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Research and Development of Innovative Environmental and Energy Technologies that Use Inorganic Membranes and Efforts for Practical Use and Industrialization

1. Introduction

The Paris Agreement began full-scale operation in 2020, and in October, 2050 Carbon Neutral was declared in Japan as well. In order to achieve this goal, it is necessary to effectively reduce greenhouse gas emissions and realize carbon recycling that utilizes CO_2 as a resource.

Inorganic membranes of silica, zeolite, and palladium have the features of excellent mechanical strength and heat and chemical resistance compared to polymer membranes. In addition, by using a membrane reactor that uses the inorganic membrane, energy consumption is significantly reduced compared to conventional packed-bed reactors that require separation and purification processes of distillation and adsorption. It also has the potential to simplify the process. Based on these excellent characters of inorganic membranes, as a technology that can realize an innovative production process, research is underway on the application of the membranes as an alternative to distillation and the effective use of captured CO_2. Furthermore, the development of hydrogen permselective membranes for CO_2-free and low-cost hydrogen production, which is indispensable for building a hydrogen society, is expected to be an innovative technology that greatly contributes to the reduction of greenhouse gas emissions.

The Inorganic Membrane Research Center (IMeRC) aims for the early practical use and industrialization of innovative environmental and energy-saving technologies using inorganic membranes. The organization is composed of two departments, the Research Department and the Industrial Cooperation Department, in order to promote activities with research and development and industrial collaboration.

In the Research Department, membrane reactors for carbon capture and utilization (CCU) are developed using silica, zeolite, and palladium membranes, which have unique characteristics, respectively. We mainly develop two-types of membrane reactors for synthesis of methanol and liquid hydrocarbon fuel via captured CO_2. In the case of liquid hydrocarbon fuel, CO_2 directly captured from the air is the raw material. In addition, we are also conducting research on hydrogen production by direct decomposition of methane for the purpose of CO_2-free and low-cost hydrogen production.

In the Industrial Collaboration Department, the Industrialization Strategy Council, which consists of 18 companies of inorganic membrane and porous-substrate manufacturers and user companies, aims to share the vision among manufacturers and user companies by planning joint research. Member companies have regular opportunities to share ideas and promote activities through study groups.

This paper introduces the main achievements and future prospects of the research division, such as CCU technology development and hydrogen production from methane, and the status of the activities of the Industrialization Strategy Council.

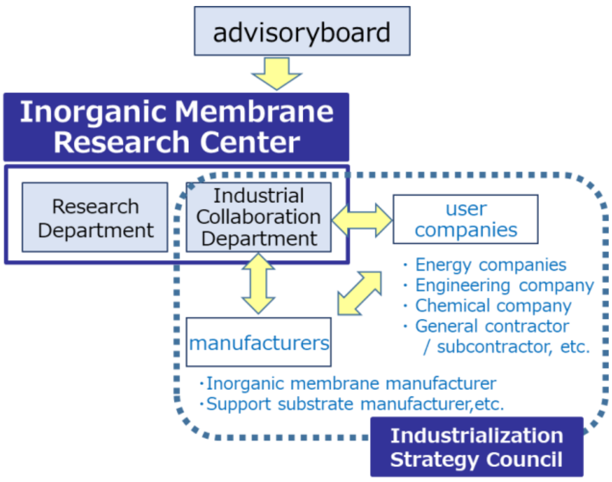

Fig. 1 Promotion system of IMReC

2. Development of CO_2-free hydrogen production technology from methane decomposition

To realize a society that relies on hydrogen, a method is required to produce hydrogen at low cost and in large quantities. With the focus on methane, which can be stably supplied for a long time because of the shale gas revolution, hydrogen and solid carbon are produced by pyrolysis, and hydrogen production costs can be reduced by selling the carbon. A membrane reactor, which is applied to that reaction, could produce hydrogen at low cost and save on energy consumption. In addition, the process has the advantage of not emitting carbon dioxide and is a technological development that contributes to a decarbonized society.

