

Development of Highly Active Pt/Alumina as Low Temperature Catalysts for Utilization of Organic Hydride Dehydrogenation Processes

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有機ハイドライド脱水素プロセスのための Pt/Al₂O₃ 系触媒の低温高活性化

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Abstract

For highly active catalysts at low temperature for dehydrogenation of organic hydrides, Pt-loaded catalysts on alumina-based supports have been investigated. For boehmite (AlOOH)-supported Pt (1.0 wt%) catalysts, well-dispersed Pt⁰ species by impregnation with Pt⁰-1,3-divinyltetramethyldisiloxane complex should be formed as highly active one for cyclohexane (CH) dehydrogenation at less than 200 °C. The activity was enhanced by silylation of boehmite surface with vinyl- or phenyl-silane due to hydrophobization. For γ -Al₂O₃-supported Pt catalysts using an impregnation of H₂PtCl₆, active Pt⁰ species are formed by UV irradiation due to reductive photo-deposition. It was presumed that stable dehydrogenation activity at low temperature is a subject because the Pt⁰ species could be aggregated reductively by produced hydrogen.

Key Words: Effective Utilization of Organic Hydrides, Dehydrogenation of Cyclohexane or Methylcyclohexane, Pt-loaded Alumina Catalysts, Pt-loaded Boehmite Catalysts

1. Introduction

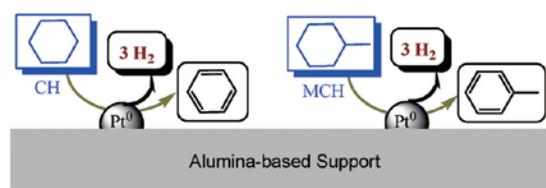
Hydrogen energy source has been more important in recent years for the glowing demand

of fuel cell vehicle (FCV), where energy stored as hydrogen should be converted to electricity by the fuel cell¹⁾. Hydrogen is a clean fuel when

consuming in a fuel cell with air, and then produces only water. Hydrogen can be produced from a variety of resources such as natural gas (LNG), coal, fuel, water, ammonia, biomass, *etc.* Many processes have been industrialized for hydrogen production, *e.g.*, reforming of LNG or renewable liquid fuels, gasification of coal or biomass, microbial biomass conversion, electrolytic hydrogen production from water, *etc.* As a hydrogen energy carrier, it must be used to store, move, and deliver energy produced from other sources. One of an important subject to employ the hydrogen energy for FCV is storage hydrogen gas stored in a tank on the vehicle. Hydrogen fueling stations need recently to supply the source, however, rapid spread of the station is difficult realistically.

The system of dehydrogenating organic hydride is very attractive for hydrogen storage in FCV. Representative systems of organic hydrides are as follows: $C_6H_{12} \rightleftharpoons 3 H_2 + C_6H_6$ (Cyclohexane-Benzene system), $C_6H_{11}-CH_3 \rightleftharpoons 3 H_2 + C_6H_5-CH_3$ (Methylcyclohexane-Toluene system), and $C_{10}H_{18} \rightleftharpoons 5 H_2 + C_{10}H_8$ (Decalin-Naphthalene system). By dehydrogenation of each organic hydride efficiently, durable hydrogen supply will be available in FCV by using highly active dehydrogenation catalysts. Since the application of this system can utilize existing gas stations, rapid spread will be possible for hydrogen energy supply.

