Dehydrogenation Catalyst for Organic Hydride on the Basis of Superheated Liquid-Film Concept

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Abstract: Reversible reaction couples of hydrogenation and dehydrogenation of organic compounds e.g. methylcyclohexane and toluene, or 2-propanol and acetone, are described in terms of hydrogen supplier to fuel cells, which will satisfy our demands of combined heat and power at various compact sizes. Carbon supported nano-sized metal particles, wetted with the liquid substrate in a reactor, was used for conversion of organic hydrides into hydrogen and organic compounds, being separable by distillation. Vigorous nucleate boiling is important for heat transfer as well as for irreversible bubble evolution, leading hydrogen to the vapor phase. Once the bubble is broken at the interface, catalytic hydrogenation will be prohibited, because gaseous hydrogen is unable to dissolve into the boiling liquid. Catalytic dehydrogenation under superheated liquid-film conditions can thus convert low-quality heats into hydrogen energy.

Keywords: Dehydrogenation catalyst, Organic hydride, Superheated liquid-film.

1. INTRODUCTION

As a storable and transportable hydrogen carrier, organic hydride can take a mediator role in energy supply chain [1], being initiated with renewable energies and utilized finally at local and small-scaled applications. In contrast to facile hydrogenation reactions, endothermic dehydrogenation should include for this purpose such difficult performances as perfect conversion at temperatures as low as possible by adopting a compact-sized reactor.

Under nucleate boiling conditions [2], superheated liquid of organic hydride was enforced to contact with catalytically-active sites after frequent removal of bubbles, by which generated hydrogen was carried out efficiently to the gas phase without return. Moreover, nano-sized metal particles supported on microporous carbon must properly be immersed with organic hydride e.g. 2-propanol, decalin or methylcyclohexane, under steep temperature gradients [3].

In the present paper, simultaneous reaction procedures of both perfect conversions and high liquid-hourly space velocities (LHSV) are explored upon the basis of irreversible thermodynamics in order to perform reactor design for supplying hydrogen to operate solid oxide fuel cell (SOFC) in domestic scales.

2. EXPERIMENTAL

2.1. Catalyst Support

Highly-porous carbon granule and carbon cloth were adopted as catalyst-support materials. Granular particles (7 μm) were made by steam activation with potassiumhydroxide from palm shell (Kansai Netsu Kagaku Co.), being bestowed with large surface area ($3100\ m^2g^{-1}$ by the BET method), huge micropore volume ($1.78\ mLg^{-1}$) and small micropore diameter (2 nm). These characteristics were brought from such processes that graphitic carbon layers were selectively eroded with repeated reactions of $C + KOH \rightarrow CO + 1/2\ H_2 + K$ and $K + H_2O \rightarrow KOH + 1/2\ H_2$ during activation. On the contrary, carbon fibres were made by tugging-calcination of poly-acrylonitrile and woven into carbon cloth with plenty nano-cracks of 1.5 nm width with the BET surface area of $1834\ m^2g^{-1}$ (Kuraray Chemicals Co.).

Organic hydrides are accepted into these micropores at low temperatures, left inside due to capillary condensation at higher temperatures and possible to migrate over the carbon surface as liquid even at superheated temperatures.

2.2. Catalyst Metal

Carbon-supported platinum catalysts (5 wt%)were prepared from an aqueous solution of K_2PtCl_4 by stirring with the granular carbon, which had been treated with a concentrated NaOH aqueous solution. Base treatment would change the micropore structures

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of granular carbon. Indeed pretreatment at pH 14 was revealed to reduce the specific surface area to 1925 m^2g^{-1} and the micropore volume to 0.97 mLg^{-1}, but the pore diameter was ascertained to retain the magnitude of 2 nm. Valency of $PtCl_4^{2-}$ was reduced to metallic Pt with a hot aqueous solution of $NaBH_4$, which was followed by water washing and prolonged heating evacuation. The average diameter of well-dispersed platinum particles was obtained as 2.7 nm in an electron-microscope image [4]. High particle dispersion would originally be ascribed to the ligand exchange of $PtCl_4^{2-}$ into $Pt(OH)Cl_3^{2-}$ inside the micropore of base-pretreated carbon, since it would be presumed for platinum to coordinate with any hydrophilic group of carbon through strong mediation of the OH ligand and to be reduced into scattered atoms all over the granule. Composite catalysts of either Pt-Fe/C or Pt-Ir/C were prepared similarly from the mixed aqueous solution of K_2PtCl_4 and $FeCl_3$ or K_2PtCl_4 and $IrCl_3$ by impregnation. Another composite couple of Pt-Re was made from mixing of the Pt/C catalyst and $Re(C_5H_5)(CO)_2$ at 240°C under hydrogen atmosphere.

Platinum catalysts supported on carbon cloth (5 wt%) were prepared by a similar impregnation method. A certain amount of carbon cloth, pre-evacuated at 150°C for 1 h, was immersed and stirred for 24 h with an aqueous solution of K_2PtCl_4, which was followed by $NaBH_4$ reduction. After water-washing, filtering and drying in vacuo at 200°C for 5 h, platinum particles supported on carbon cloth were cut into circular and rectangular shapes before setting to the reactor for hydrogen generation. According to electron-microscope image, nano-sized platinum particles were certainly prepared, but homogeneous dispersion was difficult on carbon cloth.

2.3. Reaction Apparatus

Both batch-wise and flow-type reactors were used for generating hydrogen from organic hydrides [5].

Batch-wise pursuit of catalysis was performed with a set of round-bottom flask, oil bath, refluxing condenser and gas burette (Figure **1a**). A certain amount of granular catalyst and various amounts of organic hydride were set inside the flask, from which hydrogen was transferred to gas burette under reactive distillation conditions.

A flow-type rector was consisted of carbon-cloth catalyst laid on a pan, circular ring for spraying substrate liquid, mantle-and block-shaped electric heaters monitored with thermocouples, refluxing condenser and gas flow meter (Figure **1b**). Spray rings with three and six holes were examined to know whether poring densities of liquid toward the carbon-cloth catalyst and distribution rates of substrate over the catalyst surface could affect the reaction rates or not.

Another flow-type reactor was different concerning style of substrate feed and mode of catalyst packing. The granular-carbon catalyst was set in a 1/4 inch stainless tube with length of 6 cm, containing inlet packing of carbon cloth (0.5 cm), preheating zone of granular carbon (3 cm), reaction zone of granular catalyst (2 cm) and outlet packing of carbon cloth (0.5 cm). Substrate liquid was fed from the bottom, heated

(a) Batch-wise reactor   (b) Flow-type reactor
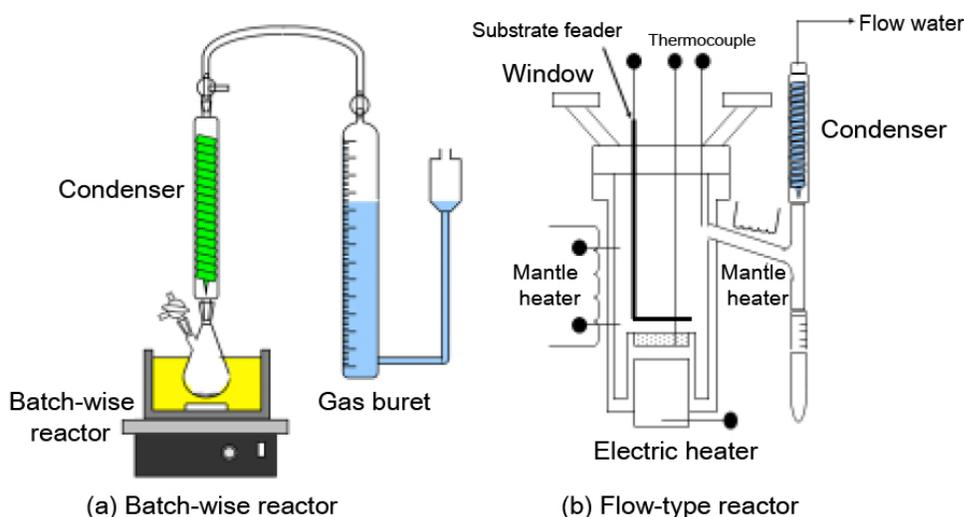
Figure 1: Experimental apparatus for catalytic dehydrogenation under boiling and refluxing conditions in batch-wise or flow-type operation.
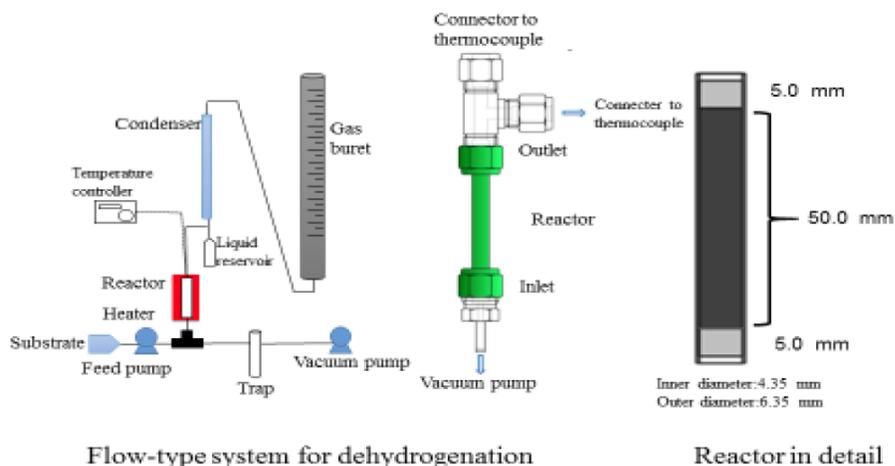
Figure 2: Experimental apparatus for catalytic dehydrogenation under boiling conditions in continuous operation with tubular flow reactor.

gradually, evolved hydrogen accompanying evaporation, and then removed out as a gaseous mixture (Figure **2**).

2.4. Reaction Procedure

Platinum nano-particles supported on highly-porous carbon must be wetted with superheated substrate liquid, even though it was fed at ambient temperatures irrespective of the reactor, either batch-wise or flow-type.In a flow-type reactor (Figure **1b**), liquid-phase substrate was supplied continuously to a certain amount of the Pt/C catalyst at various feed rates under atmospheric pressure. All vapors were removed from the reactor via a thermally protected part by a refluxing condenser. After confirming the reaction to be stationary, hydrogen generation rates were recorded every 5 min for 30 min with a flow meter, and the condensate composition was analyzed gas-chromatographically. Since the substrate was fed as droplets from a ring-shaped feeder to the catalyst in a flat-bottomed round vessel, nano-sized platinum had to be supported on carbon cloth in order to avoid jumping of the granular catalyst due to substrate droplets. Two kinds of hole densities for sending the same amount of substrate were attempted with respect to the feeder ring, one concentrated (three holes) and the other dispersed (six holes). The catalyst-layer temperatures were measured with a thermocouple, set at the bottom of the catalyst carbon-cloth.

Properly-wetted states under steep temperature gradient were essentially important for enhancing the rates of hydrogen generation and the extents of conversion. Reaction procedures should be controlled to avoid i) gas-solid contact caused by drying up, ii)

liquid-flooding to diminish temperature gradient, iii) useless evaporation from bulk liquid and iv) liquid-feed channeling induced by excessive flow.

The amount ratio of substrate liquid to catalyst solid seems to be decisive for efficient hydrogen generation in batch-wise procedures, whereas proper feed rates of substrate must be chosen for flow-type operations in order to keep the catalyst under superheated liquid-film conditions.

3. RESULTS

3.1. Batch-Wise Dehydrogenation of 2-Propanol

In the batch-wise reactor, hydrogen generation was pursued under boiling and refluxing conditions by heating at 90°C and cooling at 5°C for 2.0h,where a constant amount of granular catalyst (1.01g) and various amounts of 2-propanol (2.0, 3.0, 4.0, 5.0 and 10.0mL) were laid in a round-bottom flasks, as shown in Figure **3**. Catalytic behaviors were quite sensitive to the amounts of 2-propanol. The optimum liquid-solid amount ratio for the catalyst of 1.01g became 2-propanol of 4.0mL. As for the region of high liquid/solid ratios as 5.0 and 10.0 mL, the larger substrate amount gave the smaller catalytic activity. On the contrary, the substrates as scarce as 2.0 and 3.0mL resulted in two catalysis phases i.e. initial rapid and later suppressed generation of hydrogen even under the same reaction conditions.

Hydrogen generation (2h) was correlated with the charged amount in Figure **4a**, exhibiting a maximum at 4.0mL substrate, which was indifferent to the kinds of metal species, either platinum alone or platinum-iron composite. The present tendency may suggest that the
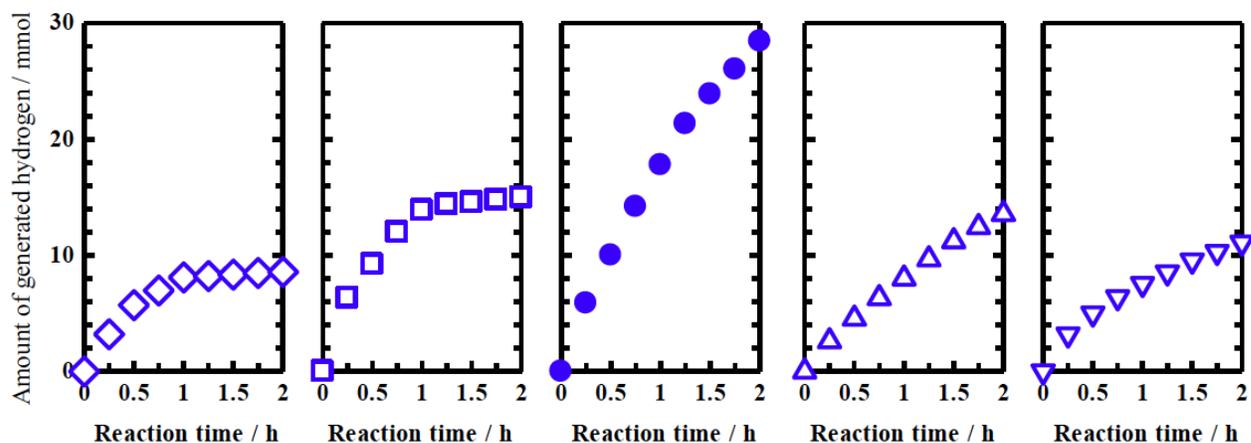
Figure 3: Dehydrogenation of catalysis for 2-propanol in a batch-wise reactor. Relationship between reaction rates and charged amounts of substrate.

Time course of hydrogen generation with carbon-supported platinum-iron catalyst at variously-charged amount of 2-proponal. Charged amount: 2.0 (◇), 3.0 (□), 4.0 (●), 5.0 (△), and 10.0 mL (▽).

Catalyst: composite nanoparticles supported on the granular activated carbon (Pt-Fe (10:1)/C 5 wt-metal%, 1.01 g). Reaction conditions: boiling and refluxing by heating at 90 °C and cooling at 5 °C.
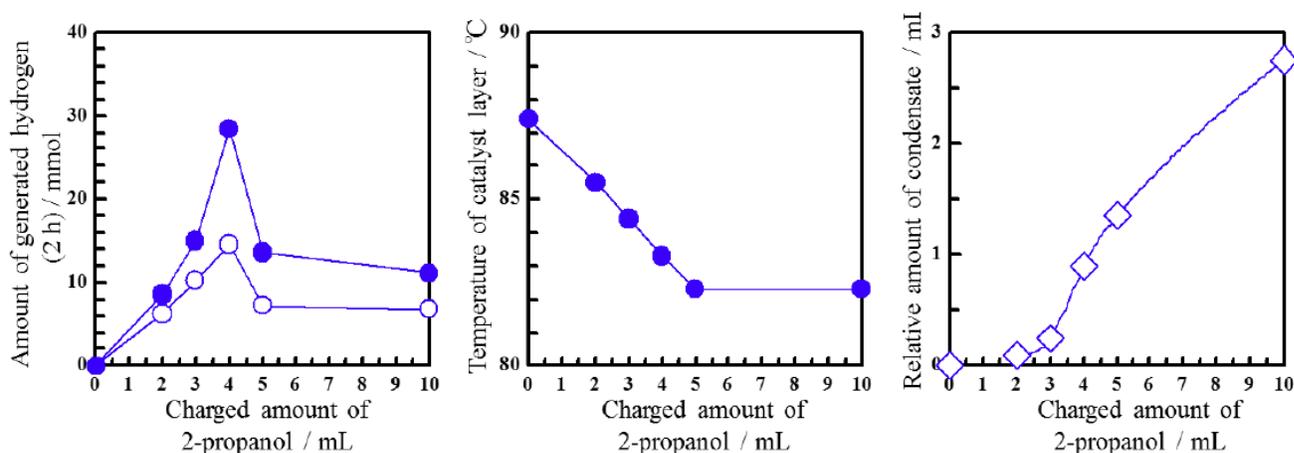
Figure 4: Dehydrogenation (**a**), catalyst temperature (**b**), and evaporation (**c**) for 2-propanol in the batch-wise reactor.

(**a**) Relationship between catalytic dehydrogenation activities and charged amounts of 2-propanol with carbon-supported platinum-iron composite (●) and platinum alone (○) catalysts.

(**b**) Temperatures monitored with a thermocouple inside the catalyst layer as a function of charged amounts of 2-propanol (●).

(**c**) Evaporation rates from the granular carbon support pursued by measuring dropped-down condensate relatively as a function of charged amounts of 2-propanol (◇).

maximum is not determined by the kinds of catalytic active sites but by the supporting carbon. Plenty amounts of micropores would be useful for substrates, which were kept in the liquid phase under working conditions. Interestingly, the catalyst-layer temperature realizing the maximum activity (4.0mL-substrate) was higher than the boiling point (82.4°C) but lower than that of the sandbath (0mL), as shown in Figure **4b**. Thus the catalytic active sites could take their important role, where capillary-condensed substrates in the carbon micropores would migrate on surface as superheated liquid toward the nano-metal sites.

Relative evaporation rates were depicted in Figure **4c**. Evaporation was rather suppressed in the scarce region (<3mL), which was quite different from the plenty region (>4mL). This might be expected from the contrast between capillary-condensed liquid and bulk liquid. Excess amounts of charged substrate would consequently result in not only reducing the catalyst-layer temperature from the external-heating temperature down to the boiling point, but also for the liquid substrate to evaporate in vain without chances to react.
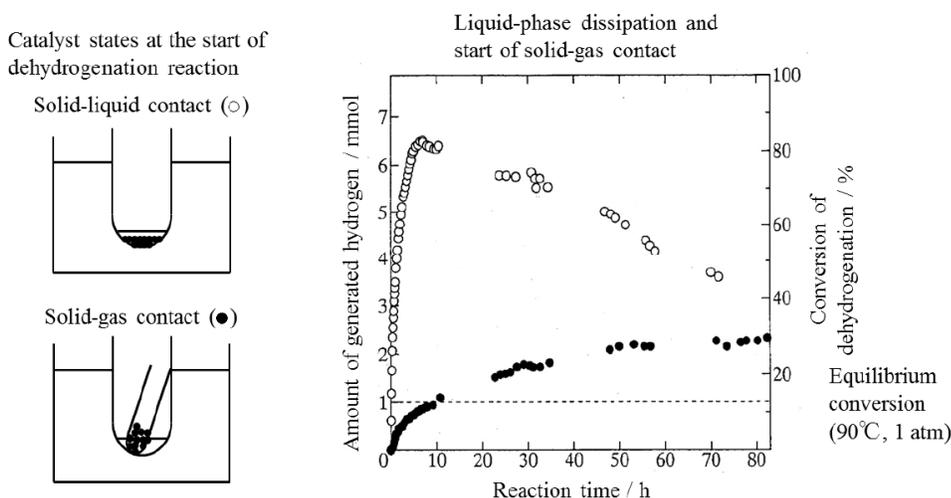
Figure 5: Batch-wise dehydrogenation of 2-propanol as contrasted in catalyst/substrate contact modes between solid-liquid and solid-gas.

Time courses of hydrogen amounts generated from different states of catalysts immersed in liquid 2-propanol (○) and adsorbed with gaseous 2-propanol (●) at the start of reaction. Charged amount of 2-propanol: 0.6 mL, Catalyst: Platinum-ruthenium composite nanoparticles supported on the granular activated carbon (Pt-Ru (1:1)/C 22 wt-metal%, 0.09 g), Reaction conditions : Boiling and refluxing by heating at 90°C and cooling at 5°C.

The catalyst/substrate contact of solid-gas or solid-liquid was compared in order to contrast the ordinary heterogeneous mode to the superheated liquid-film mode (Figure **5**). Evaporated substrate could contact with the granular catalyst only inside a narrow glass tube and gave hydrogen at a steady but rather low reaction rate all through the period. Since hydrogen was separated from condensates under refluxing conditions, conversion levels of dehydrogenation became higher than equilibrium owing to reactive separation, as realized in this solid-gas catalysis. However, the same granular catalyst generated hydrogen in a peculiar manner, when immersed with a carefully-chosen amount of substrate. Rapid evolution upto a high conversion over 80% was followed by sudden stop and by gradual decrease of gas volume, approaching to another conversion limit. In appearance, new limit is aiming at the same one with solid-gas contact. When the precharged liquid substrate was all evaporated volume increase was stopped. From the moment of observed stoppage, the catalyst surface would be enforced to contact directly with the gaseous components. The volume decrease should be attributed to solid-gas catalysis between hydrogen and acetone. Thus the presumption that the superheated liquid-film conditions would promote dehydrogenation beyond equilibrium was instituted.

3.2. Batch-Wise Dehydrogenation of Decalin

Hydrogen generation for 2.5h from a constant amount of granular catalyst (0.30 g) and various amounts of decalin (0.5, 0.75, 1.0, 1.25, 1.5 and 3.0mL) was investigated under boiling and refluxing conditions in the batch-wise reactor by heating at 210°C and cooling at 5°C (Figure **6**).

As shown in Figure **7**, the correlation pattern between the amounts of generated hydrogen and charged decalin was similar to 2-propanol (Figure **4a**). The catalyst-layer temperature at the optimum ratio of 0.30g-catalyst/1.0mL-decalin was observed also to be higher than the boiling point (192°C) and lower than the heating temperature (210°C), as shown in Figure **8** like 2-propanol (Figure **4b**).

Under common boiling and refluxing conditions of heating externally at 210°C and refluxing at 5°C, the temperatures of a constant amount of granular activated carbon (0.285 g) immersed with decalin (0,10, and 3.0mL) were measured by inserting a thermocouple directly (Figure **9a**). In the suspension state (3.0mL), the catalyst-layer temperature was almost equal to the boiling point of decalin (192°C), whereas the temperature in the liquid-film state (1.0mL) was kept at the level just between the external heating temperature (210°C) and the boiling point (192°C). In case of the sand bath state (0mL), its temperature was close to the heating temperature of 210°C.By raising the external heating temperature from 210°C to 280°C, the temperatures of the liquid-film state (1.0mL) were elevated in accordance with the heating temperatures (Figure **9b**).
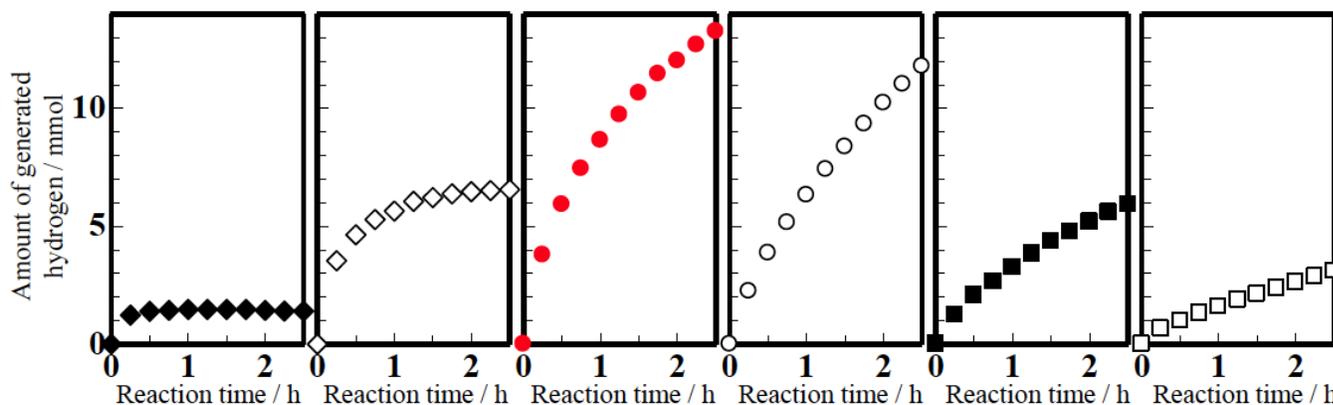
Figure 6: Dehydrogenation catalysis for decalin in the batch-wise reactor. Relationship between reaction rates and charged amounts of substrate.

Time courses of hydrogen generated from decalin with carbon-supported platinum catalyst at various charged amounts of decalin in the batch-wise reactor. Charged amount of decalin: 0.5 (◆), 0.75 (◇), 1.0 (●), 1.25 (○), 1.5 (■), and 3.0 mL (□). Catalyst: Platinum nanoparticle supported on the granular activated carbon (Pt/C 5 wt%, 0.30 g). Reaction conditions: Boiling and refluxing by heating at 90 °C and cooling at 5 °C.
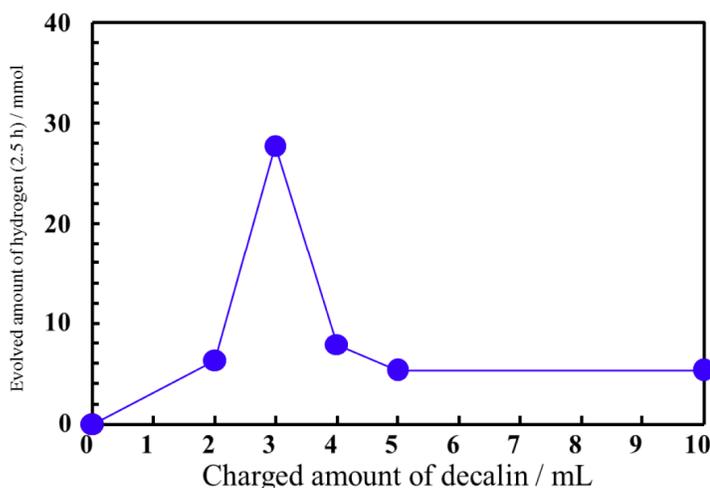
Figure 7: Relationship between catalytic dehydrogenation activities and charged amounts of decalin with use of carbon-supported platinum catalyst in the batch-wise reactor.

Amounts of hydrogen generated for 2.5 h from decalin as a commercial mixture of cis and trans-isomers (bp: 192 °C) with Pt/C catalyst (5 wt%, 0.75 g) under boiling and refluxing conditions by heating at 210 °C and cooling at 5 °C.

In Figure **10a**, time courses for decalin dehydrogenation with a Pt-Re composite catalyst were depicted at various heating temperatures. Complete conversion of decalin into naphthalene and hydrogen was attained by heating externally at 280°C. Initial reaction rates were well correlated with heating temperatures in the Arrhenius plots of Figure **10b**.

3.3. Batch-Wise and Flow-Type Dehydrogenation of Methylcyclohexane

Sharp contrast in hydrogen generation from methylcyclohexane was demonstrated among the catalyst-layer states of scarce, adequate and excess amounts for pre-immersing the catalyst (0.30g) (Figure

11). In the scarce-amount case (0.4mL), initial rapid generation was immediately changed to poor reactivities, whereas the reaction rate was suppressed all through the period in case of the excess amount (1.2mL).

Methylcyclohexane could be converted with the Pt-Ir composite catalyst (0.30 g) into toluene and hydrogen almost completely at 210°C after the 2.0h period, only when the adequate amount of substrate (0.8mL) was charged initially. Importance of the solid/liquid contact ratio should be noted for catalytic dehydrogenation of methylcyclohexane as well under boiling and refluxing conditions.
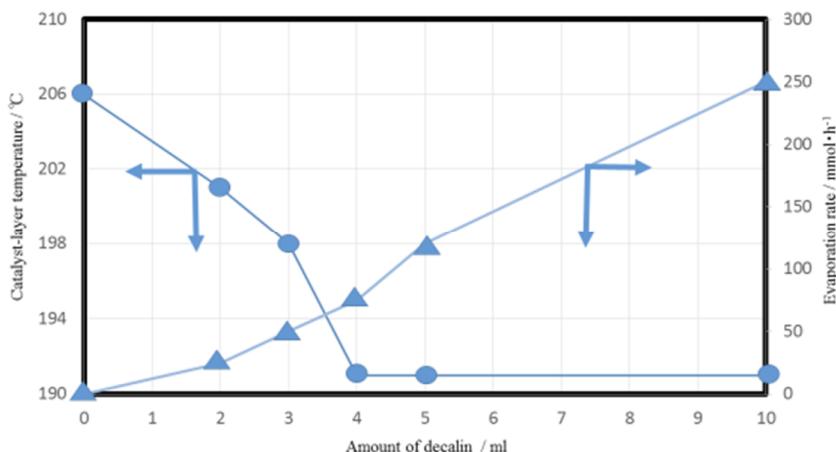
Figure 8: Correlation of charged decalin amounts with catalyst-layer temperatures and evaporation rates. The carbon support without metal was set inside the batch-wise reactor.

Catalyst: Pt/C (5 wt%) 0.75 g. Reaction conditions: Boiling and refluxing by heating at 210 $^\circ$C and cooling at 5 $^\circ$C.
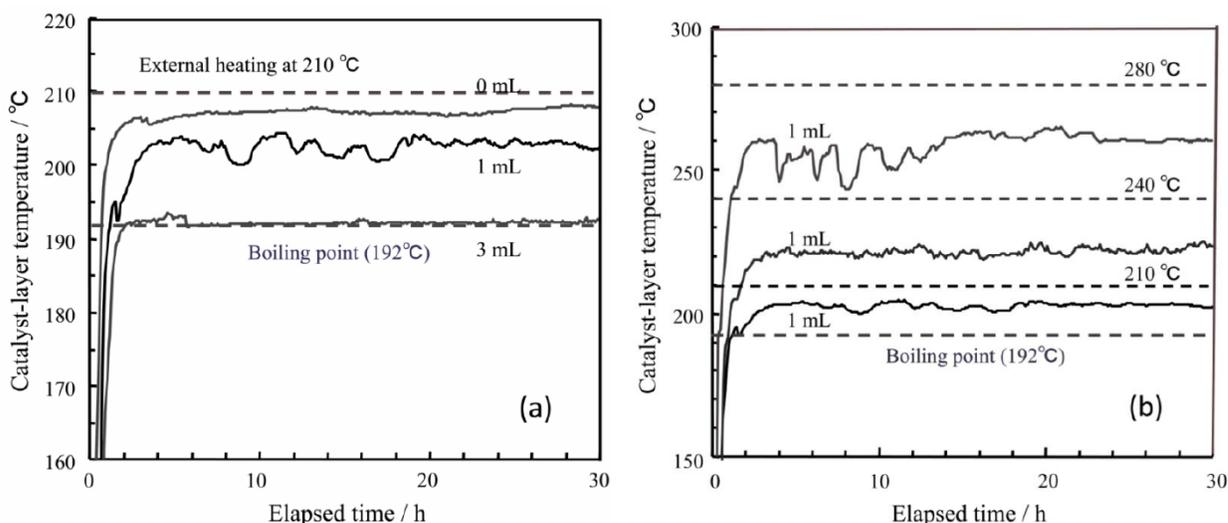
Figure 9: Correlation of catalyst-layer temperatures with the charged amounts of decalin (a) and the effect of the external heating (b) in the batch-wise reactor.

Charged amount of decalin: 0, 1.0, and 3.0 mL, Temperature: Monitoring with a thermocouple inserted to granular activated carbon adopted as catalyst support (0.285 g), Boiling and refluxing : External heating at 210 $^\circ$C, 240 $^\circ$C, and 280 $^\circ$C and cooling at 5 $^\circ$C.

In Figure **12**, hydrogen generation from cyclohexane, methylcyclohexane or decalin in the batch-wise reactor was compiled for a common liquid-film state at the same catalyst (0.30g)/substrates (1.0mL) ratio. Methycyclohexane exhibited the highest reactivity among these naphthenic substrates, as exemplified in the time course at 240°C.

Superior reactivities in the liquid-film states over the suspended states were ascertained at the common heating temperature of 210°Cfor all of these substrates. Activation energies for methylcyclohexane and decalin were given from the Arrhenius plots (Figure **13**).

As shown in Figure **14a**, methlcyclohexane conversions into toluene and hydrogen were correlated with the substrate feed rates as monotonous decreasing curves irrespective of the densities of feed-liquid holes in the flow-type reactor (Figure **1b**). In all cases, conversions were enhanced at low feed rates and at high temperatures. Under the conditions investigated, the highest conversion was attained at the substrate feed rate of 0.39 mmolmin^{-1} and the catalyst-layer temperature of 330°C. The magnitude of conversion was larger than 90%.
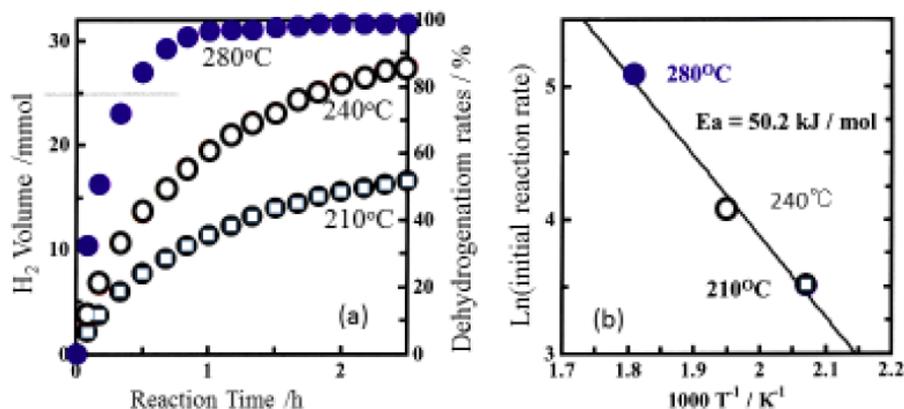
Figure 10: Dependence of catalytic dehydrogenation rates on external heating temperatures for decalin in the batch-wise reactor (**a**) and Arrhenius plot (**b**).

Catalyst: Pt-Re/C (molar ratio 4:1, 5 wt-Pt%, 0.30 g) immersed in decalin 1.0 mL. Reaction conditions: Boiling and refluxing by heating at $210\,^\circ$C, $240\,^\circ$C, and $280\,^\circ$C, and cooling at $5\,^\circ$C. Arrhenius analysis: Activation energy from initial reaction rates.
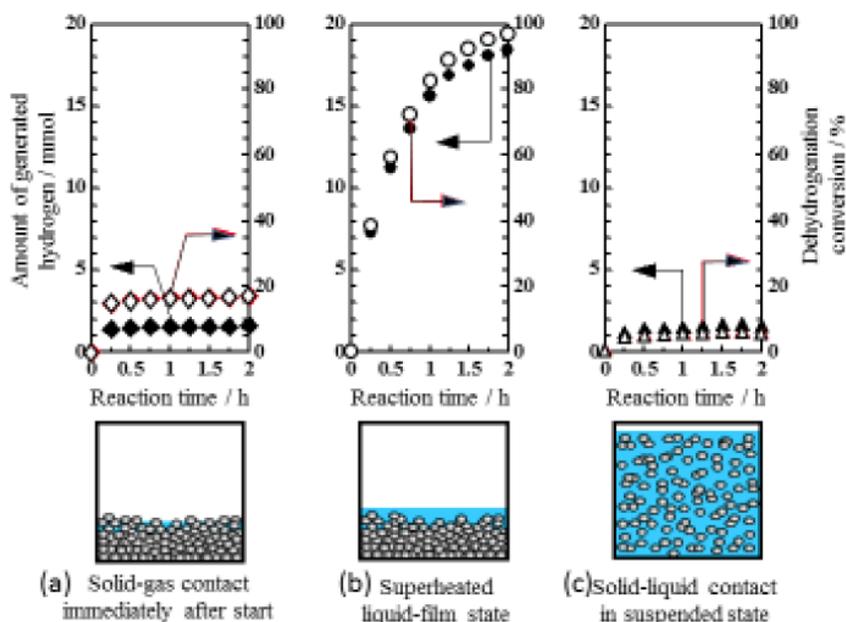
Figure 11: Dehydrogenation catalysis for methylcyclohexane in the batch-wise reactor. Relationship between reaction rates and charged amounts of substrate, with schematic description on immersed states of catalyst shown below.

Time courses of hydrogen generation with carbon-supported platinum-iridium catalyst at variously-charged amounts of methylcyclohexane. Charged amount: 0.4, 0.8, and 1.2 mL. Catalyst: Composite nanoparticles supported on granular activated carbon (Pt-Ir (4:1)/C, 5 wt-metal%, 0.30 g). Reaction conditions: Boiling and refluxing by heating at $210\,^\circ$C and cooling at $5\,^\circ$C.

In contrast, the reaction rates were not monotonous (Figure **14b**). For all of the catalyst-layer temperatures (225, 285 and 330˚C), the maximum rate was obtained at the substrate feed of about 40 mmolmin^{-1} among these continuous operations (0.39~63mmolmin^{-1}). Low feed rates would decrease total molecules of contact with the catalytic sites. Excessively high rates would increase the possibility of channeling, with substrate contact to the catalytic sites disturbed. Dehydrogenation rates would therefore exhibit maximum with respect to the substrate feed rates.

Correlation plots between methylcyclohexane conversions and catalyst-layer temperatures together with the curve of equilibrium conversion at atmospheric pressure were summarized for platinum nano-particles supported on carbon cloth with different shapes and sizes, and with liquid substrate fed at various rates (Figure **15**).

Continuous generation of hydrogen with use of a tubular flow reactor (Figure **2**) was examined for various inlet rates of methylcyclohexane under
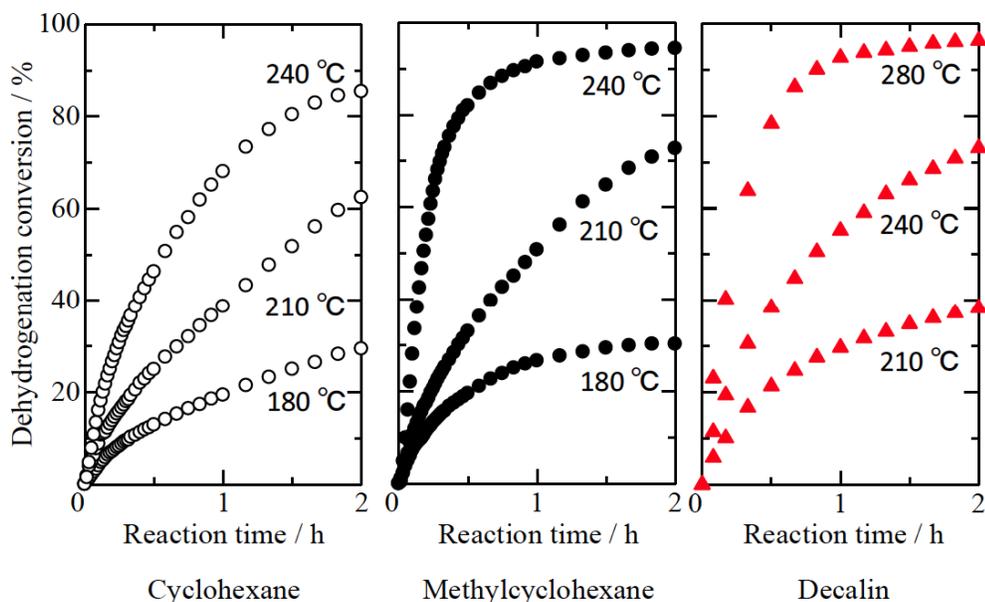
Figure 12: Comparison on dehydrogenation catalysis among naphthene substrates under superheated liquid-film conditions in the batch-wise reactor.

Time courses of hydrogen generation with carbon-supported platinum catalyst (Pt/C t wt%, 0.30 g) immersed in substrate (1.0 mL) by heating (180, 210, 240, and 280 °C) and cooling (5 °C) under boiling and refluxing conditions.
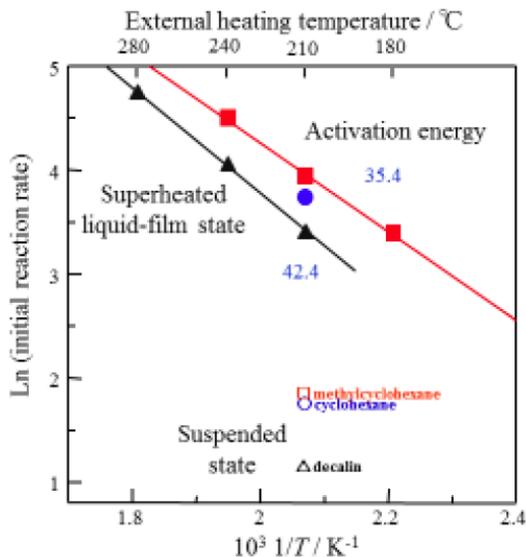
Figure 13: Comparison in plots between suspended state and superheated liquid-film state for catalytic naphthene dehydrogenation at 210°C and in lines of Arrhenius analyses for methylcyclohexane and decalin.

Initial reaction rates as a function of external heating temperature (Ln (rate) vs $1/T$) with carbon-supported platinum catalyst (Pt/C 5 wt%, 0.30 g) immersed in substrate (1.0 mL compared to 5.0 mL) under boiling and refluxing conditions in the batch-wise reactor.

controlled catalyst-layer temperatures (Figure **16**). The platinum nano-particles supported on granular activated carbon were laid at the upper part in the reactor tube. Liquid substrate was introduced from the

downside part and heated. Temperatures were monitored with thermocouples at the positions of reactor inlet and outlet, preheating zone (two sites) and reacting zone (two sites). It was evident that the preheating zone itself was superheated, since the indicated temperatures (ca.170~220°C) were in-between the boiling point (101°C) and the catalyst-layer temperatures (240~360°C).

Low feed rates would bring favorable conversions as the result of long periods of contact with catalyst. Contrastingly, hydrogen generation rates were unfavorable at low feed rates, as shown in Figure **17**. Chances for the catalyst surface sites to meet with the substrate molecules would be increased with the feed rates. Anyhow, higher catalyst-layer temperatures brought larger reaction rates.

The outlet gaseous mixture of the tubular flow reactor can be separated by fractional distillation into hydrogen and the condensate, consisting of toluene and methylcyclohexane. Dehydrogenation was expected to proceed further by re-charging condensate mixtures to the reactor, where the same reaction conditions were imposed to methylcyclohexane with toluene addend at various compositions and temperatures (Figure **18**). An inert carbon layer (0.16 g, 4 cm length) was used for preheating. Platinum nano-particles supported on granular activated carbon (Pt/C 5wt%, 0.04g, 1cm length) could therefore contact with
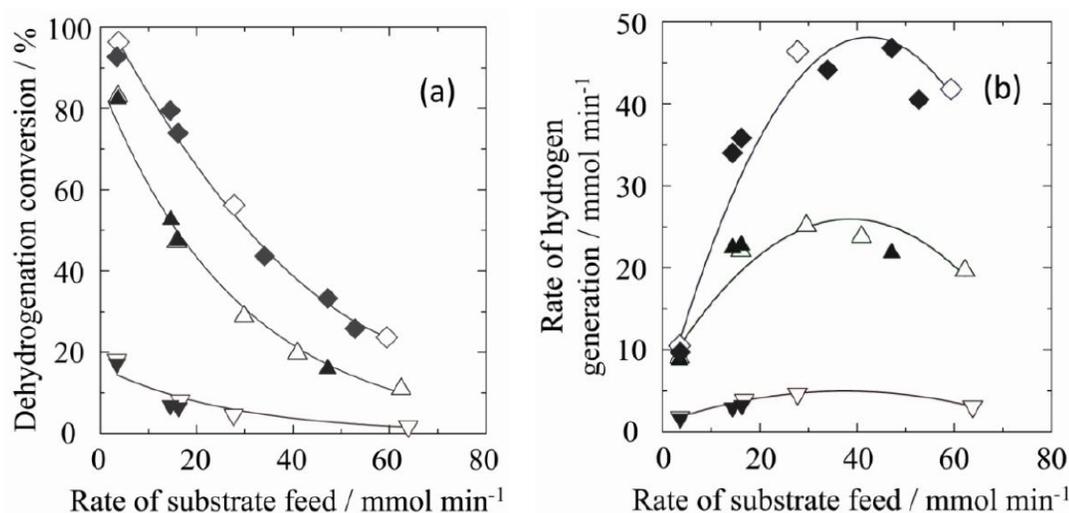
Figure 14: Dehydrogenation catalysis for methylcyclohexane in a flow-type reactor. Correlation of feed rates with conversions (**a**) and rates of hydrogen generation (**b**).

Stationary magnitudes of conversion and hydrogen generation rate pursued with platinum nanoparticles supported on carbon cloth (Pt/C 5 wt%, 3 cmΦ) at various temperatures monitored at the bottom of catalyst layer as 225 °C (▽), 285 °C (△), and 330 °C (◇), and various feed rates in both concentrated (open symbol) and dispersed (closed symbol) manners with respect to the density of holes for feeding substrate liquid.
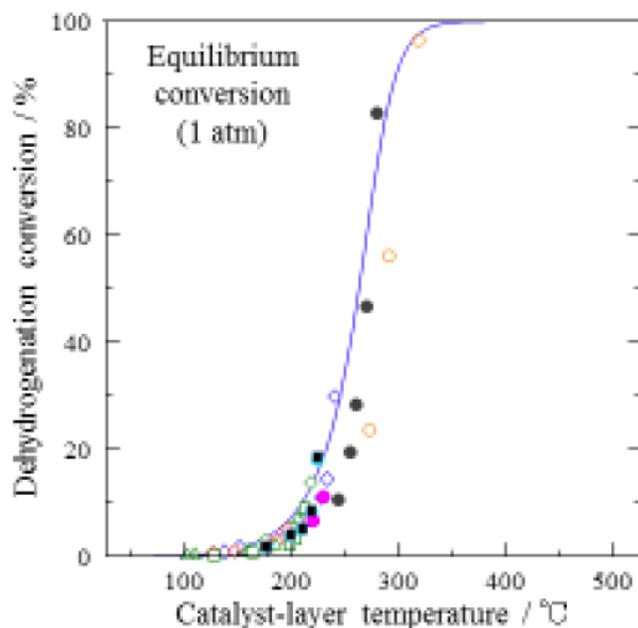
Figure 15: Dehydrogenation catalysis for methylcyclohexane in the flow-type reactor. Relationship between dehydrogenation conversions and catalyst-layer temperatures as varied with the amounts of platinum catalyst and the feed rates of substrate liquid.

Catalyst: Platinum nanoparticles supported on carbon cloth (Pt/C 5 wt%, 3 ~ 5 cmΦ circular and 10 × 20 cm^2 rectangular). Feed rate : 0.3 ~ 2.1 mL min^{-1} for circular and 0.3 ~ 3.5 mL min^{-1} for rectangular.

superheated liquid. Under the conditions of inlet toluene concentrations (8.5%~32.7%) and the catalyst-layer temperatures (200°C~260°C), catalytic dehydrogenation was found to proceed further. Attained conversions were irrelevant to equilibrium conversions given for neat methylcyclohexane (curved line in the figure). By this reason, adoption of a two-staged tubular flow reactor was decided.

Double-staged tubular flow reactors could actually increase dehydrogenation conversions, in which the outlet condensates of the 1st-stage reactor were used
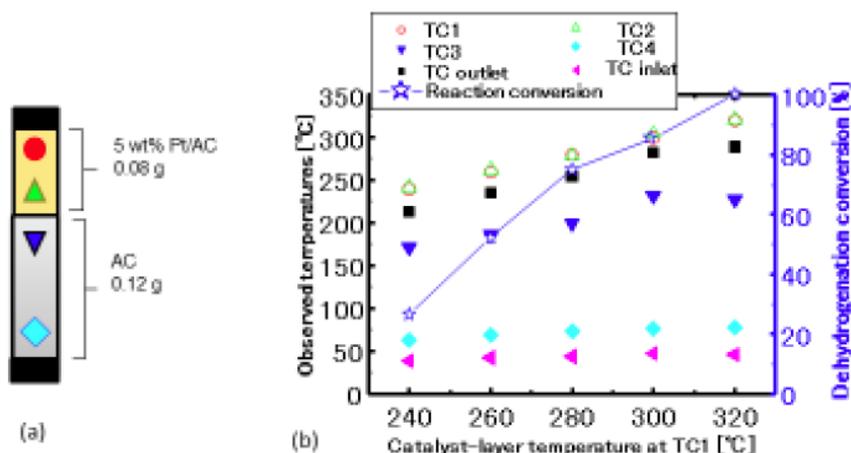
Figure 16: Dehydrogenation catalysis for methylcyclohexane in a tubular flow reactor, consisting of preheating zone (AC) and reaction zone (Pt/C) (**a**). Correlation of catalyst-layer temperatures with temperature distributions inside/outside the reactor and dehydrogenation conversions (**b**).

Catalyst: Platinum nanoparticles supported on granular activated carbon (Pt/C 5 wt%, 0.08 g filled at the upper part (2 cm) in the flow reactor (1/4 inch stainless tube)). Substrate feed: Liquid methylcyclohexane at ambient temperature introduced to the downside activated-carbon part (0.12 g, 3 cm) at the rate of 23.4mmolh^{-1}.
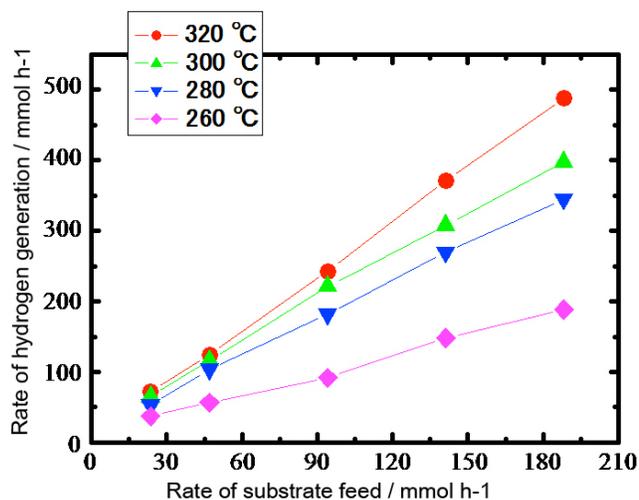
Figure 17: Dehydrogenation catalysis for methylcyclohexane in a tubular flow reactor. Relationship between the rates of hydrogen generation and the rates of substrate feed at various catalyst-layer temperatures.

Catalyst: Platinum nanoparticles supported on granular activated carbon (Pt/C 5 wt%, 0.08 g). Substrate feed: Methylcyclohexane liquid introduced to the tube at the rate of 0.39, 0.78, 1.57, 2.35, and 3.14 mmol min^{-1}.

as the inlet reactants of the 2nd-stage one. At each catalyst-layer temperature from 200°C to 300°C, further extents of reaction were confirmed, as shown in Figure **19**. Finally-attained conversions i.e. the outlet compositions of the 2nd-stage reactor, were all exceeding the equilibrium-curve line of the neat substrate. It should be emphasized that perfect conversion was attainable at 300°C. Ordinarily catalysis for this endothermic reaction requires higher temperatures than 350°C due to equilibrium restriction.

4. DISCUSSION

4.1. Thermodynamical Backgrounds of Properly-Wetted Catalysis

The inequality equation on chemical reactions of DeDonder (eq. 1) was developed by Prigogine to the extended inequality equation (eq. 2) [6].

$$AV > 0 \tag{1}$$

$$A_1V_1 + A_2V_2 > 0 \tag{2}$$

Where A is the chemical affinity and V is the time derivative of reaction extent.

Among thermodynamical couples for chemical reactions, heat transfer would be included as a partner, which brings about large entropy production rates (eq. 3).

$$A_1V_1 = T (d_iS / dt) \tag{3}$$

If this entropy term is sufficiently large (T (d_iS / dt) >> 0), the AV term for the coupled reaction would become negative ($A_2V_2 < 0$). Consequently, the chemical reaction can proceed ($V_2 > 0$), even though no Gibbs energy is affirmative ($A_2 < 0$).

The tensor order of heat flow and mass flow is classified as vector in common. Since Prigogine coupling [6] can be constituted between the same tensor order, it might be realized with nucleate boiling (Figure **20**). Steep temperature gradients for nucleate
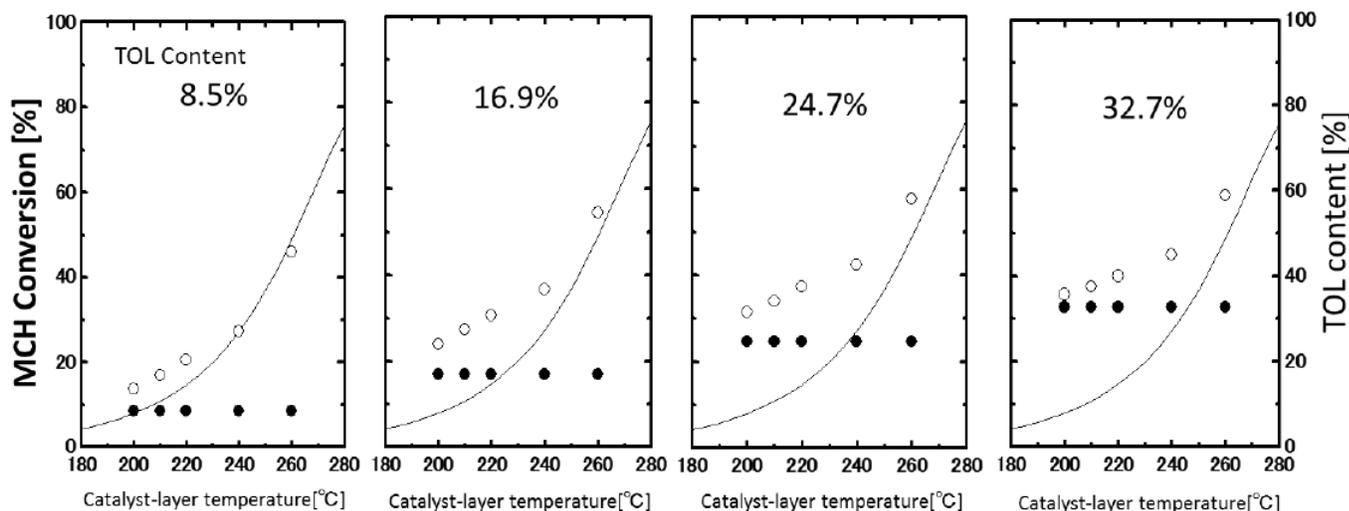
Figure 18: Dehydrogenation catalysis in a tubular flow reactor for methylcyclohexane, containing toluene addend initially at various concentrations. Rates of hydrogen generation correlated with substrate feed rates under various catalyst-layer temperatures.

Catalyst: Platinum nanoparticles supported on granular activated carbon (Pt/C 5 wt%, 0.08 g). Substrate feed: Methylcyclohexane liquid introduced to the tube at the rate of 0.39, 0.78, 1.57, 2.35, and 3.14 mmol min^{-1}.
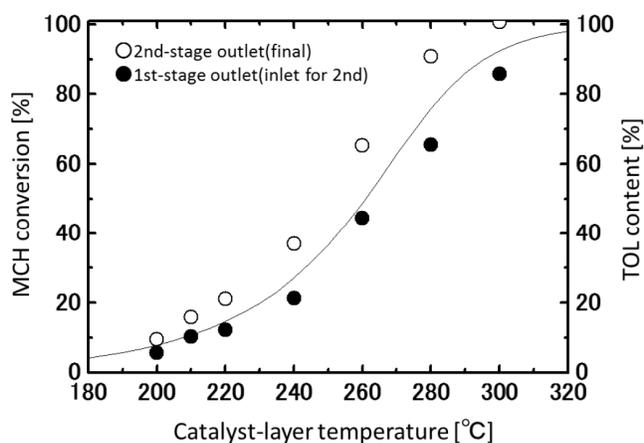
Figure 19: Dehydrogenation catalysis for methylcyclohexane in a two-staged tubular flow reactor. Two-stage performance from the MCH-TOL mixture, condensed as the first-stage output.

Catalyst: Platinum nanoparticles supported on granular activated carbon (Pt/C 5 wt%, 0.04 g laid at uppermost (1 cm), with downside (4 cm) carbon support preceded for preheating). Substrate feed: 1st-stage input (MCH 0.39 mmol min^{-1}) converted into the substrate feed for 2nd-stage input after condensation.

boiling will assure us high heat conductivities, though heat quantities are large. Irreversible mass flow will proceed at the bubble-evolving sites especially under enforced-fluid conditions [2]. Such processes that reaction products are expelled from the catalyst surface to the bubble space, and further to the gas space, will be repeated as the entropy-producing sequences (Figure **21**). Rapid heat transfer will thus enhance efficient mass transfer, and vice versa.

4.2. Necessary Conditions for Properly-Wetted Catalysis

Properly-wetted nano-metal catalysts, supported on highly-porous activated carbon, had been chosen for efficient dehydrogenation [7-10]. Reasons of choice would be summarized as follows.

Proper Liquid-to-Solid Ratio in Amounts

As shown in Figures **3**, **6** and **11** for 2-propanol, decalin and methylcyclohexane, respectively, a certain amount of solid catalyst must be immersed with a proper amount of substrate liquid initially in bach-wise operations. Scarce substrate amounts were easy to dry up partially or totally, resulting in suppressed dehydrogenation rates. On the contrary, substrate liquid in excess caused suspended states with no temperature gradient at the catalyst surface. Moreover, predominance of substrate evaporation from the bulk liquid (Figure **4**) would not favor hydrogen generation by reflecting their endothermicity difference.

Temperature Order of External Heating > Catalyst Layer > Boiling Point

The catalyst-layer temperature was higher than the boiling point at the properly-wetted state, where hydrogen generation was most favored. Catalyst-layer temperatures at the properly-wetted state were raised in accordance with external heating temperature (Figure **9b**), which brought enhanced catalytic activities (Figure **10**). It is to be noted that the catalyst-layer temperature at the properly-wetted state was

(a)Classification of boiling modes differentiated from superheated degree

(b)Definition of nucleate boiling and mechanism of highly-efficient heat transfer
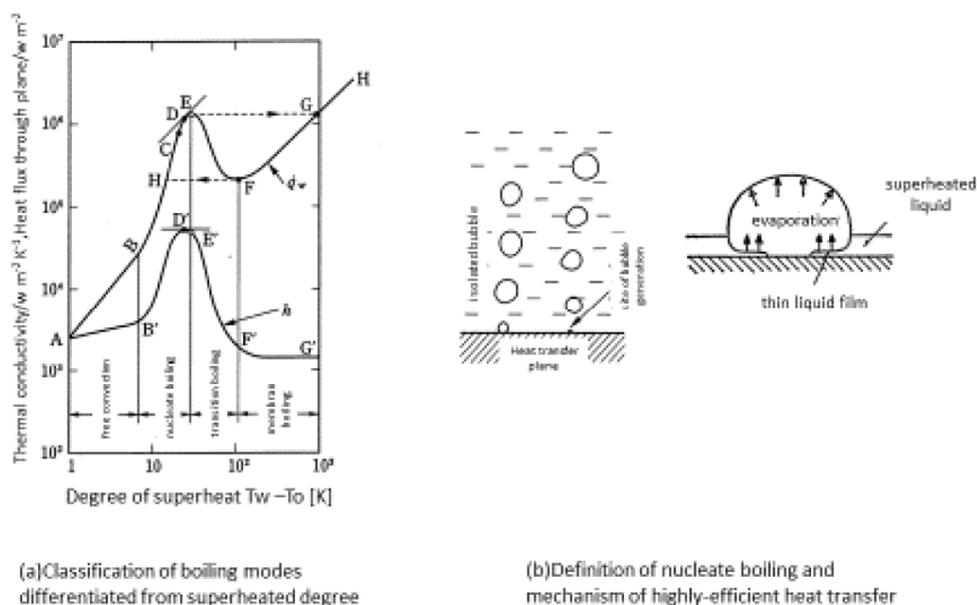
Figure 20: Classification of boiling modes in focus on nucleate boiling as the most efficient mode for heat transfer.

Chemical bond cleavage on the catalyst surface	Removal to bubble from the catalyst surface	Rapid replenishment toward the catalyst surface
$R_{ads} \rightarrow P_{ads} + H_{ads}$	$P_{ads} \rightarrow P_{gas},\ H_{ads} \rightarrow H_{gas}$	$R_{solu} \rightarrow R_{ads}$
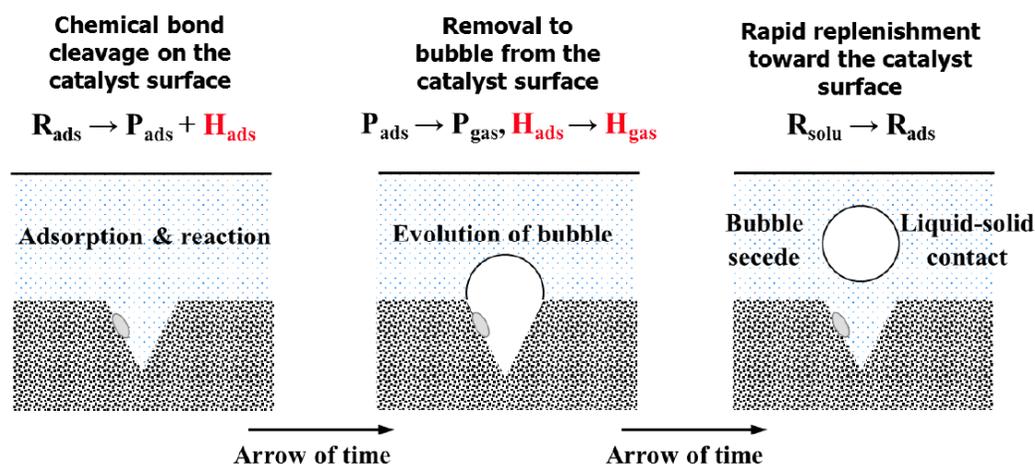
Figure 21: Repeated irreversible processes for dehydrogenation of organic hydride under superheated liquid-film conditions. Catalyst: Platinum nanoparticles supported on granular activated carbon (Pt/C 5 wt%, 0.08 g). Substrate feed: Methylcyclohexane liquid introduced to the tube at the rate of 0.39, 0.78, 1.57, 2.35, and 3.14 mmol min^{-1}.

determined by the activated-carbon support irrespective of metallic species (Pt only or Pt-Fe composite, Figure **4a**, suggesting the importance of carbon micropores.

In the batch-wise experiments, external heating temperatures with use of oil-bath heat reservoir were 90°C for 2-propanol (bp: 82.4°C), 210-280°C for decalin (bp:192°C) and 180-240°C for methycyclohexane (bp: 101°C). True reaction temperatures at the bubble-evolving sites of nucleate boiling or the temperatures of superheated substrate liquid are not yet known. However, essential importance of properly-wetted catalysis lies not on the reaction temperature itself but

on the temperature gradient from the supporting carbon, which is detectable, to the immeasurable catalytically-active sites. Activation energies were obtained from the rate dependence on heating temperatures (Figures **10** and **13**), which would partly reflect the surface densities of vacant active sites generated by enforced bubble removal from catalyst.

How to Accomplish Perfect Conversion

On account of thermodynamical characteristics of dehydrogenation: $\triangle H > 0$ and $\triangle S > 0$, equilibrium conversions will decrease at low reaction temperatures. The turning temperature for 2-propanol is 164.7°C, at which 50 % conversion ($\triangle G° = 0$) is attained. As for

dehydrogenation of 2-propanol, equilibrium limit of 12.6 % conversion at 90°C was overcome by reactive separation (Figure **5**, the case of solid-gas contact), whereas 83 % conversion was found to be realized by adopting the properly-wetted state (Figure **5**, the case of solid-liquid contact).

The flow-type experiments have demonstrated for dehydrogenation conversions to increase with diminished supply rates of substrate liquid (Figure **14**), which would be ascribed to prolonged contact for the catalyst with substrate molecules. Conversions were favored at elevated catalyst-layer temperatures, as elucidated for Pt (5 wt%) nano-particles on both carbon cloth (Figure **15**) and carbon granules (Figure **16**) in harmony with equilibrium predictions.

In the tubular flow reactor, liquid mixtures of substrate methylcyclohexane and product toluene were found to evolve hydrogen at various levels of toluene contents and catalyst-layer temperatures (Figure **18**). A double staged rector was therefore designed: the first-stage output was fractionated to separate hydrogen from a methylcyclohexane-toluene mixture, which was fed to the second stage in liquid in order to proceed the reaction further (Figure **19**). Perfect conversion was demonstrated at 300°C beyond the equilibrium conversion by adopting this two-staged flow reactor upon the concept of the properly-wetted state.

4.3. Compact Feed of Hydrogen from MCH to SOFC (Enefarm)

Continuous generation of hydrogen (490 mmolh^{-1}) from the liquid feed of methylcyclohexane (192 mmolh^{-1}) was observed with use of the granular Pt/C (5 wt%) catalyst at 320°C (Figure **17**). The extent of conversion

85.1 % was derived as the ratio from the above two rates of hydrogen generation and methylcyclohexane feed, whereas perfect conversion had been observed at the reduced feed rate (23.4 mmolh^{-1}). These experiments were performed with the same catalyst and temperature (Figure **16**). Long contact period due to diminished substrate flow is favorable to conversions. In contrast, large amounts due to high feed rates would enhance catalytic reaction rates.

The tubular flow reactor has an inside volume of 0.743 mL, consisting of a preheating zone (3 cm) and a catalyst zone (2 cm). Total catalyst volume of the two-staged reactor ought to be 0.594 (=0.743 × 2/5 × 2) mL. Liquid hourly space velocity of 41.0 h^{-1}will be attained at perfect conversion toward the adopted feed rate (192 mmol-MCHh^{-1} = 24.35 mL-MCHh^{-1}). When the conversion of 85.1 % had been attained in the 1st reactor at 320°C, perfect conversion in the 2nd reactor would be realized at the catalyst-layer temperature of 320°C. Heating temperatures of 350 ~ 400°C would sufficiently be enough to enable perfect conversion for large feed rates of methylcyclohexane.

The magnitude of LHSV for Spera Hydrogen® was reported as 2.0 h^{-1} by Chiyoda Chemical Corporation [11], which seems to be a typical magnitude as gas/solid catalysis. In other words, LHSV of 41.0 h^{-1} for properly-wetted catalysis is so huge that a dehydrogenation reactor can be designed in a compact manner. Contrast between these two types of catalysis is summarized in Table **1**. Data for properly-wetted catalysis with adoption of a two-staged reactor was cited from Figure **19**.

Solid oxide fuel cell (SOFC), driven with hydrogen from methylcyclohexane, attracts our special attention

Table 1: Contrast in Characteristics of Properly-Wetted Catalysis with Gas/Solid Catalysis for Dehydrogenation of Methylcyclohexane

	Properly-Wetted Catalysis	Gas/Solid Catalysis
Microeversibility during reaction	No	Yes
Substrate in contact with catalyst	Liquid phase	Gas phase
Substrate density [mol-MCH/L]	7.88	0.0446
Catalyst volume [mL]	1.485	4.72×10^6
Substrate feed rate in liquid [mL-MCH/h]	2.97	94.4×10^3
Product generation rate [NL-H2/h]	1.57	50.0×10^3
Catayst-layer temperature [°C]	300	350
Extent of conversion attained [%]	>99	>99
Data source	Figure 19	Ref. [11]
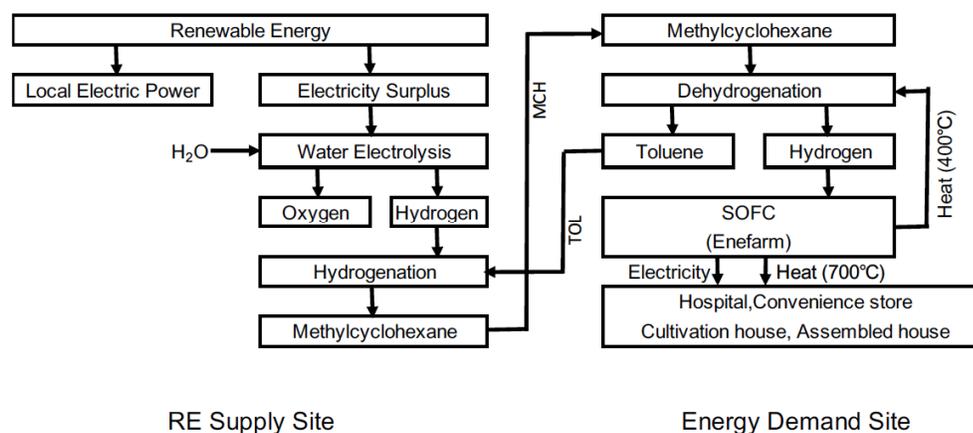
Figure 22: Energy supply chain started from renewable energy and aimed to electricity and heat of SOFC (Enefarm) by mediation of organic hydride.

to Enefarm scales (700 w and 5 kw) [12] on the following grounds.

1)   Since enthalpy change of methylcyclohexane dehydrogenation (67.5 kJ/mol-H_2) is much smaller than the combustion heat of hydrogen (241.8 kJ/mol-H_2), the endothermicity is reconciled with the exhaust heat from SOFC.

2)   The exothermic temperature of SOFC (700°C) is sufficiently higher than the endothermic temperature for hydrogen generation afforded from methylcyclohexane (350 ~400°C).

3)   In order to operate Enefarm SOFC (700 w), it is necessary to supply hydrogen of 23.94 mol-H_2h^{-1} or to feed substrate of 7.98 mol-$MCHh^{-1}$ at perfect conversion. The observed hydrogen generation rate at 320°C as well as the activation energy of 100.9$kJmol^{-1}$ would allow designing a new flow reactor under 350 ~ 400°C conditions. Metallic species, including any composite one, must be selected on the basis of both catalytic activities and preparation costs.

4)   Storable and transportable merits of the MCH/TOL hydrogen carrier are useful to any demand in small scales and/or emergency use at convenience stores or hospitals e.g. LED illumination or steam disinfection for medical operations in a hospital.

5)   Dispersed sources of renewable energies will generate hydrogen via water electrolysis and produce methylcyclohexane as a safe, easy-to-handle and cost-effective hydrogen carrier. Reproduction from toluene will be performed with an adequately-sized equipment and tiny exergy-

loss operation, if compared to liquefaction of hydrogen. Moreover, both methylcyclohexane and toluene are commodity chemicals suitable for over-land and over-sea transport.

Energy supply chain from renewable energy to SOFC would thus be supported with the MCH/TOL hydrogen carrier. A storage tank (90 L) of methylcyclohexane will give hydrogen to SOFC (700 w) for four days continuously. Compact design of a two-staged catalytic reactor coupled with Enefarm SOFC would make it possible to provide combined heat and power to hospitals, combinience stores, cultivation houses, assembled houses and so on (Figure **22**) [13].

5. CONCLUSION

Upon the basis of superheated liquid-film concept, organic hydrides were attempted to generate hydrogen under nucleate boiling conditions with use of nano-metal particles supported on highly-porous carbon.

Steep temperature gradient toward properly-wetted catalysts was found to afford perfect conversion as well as high LHSV. Methylcyclohexane hydrogen was affirmatively verified for SOFC (Enefarm) operation. Heating temperatures at 350 ~ 400°Cwill be adequate for thermal cascade utilization of SOFC exhaust heat (700°C).

Newly-designed compact reactors for supplying hydrogen to SOFC (700 w and 5 kw) would take an anticipated mediator role between renewable energy supply and local energy demand.

REFERENCES

[1]   Gupta RB. Hydrogen Fuel-Storage, Transport and Utilization, CRC Press, New York 2008; Chapt. 1 & 13.

[2]   Aihara T. Heat Transfer Engineering, Shokabo Press. Tokyo, 1994; Chapt. 5.3.5. "Enforced Fluid Boiling".

[3]   Shono A, Saito Y. Technology Assembly for Utilization of Hydrogen. NTS Press, 2014; Chapt. 2.6.1. "Organic Hydride for Storage & Transport System of Hydrogen".

[4]   Saito Y. Engineering System for Fine Particles – Applied Technology II (Ed. H. Yanagida), Fuji Techno-system Press, Tokyo 2002; Chapt. 9.2.2. "Metal Fine Particle Catalyst".

[5]   Hodoshima S, Takaiwa S, Shono A, Satoh K, Saito Y. Appl Catal A: General 2005; 283: 235-242.
https://doi.org/10.1016/j.apcata.2005.01.010

[6]   Glansdorff G, Prigogine I. Thermodynamic Theory of Structure, Stability and Fluctuations, Wiley, London 1971; Chapt. 3.

[7]   Hodoshima S, Shono A, Saito K, Saito Y. Stud Surf Sci Catal 2006; 159: 177-180.
https://doi.org/10.1016/S0167-2991(06)81562-4

[8]   Shono A, Hashimoto T, Hodoshima S, Satoh K, Saito Y. J Chem Eng Jpn 2006; 39: 211-215.
https://doi.org/10.1252/jcej.39.211

[9]   Hodoshima S, Shono A, Saito Y. Energy Fuels 2008; 22: 2559-2569.
https://doi.org/10.1021/ef700607h

[10]   Saito Y, Aramaki K, Hodoshima S, Saito M, Shono A, Kuwano J, Otake K. Chem Eng Sci 2008; 63: 4935-4941.
https://doi.org/10.1016/j.ces.2007.11.036

[11]   Okada Y. Energy Catalyst Technology, Muroi T, Ed. Science & Technology Press, Tokyo, "Catalyst Technology for Hydrogen Storage and Transport System with Use of Organic Hydride" 2010; Chapt. 7.2.

[12]   NEDO, White Paper on Hydrogen Energy. Nikkan Kogyo Newspaper Press, "Domestic, Business & Industrial Use of Fuel Cell" 2015; Chapt. 6.5.1-2.

[13]   Saito Y, Okada Y. Energy Technology Roadmap of Japan: Future Energy Systems Based on Feasible Technologies Beyond 2030, Kato Y, Koyama M, Nakagaki T, Eds., Springer, London, Topics in Primary and Secondary Sectors of Industry, "Organic Hydride for Hydrogen Energy Carrier" 2016; Chapt. 6.