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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

Inorganic membranes, such as silica membranes and zeolite membranes, have the features of excellent heat resistance and environmental resistance, in addition to high separation performance, and are expected to apply to various applications. Compared to the conventional separation and purification methods of distillation and adsorption, inorganic membranes can save energy, and they are also being developed for CO_2 separation and purification, as well as for hydrogen separation and purification, which are indispensable for a society that intends to use hydrogen in practical ways. Therefore, the use of the membranes is attracting a great deal of attention as an environmental and energy technology that contributes to the preservation of the global environment. However, practical application has so far been limited to alcohol dehydration. In the future, innovative environmental and energy technologies using inorganic membranes will be required for early commercialization and industrialization.

The Inorganic Membrane Research Center (IMeRC) has two departments: the Research Department and the Industrial Cooperation Department. In the Research Department, hydrogen separation, purification, manufacturing, separation, and recovery are performed using silica membranes, zeolite membranes, and palladium membranes, each of which offers excellent characteristics. We are conducting research on the ways to more effectively use the CO_2 produced. In the Industrial Collaboration Department, the Industrialization Strategy Council, which consists of 18 companies of inorganic separator and support 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.

In 2020, we constructed a membrane reactor (MR) using a silica membrane and a palladium membrane in a project that directly decomposes methane and produces hydrogen, which was commissioned by the New Energy and Industrial Technology Development Organization (NEDO), and confirmed the high conversion rate of the membrane reactor with this reaction system. We reported to the committee of NEDO, and the project was completed.

As for CO_2 separation, capture, and utilization (CCU: Carbon Capture and Utilization), we developed a zeolite membrane with high selectivity for water and applied it to a membrane reactor to enhance the conversion rate for methanol. We confirmed a three-fold improvement in the conversion rate compared to conversion in the reactor. In addition, NEDO's Moonshot research and development program was commissioned jointly with Kanazawa University and the Chemical Research Group for the development of highly efficient direct air capture (DAC) and carbon recycling technologies, and IMeRC conducts research to develop a process to produce liquid fuel from the CO_2 collected from the atmosphere

At the Industrialization Strategy Council, the second phase (2019–2020) of the Common Base (Reliability Evaluation Method) Research Group and the CO_2 Separation Research Group was completed, and seminars were held on the Web.

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

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. 1)

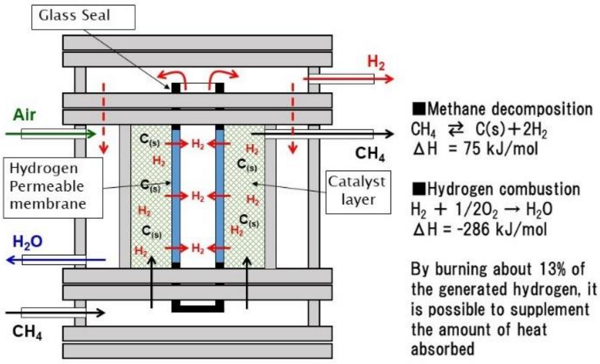

Fig. 1 Application of a membrane reactor to the hydrogen production process from methane decomposition

For the development of a hydrogen permselective membrane in a), silica and palladium membranes are candidates. The guidelines for membrane formation were narrowed down based on membrane formation experiments and literature searches. The development of silica membranes was examined using various silica sources, and the silica source was selected by evaluating permeation separation performance. As a result, we were able to achieve the target performance for this project with a membrane using dimethoxydimethylsilane (DMDMS: a silicon compound in which two methyl groups and two methoxy groups are bonded to Si as the center) as a silica source. Furthermore, by carefully examining the membrane formation conditions for DMDMS, it was possible to form silica membranes that exhibited high heat resistance (Fig. 2).

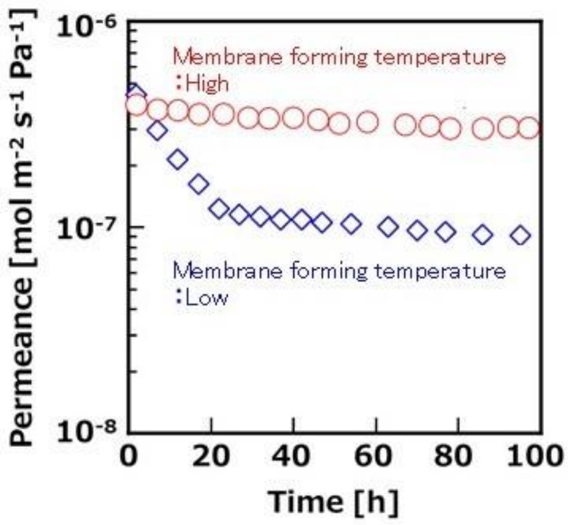

Fig. 2 Results of heat durability tests of silica membranes with different membrane forming conditions