As a typical system of dehydrogenating organic hydride, methylcyclohexane (MCH) has been studied by many workers for hydrogen source. The dehydrogenation process is highly reversible, and the industrial hydrogenation process has been commercialized, while the dehydrogenation process of MCH does not exist and the research on the catalytic dehydrogenation of organic liquid hydride is not comprehensive. The development of dehydrogenation catalysts with good stability, catalytic activity and product selectivity under low temperature and high pressure is the central issue of the industrialization²⁻³⁾. The subjects to be overcome



Scheme. 1 Schematic diagram of CH/MCH dehydrogenation over a Pt-loaded catalyst.

in this system are pointed out; (1) lowering the high activation temperature (300-400 °C) to *ca.* 200 °C, (2) control of the durable reversibility for dehydrogenation-hydrogenation cycle, and (3) suppressing the catalytic deactivation due to demethylation and/or carbonaceous deposition on the catalysts⁴⁾. As another hydrogen source, cyclohexane (CH)⁵⁾ has also been studied. Although cyclohexane dehydrogenation proceeds durably on Pt-loaded catalysts without deactivation due to demethylation, the reactivity will be relatively lower than that of methylcyclohexane. Recently, reversible dehydrogenation and rehydrogenation reactivity of cyclohexane and methylcyclohexane was presented by single site Pt⁰ catalyst⁶⁾. On the previous background, catalytic dehydrogenation activity over Pt-loaded catalysts supported on alumina-based supports have been investigated by using several preparation methods for highly active catalysts at low temperature below 200 °C. In the present study, dehydrogenation activity of cyclohexane (CH) over Pt (1.0 wt%)-loaded Al₂O₃ or AlOOH (boehmite) catalysts have been evaluated mainly. Although the dehydrogenation activity of CH is lower than that of MCH, the purpose of this study is to find the optimum Pt species for highly active CH dehydrogenation at less than 200 °C.

2. Experimental

Supported Pt catalysts (1.0 wt% as platinum) were prepared by impregnation method with aqueous hydrogen hexachloroplatinate (Pt⁴⁺) solution (denoted as Pt(Cl)) or Pt⁰-1,3-divinyltetramethyldisiloxane complex in *n*-

heptane solution (denoted as Pt(Sil)), and then followed by drying overnight and calcination at 500 °C for 6 hours. The support oxides employed in this study is γ -Al₂O₃ (2-3 μ m particle size; Kojundo Kagaku Co.), α -Al₂O₃ microparticle (AKP-50; Sumitomo Chem. Co.) boehmite (AlOOH; Fujifilm-Wako), etc. To protect -OH groups on the support for hydrophobization, surface silylation was used by means of impregnation with triethoxyvinylsilane in *n*-heptane solution at 70 °C. The silylated catalysts were also followed by drying and calcination.

As a pre-reduction of active Pt sites (to form active Pt⁰ species), thermal reduction with H₂(20%)-Ar at 200 °C for 1 h or photodeposition under UV irradiation (using a high-pressure mercury lamp in 250 W). After the pretreatment, the powdery catalyst sample was set in a glass tube reactor. The catalytic activity for CH or MCH dehydrogenation was tested by using a fixed bed flow reactor at atmospheric pressure. The Ar gas (30 mL/min) was fed into the reactant CH (vapor pressure: 16.19 kPa at 30 °C) by bubbling, and the vaporized reactant was fed to the catalyst equipped with thermally controlled electric furnace. The catalyst temperature was elevated stepwise from 100 to 200 °C (25.0 °C step), and the product reacted for 20 minutes for each temperature was analyzed by using online gas chromatography (TCD-GC; Shimadzu GC-6A).

3. Results and Discussion

3-1. Pt/Boehmite Catalysts

Fig. 1 shows the reactivity of CH dehydrogenation over Pt/ α -Al₂O₃ and Pt/AlOOH catalysts (pre-reduced thermally) by using the Pt(Cl) or Pt(Sil) precursor. CH dehydrogenation reactivity increased with elevated temperature, and detected products are only hydrogen and benzene (without cyclohexenes) in all the catalysts. In the region of 150-200 °C, the Pt(Sil)-loaded catalysts showed relatively higher activity than Pt(Cl)-loaded ones. At the same time, boehmite-supported catalysts show higher reactivity than α -alumina-supported ones. The difference on activity is

