Robust Catalyst for CO_2 Conversion to Synthetic Fuels and Chemicals

KAMATA Hiroyuki : Doctor of Engineering, Manager, Applied Physics & Chemistry Group, Technology Platform Center, Technology & Intelligence Integration

Reduction of the emission of carbon dioxide (CO_2) and its utilization as a carbon source are urgent to prevent the global warming. Conversion of CO_2 to useful chemicals or clean fuel such as methane is one of the important options for CO_2 utilization. However, CO_2 is chemically very stable thus the development of highly active but yet robust catalyst is necessary. IHI is currently dedicated to developing the process of the methanation and lower olefins production. The unique catalyst IHI developed is confirmed to be very stable in methanation process. For early deployment, we are now focusing on the system verification and demonstration for the methanation process.

1. Introduction

There is growing concern regarding global warming and climate change resulting from increased concentration of carbon dioxide (CO_2) originating from use of fossil fuels. "Global Warming of 1.5°C[(1)]," a special report published in 2018 by the Intergovernmental Panel on Climate Change (IPCC), reports that it is important for the global temperature rise to be suppressed not to 2°C but to 1.5°C or less. According to the report, the suppression will make it possible to ensure a sustainable and fair world while maintaining human and natural ecosystems although a rapid and major change is required in every aspect of society to achieve it. In line with country-specific CO_2 emission reduction goals under the Paris Agreement, Japan is aiming to reduce greenhouse gas emissions by 26% from 2013 levels by 2030. Similarly, the EU is required to reduce greenhouse gas emissions by 40% from 1990 levels, and even developing countries, such as China and India, are required to make drastic reductions[(2)]. In addition, Japan has set the goal of reducing CO_2 emissions to net-zero by 2050.

There are two ways to reduce CO_2 emissions. One is to reduce the amount of CO_2 generated, and the other is to capture CO_2, store it in a controllable manner, and utilize it. The idea of capturing CO_2 and using it as a carbon source is rapidly becoming common as the concept known as CCU (Carbon Capture & Utilization). The amount of CO_2 generated through human activities is estimated to be approximately 30 Gt per year. However, the amount of CO_2 used effectively as raw material, such as urea, is only 200 Mt per year, which is extremely small compared to CO_2 emissions[(3)]. Going forward, technologies to efficiently convert CO_2 to various valuable products are required in order to promote the capture and utilization of CO_2. The conversion of CO_2 to valuable products occurs through chemical reactions, and therefore requires catalysts that possess the new function of converting CO_2 to the desired product and enable efficient CO_2 conversion.

This paper first describes the potential technologies and technical challenges of CO_2 utilization aimed at realizing a low-carbon society, and then introduces the new process and catalyst for CO_2 utilization on which IHI Corporation is currently working.

2. CO_2 conversion technology using catalyst

2.1 Potential of CO_2 utilization

Figure 1 shows major promising valuable products that can be synthesized using CO_2 as raw material. Considering CO_2 as a carbon source enables us to recognize CO_2 as potential raw material for various valuable products, such as fuels, chemicals, and alcohol. For example, by reducing CO_2 with hydrogen, it is possible to produce methane, which is the chief component of city gas, methanol, which is a major basic chemical, and other hydrocarbons of large molecular weight, such as liquid fuels and waxes. For example, total world production of natural gas, which is mainly composed of methane, is enormous, exceeding 3 trillion cubic meters per year[(4)], and approximately 100 billion cubic meters of natural gas is consumed every year in Japan. With regard to lower olefins, the world's total supply of ethylene is 160 Mt

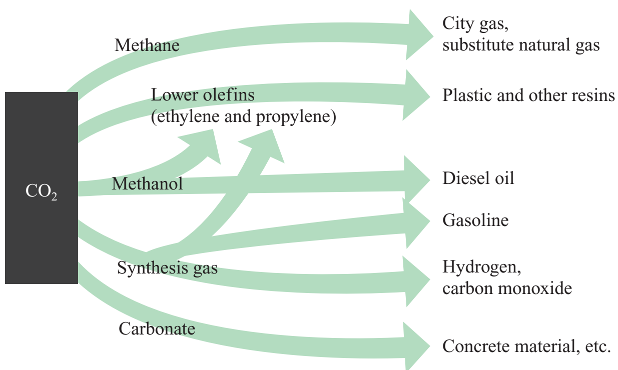

Fig. 1 Potential routes of CO_2 utilization

per year, and that of propylene is 120 Mt per year[5]. Most of them is used as raw material for plastic and other resins, which use the derivatives of these materials. In addition, the global demand for methanol is estimated to be 75 Mt per year[6]. Therefore, if valuable products can be synthesized at a fair cost using CO_2 as raw material, favorable demand can be expected.

2.2 Features and challenges of CO_2 conversion using catalyst

CO_2 is a final product of combustion of hydrocarbons and is an extremely stable substance with low reactivity. In terms of energy, the stability of a substance can be represented by its Gibbs free energy. **Figure 2** shows the energy level and catalytic reaction of CO_2. CO_2 has a Gibbs free energy ΔG^0_f of −394 kJ/mol and is extremely stable, with a lower energy level than methanol (−166 kJ/mol), methane (−51 kJ/mol) and ethylene (+68 kJ/mol). In order to synthesize hydrocarbons with high energy levels from CO_2, which is stable because of its low reactivity, it is necessary to enable reaction by activating the CO_2 using a catalyst.

When a chemical reaction proceeds, the reaction rate is generally determined by the height of the energy barrier at that time (**Fig. 2**). If the energy barrier is too high, then the reaction hardly proceeds, but the use of a catalyst lowers the energy barrier and allows the reaction to proceed more easily. In addition, since the reaction route differs depending on the type of catalyst, it is possible to use the energy barrier to selectively synthesize the desired substance.

For example, the following is a discussion of a reaction in which methane and methanol are synthesized using carbon monoxide (CO) and hydrogen (H_2) as raw materials. The reaction starts with adsorption of the CO molecule onto a metal atom surface, which serves as the catalyst. When this occurs, electrons from the metal atoms are donated to the C-O bond, allowing the CO to react more easily. When nickel (Ni) is used as the catalyst, electron donation is strong and the C-O bond is broken easily, so that reaction with H_2 occurs, forming methane (CH_4). When a catalyst consisting of copper (Cu) and zinc (Zn) is used instead of Ni catalyst, the C-O bond is less easily broken, and so methanol is formed instead of CH_4, with the C-O bond remaining unbroken. In this way, the reaction route can be controlled by changing the type of catalyst, enabling efficient formation of the desired substance. In contrast to CO, CO_2 is stable because of its lower reactivity. When using it as a raw material, the characteristic makes it important to efficiently break the C-O bonds in the CO_2 using a catalyst so as to allow the reaction to proceed effectively.

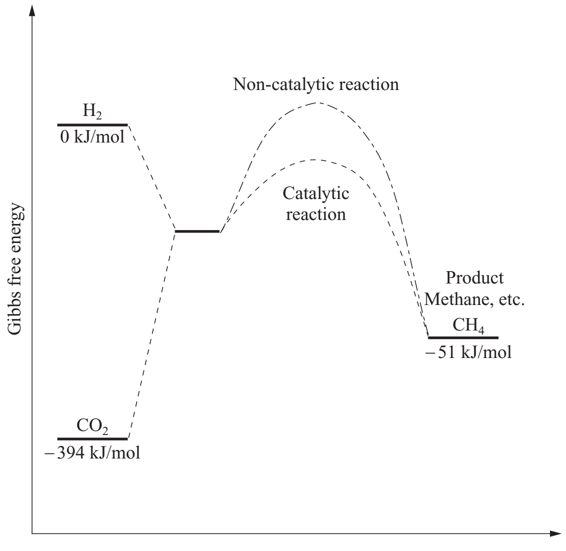

Fig. 2 Energy diagram of CO_2 conversion

3. IHI's efforts toward CO_2 utilization

3.1 CO_2 utilization process

Currently, as a CO_2 utilization process, IHI is developing technologies that use CO_2 to produce methane, which is the chief component of natural gas, and ethylene, propylene, and other olefins, which can be used as raw materials for plastic and other resins. The process to produce methane using CO_2 as a raw material is known as Sabatier reaction and often referred to as CO_2 methanation.

Flue gases from refuse incineration plants and boilers contain from a few to ten plus several percent CO_2. To promote utilization of the CO_2 in flue gases, it is necessary to separate and capture the CO_2 so as to increase its concentration. For this separation and capture, it is possible to apply separation and capture technology that IHI has been developing which uses efficient chemical adsorption[7], [8].

At the same time, hydrogen, which is necessary for the hydrogenation of CO_2, can be obtained, for example, using renewable energy, such as solar and wind power generation. By using electricity derived from sunlight and wind to decompose water by electrolysis, it is possible to produce hydrogen without generating CO_2. In addition, the surplus hydrogen generated as a by-product in petrochemical plants can be used as a hydrogen source.

Figure 3 shows the CO_2 utilization process. Using flue gas-derived CO_2 and hydrogen as raw materials, methane can be synthesized with a methanation catalyst. The methane can be used as fuel for power generation or city gas if supplied to the existing natural gas infrastructure. Similarly, in the process of producing olefin from captured CO_2 and hydrogen, the CO_2 can be immobilized as part of the plastic raw material by treating the hydrocarbon containing the synthesized olefin at a petrochemical plant.

The reaction formulas for the methanation reaction and lower olefin synthesis reaction are as follows:

- Methanation reaction formula

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$
$$\Delta H^0_{298} = -165 \text{ kJ/mol} \quad \cdots\cdots (1)$$

- Lower olefin synthesis reaction formula (for ethylene)

$$2CO_2 + 6H_2 \rightarrow C_2H_4 + 4H_2O$$
$$\Delta H^0_{298} = -128 \text{ kJ/mol.} \quad \cdots\cdots (2)$$

Both the methanation reaction and lower olefin synthesis reaction are exothermic, and therefore require removal of the heat generated. IHI's process, which uses an isothermal reactor with excellent heat exchange performance, makes it possible to increase the yield of methane, etc., by efficiently

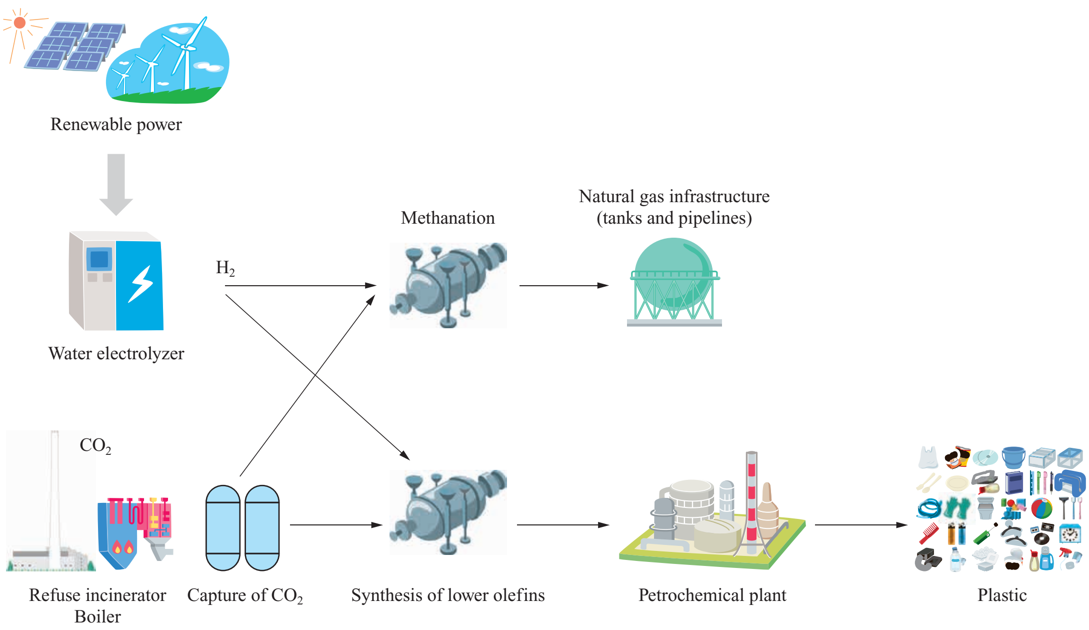

Fig. 3 Schematic process of CO_2 conversion to valuable products

removing the generated reaction heat.