Adopted as a contract project of NEDO in FY 2019, the objective was follows: a) development of a high hydrogen permselective membrane with durability under high temperature conditions (>500°C), b) development of a catalyst that activates at relatively low reaction temperatures for the membrane reactor, and c) the development of membrane reactors consisting of a hydrogen separation membrane and a catalyst with a demonstration of their effectiveness. (Fig. 2)

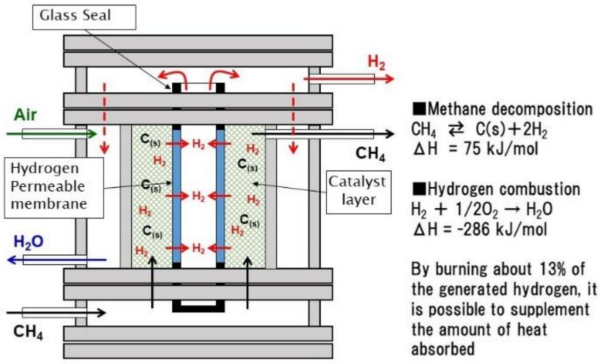

Fig. 2 Application of a membrane reactor to the hydrogen production process from methane decomposition

For the development of a hydrogen permselective membrane in a), silica and palladium membranes are candidates. We have succeeded in developing a hydrogen permselective membrane having high H_2 permeance and heat resistance at 723 K. Both of the silica and palladium membranes were showed over 5 x 10^{-7} mol m^{-2} s^{-1} Pa^{-1} of H_2 permeance, and 3,000 of H_2 selectivity. These results were exceeded the final goal of this project. In addition, $Ni/Fe/Al_2O_3$ as a catalyst for methane decomposition showed relatively high catalytic activity at 873 K.

We calculated the hydrogen production efficiency and CO_2 emissions using a membrane reactor for methane decomposition. As shown in Fig. 3, high hydrogen production efficiency and low CO_2 emissions were obtained compared with the conventional packed bed reactor (PBR). Compared with the CO_2 emissions from the methane steam reforming (SRM), which is a general hydrogen production method, CO_2 emissions from SRM are 0.95 kg-CO_2/Nm^3-H_2, whereas methane decomposition using the membrane reactor is 0.2 kg-CO_2/Nm^3-H_2. The CO_2 emissions from this membrane reactor can be suppressed to about 1/5.

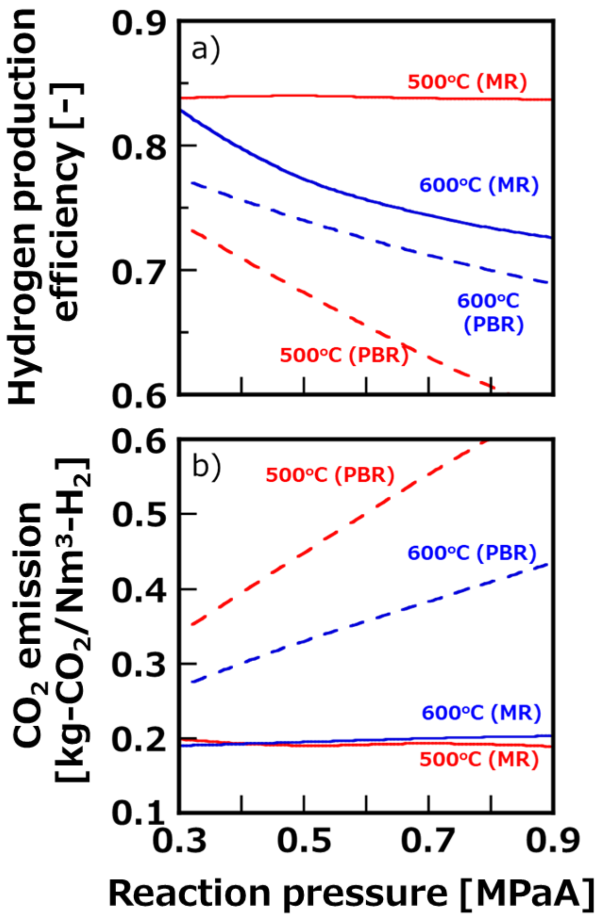

Fig. 3 Calculation results of effect to apply the membrane reactor for methane decomposition.
a) Hydrogen production efficiency, b) CO_2 emission.