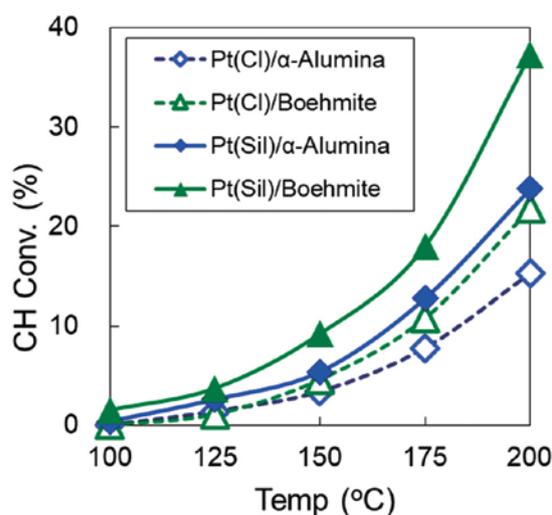


Fig. 1 Catalytic CH dehydrogenation over a Pt/ α -Al₂O₃ and Pt/AlOOH catalysts prepared using Pt(Cl) and Pt(Sil) precursors.

presumably due to the dispersibility of Pt⁰ species after thermal pre-reduction because of higher surface area on AlOOH than that on α -Al₂O₃. For Pt(Sil)-loaded catalysts, metallic Pt can be well-dispersed based on the effect of bulky ligands in the Pt⁰-1,3-divinyltetramethyldisiloxane precursor which prevents aggregation of Pt⁰ metal. In this case, silicon (Si⁴⁺) will remain on the alumina or boehmite support after the pre-reduction, and remaining silicon will affect the surface acid-base properties of the support. As well known, dehydrogenation of CH proceeds Pt⁰ species⁴⁾ and produced hydrogen will be sorbed partly. At the same time carbonaceous products will spillover on the support. It is important to affect the alumina or boehmite surface property for dehydrogenation reactivity on Pt⁰ active sites. Based on these backgrounds, effects of the alumina surface supporting platinum was investigated. Fig. 2 shows the CH dehydrogenation reactivity over a Pt(Sil)/boehmite catalysts modified using various organosilane modifiers (50/mol/g). By modification with triethoxyvinylsilane and triethoxyphenylsilane, hydroxyl groups on the surface (due to the support surface over Al₂O₃ or AlOOH) will be blocked and hydrophobic surface will be formed. In case of silylation with triethoxy-aminopropylsilane, hydrophobic surface

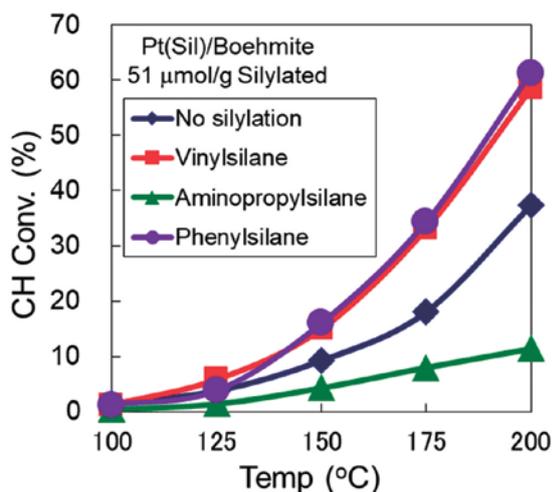


Fig. 2 CH dehydrogenation over Pt(Sil)/ AlOOH catalysts modified using various organosilane modifiers (50 mmol/g).

will not be formed because of modified amino group. The CH dehydrogenation reactivity is enhanced definitely by modification of vinylsilane and phenylsilane, although the reactivity became low by modification of aminopropylsilane. This result indicates that hydrophobicization of the AlOOH surface as well as blocking of hydroxyl groups is a noted factor for high activity. The effect of the silylated amount using triethoxyvinylsilane was also investigated as shown in Fig. 3. It is summarized that the reactivity increased with the amount of modification up to 75 mol/g, and remained constant in 75-100 mol/g. The silylation less affect the Pt⁰ species because of absence of OH groups. It is suggested that surface hydrophobicization of AlOOH support will bring about an enhancement of desorption of produced benzene, and thus, dehydrogenation on Pt⁰ exposed on the surface does not disturb with efficient desorption of the produced hydrogen and benzene. From these results, the activity of Pt⁰ species on γ -Al₂O₃ (with a high specific surface area) support instead of AlOOH (containing abundant hydroxyl groups) one was studied as follows.

