Technical Report

Overview and Research Examples of CCU, Carbon Dioxide Capture and Utilization from Steel-making Industry

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Abstract

CO_2 utilization and storage technology is one of the most essential research issues to be addressed in order to realize zero-carbon steel. Nippon Steel Corporation has been investigating these technologies in collaboration with leading researchers in the C1 chemistry field through the development of a number of catalysts in the steel-making and energy sector. At present, research, which will be practically realized in the short-term, mid-term or long-term, is being conducted through industry-government-academia cooperation. This paper introduces such research, and compares it to the national research roadmap on CO_2 reduction technologies. In the future, we hope to realize these research projects by promoting interindustry cooperation together with business partners in the field of chemicals, energy, etc.

1. Introduction

In order to realize zero-carbon steel for the steel-making industry, it is essential to develop innovative technologies that are not an extension of the energy-saving technologies cultivated by our predecessors. At Nippon Steel Corporation that predominantly employs the blast furnace-converter process, it is very effective to apply CO_2 emission reduction technologies to the blast furnace that emits the greatest amount of CO_2 in the steelworks. This is because CO_2 is inevitably produced in the blast furnace by reducing iron ore with coke. In future, the development of a carbon-free steelmaking process, where the iron ore is reduced by hydrogen (hydrogen reduction steelmaking) will nullify CO_2 emission, replacing the present process. However, in consideration of the way forward for the establishment of the hydrogen reduction technology and the establishment of the supply system of low cost CO_2-free hydrogen in large quantities, the production that employs both processes compatibly is expected in the interim. Under these circumstances, it is a crucial issue to fix and add value to the emitted CO_2 by Carbon dioxide Capture, Utilization and Storage (CCUS) (**Fig. 1**), while reducing the CO_2 emission volume by utilizing the technologies developed in the COURSE50 [1] for the blast furnace process.

This article features Carbon dioxide Capture and Utilization (CCU) (shown in the dotted line box in Fig. 1), and introduces the contents of the various R&Ds conducted under the industry-government-academia cooperation based on the catalytic technologies owned by Nippon Steel.

CO_2 is the combustion emission of the carbon and/or the hydrocarbon of the fossil resource that is generated when it is used for energy and/or chemical use, and is a highly stabilized and chemically inert oxide under the general environment. In order to convert such a chemical compound to other useful chemical compounds (basic chemicals, functional chemicals, pharmaceutical and crop protection products, fuels and so forth), in principle, four methods for reduction can be applied: (1) to provide electrons, (2) to apply heat, (3) by means of hydrogen and (4) by means of other agents having high reducing capability except for hydrogen. Accordingly, CCU technologies should also be developed from these viewpoints. For such a purpose, it is strongly required to make full use of the elemental technologies such as electrochemistry, thermodynamics, catalyst chemistry, chemical reaction engineering, materials science, process engineering, analytical science and computational science. Furthermore, although new markets need to be formed from now on which is difficult to predict, it is reported that the potential amount of fixed CO_2 by CCU technologies is estimated to reach several billion tons. [2]

To date, Nippon Steel has introduced and been operating various catalytic processes to render the in-house exhaust gases harmless (e.g. desulfurization, denitrification), and operates the equipment. In addition, on the other hand, Nippon Steel has also dealt actively with the development of the catalyst for the steel-making and energy

