

# A review of topics in hydrogen-related innovative materials in Japan

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## Abstract

R&D on hydrogen energy technology had been conducted in world energy network (WE-NET) Project in Japan, which was followed by the project “Development of Safe Utilization Technology and an Infrastructure for Hydrogen Use” with the emphasis on the fuel cell deployment. These projects, both supported by New Energy and Industrial Technology Development Organization (NEDO), have contained the subproject “Research on Innovative Technologies” to ensure discovery and incubation of innovative technologies that are considered indispensable for introduction and dissemination of hydrogen energy into the society. In this paper, some significant results achieved in this subproject together with the framework of the project will be reported.

In the exploratory research on the alternative materials to platinum group metals for fuel cells and hydrogen production, tantalum oxynitrides were found potentially applicable as new electrodes; the development of magnetic refrigeration of hydrogen is under way with the finding of materials with feasible magneto-caloric properties; in search of innovative hydrogen storage systems, a new process of decalin dehydrogenation/naphthalene hydrogenation based on superheated liquid-film-type catalysis was developed.

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*Keywords:* Hydrogen; Catalyst; Platinum; Liquefaction; Storage

## 1. Subproject of “Research on Innovative Technologies” in hydrogen-related technologies

### 1.1. Introduction

It has been made clear that the necessity for innovative technology has become more important and essential to realize the hydrogen economy. The innovative technologies are defined in this paper that the technologies, which have potentiality to make breakthroughs in the future but have been kept remained at early stages of development because of their uncertainty in technological values.

Since these innovative technologies seldom have explicit relations to succeeding commercialization and tend to be abandoned, it is important to strategically and intentionally deploy these innovative technologies for the development of innovative technologies.

In Japan, R&D on technologies for hydrogen energy has been conducted in the consecutive projects of “World Energy Network” (WE-NET), which was followed by the project “Development of Safe Utilization Technology and an Infrastructure for

Hydrogen Use” with the emphasis on the fuel cell development. Both projects were supported by New Energy and Industrial Technology Development Organization (NEDO).

The subproject named “Research on Innovative Technologies” has been continuously practiced to explore and incubate innovative technologies. It is the objective of this report to outline the framework and characteristics of this subproject along with the typical research topics on innovative materials.

### 1.2. The framework and characteristics of the project

The subproject, “Research on Innovative Technologies” has been practiced for 12 years as one of the tasks of “World Energy Network” (WE-NET) (1993–2002) and “Development of Safe Utilization Technology and an Infrastructure for Hydrogen Use” (2003–2007).

The framework of this subproject has been unchanged since the beginning as shown in Fig. 1. NEDO entrusts this task to The Institute of Applied Energy (IAE), which conducts public offering of innovative research themes, adoption of appropriate themes, conduction of collaborative research projects with organizations in charge of adopted research themes, and finally evaluation of the research achievements.

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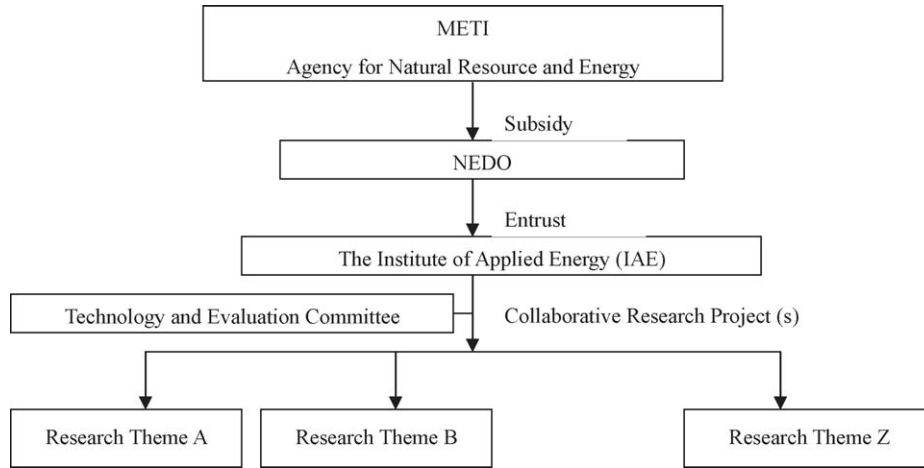


Fig. 1. Framework of the project of “Research on Innovative Technologies”.

The first characteristic of this subproject is its wide research areas. This project covers “hydrogen production, storage, transport and utilization”. This gives opportunity researchers working in the wide variety of research fields to be involved in this project.

Second characteristic is the partial turnover of research projects that takes place annually. Whole scheme of the activities is summarized in Fig. 2. Public offering for new research themes is held every year. This is followed by evaluation of applied research themes and adoption of new research themes. Towards the end of each fiscal year, research achievements are evaluated which results in the partial turnover of research projects. These annual activities are designed mainly for effective conduction of research on newly emerging technologies having potentiality.

Finally, this project has the function of making recommendations on certain research themes to NEDO. Research organization conducting a research theme which achieved promising results is recommended to prepare new proposals to NEDO for further research with larger fund.

1.3. The output of the project

In the first 2 years of WE-NET, the efforts were concentrated to construct the structure of this project. The problem in the early days was the establishment of the method of evaluation of applied proposals. This was not an easy process because of the wide variety of research fields and uncertainty of values of

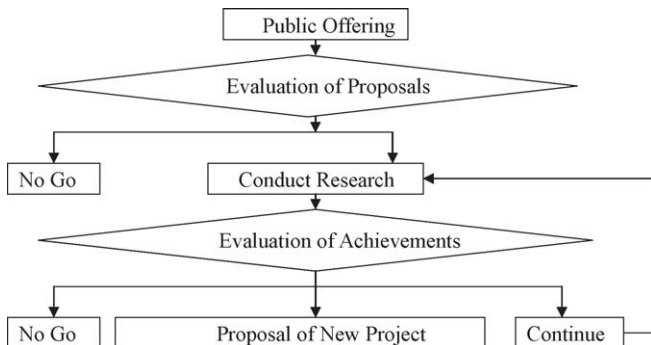


Fig. 2. Whole scheme of annual activities.

Table 1

Proposals and conducted research themes of research on innovative technologies

Fiscal year	Proposals	Accum. proposals	Conducted themes	Accum. themes	Note
1993–1998		34		12	
1999	8	42	3	15	
2000	5	47	5	20	
2001	3	50	8	28	
2002	26	76	11	39	P.O.
2003	11	87	11	50	P.O.
2004	35	122	14	64	P.O.

P.O.: public offering conducted; 1993–1998: WE-NET I, 1999–2002: WE-NET II; 2003–2004: development of safe utilization technology and an infrastructure for hydrogen use.

the proposals. This problem was solved by the application of “Analytic Hierarchy Process” which was developed by Saaty and Alexander [1].

The efficient collecting good proposals with the limited fund were realized by practice of public offering using website of NEDO and IAE in 2002.

Table 1 shows the numerical results of proposals and conducted research themes, which shows the remarkable effect of the systematic public offering.

Adopted research themes in the fiscal year of 2004 are summarized in Table 2. Table 3 shows the output of this project expressed in the number of presentations, paper publication and patent application. The small number of patent application is considered to be due to the preliminary phase of the research in this project. But it is expected to increase drastically in the current academic situation in Japan where intellectual property has been considered more important than before.

2. Research topics

2.1. Tantalum oxynitrides for new cathode of polymer electrolyte fuel cells

This research [2] is conducted in collaboration with Yokohama National University, Tokyo Institute of Technology and IAE.

Table 2  
Adopted themes in FY 2004

No.	Research themes
Hydrogen production	
1	Platinum group metal substituted catalysts for FC and H <sub>2</sub> production
2	Production of pressurized high purity H <sub>2</sub> hydrogen from reformed natural gas combined with carbon dioxide capture
3	A study on hydrogen production by high-performance fermentation bacteria
4	Feasibility study of mass production of cost-effective hydrogen by using industrial waste heat
5	Development of hydrogen production process at low temperature from methane by using hydrogen permeating membrane reactor
6	Research and development on hydrogen production technology using shape selectivity of zeolites
Storage and transportation; safety	
7	Surveillance study concerning efficient hydrogen liquefaction and stable storage of liquid hydrogen over a long period of time
8	Magnetic refrigeration for hydrogen liquefaction
9	Development of high performance magnetic refrigerants for hydrogen liquefaction by magnetic refrigeration
10	Study on diamond-like-carbon films for hydrogen gas barrier
11	Acoustical approaches for detecting leakage of gaseous hydrogen
Storage and transportation; safety	
(1)	Research project on the possibility of platinum group metal substituted catalysts for fuel cell and hydrogen production
12	Development of a matrix-supported micro fuel cells system operated at the intermediate temperature
13	Fundamental study on combustion improvement method of composition controlled hydrogen mixtures
14	Research and development of ultra low No <sub>x</sub> hydrogen engine

Although the theoretical efficiency is high, the practical efficiency of PEFC is not so high due to large cathode overpotential, which results in the large energy and exergy loss. Highly dispersed platinum or platinum alloy on carbon powder are used as a commercial cathode catalyst at present. Though platinum is generally used as the catalysts in many fields, its catalytic activity for oxygen reduction reaction (ORR) is not enough to obtain the sufficient exergy efficiency. Furthermore, the estimated global amount of the Pt deposits was too small to manufacture many fuel cell systems, especially systems for fuel cell vehicles. Thus, in order to attain the popularity of the fuel cell systems in the future, the development of alternative Pt catalysts

Table 3  
Presentations, paper publication and patents application generated from the subproject

Fiscal year	Oral presentations	Paper published	Applied patents
1999	0	0	0
2000	2	0	0
2001	6	4	0
2002	43	13	1
2003	33	14	7
2004	44	28	7
Total	128	59	15

1993–1998: WE-NET I; 1999–2002: WE-NET II; 2003–2004: Development of Safe Utilization Technology and an Infrastructure for Hydrogen Use.

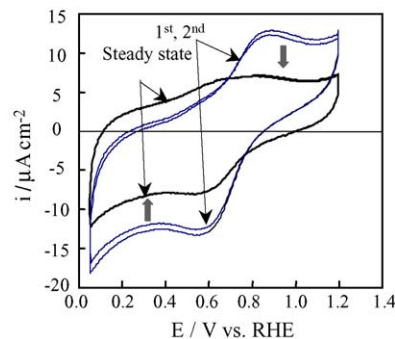


Fig. 3. Cyclic voltammogram of TaO<sub>0.96</sub>N<sub>1.04</sub> under N<sub>2</sub> atmosphere. Scan rate: 50 mV s<sup>-1</sup>.

is inevitable. We tried to apply tantalum oxynitrides (TaON) and nitrides (Ta<sub>3</sub>N<sub>5</sub>) to cathode catalysts. These compounds are known as visible light driven photocatalysts. However, these catalytic activities of oxygen reduction were unknown.

Fig. 3 shows the typical cyclic voltammogram of TaON under N<sub>2</sub> atmosphere. At first several cycles, the anodic peak at 0.9 V and cathodic peak at 0.6 V were observed and the anodic and cathodic currents decreased with potential cycling as shown in Fig. 3. However, the current change was found to be due to the Nafion<sup>®</sup> on the electrode surface. In case of the carbon rod with only Nafion<sup>®</sup>, the similar current change was observed. After several potential cycles, the potential–current curve became unchanged to achieve the steady state, which showed that the corrosion resistance of TaON is high in acid electrolyte. Because all of TaON, Ta<sub>2</sub>O<sub>5</sub> and Ta<sub>3</sub>N<sub>5</sub> had similar voltammogram, all samples were considered to have high corrosion resistance in acid solution.

Fig. 4 shows the slow scan voltammogram under oxygen atmosphere. Ta<sub>2</sub>O<sub>5</sub>, Ta<sub>3</sub>N<sub>5</sub> and TaON except TaO<sub>0.92</sub>N<sub>1.05</sub> (nitrogen content: 7 wt.%) had little catalytic activity for ORR. However, the reduction current of TaO<sub>0.92</sub>N<sub>1.05</sub> (nitrogen content: 7 wt.%) for ORR was clearly observed in the range of less than ca. 0.8 V vs. RHE. Because of the phenomena that such a reduction current was not observed under nitrogen atmosphere, the reduction current was considered to be responsible for oxygen reduction reaction.

It was shown that the catalytic activity was very sensitive to bulk composition and/or surface state, because of the fact that only TaO<sub>0.92</sub>N<sub>1.05</sub> (nitrogen content: 7 wt.%) sample had some

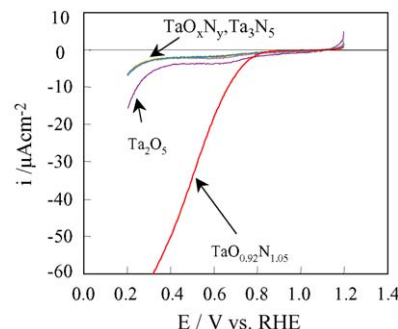


Fig. 4. Potential–current curve for oxygen reduction reaction. Scan rate: 5 mV s<sup>-1</sup>.

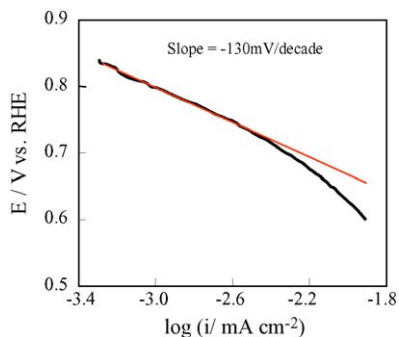


Fig. 5. Tafel plot for oxygen reduction of TaO<sub>0.96</sub>N<sub>1.04</sub>.

catalytic activity. Fig. 5 shows the Tafel plot of TaO<sub>0.92</sub>N<sub>1.05</sub> for ORR where the current was taken as the difference between the reduction current under oxygen and that under nitrogen. Tafel slope was ca. -130mV/dec indicating that the number of transferred electron of the rate-determining step was estimated to be unity. According to XPS analysis, oxygen species, such as hydroxide ions, on the catalyst affected the catalytic activity for oxygen reduction.

In summary, to increase the catalytic activity of oxygen reduction reaction and to reduce the use of platinum which is utilized as a commercial cathode catalyst, non-platinum material such as tantalum oxynitride, TaON, were examined for the application to the cathode materials of polymer electrolyte fuel cell. Ta<sub>2</sub>O<sub>5</sub>, TaON and Ta<sub>3</sub>N<sub>5</sub> had high stability in acid solution. Among them, TaO<sub>0.92</sub>N<sub>1.05</sub> (nitrogen content: 7 wt.%) clearly showed catalytic activity for ORR.

2.2. Magnetic refrigeration and liquefaction of hydrogen

This research [3,4] is conducted in collaboration with National Institute of Materials Science, Kanazawa University and IAE.

Liquid hydrogen is one of the promising media for transporting and storing hydrogen efficiently and economically due to its high volumetric density. For liquefaction of gaseous hydrogen, conventional systems use the J-T valve or heat exchanger at the liquid hydrogen temperature of 20.7 K, and the figure of merit in those systems is less than or comparable to approximately 35%. In order to attain much higher efficiency, magnetic refrigeration is one of the hopeful cooling methods, because the direct condensation of gaseous hydrogen can be realized with high thermal efficiency by using the sub-cooled surface of the magnetic material. The liquefaction efficiency of the hydrogen magnetic refrigeration is expected to be higher than 50% based on the analogy from the helium liquefaction in the previous study. This method is also expected to be useful for the higher reliability than that of the J-T valve, where contaminations of gas easily block the gas flow passes. The goal of this research is to realize a hydrogen liquefaction system with Carnot efficiency higher than 50% by the magnetic refrigeration. Magnetic refrigeration which is based on the magneto-caloric effect of solid material has potential for high thermal efficiency based on the principle of reversible cycle and the advantage of compactness due to high entropy density of the magnetic material.

Magnetic refrigeration has been used in laboratories for over 75 years and is unique technique to realized temperatures below 1 mK. Application of this technique above 1 K has been done for various temperature ranges such as room temperature, helium temperature and superfluid helium temperature in the past 25 years.

The research areas are divided in to two fields, namely, Carnot magnetic refrigeration for hydrogen liquefaction and active magnetic regenerative refrigeration (AMRR).

2.2.1. Carnot magnetic refrigeration for hydrogen liquefaction

Carnot magnetic refrigeration with condensation-liquefaction process at high efficiency is proposed to substitute the

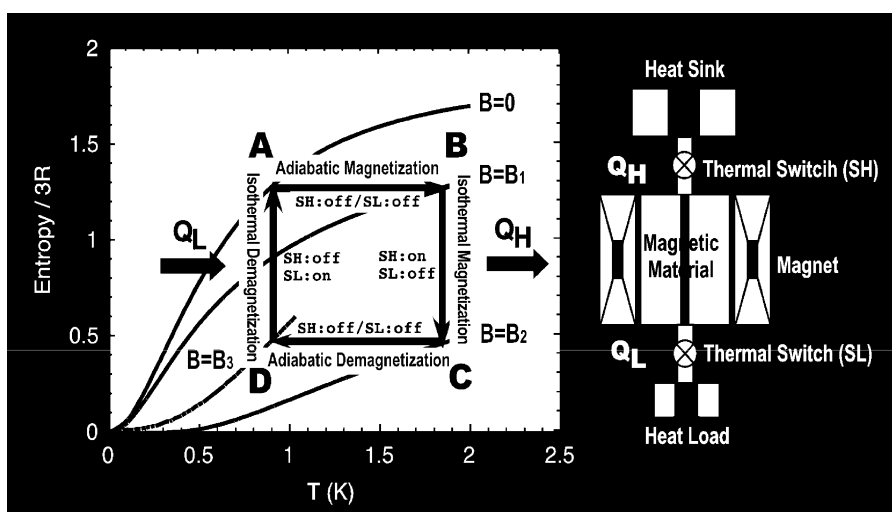


Fig. 6. Principles of Carnot magnetic refrigeration. Carnot Cycle operation; 1, adiabatic magnetization (A–B),  $B = 0$ – $B_1$ , thermal switches off; 2, isothermal magnetization (B–C),  $B = B_1$ – $B_2$ , Sw. SH on, SL off; 3, adiabatic demagnetization (C–D),  $B = B_2$ – $B_3$ , switches off; 4, isothermal demagnetization (D–A),  $B = B_3$  to 0, Sw. SH off, SL on.

conventional J-T method. The principle of Carnot magnetic refrigeration is shown in Fig. 6.

Serious difficulty occurs to choose the magnetic materials for 20 K magnetic refrigeration, because the conventional magnetic materials are mostly metallic compounds which are reactive under the hydrogen atmosphere. On the other hand, some oxide magnetic materials such as rare-earth garnets are generally stable in the hydrogen. As this study seeks for a realistic cooling system under the current technology level, the following points are especially considered:

- Polycrystal magnetic refrigeration materials because of their easy fabrication and flexibility;
- Magnetic field of 6 T provided by a helium free magnet system.

Since the magnetic material  $Gd_3Ga_5O_{12}$  (GGG) is one of the standard materials in the low temperature magnetic refrigeration, our research has been focussed on new magnetic materials having higher magneto-caloric effect (MCE) than GGG.

GGG is known as a good oxide magnetic material, but shows poor MCE in the range of 20 K. Some magnetically anisotropic materials like  $Dy_3Al_5O_{12}$  (DAG) are useful to provide the large MCE, when the magnetic field is applied to the easy axis direction of the single crystal as shown in Fig. 7. But if those samples are to be fabricated as the polycrystals, the entropy change reduction occurs by averaging the anisotropy. It is suggested that replacing the anisotropic element with isotropic one is an effective method to increase the MCE. Especially in the  $(Gd_xDy_{1-x})Al_5O_{12}$  system, this is useful not only to weaken the anisotropy, but also to increase the magnetic saturation entropy (Fig. 8). For the  $X=0.2$  sample, about 260 J/kg of MCE can be estimated at 20 K by applying the magnetic field of 6 T. It showed 80% increase in MCE to GGG (Fig. 8) and suggested that this compound is practically applicable.

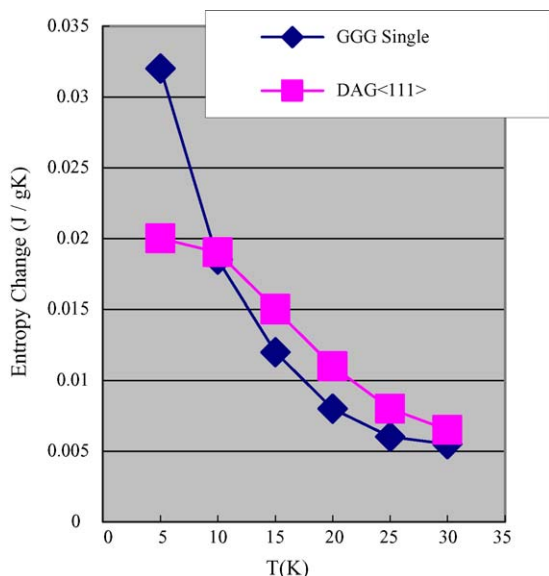


Fig. 7. Entropy change of GGG and DAG single.

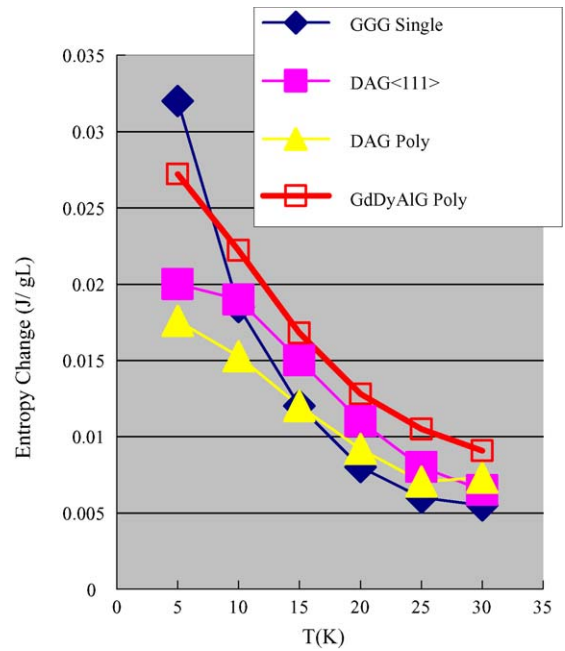


Fig. 8. Entropy change of DAG poly and GdDyAlG poly.

### 2.2.2. Active magnetic regenerative refrigeration (AMRR)

A regenerative cycle is required to achieve magnetic refrigeration over a wide range of temperature under the practical magnetic fields of superconducting magnet because the adiabatic temperature change in most of the rare earth compounds is typically  $1\text{--}2^\circ\text{K T}^{-1}$  field change. As a basic cycle of magnetic regenerative refrigeration that follows liquefaction by magnetic refrigeration, temperature range from 20 to 77 K or LNG temperature was set as the goal. Active magnetic regenerator (AMR) is thought to be a useful regenerative magnetic refrigerator and it is called active because it produces refrigeration independently using the magneto-caloric effect, whereas an ordinary thermal regenerator behaves as a thermal sponge and a passive heat exchanger. Performance evaluation (Fig. 9) and the basic thermal analysis of active magnetic regenerative refrigeration was conducted. As a result:

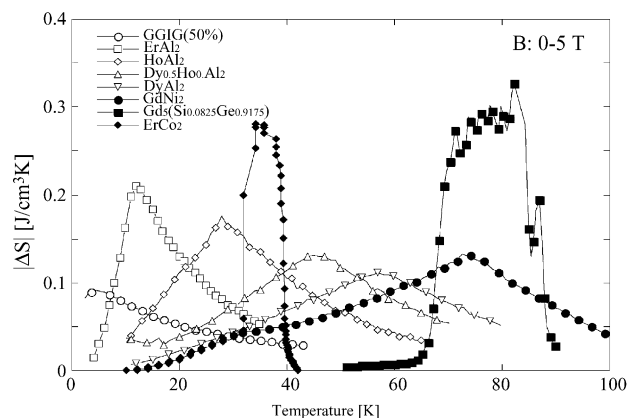


Fig. 9. Magnetic entropy change.



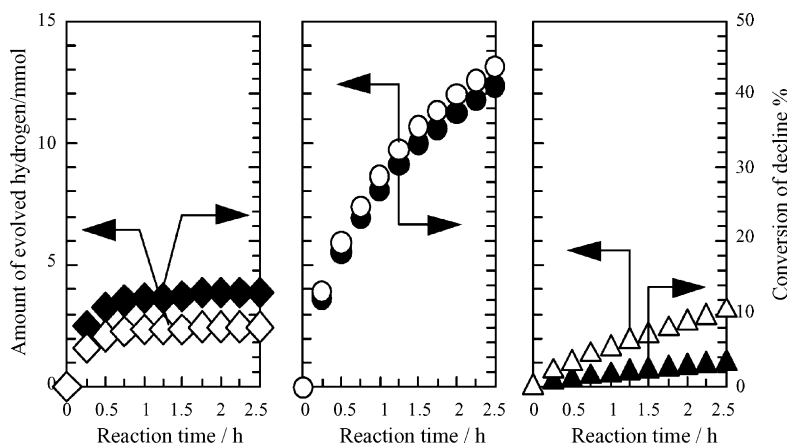


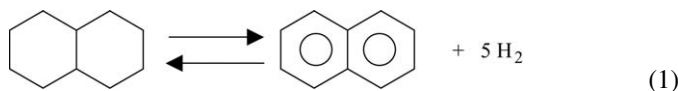
Fig. 10. Time courses of hydrogen evolved from decalin and conversion of decalin with carbon-supported platinum catalyst at various charged amounts of decalin. Catalyst: platinum nano-particles supported on granular activated carbon (Pt/C, 5 wt.-metal%) 0.30 g charged amount of decalin: 0.5 (□, □), 1.0 (○, ●) and 3.0 ml (□, ▲), Reaction conditions: boiling and refluxing by heating at 210 °C and cooling at 5 °C.

- (1)  $Gd_5(Si_xGe_{1-x})_4$  was found to be a hopeful material in the wide range of temperatures and its entropy diagram was determined along with effect of hysteresis which is peculiar to primary conversion materials.
- (2)  $ErCo_2$  was found to be hopeful at around 30 K by inspection of its entropy diagram.

### 2.3. Efficient hydrogen supply from organic chemical hydrides with superheated liquid-film-type catalysis for operating fuel cells

This research [4] was conducted in collaboration with Tokyo University of Science, Nippon Oil Research Institute Co., Ltd. and IAE.

Hydrogen for fuel cells affords us an important alternative energy from environmental standpoints, any breakthrough is urgently required to mobile storage of hydrogen. By this reason, a catalytic reaction pair of decalin dehydrogenation/naphthalene hydrogenation (Eq. (1)) has been proposed by our group as an organic chemical hydride.



As for storage capacities of hydrogen in weight and volume, decalin (7.3 wt.%, 64.8 kg-H<sub>2</sub>/m<sup>3</sup>) is able to store hydrogen more than the values (6.5 wt.%, 62.0 kg-H<sub>2</sub>/m<sup>3</sup>) targeted in the U.S. Department of Energy (DOE) Hydrogen plan. We found that reactive distillation conditions and “superheated liquid-film-type catalysis” made it possible to evolve hydrogen efficiently from organic hydrides, namely for decalin at lower heating temperatures than 300 °C.

Catalytic decalin dehydrogenation in batch-wise operation is explained in detail as follows. Catalytic rates of hydrogen evolution from various charged amounts of decalin (0.5, 1.0 and 3.0 ml) with a constant amount of the carbon-supported platinum catalyst (Pt/C, 0.30 g) were compared with each other under common boiling and refluxing conditions at 210 °C. The

time courses of hydrogen evolution as well as conversion (2.5 h) reveal us that the ratios of catalyst-to-decalin are quite sensitive to the catalytic activities (Fig. 10).

When the catalyst was suspended uniformly in 3.0 ml decalin, low initial rates of hydrogen evolution and poor 2.5 h conversions were obtained. In the case of 1.0 ml decalin, the catalyst could not be suspended, but its surface layer became just wet with the substrate solution. The present state of catalyst was designated as a “superheated liquid-film state”. Both the highest initial rate of hydrogen evolution and the highest decalin conversion (2.5 h) were accomplished simultaneously only by adopting this superheated liquid-film-type catalysis. Under this conditions of reactive distillation, chemical equilibrium can be shifted toward the dehydrogenation side to even at 210 °C, which is the unfavorable temperature range for decalin conversion.

In case that the initially charged amount of decalin was as small as 0.5 ml, the catalyst surface became dry within an hour as if the catalyst behaved as a sand bath. The substrate supply to the catalyst surface was apt to become deficient especially after the reaction time elapsed. Under boiling conditions, the catalyst temperature in the liquid-film state was higher than the boiling point of the solution, whereas its temperature in the suspended state was equal to that of the boiling bulk solution. Superheated active sites in the liquid-film state are certainly advantageous to the suspended one for liquid-phase decalin dehydrogenation.

It was demonstrated that a rather wide range of feed rates were allowed in the continuous operation, which leads us to the expectation that reactor designing is not difficult to keep high reaction rates.

The updated results of this decalin/naphthalene pair for hydrogen mobile storage for fuel cell vehicles were summarized as follows.

- (1) Efficient hydrogen evolution from decalin over carbon-supported platinum-based catalysts was well demonstrated by heating at the temperature range of 210–280 °C in a

batch-wise operation under the concept of “superheated liquid-film type catalysis”.

- (2) Similar superheated liquid-film conditions were realized at more flexible rate range of decalin feed in a continuous operation, giving high stationary-rate of hydrogen evolution at the same temperature.
- (3) According to a correlation curve based on experimental results in the continuous operation, the reaction area necessary to a 50 kW power could be decreased down to below 1.0 m<sup>2</sup> at one-pass conversion above 70% on the fuel-cell vehicles. An additional function of internal refluxing and arrangement of suitable composite catalysts would be helpful to load it on the fuel-cell vehicles.

### 3. Summary

By the project “Research on Innovative Technologies”, the deployment of subprojects for innovative technology has been successfully conducted. And the research conducted in this project is contributing to development of hydrogen-related tech-

nologies. New Projects have been proposed based on the results of this project.

### Acknowledgement

The authors are grateful to New Energy Development Organization (NEDO) for the financial support of this research.

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