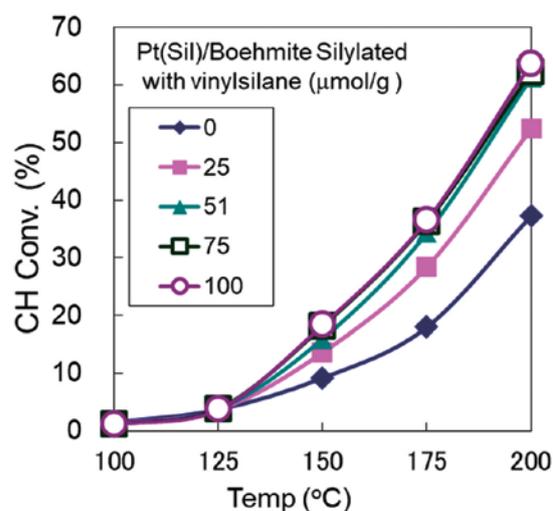


Fig. 3 CH dehydrogenation over Pt(Sil)/ AlOOH catalysts modified using various amount (0-100 mmol/g) of vinylsilane.

3-2. Pt/ γ -Alumina Catalysts

To form active Pt⁰ species for dehydrogenation on the support, inhibition of Pt⁰ aggregation cannot be avoided. On α -Al₂O₃ with both low surface area and surface OH group, less interaction between Pt and the support affects the aggregation easily to form large Pt particles. By reductive photo-deposition of platinum, Pt catalyst supported on optimal alumina with a low aggregation degree can be obtained with a large surface area and appropriate hydroxyl groups⁷⁾. On this background, Pt(Cl) supported on γ -Al₂O₃ (2-3 nm of particle size, and *ca.* 200 m²/g of specific surface area) was employed to evaluate the CH hydrogenation activity. To form well-dispersed Pt⁰ nanoparticles using the Pt(Cl) precursor,⁸⁾ UV irradiation using mercury lamp was introduced for reductive photodeposition. Fig. 4 shows the CH dehydrogenation reactivity over a Pt(Cl)/ γ -Al₂O₃ catalysts prepared by reductive photo-deposition (without thermal pretreatment with H₂-Ar prior to CH dehydrogenation). The Pt(Cl)/ γ -Al₂O₃ after UV irradiation for 1 hour shows the highest reactivity apparently, indicating the formation of optimum Pt⁰ species. However, color of the catalyst irradiated for 1 hour is almost white with light gray, and thus, Pt sites maybe reduced partly and Pt⁰-Pt²⁺ mixture exists on the support. The

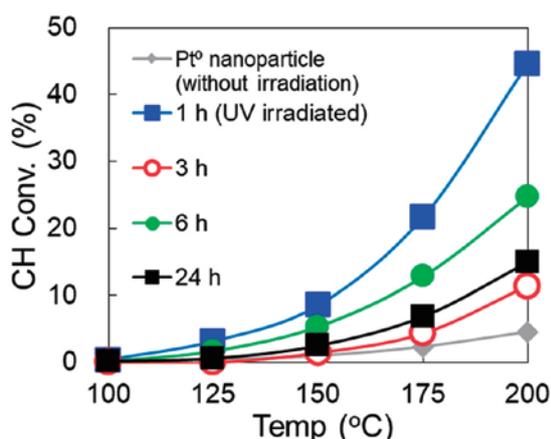


Fig. 4 CH dehydrogenation over Pt(Cl)/ γ -Al₂O₃ catalysts prepared by photodeposition with several times (1-24 hours).