3.2 Development of catalyst – using methanation catalyst as example

The methane reaction using CO_2 as a raw material requires not only high catalyst activity in order to activate the CO_2 to react efficiently, but also a robust catalyst without deterioration even after prolonged use. **Figure 4** shows the challenges regarding catalysts for CO_2 utilization, and the sintering of active metal on the catalyst surface. There are various factors causing deterioration of the catalyst, but typical ones are the following three: reduced surface area caused by the sintering of active metal particles at high temperature, deposition of carbon derived from CO_2 or hydrocarbons on the catalyst surface, and poisoning of the catalyst by trace impurities contained in the source gas[4] (**Fig. 4-(a)**). For example, with regard to deterioration of catalyst performance due to sintering, the active metal particles supported on the surface of the carrier aggregate at high temperature and the effective reaction surface area of fine structure decreases, causing performance to deteriorate (**Fig. 4-(b)**). These deterioration factors do not operate individually but interact with each other, and the catalyst must therefore be designed so as to achieve both high activity and robustness.

To overcome these technical challenges, IHI is working with the Institute of Chemical and Engineering Sciences (ICES), which is an affiliate of the Agency for Science, Technology and Research (A*STAR) of Singapore, to develop catalysts with a unique structure that exhibits both high activity and robustness[9].

Figure 5 shows a transmission electron microscope (TEM) photograph of the developed methanation catalyst, together with a diagram that schematically illustrates its structure. The catalyst is made up of a porous oxide matrix containing nickel nanoparticles, which have an extremely small particle

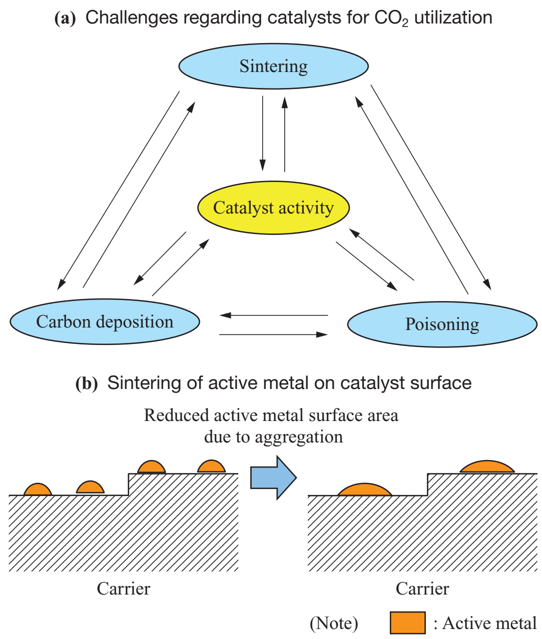

Fig. 4 Sintering of active metals on catalyst surface

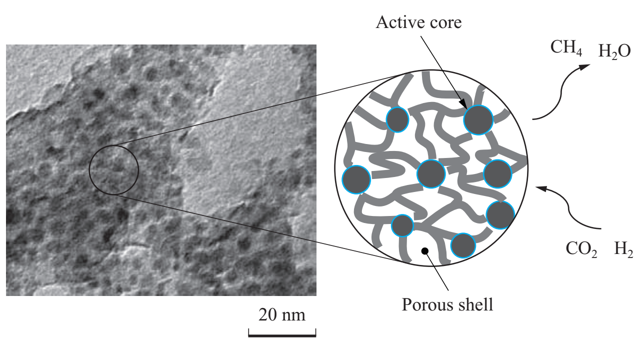

Fig. 5 TEM and schematic images of IHI Methanation catalyst

size of 3 nm, that function as the active metal. In contrast to conventional catalysts that have a two-dimensional structure in which the active metal is supported on the surface of a carrier, the developed catalyst has a three-dimensional network structure. The reaction gas is supplied to the active metal through the porous oxide matrix, and this matrix also helps prevent the Ni nanoparticles from sintering in the high-temperature reaction field.

