Organic chemical hydrides as storage medium of hydrogen on the basis of superheated liquid-film concept

Shinya Hodoshima, Atsushi Shono, Kazumi Satoh, Yasukazu Saito

a(Department of Industrial Chemistry, Faculty of Engineering, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan, hodosima@ci.kagu.tus.ac.jp)

ABSTRACT:

A catalysis pair of tetralin dehydrogenation / naphthalene hydrogenation has been proposed in the present paper as an organic chemical hydride for operating stationary fuel cells. Catalytic naphthalene hydrogenation, having been commercialized since the 1940s, proceeds to generate decalin via tetralin as an intermediate. The storage capacities of tetralin (3.0 wt%, 28.2 kg-H₂ / m³) are lower than decalin (7.3 wt%, 64.8 kg-H₂ / m³) but both tetralin dehydrogenation and naphthalene hydrogenation are much faster than the decalin / naphthalene pair. Moreover, existing infrastructures, e.g., gas station and tank lorry, are available for storage, transportation and supply of hydrogen. As for the stationary fuel cells with large space for hydrogen storage, tetralin as a hydrogen carrier is superior to decalin in terms of fast hydrogen supply.

Rapid hydrogen supply from tetralin under mild conditions was only accomplished with the carbon-supported metal catalysts in the “superheated liquid-film states” under reactive distillation conditions. In contrast to the ordinary suspended states, the catalyst layer superheated in the liquid-film state gave high catalytic performances at around 250°C. As a result, serious coke formation over the catalyst surface and excessive exergy consumption were prevented simultaneously.

KEYWORDS: Organic chemical hydrides; Stationary fuel cells; Carbon-supported metallic nano-particles; Superheated liquid-film-type catalysis

INTRODUCTION:

Hydrogen is expected to contribute definitely to the coming sustainable society as a clean energy carrier [1]. However, some technological tasks regarding its production, transportation, storage and safety must be solved in order to realize hydrogen energy systems such as fuel cells. In particular, development of the suitable medium for hydrogen storage and the efficient methods for absorbing and desorbing hydrogen through the medium are urgent issues. With respect to hydrogen storage, hydrogen carrier requires the following characteristics: (1) High storage capacity; (2) Safe and cost-effective; (3) Facile reversibility.

Reversible catalysis pairs of cyclichydrocarbons dehydrogenation / aromatics hydrogenation have been proposed by our group (e.g., a pair of decalin / naphthalene (Eq. (1))) [2-13]. A target storage value (6.5 wt%, 62.0 kg-H₂ / m³), presented by the DOE hydrogen plan, U.S. [14], is well satisfied with decalin (7.3 wt%, 64.8 kg-H₂ / m³). Both decalin and naphthalene are accepted socially as safe commodity chemicals, since they have been utilized as a solvent and an insect killer at home, respectively, for long periods. The catalytic process for naphthalene hydrogenation has been commercialized since the 1940s [15]. In addition, existing gas stations or tank lorries are available for using either decalin or naphthalene oil [11,12]. All of these advantages for storage and transportation of hydrogen suggest that decalin is suitable as one of the on-board liquid organic hydrides for operating fuel-cell automobiles [5,7,11] or vehicles powered by hydrogen-fueled internal combustion engines [12].

On the other hand, much attention should be paid to another pair of tetralin dehydrogenation / naphthalene hydrogenation (Eq. (2)), the storage densities of which (3.0 wt%, 28.2 kg-H₂ / m³) are lower than those of decalin. However, the dehydrogenation rate of tetralin [6,13] can exceed the magnitude of decalin, as well conceived with rapid partial hydrogenation of naphthalene into tetralin in a successive reaction process [15]. Tetralin would therefore be adoptable to hydrogen storage for stationary fuel cells, with the advantage of large space for storage taken into consideration.

Efficient hydrogen supply from tetralin at mild heating temperatures is required for preventing from not only serious coke formation that would cause catalyst deactivation but also excessive consumption of exergy. Though endothermic tetralin dehydrogenation is thermodynamically restricted at temperatures lower than 250°C [16], “superheated liquid-film-type catalysis” under reactive distillation conditions [17] would make it possible to evolve hydrogen from organic hydrides quite efficiently in this temperature range [2-13],
at which carbonaceous deposit over the catalyst surface would be avoided. As for sources of heat for endothermic dehydrogenation, waste heats recovered from various industrial processes or solid oxide fuel cells would be available.