Fig. 4 shows results of the membrane reactor tests using palladium and silica membranes as hydrogen permselective membranes. A broken line in this figure shows methane conversion using the packed bed reactor, and a solid line shows the maximum methane conversion theoretically obtained using the membrane reactor. From these results, methane conversion using the membrane reactor showed 0.8 (palladium membrane), and 0.7 (silica membrane) at 873 K as the reaction temperature and 0.4 MPa as the reaction pressure. Compared to a packed bed reactor, both membrane reactors obtained higher methane conversion. On the other hand, in the case of a reaction temperature of 773 K, methane conversion using a membrane reactor was approximately the same as when using a packed bed reactor. It is assumed that the Ni/Fe/Al_2O_3 catalyst showed low catalytic activity at 773 K. Thus, these results propose that the development of a catalyst having higher catalytic activity in lower reaction temperatures is indispensable. This is one of the major issues in the development of membrane reactors using inorganic membranes and is not limited to methane decomposition. In the future, the research and development of a membrane reactor should be promoted by integrating catalyst development and membrane development.

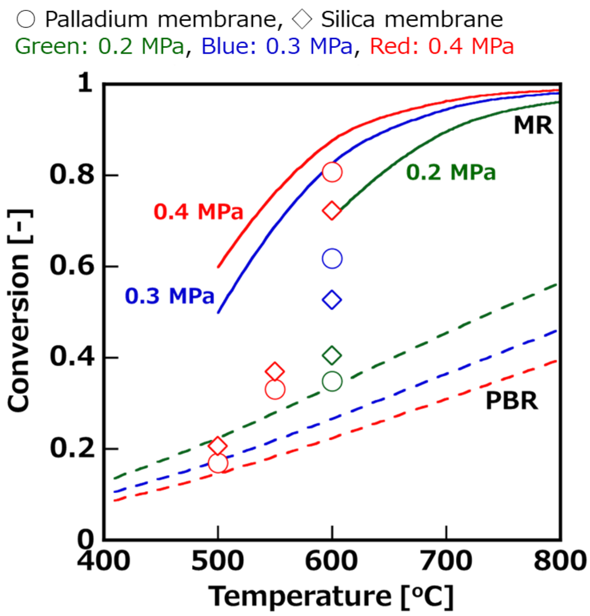

Fig. 4 Effect of methane conversion increasing using membrane reactor.

3. CO_2 utilization technologies in RITE

Recently, CO_2 utilization technologies have been actively researched and developed in countries around the world, including the EU, as being effective in reducing CO_2 emissions. On the other hand, in the hydrogenation of CO_2, water is generated by the reaction, which decreases the reaction rate. In addition, most reactions are exothermic, and the removal of the reaction heat is one of the problems. In order to solve these problems, highly efficient, energy-saving CO_2 utilization technology has been developed at the Inorganic Membranes Research Center using a membrane reactor.

3.1. Development of effective methanol synthesis from CO_2 hydrogenation

Methanol is an important intermediate for chemical products, and demand is expected to grow in the future. Methanol is mainly synthesized using syn-gas (mixture gases of CO and H_2); however, synthesis requires high temperatures and high pressures. Generally, Cu/ZnO-based catalysts are used with the reaction within the temperature range of 473–573 K. On the other hand, the one-pass yield shows low values owing to equilibrium limitations. This is remarkable in the methanol synthesis from CO_2 hydrogenation represented by the following reaction formula.

$$CO_2 + 3H_2 \rightleftarrows CH_3OH \text{ (methanol)} + H_2O$$

CO_2 emission reduction potential can be expected at about 100 million tons/year (assuming demand methanol production of 50 million tons/year) when methanol production process will change to that via CO_2 as the raw material. Thus, highly efficient methanol synthesis processes from CO_2 have been required. If the produced water is removed from the methanol synthesis reaction system, it can be improved to a one-pass yield with synthesized methanol at a relatively mild condition of lower reaction pressure and temperature. The membrane reactor with the water permselective membrane is expected to be one of the highly efficient methanol production processes.