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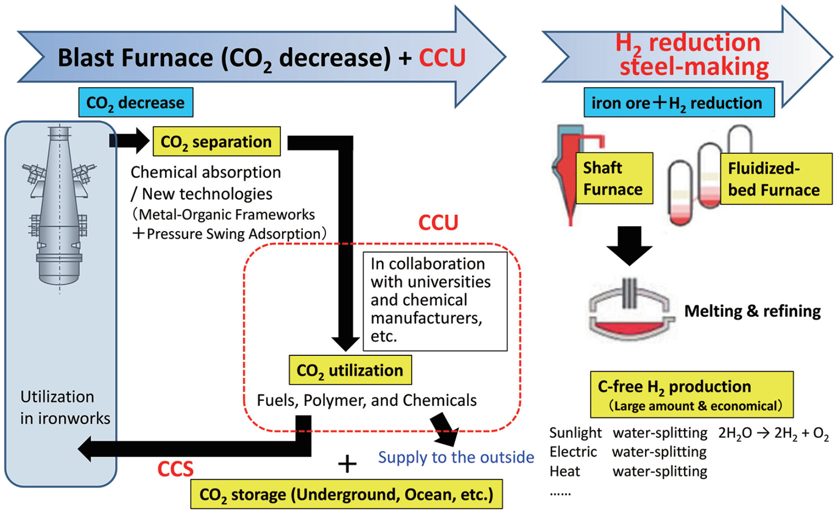

Fig. 1 Illustration of research strategy idea for decarbonization in Nippon Steel

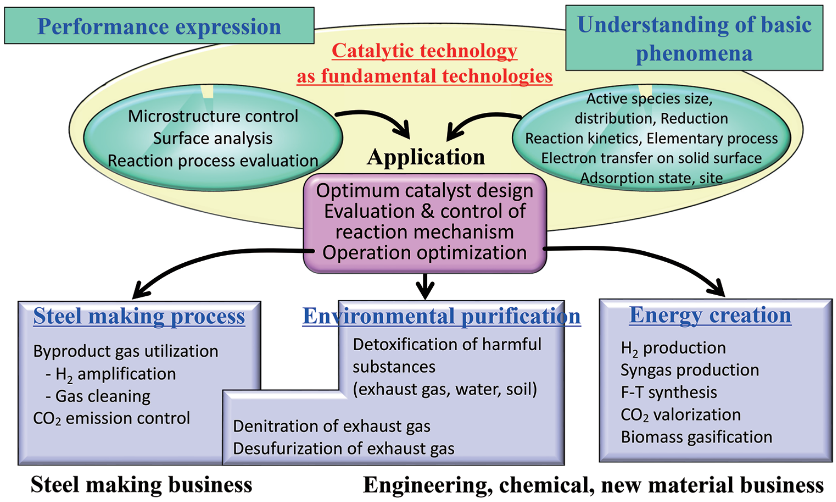

Fig. 2 Image of our elemental technologies for the catalyst field and their application

field based on its own elemental technologies such as material design, material analysis, surface control and chemical reaction analysis (**Fig. 2**).

As the development examples thereof, Nippon steel managed the waste gas in steel-making that is characterized by poor cleanliness and by the high content of hydrogen sulfide that is harmful to the catalyst[3] for the purpose of producing hydrogen from the tar contained in the high temperature coke oven gas (COG) by means of catalytic reforming with steam. Nippon Steel also addressed, in the field of C1 chemistry,[4] the production of synthetic gas (Syngas) from natural gas by means of methane steam reforming and liquid fuel from Syngas by means of the Fischer-Tropsch (FT) synthetic reaction.

With these background technologies, Nippon Steel aggressively tackled the development of the CCU technologies. Then, based on the research examples so far conducted with respect to the CO_2-based catalytic conversion[5] (**Fig. 3**), we investigated the technical trends and the possibilities of development of the technologies. Starting with the study on the synthesis of cyclic carbonate by copolymerization with epoxide in the 1990s, various chemical reaction systems have been studied by a number of domestic and overseas

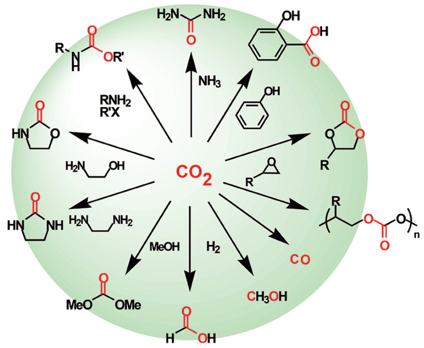

Fig. 3 Examples of research on CO_2-based catalytic conversion

research institutes. However, it was found that the successful cases put into practical use were very scarce. This is because CO_2 is highly inert, and therefore the reactivity and the reaction yield can hardly be enhanced, and the product cost can scarcely be reduced. Furthermore, it is considered that the R&D resources were concentrated on CO-based C1 chemistry.