For the purpose of generating hydrogen rapidly from tetralin at around 250°C, catalytic tetralin dehydrogenation with carbon-supported metallic nano-particles was performed in continuous operations on the basis of “superheated liquid-film concept” [2-13], with comparing dehydrogenation catalysis for decalin under the same reaction conditions.

\[ \text{C}_8 \text{H}_{10} + 5 \text{H}_2 \rightarrow 8 \text{H}_2 \text{O} \]  \hspace{1cm} (1)  

\[ \text{C}_8 \text{H}_{10} + 2 \text{H}_2 \rightarrow 8 \text{H}_2 \text{O} \]  \hspace{1cm} (2)

**EXPERIMENTAL:**

**Catalyst preparation**

A pretreatment was carried out by immersing granular activated carbon (KOH-activation, BET specific surface area: 3100 m² / g, pore volume: 1.78 cm³ / g, average pore size: 2.0 nm, Kansai Netsukagaku Co. Ltd.) [18] with an aqueous solution of NaOH (pH 14) for 24 h in order to promote the anion exchange between the ligand chloride of impregnated metal precursors (K₂PtCl₄) and the aqueous hydroxide ion inside the micropores of catalyst supports [19].

A platinum catalyst supported on this granular activated carbon (Pt / C, 5 wt-metal%) [2-13,19] was prepared by a conventional impregnation method in the following manner. Firstly, granular powders of the base-pretreated activated carbon were stirred with a K₂PtCl₄ aqueous solution at room temperature for 48 h. This step was followed by drop-wise addition of a NaBH₄ aqueous solution at room temperature for 10 min. After the solution was kept standing for another 30 min, the catalysts were filtered and then washed with a large amount of water. Finally, the Pt / C catalyst was evacuated at 70°C for 10 h.

A platinum catalyst (5 wt-metal%) supported on activated carbon cloth (BET specific surface area: 1834 m² / g, average pore size: 1.5 nm, Kuraray Chem. Co.) was also prepared by an impregnation method [11,12]. A piece of the activated carbon cloth (ACC) was cut into a disk with a diameter of 5 cm and a thickness of ca. 0.8 mm. The disc-shaped ACC was stirred with a K₂PtCl₄ aqueous solution at room temperature for 24 h. This step was followed by drop-wise addition of a NaBH₄ aqueous solution at room temperature for 10 min. After the mixture was kept standing for another 30 min, the catalysts were filtered and then washed with a large amount of water in order to remove the residual ions. Finally, the Pt / ACC catalyst was evacuated at 200°C for 5 h.

**Measurement of catalytic dehydrogenation activities for decalin and tetralin**

Fig. 1(A) shows a continuous dehydrogenation reactor (eggplant-type flask, volume: 50 ml) at laboratory scale. In this operation, both catalytic dehydrogenation for decalin and tetralin were performed with a constant amount of the platinum catalyst supported on granular activated carbon (Pt / C, 1.1 g) by heating at 230°C. Here liquid-phase substrates were supplied continuously to the catalyst at various feed rates (0.28, 0.5, 1.1, 1.7 and 2.3 ml / min for decalin, 0.26, 0.5, 1.2, 1.7 and 2.1 ml / min for tetralin). All of the vapor were removed from the reactor through a thermally-protected part to a condenser cooled at 25°C (see Fig. 1(A)). After confirming stationary rates of hydrogen evolved from decalin or tetralin by a flow meter, the rates of evolved hydrogen were recorded every 5 min for 30 min by the flow meter and the liquid compositions, consisting of naphthalene, tetralin and unconverted reactants, were analyzed with gas-chromatographic analysis. The temperature of each catalyst layer during reaction was measured by directly inserting a thermocouple into the catalyst layer. In this way, the relationship of catalytic dehydrogenation activities with both the feed rate and the catalyst-layer temperature was investigated. In addition, a long-term reaction test for examining catalyst deterioration was performed at the amount ratio of catalyst to tetralin solution of 1.1 g / 0.5 ml min⁻¹, regarding tetralin dehydrogenation over the Pt / C catalyst at heating temperature of 240°C.

In a continuous reactor at bench scale (SUS-type, volume: 1.2 L) (Fig. 2(B)) [11,12], catalytic tetralin dehydrogenation was performed with a constant amount of the platinum catalyst supported on activated carbon cloth (a disk-shaped Pt / ACC catalyst (5 wt-metal%) with a diameter of 5 cm, 0.30 g) by heating at 260°C [11,12]. Liquid-phase tetralin was supplied continuously to the catalyst bed at various feed rates (0.25, 0.5, 1.0, 1.5 and 2.0 ml / min). The rates of evolved hydrogen were recorded every 5 min for 30 min by the flow meter and the liquid compositions, consisting of naphthalene and unconverted tetralin, were analyzed gas-chromatographically at the final stage. Temperatures of the catalyst layer during reaction were also measured with the same manner as described above. The relationship of catalytic dehydrogenation activities with the feed rate was similarly examined [11,12].
RESULTS AND DISCUSSION:

