Technical Review

Development of Technology for Advanced Utilization of Hydrogen from By-product Gas of Steelmaking Process

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1. Introduction

Huge volumes of by-product gases are generated during the steelmaking processes. In particular, coke oven gas (COG)—which is generated from the coal carbonization process to produce coke for iron ore reduction—contains about 55% hydrogen and about 30% methane. With the arrival of a hydrogen society in the offing, COG may be considered a very promising source of hydrogen.

In response to "Cool Earth 50" declared by ex-Prime Minister Abe in 2007, the steel industry also decided to develop new technologies that would help reduce CO_2 emissions by 30% by around 2030 and to put those technologies to practical use and popularize them.

Since fiscal 2008, the New Energy and Industrial Technology Development Organization (NEDO) has pursued the "CO_2 Ultimate Reduction in Steelmaking Process by Innovative Technology for Cool Earth 50: COURSE50 Project" to help achieve the reduction in CO_2 emissions from steelmaking processes.[1]

This project has two main pillars. One is the technology that permits introducing hydrogen-enriched COG into the blast furnace to reduce the iron ore so as to decrease the amount of CO_2 generated in the blast furnace. The other is the technology that permits separating out and recovering CO_2 from the blast furnace gases. The authors et al. are now engaged in the development of technology to produce hydrogen-enriched COG ("reformed COG") to be fed into the iron ore reducing process. Specifically, they are developing a reformed COG manufacturing technology that decomposes tar contained in the hot crude COG (about 800℃) from the coke oven ascension pipe into hydrogen and other types of gases with the aid of a suitable catalyst by effectively utilizing the sensible heat of the COG.

Prior to the start of the above COURSE50 Project, Nippon Steel Corporation took part in the "Development of technology for manufacturing hydrogen from steelmaking process gases: COG Project" that was pursued by the Ministry of Economy, Trade and Industry from fiscal 2001 to 2005. In that project, the company developed a technology for catalytic reforming of tar contained in COG. Ultimately, using a test facility with a capacity of about 10 Nm^3/h ("Process Development Unit: PDU") constructed in the grounds of Nippon Steel's Yawata Works, the company verified its hydrogen amplification technology and extracted several problems involved in industrialization of the technology using simulated COG and simulated tar obtained by the carbonization of coal in a rotary kiln.[2]

After completion of the project, the company energetically pursued, until 2009, its research and development into the improvement of catalysts used for tar reforming (low-temperature activity and anti-deposition of carbon, in particular), which was one of the important development themes. As a result, catalytic performance could be improved dramatically. The above R&D results prompted the authors et al. to also joined COURSE50 Project from fiscal 2010.

The research and development concept of the project is shown in
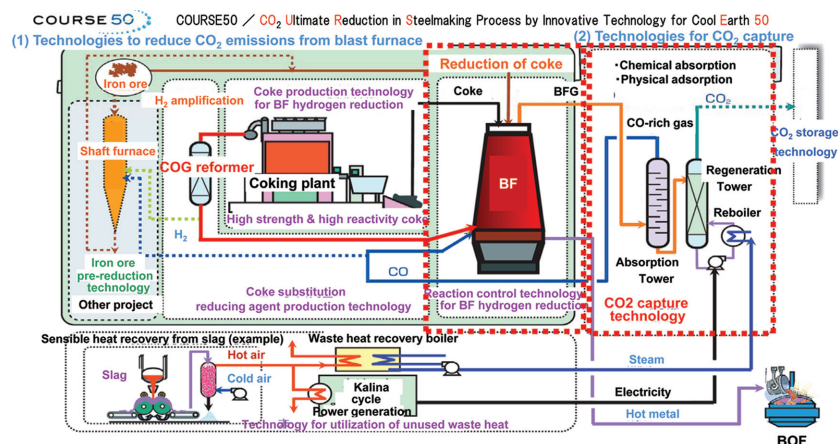

Fig. 1 Conceptual figure of R&D in the COURSE50 project (red arrow indicates our share of developments)

