Plenary Lecture

Carbon Dioxide as a Chemical
Feed Stock

by

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INTRODUCTION

Far-reaching implications with regard to greenhouse gases in the atmosphere are being discussed in many terms including climate change. Especially build up of carbon dioxide in the atmosphere has attracted keen global concerns. So for energy and chemical industries have utilized fossil fuels liberating vast amounts of carbon dioxide. They are requested to be reduced to the possible maximum extent. Apparently, increase in the efficiency of energy use, in particular that of fossil fuels, is the best practicable counter measure. On the other hand, recycle use of carbon dioxide for manufacture of chemicals may possibly provide another answer.

In this paper, discussions will be made on several examples of the chemistry related to the latter approach followed by the needs of basic research for sustainable development of mankind in future.

Carbon dioxide, together with water, is the final product of combustion of fossil fuels of hydrocarbons. Since these are the most stable compounds thermodynamically, a large amount of energy is released, in the combustion of hydrocarbons, of which we can make use. On the contrary, conversion of carbon dioxide to organic chemicals requires a significant amount of energy in various forms such as thermal, electric, radiant and chemical. The recycle use could be practiced, therefore, provided it is justified in terms of both energy and carbon dioxide balance.

USE OF CARBON DIOXIDE FOR OXIDATION OF HYDROCARBONS TO GIVE OLEFINS AND/OR AROMATICS

As mentioned above, hydrogenation of carbon dioxide by hydrogen to methanol may not be rational since hydrogen is now produced mostly through partial oxidation of hydrocarbons yielding carbon dioxide. However, the use of natural hydrocarbons as the reducing agent for carbon dioxide seems to make sense. In other words, oxidative dehydrogenation of hydrocarbon by the use of carbon dioxide might represent a promising approach to the above issue, in particular, if the hydrocarbon produces a compound of high value while carbon dioxide is converted to carbon monoxide that is a useful raw material of C1 chemistry.

Extensive studies (1) are being made on catalytic reduction of carbon dioxide by lower alkanes

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such as propane, which is converted into aromatics. In this connection, aromatization of lower alkanes is known to be promoted by metallosilicates or transition metal loaded ZSM-5 zeolites. Introduction of carbon dioxide has been found to promote significantly the conversion of propane and yield of aromatics over 10%Zn/HZSM-5 catalyst at 873 K.

Based on the above experimental findings, a preliminary study is made on economic feasibility of the process. A commercial plant is assumed to produce $150 \times 10^3$ and $67.5 \times 10^3$ t/y of BTX and methanol, respectively. The latter is derived from carbon monoxide by hydrogenation in the second reactor. To this end, hydrogen to carbon monoxide ratio is controlled by adjusting the introduction of carbon dioxide into the first reactor. The cost of BTX produced is estimated to be 40 Yen/kg, which is close to that of a competitive process of manufacturing aromatics, namely Z-Forming. The above cost depends largely on the by-product methanol credit that is presumed rather cheap or at 15 Yen/kg : methanol price imported to Japan. This process clearly has an advantage over the hydrogenation of carbon dioxide into methanol, since it is reduced by hydrogen of propane.

The oxidative coupling of methane using carbon dioxide and oxygen is another example where the main products aimed at are ethene, ethane and carbon monoxide. Incidentally, numerous works have been done on the similar reaction using oxygen alone, where poor selectivity with respect to C2 hydrocarbons had remained as the problems to be solved. Improvement in the selectivity is effected (2) by replacing one-half mole of the oxygen by one mole of carbon dioxide. Namely, C2 selectivity higher than 95% is attained at methane conversion 4%.

Metal oxide catalysts comprising PbO/MgO, PbO-Na2O/MgO, CaO, PbO/CaO and BaO-CaO are developed for this reaction. Preliminary study of the economics of the carbon dioxide process is attempted following after the work of Eindhoven University on oxidative coupling of methane using solely oxygen. In this study, ethene to carbon monoxide ratio is assumed to be 1 : 1 in mole as is indicated by the stoichiometry:

$$4 \text{CH}_4 + 2 \text{CO}_2 + \text{O}_2 \longrightarrow 2 \text{C}_2\text{H}_4 + 2 \text{CO} + 4 \text{H}_2\text{O}$$

Since oxygen is reported, in the previous study mentioned, to share approx. 25% of the total cost of ethene production, it is assumed that use of carbon dioxide in this study could reduce the total cost by 12.5% affording the additional investment cost for the use of carbon dioxide. The previous study claims that ethene cost would be competitive in Europe provided C2 selectivity of 80% were held at methane conversion of 30%. Since by product credit of carbon monoxide may improve largely the economy, the target of improving catalyst performance may be much lowered.

The reduction in carbon dioxide emission effected by the commercial introduction of the above invention is estimated but not large. Even if all of the ethene plants (naphtha cracking) in Japan ($6.3 \times 10^4$ t/y) were replaced by the oxidative methane coupling process, the consumption of carbon dioxide would be $9.9 \times 10^4$ t/y, or roughly 1% of the total emission of carbon dioxide in Japan. This might fall down to 1/3% when the carbon monoxide were converted to methanol by use of hydrogen, which is manufactured by shift reaction of the two third of carbon monoxide yielding carbon dioxide.

**CARBON DIOXIDE FOR POLYMER SYNTHESIS**

Research and development work has been done (3) to produce carbon dioxide polymers with alkylene oxide in the presence of organometallic catalyst. In the case of ethylene oxide or propylene
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oxide, carbon dioxide copolymerizes alternately with epoxide to give an aliphatic polycarbonate of high molecular weight, from 50,000 to 150,000.

\[
\text{RCH-CHR’} + \text{CO}_2 \rightarrow (\text{CHR-CHR’-O-C-O-})_n
\]

Representative catalysts are manufactured by reaction of diethylzinc with equimolar amount of either one of the following compounds: water, primary amine, aromatic dicaarboxylic acid, and aromatic hydroxycarboxylic acid. A solid catalyst is obtained by reaction of zinc oxide with dicarboxylic acid in close contact. Polymerization reaction is usually carried out in a solvent system, where carbon dioxide pressure of 5 to 50 atm and temperature 50 to 150°C are preferred.

The carbon dioxide-epoxide copolymer has several features such as high oxygen content, thermal decomposition yielding cyclic carbonate monomer at moderate temperature, easy hydrolysis under alkaline condition, etc. Some preliminary studies are made on the economics giving the copolymer price around 200 yen/kg. In this assessment, carbon dioxide cost is assumed zero, and that of catalyst 1000 yen/kg.

The first commercial plant are now in operation in USA producing polypropylene carbonate to be sold as a binder for electronics industry. Amount of carbon dioxide consumed for producing copolymer of 100×10^3 t/y is 50×10^3 t/y, where ethylene oxide is the counterpart. In order to effect the carbon dioxide fixation in sizable amount, exploration of the market is essential where the features of the copolymer are enjoyed for long time without decomposition yielding carbon dioxide.

CARBON DIOXIDE DERIVED CHEMICALS

An investigation was made on the chemicals which are possibly derived from carbon dioxide and could be responsible for its fixation. Obviously the chemicals containing as many oxygen atom as possible in a molecule are preferred because less reducing agent is required. These are exemplified by urea (-N(CO)-), acid (-C(O)O-), ester (-C(O)O-), organic carbonate (-OC(O)O-), carbamine (-N(CO)-) etc. Among these, urea is the largest commodity chemicals of which annual production is 0.7×10^6 t in Japan or 42×10^6 t worldwide. Carboxylation of aromatics by Kolbe-Schmitt process is another example of industrial importance.

In the long run, dimethyl carbonate (DMC) is expected to be be produced from carbon dioxide and methanol and used not only as chemical reagent and solvent but also as octane booster for gasoline. Although conventional synthesis of DMC had been based on the use of toxic phosphine, a novel reaction has been developed and put into commercial production, where a slurry catalyst comprising CuCl and CuCl₂ is employed.

\[
\text{CO} + 1/2\text{O}_2 + 2\text{CH}_3\text{OH} \rightarrow (\text{CH}_3\text{O})_2\text{C} = \text{O} + \text{H}_2\text{O}
\]

In view of stoichiometry, carbon monoxide and oxygen can be substituted for carbon dioxide, namely,

\[
\text{CO}_2 + 2\text{CH}_3\text{OH} \rightarrow (\text{CH}_3\text{O})_2\text{C} = \text{O} + \text{H}_2\text{O}
\]

A number of research work are currently conducted to explore the catalyst, such as Sn, Ti, Co, and Th, for the above reaction. Although the use of dimethyl carbonate as an additive for fuel releases carbon dioxide upon its combustion, improved fuel economy resulting from the octane increase might effect a significant reduction in gasoline consumption and that in carbon dioxide emission as well.
R & D NEEDS FOR THE FUTURE

Needless to say that further research and development are needed for bringing the above mentioned chemical processes into practical use to effect the reduction in carbon dioxide emission. First of all, the key subject lies in the increased activity and selectivity of the catalyst for the process. Thus, energy saving and economy of the process will be resulted. Secondly, exploration of the market for the products is essential. Such are the cases in the production of carbon dioxide-epoxide polymer and dimethyl carbonate. Thirdly, the full and detailed assessment of the process in terms of energy and carbon dioxide balance is indispensable before the commercial practice. The standard and methodology should be developed to this end.

CONCLUDING REMARKS

A survey of chemical use of carbon dioxide has revealed that several bulk chemicals such as urea, methanol, carboxylic acids and carbonates are being produced in sizable amounts, respectively. Remarkable advances in carbon dioxide chemistry are also being made such as its use for oxidative dehydrogenation of hydrocarbons to produce aromatics, oxidative coupling of methane to form ethene, polymerization with epoxide, and production of dimethylcarbonate etc. These innovations, together with conventional processes, may offer one of the practicable measures to reduce emission of carbon dioxide. The effect, however, may not be so large as to ameliorate significantly the carbon dioxide build-up in the atmosphere, since the market of chemicals are smaller than that of energy in one order of magnitude.

All the more, fixation of carbon dioxide as organic chemicals has an inherent deficiency that the organic chemicals are not necessarily stable and eventually oxidized either naturally or artificially, for example by incineration of their wastes, producing carbon dioxide. Therefore, an introduction of the social infrastructures is indispensable to enable the recycle use of carbon resources, including the dioxide, with minimum use of energy especially that of fossil fuels.

Eventually, it should be stressed that chemical technology in future are to be in conformity with the global environment with little perturbation to carbon dioxide recycle. To this end, further progress in science and technology for making best use of the renewable resources and solar energy are highly expected.

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REFERENCES