Catalytic hydrogen supply from tetralin at laboratory scale

In a continuous reactor at laboratory scale (Fig. 1(A)), catalytic dehydrogenation for tetralin was performed with a continuous supply of tetralin at various feed rates (0.26, 0.5, 1.2, 1.7 and 2.1 ml / min) into the reactor, containing a constant amount of the platinum catalyst supported on granular activated carbon (Pt/C, 1.1 g), under boiling and refluxing conditions by heating at 230°C and cooling at 25°C. Fig. 2(A) shows a relationship of the catalyst-layer temperature during reaction with the feed rate of tetralin in the continuous operation. The smaller the feed rate of tetralin, the larger the temperature of catalyst layer. Dehydrogenation activities for tetralin were also changed dramatically in accordance with the feed rate (Fig. 2(B)(C)).

In cases of 2.1, 1.7 and 1.2 ml / min, the temperature of each catalyst layer was almost equal to boiling point of tetralin (207°C). These catalysts were suspended uniformly in sufficient amounts of tetralin, resulting in low catalytic conversions comparatively (Fig. 2(B)).

At below 1.2 ml / min, the temperatures were higher than the boiling point (Fig. 2(A)). Catalytic tetralin conversions were remarkably enhanced in this range of feed rate (e.g., 61.5% at 0.26 ml / min). Though the catalysts were not suspended, their surface parts of the catalysts became just wetted with the tetralin solution. According to the previous studies on dehydrogenation catalysis in a batch-wise operation [2-13], these states of catalysts were designated as the “superheated liquid-film state” [2-13], since the carbon-supported catalysts were covered with thin films of liquid substrates. On the other hand, the highest rate of evolved hydrogen was attained in a certain range of feed rate, as shown in Fig. 2(C). In this continuous operation, a stationary reaction rate is determined from both the feed rate and the stationary conversion. Therefore, the highest magnitude was apparently obtained at around 1.7 ml / min.

Temperatures higher than the boiling point in the small feed rates were caused by “superheating” [20], because the catalyst layer in the liquid-film state, being directly on the reactor bottom, is just wetted with a thin liquid-film of the solution under boiling conditions. Stationary thermal flow from the external heating reservoir to the catalyst layer results in its temperature keeping higher than the boiling point. As illustrated in Fig. 3, therefore, a temperature gradient exists between the catalyst layer and the liquid phase stationarily. This temperature gradient accelerates product desorption (e.g., hydrogen and naphthalene) from the surface and regenerates the catalytic active sites [2-13], giving the high catalytic performance. It was also revealed that this effect strongly depended on the extent of superheating, on the experimental basis that the catalytic conversion increased with the catalyst-layer temperature (Fig. 2(B)). In the suspended state, on the contrary, the temperature gradient existed only around the reactor wall irrespective of the liquid bulk. Most of the catalyst particles here were in contact with the solution at the same temperature as the boiling point, resulting in the poor activities.

Fig. 1 Experimental apparatus for catalytic hydrogen evolution from organic chemical hydrides under reactive distillation conditions.
Catalyst: Platinum nano-particles supported on granular activated carbon (5 wt-metal%) 1.1 g
Reaction conditions: Boiling and refluxing by heating at 230°C and cooling at 25°C

Fig. 2 Relationship of catalyst-layer temperature and dehydrogenation activities with feed rate of tetralin in continuous operation.

Long-term reaction test for catalytic tetralin dehydrogenation

To investigate the deterioration of catalysts, a long-term test for tetralin dehydrogenation was performed under superheated liquid-film conditions by using the continuous reactor (Fig. 1(A)) at the amount ratio of Pt / C catalyst to tetralin of 1.1 g / 0.5 ml min⁻¹ (heating temperature: 240°C). Fig. 4 shows time courses of rate of evolved hydrogen and catalytic conversion in the tetralin dehydrogenation. High conversion (ca. 50%) was maintained for longer than 5 h.

The catalyst deactivation is generally ascribed to coke formation over the catalyst surface in addition to sintering or aggregation of metal particles. Exothermic catalysis often suffers from catalyst sintering caused by the rise of temperature during the reaction. On the other hand, the present endothermic reaction of tetralin dehydrogenation was performed at mild temperature of 240°C, being low enough to avoid the coke formation. Moreover, the products (e.g., naphthalene and hydrogen) or any poisoning impurities adsorbed on the catalyst surface were removable easily by vigorous bubbling due to the temperature gradient in the superheated liquid-film state under boiling conditions, resulting in preventing catalysts from deterioration [9].