At the RITE Inorganic Membranes Research Center, we successfully developed a novel hydrophilic zeolite membrane, which has higher hydrothermal stability and water/methanol permselectivity compared to the conventional LTA-type zeolite membrane. This membrane was applied to the membrane reactor for methanol synthesis, and CO_2 conversion was achieved at a rate three times higher compared to the conventional packed-bed reactor at a reaction temperature of 473 K and a reaction pressure of 4 MPa.

In near future, we will improve dehydration zeolite membrane performance, and produce a membrane having a higher effective membrane area. A new project for that purpose was adopted in 2021.

3.2. Development of liquid hydrocarbon fuel synthesis technology using CO_2 as a raw material captured from the air

Liquid hydrocarbon fuels by recycling CO_2 through the existing infrastructures for transportation and storage have a lower cost than new fuels, so they should be established to achieve carbon neutrality. The NEDO project Moonshot Research & Development Program was adopted in collaboration with Kanazawa University and the RITE Chemical Research Group in 2020. At the IMeRC, we accepted the challenge of developing the technology to convert the captured CO_2 into liquid hydrocarbon fuel by FT (Fischer-Tropsch) synthesis (Fig. 5). Similar to methanol synthesis, the water produced from the reaction causes catalyst deactivation and a reaction rate reduction in FT synthesis. Another problem is the difficult reaction control for liquid fuel because the product followed the ASF (Anderson-Schulz-Flory) distribution.

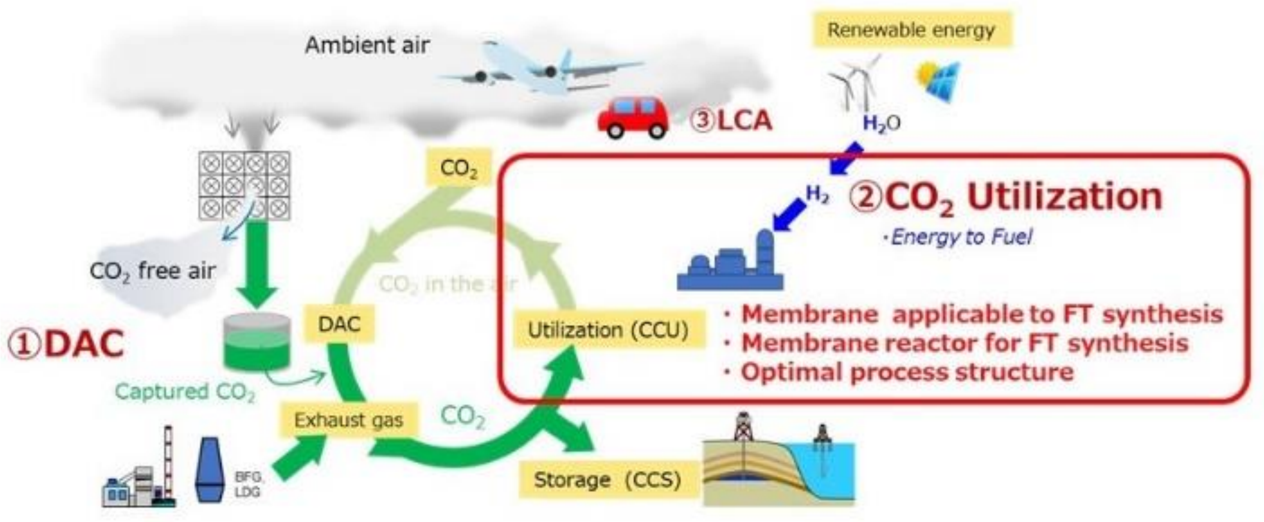

Fig. 5 Overview of the Moonshot project at RITE

Therefore, in this project, we will develop high efficiency, energy-saving CO_2 utilization technology from the CO_2 captured from the air as the raw material for the membrane reactor. Research and development items are as follows.

a) Development of membranes applicable to FT synthesis

b) Development of a membrane reactor for FT synthesis

c) Search for the optimal process structure

The target membranes are hydrophilic membranes and hydrogen permselective membranes. Catalyst deactivation can be suppressed if the generated water can be removed from the reaction side by using a hydrophilic membrane, such as zeolite. Furthermore, the reaction can be controlled by supplying H_2 to the reaction field via hydrogen permselective membranes, such as silica and palladium. We succeeded in developing the Si-rich LTA-type zeolite membrane with improved hydrothermal stability compared to the conventional LTA-type zeolite membrane. We are also involved in the development of silica membranes with excellent hydrogen permselectivity.

The membrane reactor for FT synthesis was designed and will be put into operation. A simulation model was constructed prior to the experiments, and it was confirmed that the membrane reactor can obtain a higher CO_2 conversion rate than the conventional catalyst-packed bed reactor.

In the future, we will make the best use of the knowledge we acquired and strongly promote the development of inorganic membranes and membrane reactors applicable to FT synthesis. We then intend to unravel the science of inorganic membranes that we have left unattended.

4. Activities and efforts toward commercialization and industrialization

The core of the Industrial Collaboration Department of the IMeRC is the Industrialization Strategy Council. A total of 18 separation membrane and support manufacturers and user companies (as of January 2022) participate on this council. Our goal is to establish an inorganic membrane industry that contributes to innovative environmental and energy technologies by promoting a common vision for manufacturers and user companies, as well as a joint research plan involving national projects and other initiatives.

We are promoting a variety of activities, which include the following:

a) Sponsoring needs and seeds matching meetings toward the practical use of innovative environmental and energy technologies that use inorganic membranes, and the establishment and operation of a research group that will prepare the future roadmap

b) Planning joint implementation projects funded by the government and NEDO

c) Acceptance of researchers from council members to the Research Section of the IMeRC and the implementation of training workshops

d) Offering technical guidance from the IMeRC Advisory Board and Research Section

e) Hosting exclusive technology seminars for council members

f) Offering exclusive supply services (Needs and Seeds Technology Information) to council members

In 2021, because of the spread of the COVID-19 virus, we had to refrain from face-to-face activities, but we actively promoted study group activities and seminars using the Web.

Two study groups, the Membrane Reaction Process Study Group and the Common Infrastructure (Performance Evaluation) Study Group, have started new studies. The Membrane Reaction Process Study Group examined a computational platform that enables comparative studies of performance, energy balance, and cost, which are indispensable for social implementation of membrane reactors. The Common Infrastructure (Performance Evaluation) Study Group conducted a basic study toward standardization of separation membrane performance evaluation methods with the aim of promoting the industrialization of inorganic membranes.

We also held a seminar for council members online. There were lectures from universities, member companies, membrane-related companies, etc. on the latest R & D trends and introduction of needs, seeds, practical development cases of membranes, and lively questions, answer. In addition, we conduct patent and literature searches related to the content of the lecture, and regularly provide members with needs seeds information with comments from the IMeRC in the summary.

5. In conclusion

In November 2021, the Inorganic Membrane Environment and Energy Technology Symposium to Explore the Future was held online for the first time in two years with the attendance of 389 people. At this symposium, under the theme of carbon recycling, universities and companies gave lectures on the latest trends in CO_2 separation / recovery / effective utilization, carbon cycle technology and efforts toward practical application. We introduced the latest research results of the IMeRC and the efforts of the Industrialization Strategy Council.

The audience commented that they were able to deepen their understanding of carbon recycling, as well as understand the specific efforts toward practical use and the effectiveness of inorganic membranes in separation technology.

The need for innovative environmental and energy technology development that contributes to decarbonization is increasing toward 2050 carbon neutrality. As the IMeRC, we would like to deepen basic and applied research that makes the best use of the advantages of inorganic membranes, and accelerate the movement toward social implementation