Then, Nippon Steel started new joint studies in the field of CCU with the leading researchers in the field of C1 chemistry represented by Professor Keiichi Tomishige of Tohoku University and Professor Noritatsu Tsubaki of University of Toyama who had provided us with guidance during the past research on the catalyst development. Through such joint studies, Nippon Steel decided to promote the creation of seed technologies and study on the practical application. As a result of such endeavor, with respect to a number of the research subjects which are expected to be put into practical application on a short-term basis, mid-term basis and long-term basis as shown in **Fig. 4**, R&D is being promoted under industry-government-academia cooperation. (Details of the items in the box will be explained later.)

On the other hand, in the 5th Basic Energy Plan after the conclusion of the Paris Agreement, the Government of Japan announced the following policy: the Government maintains all the options of the decarbonization technologies, promotes the research thereof under industry-government cooperation, takes initiative in the challenge to realize decarbonization, and the achievements of the challenge to the energy conversion and the decarbonization shall constitute the basis of the decision in selecting energy in 2050. With this plan, the carbon recycling promotion office was established in the Ministry of Economy, Trade and Industry, and based on the investigation on the relevant technologies, a road map (R&D policy) was formulated and disclosed. (**Fig. 5** shows its concept.[6])

In the conceptual diagram, the government intends to promote the socially recycled use (i.e. carbon recycling) of the CO_2 separated

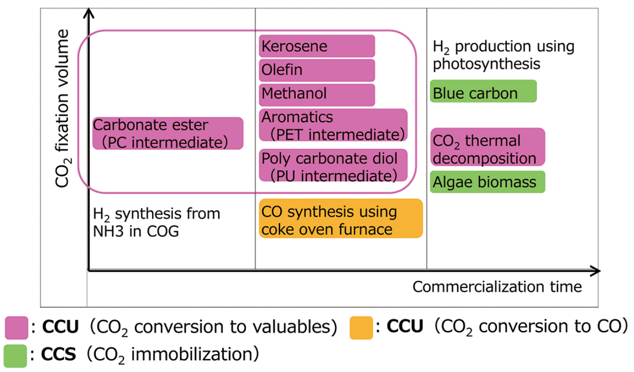

Fig. 4 Overview of research on CCUS in Nippon Steel

and captured from the fixed emission sources like those in the steelworks, and from the air, considering carbon as a resource, and by converting CO_2 to fuel and chemicals by utilizing various types of elemental technologies. Overlapping this conceptual diagram with the technology development group at Nippon Steel currently ongoing (Fig. 4), the research at Nippon Steel in the red-marked box corresponds to the government's concept in Fig. 5, and it is found that they cover most of the carbon recycling technologies. Accordingly, the steady promotion of the research of Nippon Steel toward the practical application aligns with the government policy, and simultaneously is expected to serve the best interests of the nation.

The technology development roadmap shown in **Fig. 6**[7] consists of three phases. In Phase 1, the products that do not require hydrogen and the products with high value added by hydrogen are selectively pursued. In Phase 2, the cost reduction in using the phase 1 technologies and the chemical commodities having a great demand and produced by using hydrogen are selectively pursued. In Phase 3, further cost reduction is pursued, and the government policy based on the establishment of the low cost hydrogen production process and the hydrogen procurement timing is shown.

Furthermore, in each phase, the group of products to be developed is shown, and as compared with Nippon Steel's R&D map (Fig. 4), a considerably high degree of conformity is observed in terms of practical application timing and developed products.

2. Main Discourse

This chapter explains the examples of research and development now being conducted.

2.1 New synthesis technology for polycarbonate (PC) manufacturing intermediates using CO_2 as a raw material

In 2020, Nippon Steel conducted research on "New synthesis technology for PC manufacturing intermediates using CO_2 as a raw material" in the advanced research program of the New Energy and Industrial Technology Development Organization (NEDO), a national research and development agency, jointly with Tohoku University, Mitsubishi Gas Chemical Company, Inc. and Nippon Steel Engineering Co., Ltd.

This technology development concerns the synthesis of organic carbonate from CO_2 and alcohol, and is based on the research results obtained in the joint research with Professor Keiichi Tomishige of Tohoku University. As opposed to the conventional synthesis of the

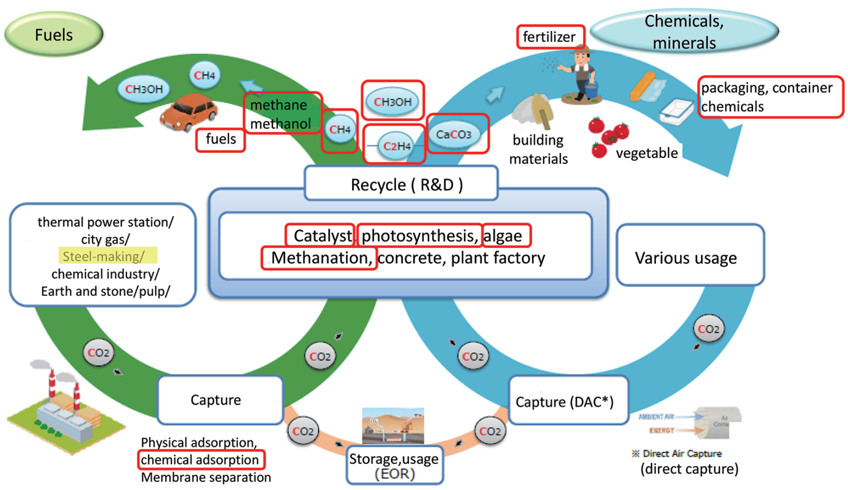

Fig. 5 Conceptual diagram of Carbon Recycling Technologies[6]

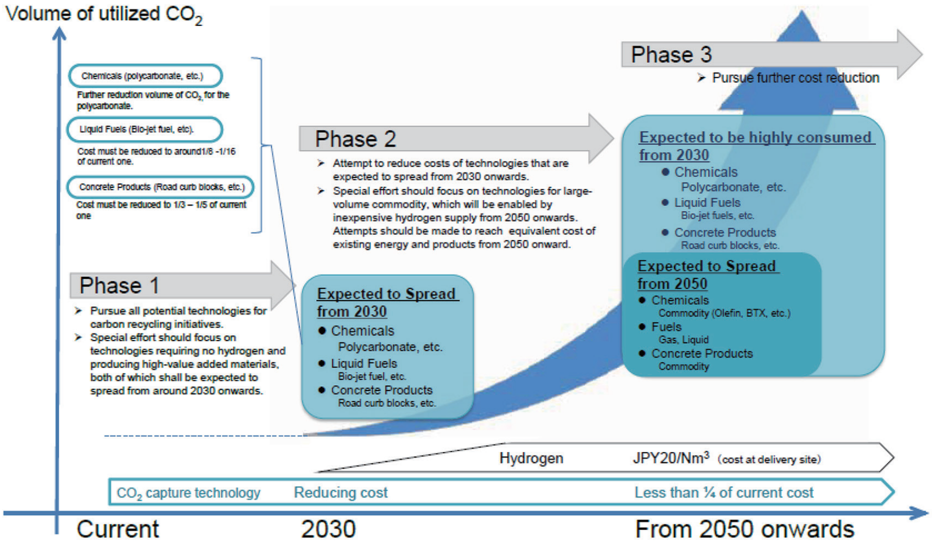

Fig. 6 Roadmap for Carbon Recycling Technologies[7]

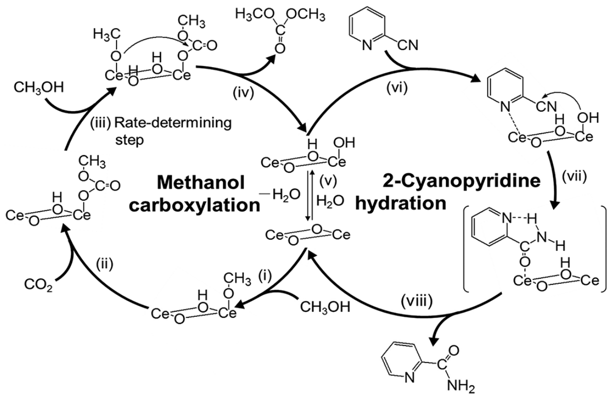

Fig. 7 Reaction mechanism of DMC (dimethyl carbonate) formation from CH_3OH+CO_2+2-cyanopyridine

organic carbonate from alcohol and phosgene, a deadly toxic compound, CO_2 is used as the substitute for the phosgene. This process was initiated by the concept of green chemistry where the chemical reaction is progressed in the presence of a catalyst. Under the circumstance where the chemical reaction hardly progresses by simply optimizing the catalyst, the coexistence of a dehydrating agent in the system was conceived. With this, the dehydrating agent was hydrated by the water produced simultaneously with the organic carbonate, removing the water from the system thereby. Thus, the equilibrium is shifted toward the formation system. As a result thereof, the progress of the reaction was found to be highly efficient.[8] (The reaction mechanism is shown in **Fig. 7**). From the viewpoint of commercialization, since the market for the equivalent amount of the byproduct produced in the hydration reaction is small, we have developed a regeneration process for the dehydrating agent to solve the problem. Furthermore, during the course of the research, a stainless steel honeycomb type catalyst structural body (**Fig. 8**) with high thermal conductivity and mass transfer and diffusion characteristics was developed, where the catalyst powder was fixed on the stainless steel honeycomb, thus preventing the catalyst from being further powdered during the reaction.[9]

The organic carbonate thus produced is used on its own for such usage as a lithium ion battery solvent, and furthermore, is used as an

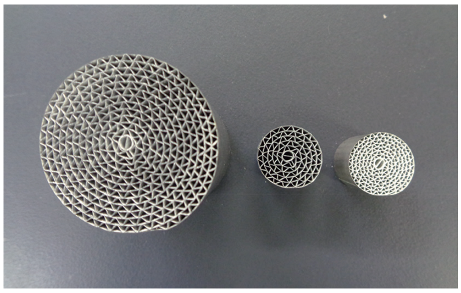

Fig. 8 Photograph of catalysts coated on stainless steel honeycomb

intermediate material of polycarbonate (hereinafter referred to as PC), a type of general purpose engineering plastic. Until 2019, we conducted bench-scale research jointly with Mitsubishi Gas Chemical Company, a PC producing company, and Nippon Steel Engineering that is in charge of designing the reactor, and confirmed that the physical property of the PC produced based on this process is not inferior to that commercially produced by the phosgene-based process.

In this NEDO project,[10] we investigate by experiment and by calculating life cycle assessment (LCA) whether or not our developed process consumes less energy in the production process as compared with that of the preceding PC production technology (**Fig. 9**[10]). Hereafter, depending on the result obtained, we will study the feasibility of the actual installation of the equipment in the pilot plant, using the CO_2 from a fixed emission source, and will advance to practical application.

2.2 New Gas-to-Liquid catalytic technology using carbon dioxide

In the framework of the realization of a low-carbon society by "game changing technology" in realization of a low carbon society mission area of MIRAI PROGRAM of the Japan Science and Technology Agency (hereinafter referred to as JST), a national research and development agency, Nippon Steel is now conducting a joint study with University of Toyama on the "New Gas-to-Liquid catalytic technology using carbon dioxide" from 2017 to 2021.[11]

This technology development concerns the catalytic process for the production of various chemical products by utilizing the Gas-to

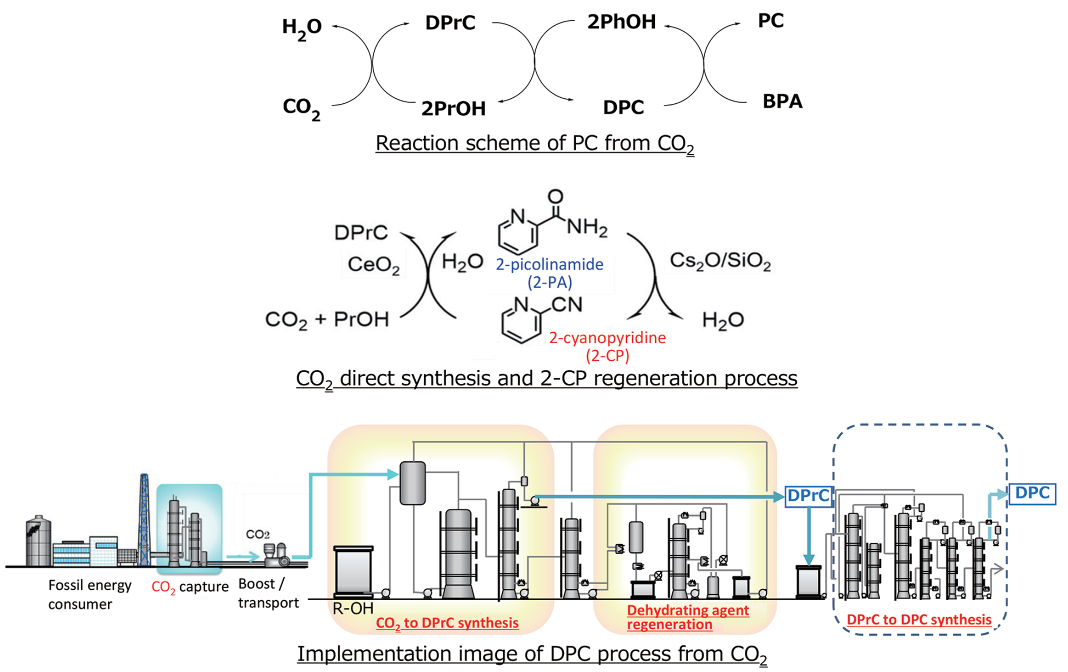

Fig. 9 Schematic manufacturing flow of DPC (Di-phenyl carbonate) from CO_2[10)]

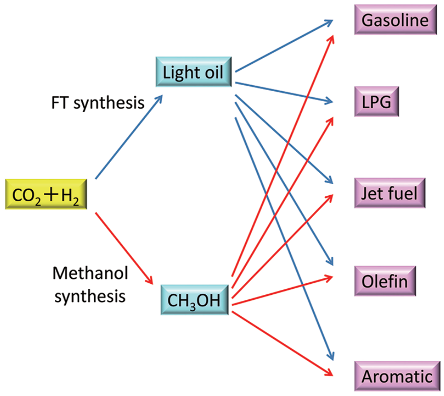

Fig. 10 Various reaction routes for CCU

Liquid (GTL) conversion technology from CO_2 and H_2 (**Fig. 10**). Conventionally, the same technology development (C1 chemistry) was conducted on the basis of the synthesized gas of CO+H_2 as the starting material as shown in the figure, and the process is the same as the conventional process except for the change of CO to CO_2 in the material gas. However, CO_2 as the base material greatly enhances the technical difficulty. Specifically, to convert an inert material, a highly active catalyst is required, and/or the intensified countermeasures that prevent the deterioration of the catalytic performance due to the generation of a great amount of by-product water. Thus, the unprecedented creative catalyst-designing concept and the process development therewith become necessary. Given the circumstances, in this JST project, we are conducting joint research with Professor Noritatsu Tsubaki of University of Toyama from the viewpoints of catalyst and process with respect to the direct synthesis of aromatics (para-xylene in particular), methanol, kerosene, light oil and olefin from CO_2, targeting the world-leading reaction efficiency and the product yield, and so far, remarkable results have been obtained.[12)] Since the subject of the R&D now being promoted is the basic materials of the chemicals and/or the fuels, when the entire global demand of the respective product is assumed to be CO_2-based, it is estimated that the amount of fixed CO_2 will be enormous. Therefore, the R&D contributes greatly to the carbon-recycling technologies in which the government is taking initiative. Hereafter, based on the result obtained in this project, and with the companies in the fields of chemistry and energy, we would like to verify the technology at the bench plant and advance to the social implementation research at the pilot plant.

2.3 Technology development for para-xylene production from CO_2

Nippon Steel is currently conducting the "Technology Development for Para-xylene Production from CO_2" in the NEDO project for the Development of Technologies for CO_2 Utilization for Chemicals, the Development of Technologies for CO_2 Reduction and Utilization , the Development of Technologies for Carbon Recycling and Next-Generation Thermal Power Generation.

This technology development is now conducting joint research with University of Toyama, Mitsubishi Corporation, Chiyoda Corporation, HighChem Company Limited and Nippon Steel Engineering during the period from 2020 to 2023.

In this NEDO project, the direct synthesizing technology of the aromatics (para-xylene) from CO_2, one of the seed technologies developed in the abovementioned JST project, on the bench plant is being verified and studied. As shown in **Fig. 11**, in this direct synthesizing technology, the hybrid catalyst consisting of Cr_2O_3 that is equipped with the function of converting CO_2 and H_2 to methanol, and the zeolite (H-ZSM-5) having the function of converting methanol to para-xylene is developed, and by arranging the catalysts in close proximity, the direct formation of the para-xylene from CO_2 in a highly efficient manner is realized.[13)]

Conventionally, the para-xylene is produced by the contact reforming process from crude oil, and is a chemical compound that is processed into polyester fibers and/or polyethylene terephthalate (PET) bottle resin via high purity terephthalic acid (PTA), and is a highly important industrial-use fundamental chemical. Due to the compositional factor of the small hydrogen/carbon ratio (H/C) of the product, among the carbon recycling technologies that produce chemicals, the process has the advantage of fixing CO_2 while suppressing the amount of use of the hydrogen source, and therefore, the feasibility of this process is considered to be very high from the viewpoints of both economy and environment. The annual global demand for para-xylene is about 49 million tons, and assuming that the entire amount of the current para-xylene demand is replaced by CO_2-based products, the amount of the fixed CO_2 is expected to reach 160 million tons annually.

In this project, we promote the sharing of roles and information with the respective research organization forming the joint research, and conduct studies on the improvement of the innovative catalyst to produce para-xylene from CO_2, the development of the industrial production technology of the catalyst and the process development therefor, and together with this, we conduct the business feasibility study including the overall economic efficiency and the CO_2 reduction effectiveness, and pursue the establishment of a route to the actual proof stage (**Fig. 12**[14]).

2.4 Development of solid catalyst processes for direct polymerization of CO_2 and diols

In the effective CO_2 utilization technology to realize the Net Zero Emission (NZE) in NEDO's unexplored challenge 2050, Nippon Steel is now conducting the "Development of Solid Catalyst Processes for Direct Polymerization of CO_2 and Diols", jointly with Osaka City University and Tohoku University from 2018 to 2022 (**Fig. 13**[15]).

In this research, we pursue the fixation of carbon dioxide by developing the solid catalytic process effective for the direct synthesis of polycarbonate diol from carbon dioxide and diol. The research originates from the synthesizing technology of organic carbonate from CO_2 and alcohol described in section 2.1. However, this research is greatly characterized by the efficient promotion of the chemical reaction without introducing a dehydration agent into the system. The polycarbonate diol so synthesized becomes the source of polyurethane, a type of engineering plastic. Therefore, it is a very important industrial fundamental chemical, and judging from the global demand, the amount of CO_2 fixation is forecast to become large.

Furthermore, in the future, by combining with the diol-synthesizing technology from biomass, diol becomes biomass-based from petrochemical based, and further fixation and reduction of carbon dioxide are expected. In this research, in addition to the experimental investigation on the improvement of the reaction efficiency, life cycle assessment (LCA) is promoted to compare the entire process and other processes. Hereafter, with a prospective result is obtained in this project, we would like to verify the technology at the bench plant with polyurethane manufacturer and advance to social implementation research at the pilot plant.

3. Conclusion

In order to realize zero-carbon steel for the steel-making industry, the technology development of the fixation of CO_2 and the addi-

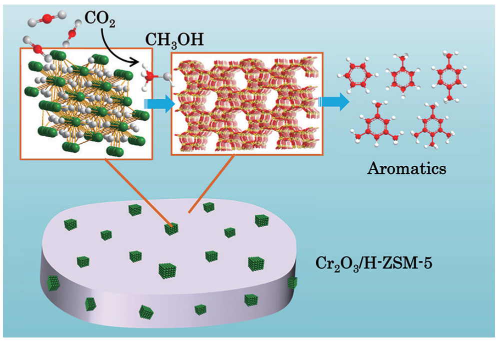

Fig. 11 Illustration of direct conversion of CO_2 to aromatics over bi-functional catalyst

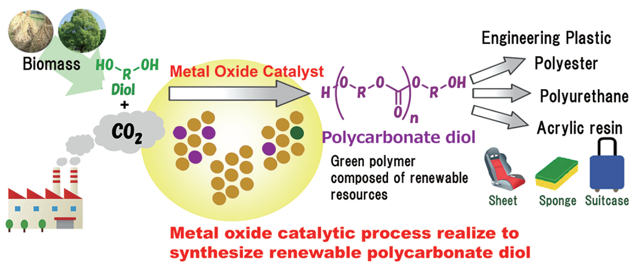

Fig. 13 Schematic manufacturing flow of polycarbonate diol from CO_2[15]

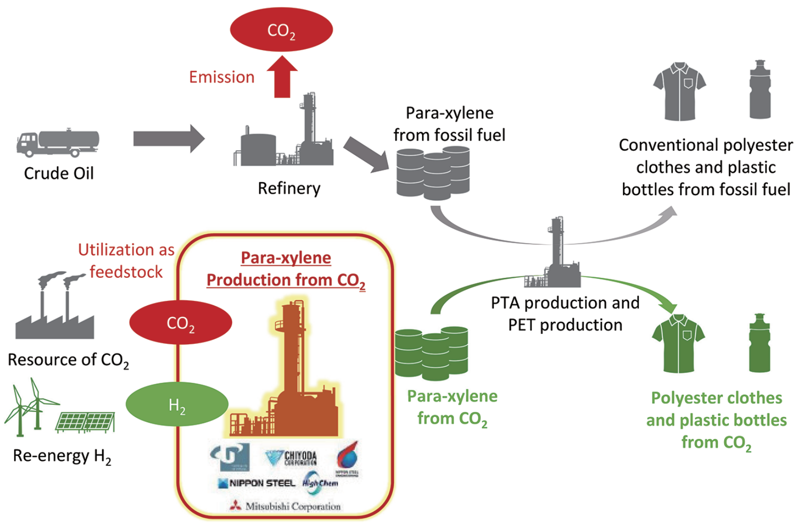

Fig. 12 Conceptual manufacturing image of PET production via para-xylene with our technology compared to conventional commercial process[14]

tion of value thereto are crucial. In its efforts made in developing catalysts for the steel-making and energy sector, Nippon Steel has conducted joint research in the field of CCU in collaboration with leading researchers in the C1 chemistry field. As a result thereof, Nippon Steel is now conducting a number of R&Ds through industry-government-academia cooperation with respect to a number of research subjects which are expected to be practically realized on a short-term, mid-term or long-term basis. Hereafter, also receiving the support of the government, we will make our utmost efforts so that the technology development group steadily produces results. Through verification of the technology at the bench plant and social implementation research in the chemical and energy fields, we will do our utmost to put it into practical use at our earliest convenience through interindustry cooperation between the steel-making industry and other industries.

Acknowledgements

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