Fig. 3 Temperature gradient from external heating reservoir toward reactor wall, catalyst layer and finally to liquid bulk under superheated liquid-film conditions.
Comparison of dehydrogenation activities for decalin and tetralin

Fig. 5(A)(B) shows a comparison of dehydrogenation activities for decalin and tetralin by heating at 230°C with the same continuous reactor. Both rates of evolved hydrogen and conversions for tetralin were much higher than those for decalin at all the feed levels. Regarding the stationary one-pass conversion, tetralin exhibited ca. 6-7 times larger conversions than the decalin under the same superheated conditions (0.26-0.5 ml/min). It is noted that high catalytic conversion above 60% was attained at 0.26 ml/min (Fig. 2(B)), though the heating temperature (230°C) is thermodynamically unfavorable for endothermic tetralin dehydrogenation. Facile dehydrogenation of tetralin would certainly be ascribed to advantageous adsorption due to the bonding capability of its aromatic part [15]. It was therefore confirmed experimentally that tetralin as an organic hydrogen carrier for stationary use is superior to decalin in terms of rapid hydrogen supply or power density [13].
Catalytic hydrogen supply from tetralin at bench scale

In order to realize the superheated liquid-film state at large scale, catalytic tetralin dehydrogenation in a continuous reactor was investigated at bench scale (Fig. 1(B)) [11,12]. Instead of the granular activated carbon, moreover, an activated carbon cloth was adopted as a catalyst support in this reaction because of its practical advantages [11,12]. Under the boiling and refluxing conditions by heating at 260°C and cooling at 25°C, dehydrogenation was performed with a continuous supply of tetralin at various feed rates (0.25, 0.5, 1.0, 1.5 and 2.0 ml / min) into the catalyst bed, containing a constant amount of platinum particles loaded on a sheet of activated carbon cloth (Pt / ACC, 0.30 g, 5 cm).

Time courses of catalyst-layer temperatures and tetralin conversions at both feed rates of 0.25 and 2.0 ml / min are shown in Fig. 6(A)(B). The temperature of catalyst layer at the feed rate of 2.0 ml / min was equal to the boiling point of tetralin (207°C), whereas the catalyst at 0.25 ml / min was superheated stationarily and gave much higher conversion than the case of 2.0 ml / min (Fig. 6(B)). In addition, the same tendencies as the laboratory-scale reaction were observed with respect to the relationships of dehydrogenation activities with the feed rate (Fig. 7(A)(B)).

It was revealed from these results that catalytic tetralin dehydrogenation under superheated liquid-film conditions was well demonstrated in the continuous operation at bench scale.

![Fig. 6](image1.png)  
(A) Temperature of catalyst layer, (B) Catalytic conversion of tetralin  
Catalyst: Platinum nano-particles supported on activated carbon cloth (5 wt-metal%) 0.3 g  
Feed rate of tetralin solution: 0.25 ml / min ( ) and 2.0 ml / min ( )  
Reaction conditions: Boiling and refluxing by heating at 260°C and cooling at 25°C

![Fig. 7](image2.png)  
(A) Stationary conversion of tetralin, (B) Stationary rate of evolved hydrogen  
Catalyst: Platinum nano-particles supported on activated carbon cloth (5 wt-metal%) 0.3 g  
Reaction conditions: Boiling and refluxing by heating at 260°C and cooling at 25°C
CONCLUSIONS:
The present study on hydrogen storage by a pair of tetralin / naphthalene and hydrogen supply from tetralin with the superheated liquid-film-type catalysis can be summarized as follows.

(1) At mild heating temperatures of 230-240°C, hydrogen supply from tetralin over carbon-supported platinum catalysts in the superheated liquid-film states was quite efficiently attained under reactive distillation conditions in the continuous operation at laboratory scale.
(2) A long-term test for tetralin dehydrogenation over carbon-supported platinum catalyst was performed under superheated liquid-film conditions, with high stationary conversion (ca. 50%) maintained for longer than 5 h.
(3) Catalytic tetralin dehydrogenation proceeded much faster than decalin under the same superheated liquid-film conditions. It was experimentally confirmed that tetralin as a hydrogen carrier for stationary use is superior to decalin in terms of rapid hydrogen supply to fuel cells.
(4) It was revealed that catalytic hydrogen supply from tetralin under superheated liquid-film conditions was well demonstrated with platinum particles supported on activated carbon cloth by heating at 260°C in the continuous operation at bench scale.

REFERENCES: