



Short communication

Hydrogen production by catalytic decalin dehydrogenation over carbon-supported platinum catalyst: Effect of catalyst preparation method



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ABSTRACT

Preparation method strongly affected the platinum dispersion of carbon-supported platinum catalysts, and accordingly, their catalytic activity in the decalin dehydrogenation. The catalyst prepared by an advanced method (ion-exchange method or polyol method) exhibited a better catalytic performance than that prepared by a conventional method (impregnation method or precipitation method) in terms of initial hydrogen evolution rate and total amount of hydrogen evolution. Platinum dispersion played a key role in determining the catalytic activity in this reaction, and thus, the high platinum dispersion of the catalysts prepared by an ion-exchange method and a polyol method resulted in their high catalytic activity.

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1. Introduction

Although petroleum has been utilized as a main energy source in the past century, the expected depletion of fossil fuels such as petroleum and coal has triggered extensive researches for sustainable energy source [1–3]. Among the various sustainable energy sources, hydrogen is regarded as a promising energy carrier. It is because that hydrogen is renewable and high energy-containing compound (>120 kJ/g) [4,5]. In addition, hydrogen energy has been called as a clean energy in the consideration of no emission of greenhouse gases such as carbon dioxide and methane [4–6]. Hydrogen storage and supply have been considered as key technologies for the hydrogen economy, which is a system delivering energy using hydrogen. In particular, onboard storage and supply of hydrogen are an important issue for the successful utilization of hydrogen in the fuel cell vehicle system. Also, when considering the fact that hydrogen is a very flammable gas, the safe transportation of hydrogen between the gas station and the production facility is absolutely required [7–9].

Various organic and inorganic materials, including metal hydride, carbon nanostructure, hydrogen-absorbing alloys, and liquid organic hydride (LOH), have been investigated as candidate materials for onboard storage and supply of hydrogen [10–12]. Particularly, the utilization of the catalytic dehydrogenation–hydrogenation system of liquid

organic hydrides (e.g., cyclohexane, methylcyclohexane, tetralin, decalin, and bicyclohexyl) has been proposed as one of the promising technologies to store and supply hydrogen for the fuel cell vehicle [13–15]. The catalytic reaction system using liquid organic hydride has the following advantages; (i) When comparing to other processes (e.g. methanol-reforming, LNG, LPG, and gasoline), this reaction system does not produce by-products such as carbon monoxide and carbon dioxide. (ii) This reversible reaction technology, in which the reactants and products can be recycled, is simpler than the system with metal hydride. (iii) Liquid organic hydrides retain comparatively a high hydrogen density and a high boiling point. (iv) Liquid organic hydrides existed in the liquid phase around room temperature, indicating that this catalytic process can use the present infrastructures such as oil tank and tank lorry for long-term storage and transport [16,17].

Decalin with considerable high hydrogen contents of 7.3 wt.% and 64.8 kg H₂/m³ is thought to be an excellent mobile storage medium of hydrogen [16]. Catalytic decalin dehydrogenation is also suitable for the hydrogen supply to the fuel cell vehicle, because decalin can be converted to naphthalene at low reaction temperature of about 200 °C. Naphthalene, which is produced by decalin dehydrogenation, can be easily recycled to decalin through the commercial process of naphthalene hydrogenation. Moreover, the amount of evaporated decalin during the storage and transport is negligible owing to its high boiling point; 187 °C (trans-decalin) and 196 °C (cis-decalin) [18]. Therefore, it can be deduced that the catalytic reaction pair of decalin dehydrogenation/naphthalene hydrogenation is regarded as one of the most

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suitable hydrogen evolution processes for the fuel cell vehicle due to its high selectivity, high reversibility, and high energy density [19].

It is well known that the catalytic dehydrogenation of decalin could be efficiently performed over carbon-supported platinum catalyst (Pt/C). The physical properties of platinum catalysts such as platinum dispersion and platinum particle size are also known to be crucial factors for the efficient hydrogen production in this reaction. It is noteworthy that these physical properties of catalyst can be much different depending on the preparation method [20]. Therefore, any systematic investigation to see the effect of preparation method on the catalytic activity of platinum catalyst in this reaction would be worthwhile. In this work, we prepared a series of carbon-supported platinum catalysts using four different preparation methods such as impregnation method, precipitation method, ion-exchange method, and polyol method. Especially, advanced methods (polyol method and ion-exchange method) were employed for the preparation of carbon-supported platinum catalysts to obtain high platinum dispersion. Catalytic dehydrogenation of decalin over the prepared catalysts was carried out in a batch-type reactor. The prepared catalysts were characterized by XRD, CO-chemisorption, and TEM analyses. Finally, effect of preparation methods on the catalytic activity of carbon-supported platinum catalyst in the decalin dehydrogenation was studied. Moreover, correlation between the catalytic performance of platinum catalyst and its physical properties was investigated.

2. Experimental

2.1. Catalyst preparation

A series of carbon-supported platinum (Pt/C) catalysts were prepared using four different preparation methods. The platinum precursors (H_2PtCl_6 and $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$) for Pt/C catalysts were provided from Wako Pure Chemical, and the palm activated carbon (Samchun Inc.) was employed as a carbon support. N_2 adsorption/desorption isotherm analysis (BELSORP-mini II, BEL Japan) revealed that the palm activated carbon retained typical characteristics of microporous carbon (surface area: $1304 \text{ m}^2/\text{g}$). The amount of platinum was fixed at 3 wt.% in all Pt/C catalysts.

2.1.1. Pt/C_{Im} (impregnation method)

Pt/C_{Im} catalyst was prepared by an incipient wetness impregnation method using an aqueous solution of platinum precursor (H_2PtCl_6). After drying the impregnated catalyst overnight at 120°C , it was reduced at 250°C for 3 h with a mixed stream of nitrogen and hydrogen to yield Pt/C_{Im} catalyst.

2.1.2. Pt/C_{Pr} (precipitation method)

A known amount of activated carbon was added into the aqueous solution of platinum precursor (H_2PtCl_6), which was followed by stirring the mixed solution at room temperature for 48 h. NaBH_4 aqueous solution as a reducing agent was then dropwise added to the mixed solution at 90°C for 30 min. After aging the resulting solution for another 30 min, solid product was obtained by filtration. The solid was washed with distilled water several times to remove the residual ions. The resulting solid was finally dried in a convection oven overnight at 80°C . The catalyst prepared by a precipitation method was denoted as Pt/C_{Pr}.

2.1.3. Pt/C_{Ex} (ion-exchange method)

Ion-exchange method was employed for the preparation of Pt/C_{Ex} catalyst with the similar preparation method as reported in the literature [17]. Prior to the ion-exchange method, activated carbon was oxidized with concentrated nitric acid for 30 min under boiling and refluxing conditions to create an oxygenated functional group on the surface of activated carbon. A known amount of oxidized activated carbon was added into the aqueous solution of platinum precursor

($\text{Pt}(\text{NH}_3)_4\text{Cl}_2$). NH_3 solution was then added into the solution to adjust the pH value of the mixed solution (pH = 9). The mixture was vigorously stirred overnight at room temperature to exchange the protons of the oxidized activated carbon into the platinum cations. The precipitate was filtered to obtain a solid product, while platinum concentration in the filtrate was investigated by ICP-AES (Prodigy, Teledyne Leeman Labs) analysis. The solid product was dried overnight at 80°C . The dried solid was calcined at 350°C for 2 h in a nitrogen stream, and subsequently, it was finally reduced at 250°C for 3 h in a mixed stream of nitrogen and hydrogen to yield carbon-supported platinum catalyst (Pt/C_{Ex}).

The platinum concentration in the filtrate, which was determined by ICP-AES analysis, was found to be negligible. This means that most of platinum cations in the precursor participated in the ion-exchange process. Therefore, we could confirm that Pt/C_{Ex} catalyst retained the designed platinum content (3 wt.%), and accordingly, was successfully prepared by an ion-exchange method.

2.1.4. Pt/C_{Po} (polyol method)

According to the similar preparation method as previously reported [21], Pt/C_{Po} catalyst was prepared by a polyol method, which is one of the promising methods for the preparation of well-dispersed metal catalyst. Ethylene glycol was used as both a solvent and a reducing agent to prepare the nanosized platinum catalyst. A known amount of activated carbon was added into the ethylene glycol solution of platinum precursor (H_2PtCl_6), and then the suspension was stirred at room temperature for 30 min. Aqueous NaOH solution (1 M) was added to adjust the pH value of the solution to 11 followed by continuous stirring for 1 h. The solution was maintained at 130°C for 3 h, and the resulting mixture was cooled down to room temperature. The mixture was filtered and washed by water and ethanol, and then, it was finally dried at 70°C in vacuo.

2.2. Catalyst characterization

XRD patterns of the prepared catalysts (Pt/C_{Im}, Pt/C_{Pr}, Pt/C_{Ex}, and Pt/C_{Po}) were obtained with a Shimadzu XRD-7000 instrument using $\text{Cu-K}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$) operated at 40 kV and 40 mA. Platinum dispersion and particle size in the catalysts were examined by CO-chemisorption (BELCAT-B, BEL Japan) and TEM (JEM-2100F, JEOL) analyses. In the CO-chemisorption analysis, metal dispersion and particle size were calculated on the basis of the adsorption stoichiometry of Pt/CO = 1.4 [22,23].

2.3. Catalytic dehydrogenation of decalin

As previously reported [17,18], catalytic dehydrogenation of decalin over the prepared catalysts was performed in a batch-type dehydrogenation reactor under boiling (210°C) and refluxing conditions (5°C) in nitrogen atmosphere. Decalin (cis- and trans-mixture) was purchased from Sigma-Aldrich. In a typical experiment, 0.3 g of catalyst was employed as a thin layer form at the bottom of the reactor. The reactor was heated to the reaction temperature, and then, the reactor was thoroughly purged with nitrogen for 30 min. After purging the reactor, a known amount of decalin was dropwise added into the reactor using a microsyringe. The evolved hydrogen from decalin was collected by a gas burette, and the amount of evolved hydrogen was periodically checked for 60 min. The evolved gas composition was also analyzed by a gas chromatography (Yong Lin Instrument, YL6500) equipped with a thermal conductivity detector (TCD).

3. Results and discussion

The analysis of the evolved gas composition clearly revealed that no by-products were observed over the all catalysts tested in this work. This indicates that the prepared carbon-supported platinum catalysts

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