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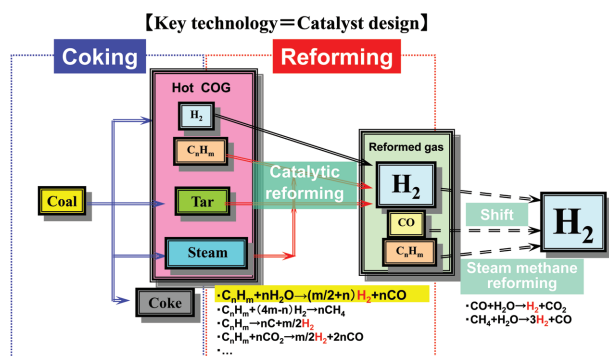   20-1, Shintomi, Futtsu, Chiba 293-8511

Fig. 2 Basic concept of H_2 amplification by catalytic reforming of tar in crude COG
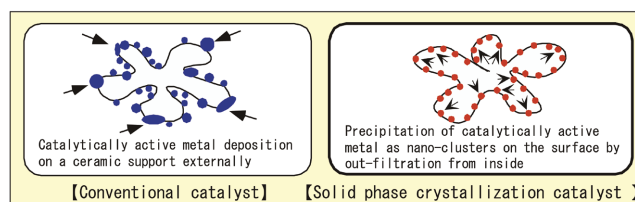

Fig. 3 Comparison of concept between conventional catalyst and our new solid phase crystallization catalyst

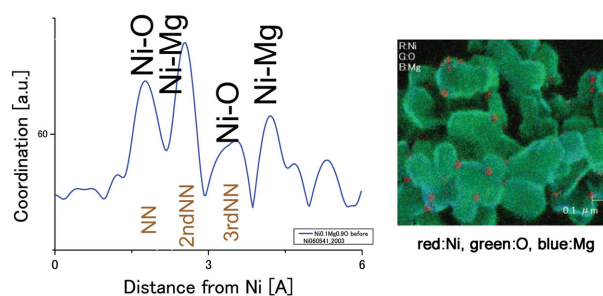Fig. 4 Analytical result of Ni-MgO by XAFS (left figure) and observation image of Ni-MgO after reduction by AES (right figure)

Fig. 1, and the concept of hydrogen amplification by catalytic reforming of tar in COG is shown in Fig. 2.

At present, for the purposes of the project, a catalytic reforming bench plant with a capacity of about 30 Nm³/h (COG dry gasification test facility using actual COG) is under construction on the grounds of Nippon Steel's Kimitsu Works. The company plans to carry out confirmation research on its hydrogen amplification technology using the bench plant in fiscal 2012 (target hydrogen amplification ratio: double, target durability: 24 hours). In the sections that follow, we focus on the results of demonstrative research on catalysts (COG Project) that Nippon Steel has been tackling to date in this particular field of technology.

2. Characteristics of Reforming Catalyst Used in the Present Research

The purpose of the present research is to develop a catalyst that permits the steam reforming reaction, hydrogenolysis, etc. to take place efficiently when COG containing tar—which is hard to separate from COG at high temperatures—is used to produce large volumes of hydrogen from the tar at high temperature. In the above reaction system, the raw source gas used contains hydrogen sulfide in concentrations as high as 2,000 ppm (about 10^5 times the sulfur concentration of raw material gas normally allowed in the field of catalysts) and tar—a heavy hydrocarbon which tends to deposit carbon easily—needs to be decomposed. Therefore, it is necessary to develop a new catalyst that is far superior to conventional catalysts in sulfur-poisoning resistance and anti-deposition of carbon.

In the present research, the company has been developing Ni-MgO-based catalysts (see Fig. 3) with an eye not on the conventional process of impregnating catalyst support with the catalytically active metal from the outside, but on the solid phase crystallization process in which a host matrix (mainly oxide) that is previously provided with a catalytically active metal species is subjected to suitable pretreatment (reduction, etc.) to cause the active metal species to coagulate on the material surface and precipitate in the form of fine metallic clusters. Compared with conventional supported catalysts, the Ni-MgO-based catalysts manufactured by the solid phase crystallization process are expected to offer these advantages: (1) little carbon deposition, (2) high reaction rate, (3) good sintering (coagulation) resistance, and (4) regeneration ability.

The nanostructure of a Ni-MgO catalyst was analyzed by the Materials Characterization Research Laboratory at the Advanced Technology Research Laboratories. The radial distribution function around Ni was evaluated using an XAFS spectrum. As a result, it was found that the Ni-MgO structure was such that the Mg within the MgO crystal lattice was partially replaced by Ni as expected (left-hand diagram in Fig. 4). In addition, a Ni-MgO catalyst in a reduced state was observed by AES. As a result, the presence of fine Ni particles on the MgO particle surface was observed (right-hand diagram in Fig. 4), validating the concept shown in Fig. 3.

3. Experiment on Catalytic Reforming of Tar in Hot COG

3.1 Experiment using actual coal carbonization gas in batch furnace[3]

Using a newly developed, Ni-MgO oxide-based catalyst and a small simulated batch-type coke oven, the company conducted an experiment on catalytic reforming reactions by passing actual carbonization gas through the catalytic reactor. As the catalyst, a Ni-MgO-based catalyst formed into a ring (12-mm ϕ × 12-mm L) was used. For comparative purposes, a commercial ring-shaped catalyst for naphtha reforming was also used.

For the catalytic tar reforming reaction, a fixed-bed flow reactor connected to the small simulated coke oven was used. The reactor was of such a construction that it could be heated from the outside by an electric furnace. The catalyst was put into the center of the reactor. Coal was charged into the above coke oven and heated to 800℃ for carbonization. In the first half of the carbonization process, the carbonization gas contains a considerable proportion of water. Therefore, the experiment was carried out once the gas composition had become relatively stable, that is, after five to 9.5 hours from the start of carbonization.

With the temperature of the catalyst bed kept at 800℃ by the electric furnace, the reactor was subjected to nitrogen purging, the catalyst was reduced in a hydrogen stream for two hours, and then the carbonization gas was introduced into the reactor. The gas flow rate was adjusted so that the space velocity (SV) relative to the feed gas became 500 h⁻¹.

Beginning twenty minutes after the start of the experiment, the gas before and after the reactor was sampled every hour to analyze

the concentrations of tar, water, hydrogen, oxygen, nitrogen, carbon monoxide, carbon dioxide, methane, ethylene, ethane, propylene, propane, butane, ammonia and hydrogen sulfide in the gas. In addition, the amount of carbon deposited on the catalyst and the amount of carbon deposited on the reactor exit-side tube were measured at the end of the experiment. **Photo 1** shows the change in appearance of the experimental gas before and after the catalytic reforming reaction. The gas after the reaction is almost colorless and transparent, whereas the gas before the reaction was yellow-colored due to the tar. Just from the change in appearance of the experimental gas, it can be seen that the catalyst reformed the tar.

Fig. 5 shows the time on stream in gas amplification ratio (i.e., the ratio in gas volume before and after reaction) of each of the main gases with the developed catalyst. Both the newly developed catalyst and commercial catalyst showed nearly the same changes in gas amplification ratio. Compared with the commercial catalyst, the developed catalyst showed higher initial activity, giving an amplification ratio of more than two for each of the beneficial gases—hydrogen and carbon monoxide.

The amplification ratio of methane also exceeded one, suggesting that the tar-decomposition reaction was progressing. On the other hand, with the commercial catalyst, the amplification ratios of hydrogen and carbon monoxide were higher than two as with the developed catalyst, but the methane amplification ratio was less than one; that is, the amount of methane decreased. The implication is
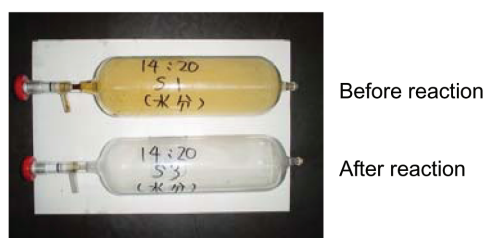

Photo 1 Appearance change of COG accompanied with tar between before and after reaction
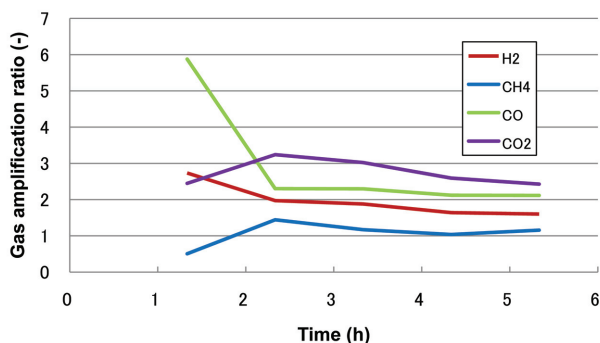

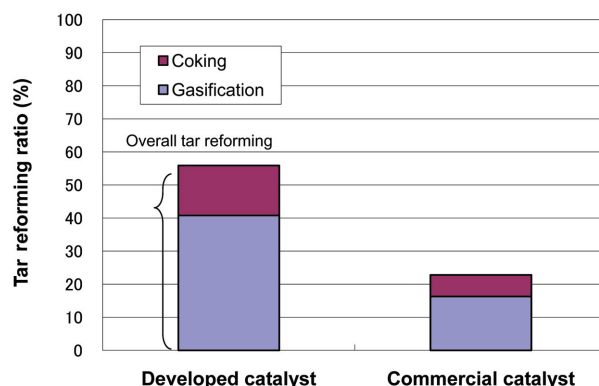Fig. 5 Time on stream of amplification ratio of main components

Fig. 6 Comparison of tar reforming ratio between developed catalyst and commercial catalyst

that the amounts of hydrogen and carbon monoxide increased as the methane reforming reaction progressed.

Fig. 6 compares the tar-reforming ratio, coking ratio and gasification ratio between the developed and commercial catalysts. With the developed catalyst, the gasification ratio was about 40% and the coking ratio was about 16%, making the overall tar-reforming ratio about 56%. By contrast, the overall tar-reforming ratio with the commercial catalyst was less than half that of the developed catalyst.

3.2 Experiment on continuous dry gasification of tar in hot COG by catalyst using PDU test facility[4]

Using the PDU test facility, the company conducted an experiment on continuous dry gasification of hot COG and studied the reforming characteristic of simulated tar, durability of the catalyst, etc.

A process flowchart of the PDU test facility is shown in **Fig. 7** and the appearance of the facility is shown in **Photo 2**. This facility carbonizes coal at about 600℃to 700℃ to generate simulated COG and reforms tar contained in the simulated COG into dry gas via a
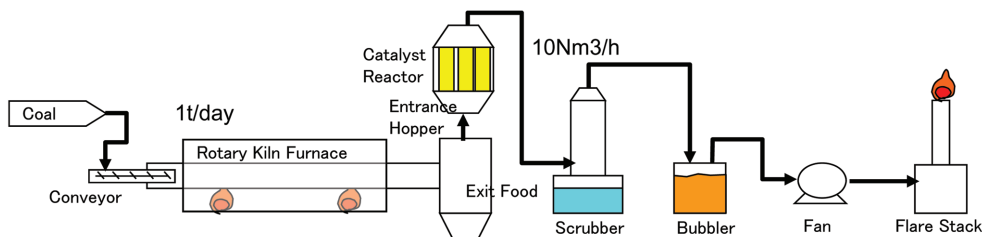

Photo 2 Appearance of PDU experimental facility

Fig. 7 Process flow diagram of PDU experimental facility

catalyst. It consists of coal carbonization facility (externally heated rotary kiln) to generate carbonization gas, dry gasification facility for catalytic reforming of COG containing tar, and gas cooling and treatment facility. From the hopper, a fixed amount of coal (20 to 40 kg/h) is put into the kiln whose internal temperature is controlled at about 630℃ by an external burner to obtain coal carbonization gas.

The coal carbonization gas generated enters the dry gasification facility (catalytic reactor) filled with catalyst, where the tar/hydrocarbon reforming reaction takes place. The setting conditions for the PDU test facility are shown in **Table 1**.

The gas that comes out of the dry gasification facility passes through a scrubber, oil bubbler, and induced draft fan to a flare stack where it is burned and exhausted. The catalyst used for dry gasification is a ring-shaped Ni-MgO-based catalyst identical to the one that was used in the experiment using a batch-type coke oven for coal carbonization described in the preceding section.

Fig. 8 shows the time on stream in amplification ratio (i.e., the volume ratio before and after the reforming reaction) of each of the main gases. Since the amounts of hydrogen, carbon monoxide and carbon dioxide after the reaction are larger than those before the reaction, it is considered that the steam reforming reaction was dominant. The amplification ratios of hydrogen, carbon monoxide and carbon dioxide showed a tendency to decrease over time. Probably, the reason for this is that the activity of the catalyst declined owing to poisoning by hydrogen sulfide contained in the COG and the deposition of carbon by thermal decomposition of tar also contained in the COG. For about seven hours of testing, the hydrogen amplification ratio remained at around two.

During the dry gasification test, not only was there a pressure drop increase due to clogging of the catalyst bed caused by carbon deposition on the catalyst as a result of the thermal decomposition of tar and by coal dust deposition on the catalyst, but also a decline in catalytic activity due to the reaction of nickel—the active metal—with hydrogen sulfide (formation of NiS).

Therefore, once the test has operated for a certain period, it is necessary to regenerate the catalyst. The purpose of catalyst regeneration is to restore the activity of the catalyst and recover the pressure drop by removing the deposit of carbon and the adsorbed sulfur from the catalyst surface by means of oxidation.

Our catalyst was regenerated by admitting air into the kiln through the air suction port in the entrance of the kiln. In order to prevent heat from being generated by sudden oxidation, the air was thinned with nitrogen to reduce its oxygen concentration below 10%. **Fig. 9** shows the change in hydrogen amplification ratio after regeneration of the catalyst.

During the reforming test carried out three times (for eight hours), the catalyst was regenerated twice. The regeneration was continued for 12 hours using a mixture of air and nitrogen whose oxygen concentration was about 6%. Although the catalyst activity decreased slightly from the original high level as a result of the repeated regeneration, the catalyst showed almost the same activity throughout the three test cycles and the hydrogen amplification ratio remained at
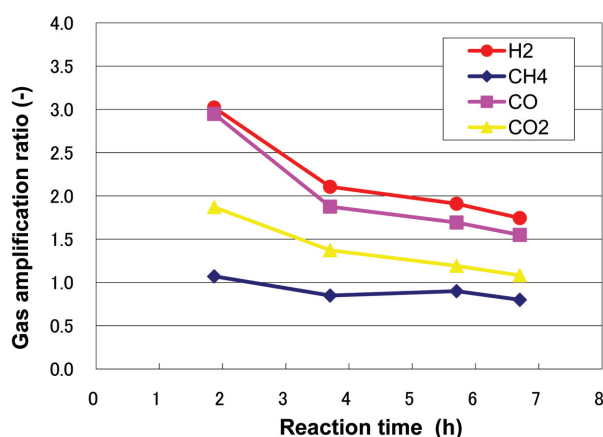
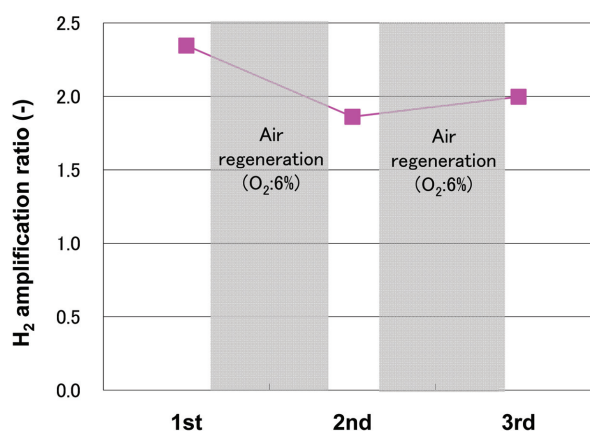**Fig. 8 Time on stream of amplification ratio of main components**

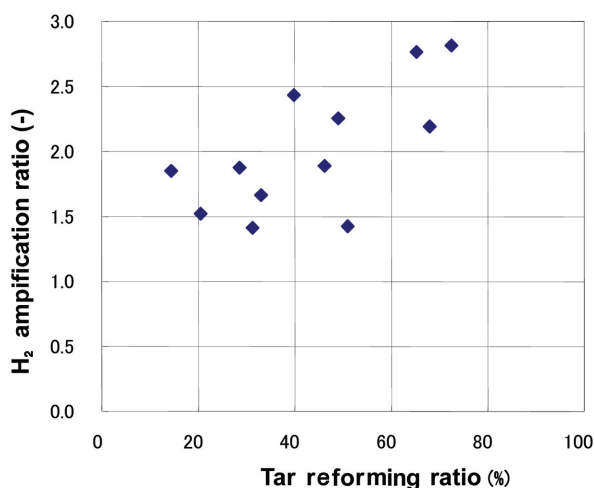**Fig. 9 H₂ amplification ratio change by regeneration**

Fig.10 Relationship between tar reforming and H₂ amplification ratio

Table 1 PDU experimental conditions

Coal feed speed	Residence time in kiln furnace	Setting temp. of kiln furnace heating burner	Setting temp. of exit food heater	Setting temp. of entrance hopper heater	Setting temp. of catalyst reactor heater
(kg/h)	(h)	(℃)	(℃)	(℃)	(℃)
20	1	750	600	600	850

around the target ratio of two. Thus, by appropriately regenerating the catalyst from time to time, it was considered possible to run the catalyst operation for a long time while maintaining the necessary catalytic activity.

Fig. 10 shows the relationship between the tar-reforming ratio and hydrogen amplification ratio, obtained by the dry gasification test. The tar-reforming ratio varied between 20% and 80% [maximum value: 73% (average value: 46%)] according to experimental conditions. The hydrogen amplification ratio shows a positive correlation with the tar-reforming ratio, indicating that hydrogen was amplified as a result of the decomposition and steam reforming of tar.

4. Conclusion

As has been described above, the company carried out a continuous dry gasification test of simulated hot COG using the PDU test facility. As a result, a measure of the prospects for hydrogen-amplification technology based on catalytic reforming of the tar could be obtained.

In the future, under the COURSE50 Project, the company plans to proceed with the performance qualification testing of the developed catalyst, with the process verification for practical application, and with the extraction of problems in the way of industrialization, through a bench plant experiment using actual crude COG in accordance with the schedule shown in **Fig. 11**. The company intends to make an all-out effort to achieve this objective.

Today, the amount of hydrogen generated from all steelworks in Japan is some eight billion Nm^3 every year. Even with the ordinary pressure swing adsorption process for separation and recovery of hydrogen, it would be possible to recover nearly five billion Nm^3 of hydrogen from all steelworks annually. This is equivalent to the hydrogen required to run as many as about six million fuel-cell vehicles. That figure would rise further if the hydrogen amplification could be conducted as described in the text.

In this context, in order for Nippon Steel to continue making positive contributions to the regeneration of the global environment in the future, we consider it vitally important not only to press ahead with the COURSE50 Project, which aims to utilize hydrogen—a by-product of the steelmaking process—to restrain CO_2 emissions from the same process, but also to search for the optimum mode of hydrogen utilization on a global basis so as make the most effective use of hydrogen arising from the steelmaking processes.

References
1) For example, http://www.jisf.or.jp/course50/index.html
2) Japan Research and Development Center for Metals: Development of Technology for Manufacturing Hydrogen from Steelmaking Process Gases, Fiscal 2004 Report on Research Results, Section 2-3. 2005
3) Japan Research and Development Center for Metals: Development of Technology for Manufacturing Hydrogen from Steelmaking Process Gases, Fiscal 2004 Report on Research Results, Section 2-5. 2005
4) Japan Research and Development Center for Metals: Development of Technology for Manufacturing Hydrogen from Steelmaking Process Gases, Fiscal 2005 Report on Research Results, Section 2-5. 2006
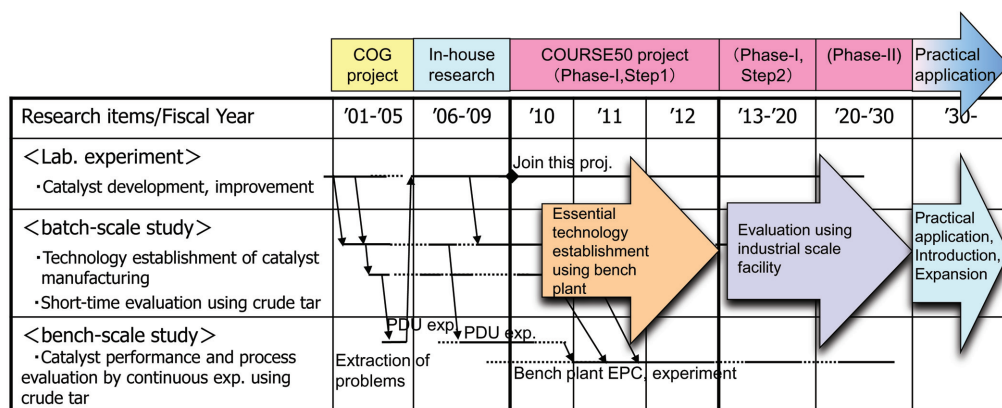
Fig.11 Schedule of the COURSE50 project for the future

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