Regarding the development of palladium membranes, we examined the membrane formation conditions of Pd-Cu alloy membranes, which are expected to improve heat resistance while maintaining high hydrogen permeability, as a pore-filled membrane, which is an inorganic membrane developed by the RITE Research Center of Technology. It was confirmed from the SEM-EDX of the formed membrane that the membrane could be formed with the desired composition (Pd 60 Cu 40 wt%). Furthermore, by scrutinizing the membrane formation conditions, the hydrogen permeability of the intrapore-filled Pd membrane at 500°C was improved to 1.3 x 10^{-6} mol m^{-2} s^{-1} Pa^{-1} (previously 8 x 10^{-7}). We developed a hydrogen permeable membrane with heat resistance and achieved the target performance.

Regarding the catalyst development in b), we conducted a literature survey targeting hydrogen production by direct decomposition of methane in Japan and other countries, grasped the technological development trends, and investigated catalysts that could be applied to membrane reactors. As a result, $Ni/Fe/Al_2O_3$ catalysts, which have been reported to produce high yields at relatively low temperatures, were selected as candidates. Regarding the catalysts, 20 types with different preparation conditions, such as coprecipitation temperature, dropping method, type of precipitant, and composition, were prototyped, and as a result of evaluating the reactivity, a catalyst with relatively high performance was selected for the membrane reactor. (Fig. 3)

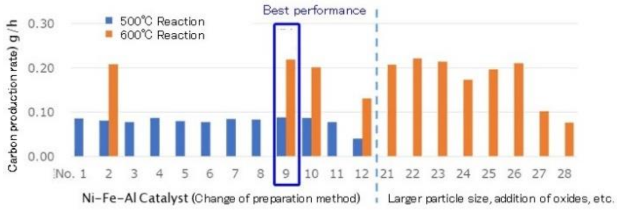

Fig. 3 Trial production and performance evaluation of catalysts for methane decomposition

Regarding the development of the membrane reactor in c), a membrane reactor was designed and manufactured, and a membrane reaction test was conducted using the $Ni/Fe/Al_2O_3$ catalyst selected in b) and a palladium membrane and a silica membrane were chosen for use as the hydrogen separation membrane. A reaction test was performed. It was confirmed that the conversion rate was improved by applying the Pd membrane and the silica membrane under the conditions of a reaction temperature of 600°C and a reaction pressure of 0.4 MPa, the effectiveness of the membrane reactor was demonstrated, and it was confirmed that the obtained carbon has a structure in which graphene is laminated around the catalyst (Fig. 4).

On the other hand, the hydrogen permeation performance of the Pd membrane after the test was reduced to about one-half. From the SEM-EDX results of the membrane after the test, it was confirmed that carbon was dissolved in the Pd layer, suggesting that the decrease in hydrogen permeation performance was due to the solid solution of carbon. We are working on countermeasures for the new issue.

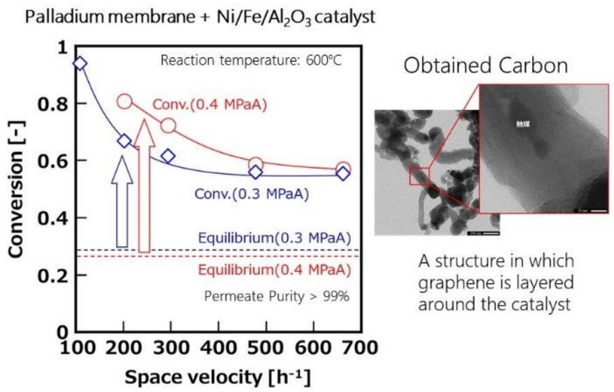

Fig. 4 Results of membrane reaction test using palladium membrane and SEM image of obtained carbon

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 pressure. 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 thermodynamic equilibrium limitations. This is remarkable in the methanol synthesis from CO_2 hydrogenation represented by the following reaction formula.

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

To solve these problems, a membrane reactor can be applied to the application because generated water can be removed from the reaction system through the membrane, and the reaction will be promoted to the methanol producing side. However, it is difficult to apply the A-type zeolite (LTA) membrane, which is often used for water separation, from the viewpoint of hydrothermal stability.

Herein, we successfully developed a novel zeolite membrane for water separation, which has higher hydrothermal stability compared to the conventional LTA-type zeolite membrane. The membrane was applied to the membrane reactor for methanol synthesis via CO_2 hydrogenation, and the CO_2 conversion from the membrane reactor showed higher rates than those from a conventional packed-bed reactor (Fig. 5). In the future, we will proceed with research and development of practical uses for the methanol synthesis membrane reactor.

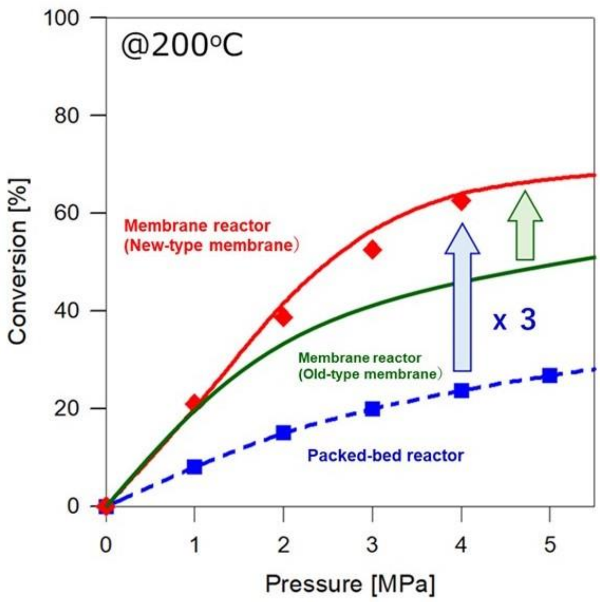

Fig. 5 Membrane reactor for methanol synthesis using a zeolite membrane

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

The NEDO project Moonshot Research & Development Program was adopted in collaboration with Kanazawa University since 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. Similar to methanol synthesis, the water produced from the reaction causes catalyst deactivation and a reaction rate reduction in FT synthesis. Another problem was that reaction control was difficult because the product followed the ASF (Anderson-Schulz-Flory) distribution.

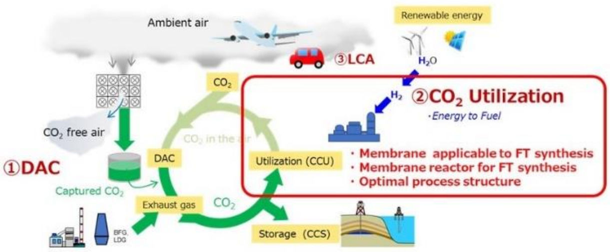

Fig. 6 Overview of the Moonshot project at RITE

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 a membrane applicable to FT synthesis
b) Development of a membrane reactor for FT synthesis
c) Search for the optimal process structure

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 a 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 pore-filled Pd membranes and silica membranes with excellent hydrogen permselectivity. 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 2021) 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 2020, because of the relationship with the COVID-19 virus, although there were some changes from the original plan, such as postponing the holding of workshops, a working group was established that would use the Web and promote studies as the CO_2 Separation Study Group and the Common Infrastructure (reliability evaluation, etc.) Study Group and subordinate organization. The group met a total of four times as the CO_2 Separation Study Group and a total of seven times as the Common Infrastructure (reliability evaluation, etc.) Study Group, and they further deepened the investigation. The Common Infrastructure Study Group aims to launch a government-sponsored project after 2021 by conducting a concrete preliminary test for accelerated deterioration of zeolite membranes and to acquire basic data for establishing long-term reliability. The CO_2 Separation Study Group studied the main theme of the applicability of inorganic membranes to natural gas fields containing high concentrations of CO_2.

In addition, seminars for council members were held on the Web (three times a year in FY 2020). In the future, we plan to give lectures on the latest R&D trends and needs, seeds, and practical development cases of membranes from advisory boards, member companies, and membrane-related companies, and there will be lively questions, answers, and discussions. It is done. In addition to gaining useful knowledge related to the practical application and industrialization of inorganic membranes, the seminars have been highly rated as meaningful places for interaction between member companies and front-line researchers.

Fig. 7 Lecture at the Seminar (April 2019)

5. In conclusion

In 2020, we constructed a membrane reactor (MR) in a project that directly decomposes methane and produces hydrogen, which was commissioned by NEDO, and confirmed the high conversion rate of the membrane reactor with this reaction system. We reported to the committee of NEDO. Regarding this project, a new project is scheduled to start in 2021, and we plan to work toward more practical use through this project.

Steadily achieved results in research and development made effective use of CO_2; in addition, NEDO's Moonshot research and development program was commissioned for the development of highly efficient direct air capture and carbon recycling technologies, and we conduct the research to develop the process on produce the liquid fuel from collected CO_2 from the atmosphere. With the acquisition of a long-term funded project, it will be possible to organize the IMeRC, and in the future, we would like to work diligently to become a core organization that leads the development and practical application of inorganic membranes in the world.