Figure 6 shows an example of a life test performed with the catalyst. It shows that the catalyst can be used stably without performance deterioration for a long period exceeding 1 000 hours even in a severe environment in which, in addition to CO_2 and H_2, the source gas contains CO, which accelerates carbon deposition. In addition, the results of analysis of the catalyst after the test show that the Ni nanoparticles in the catalyst did not aggregate due to sintering, and that the amount of carbon deposition, which causes the catalyst to deteriorate, was extremely small(9). Hence, by utilizing IHI's unique methanation catalyst, it is possible to provide a methane production process that uses CO_2 as a raw material and operates efficiently for a long period of time.

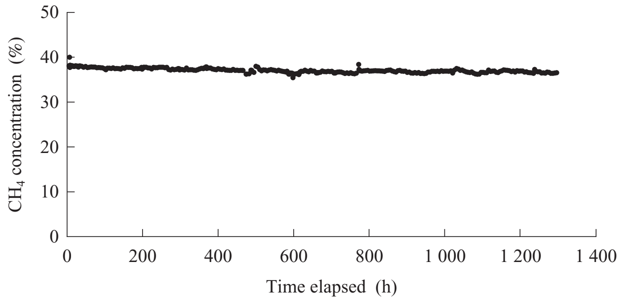

Fig. 6 Long term stability test of IHI's methanation catalyst

4. Conclusion

In order to prevent global warming, it is necessary to establish technologies to separate, capture, and utilize CO_2, which is a greenhouse gas. This paper has described CO_2 utilization technologies on which IHI is currently working, i.e., methanation of CO_2 and synthesis of lower olefins, together with the potential possibilities and technical challenges of CO_2 utilization technologies that use catalysts. IHI is working to verify and demonstrate the performance of the methanation process and the CO_2 conversion process and will strive to put these technologies to practical use as early as possible with the aim of achieving a carbon neutral society.

REFERENCES

(1) Global Warming of 1.5°C, IPCC, < https://www.ipcc.ch/sr15/ >, accessed 2018-12-20

(2) The Paris Agreement, United Nations, < https://unfccc.int/process-and-meetings/the-paris-agreement/the-paris-agreement >, accessed 2021-2-2

(3) M. Aresta et al. : The changing paradigm in CO_2 utilization, J. of CO_2 Utilization, Vol. 3-4, 2013, pp. 65-73

(4) J. R. Nielsen and L. J. Christiansen : Concepts in Syngas manufacture, Imperial College Press, 2011, p. 4

(5) Ministry of Economy, Trade and Industry :Forecast of Global Supply and Demand Trends for Petrochemical Products, < https://www.meti.go.jp/english/press/2018/1019_003.html >, accessed 2021-2-2

(6) Methanol Institute : < https://www.methanol.org/the-methanol-industry/ >, accessed 2018-12-20

(7) IHI Corporation : Toward the Realization of Low Carbon Coal-Fired Power Plant for the Sustainable Low-Carbon Society, IHI Engineering Review, Vol. 50, No. 1, 2017, pp. 22-25

(8) S. Okuno, S. Nakamura, K. Hamada, K. Takano and T. Matsuyama : Development of a Design for a Carbon Capture and Storage Facility by Utilizing a Process Simulation Technology, IHI Engineering Review, Vol. 52, No. 1, 2019, pp. 36-40

(9) H. Kamata et al. : Dispersed and high loading Ni catalyst stabilized in porous SiO_2 matrix for substituted natural gas production, Catalysis Today, Vol. 299, 2018, pp. 193-200

INFORMATION

Thank you very much for reading the article of IHI ENGINEERING REVIEW.
We hope you will take a look at other articles.

Webpages of our journals on technology are as follows:

Journal of IHI technologies (in Japanese)

IHI ENGINEERING REVIEW (in English)

Vol. 54 No. 2

Contents page of Vol.54 No.2

Our corporate website introduces our technology categorized according to social issues: “IHI Challenges with Society”. The articles of IHI ENGINEERING REVIEW are also provided there. We would appreciate it if you would visit our website.

IHI Challenges with Society

Technologies supporting IHI Products