 to fuels like Methanol, Ethanol, DME, DMC etc., using renewable or nuclear power produces no net emission of carbon dioxide (excluding CO_2 produced by energy consumption in the reduction process). The objective of such fuel production is to reduce the CO_2 footprint and to generate a fuel that lasts till eternity. Hydrogenation of carbon dioxide to methanol is slightly exergonic, and to methane to a greater extent, because of the favorable thermodynamics of water formation Use of hydrogen for reduction is not economical at present because of its cost & difficulty in transportation.

6.2 Electrolysis

It uses electricity to break water up into hydrogen and oxygen. Hydrogen then reacts with CO_2 to form methane, methanol or DME, along with other chemical building blocks. If solar or wind power is used for this process, then this kind of system can be described as "artificial photosynthesis". The overall efficiency of solar to methane can already attain 10% today, thereby exceeding the efficiency of plants (approximately 0.5% through to biogas or biofuel). The advantage of this path is rapid implementation.

6.3 Artificial Leaves – Catalytic Water Splitting Plus Co₂ Reduction

This process does not use sunlight to produce electricity. Individual photon splits the water directly via catalyzer(s), then reduction of the resulting hydrogen using CO_2 into methane, methanol or formic acid. This technology leads to artificial leaves that would produce chemical building blocks from sunlight, water and CO_2 in large-scale. Currently it achieves an efficiency rate of less than 1%, but with significant research & development over a period of time, this technology would have the greatest efficiency in the long term. The problems with this technology are linked to choosing the most appropriate catalyzer materials, which should, for instance, contain no rare metals, have a good lifespan and be recyclable. Also, only purified CO_2 can be used without damaging the catalyzer.

7. Conclusion

CO_2 is available in abundant quantities worldwide. Which is the most attractive source? Carbon dioxide emissions from fossil-burning power station and industries such as the steel industry, as well as bioethanol plants, produce large volumes of CO_2 that would have to be cleaned so as not to destroy the catalyzer or the electrolysis unit. CO_2 can be tapped directly from the atmosphere. This would generate almost limitless potential, the only constraint being the quantity of available renewable energy. How significant could CO_2-based technologies be for protecting the climate and securing raw material supplies?

8. References

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