longer the irradiation time, the deeper the gray color of the sample. If oxidized Pt state (Pt²⁺) remain on the support, the species should be reduced to Pt⁰ during the CH dehydrogenation because produced H₂ will consume the reductive treatment of Pt site thermally. Since it is not desirable, sufficient photoreduction needs to form metallic Pt species with less aggregation. For reference, γ -Al₂O₃-supported Pt⁰ nanoparticle (3-4 nm of particle size mainly) was employed to evaluate the reactivity without any reductive pretreatment. As shown in Fig. 4, the reactivity is lower than that of Pt(Cl)/ γ -Al₂O₃ after UV irradiation. It indicates the low activity on the Pt⁰ nanoparticle for CH dehydrogenation.

In Fig. 4, discontinuity was observed between the UV irradiation time and CH dehydrogenation reactivity, and a relatively high activity was shown with an irradiation time of 6 hours. Assuming that most of the Pt⁴⁺ (in Pt(Cl) precursor) species were reduced to Pt⁰ by UV irradiation for 6 hours, the catalytic stability of the active Pt⁰ species can be evaluated by investigating the steady-state activity of this catalyst. If the activity is not constant and unstable observed at the steady-state reaction, the active Pt species is in a thermally unstable state due to remaining partially oxidized species or aggregation of platinum metal further progressing during the reaction.

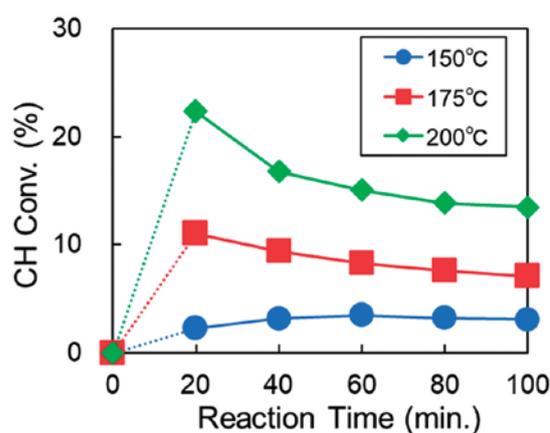


Fig. 5 Steady state CH dehydrogenation reactivity over Pt(Cl)/ γ -Al₂O₃ catalysts after UV irradiation for 6 hours at several reaction temperature (150-200 °C).

Fig. 5 shows the steady state CH dehydrogenation reactivity over Pt(Cl)/ γ -Al₂O₃ catalysts after UV irradiation for 6 hours at 150, 175, and 200 °C for 100 minutes. At 150 °C, the reactivity is almost stable. In contrast, gradual deactivation is clearly observed in the reaction at 175 and 200 °C. This result implies that aggregation of platinum proceeds during the reaction. If there were residual platinum oxidized species, the steady-state activity would increase as the Pt⁰ species increased. Whereas if the Pt⁰ species aggregated, the activity would decrease sequentially. Even at 200 °C, thermal aggregation of Pt nanoparticles proceeds slowly as reported previously⁹. It is summarized that appropriate Pt⁰ species can be prepared on γ -Al₂O₃ support, however the species will be unstable thermally.

Fig. 6 shows the product ratio of hydrogen vs. benzene on the steady-state reaction as presented in Fig. 5. If the CH dehydrogenation (C₆H₁₂ → C₆H₆ + 3 H₂) activity were to proceed steadily, the ratio should be 3. However, a ratio of about 0.9 was observed for reactions at 175-200 °C, and an even smaller ratio at 150 °C was observed. It is presumed that the generated hydrogen is consumed for reduction of the catalyst or sorbed to Pt⁰ during the aggregation. Since the Pt(Cl)/ γ -Al₂O₃ catalysts using the photo-deposition were not pretreated for thermal reduction with H₂ (in case

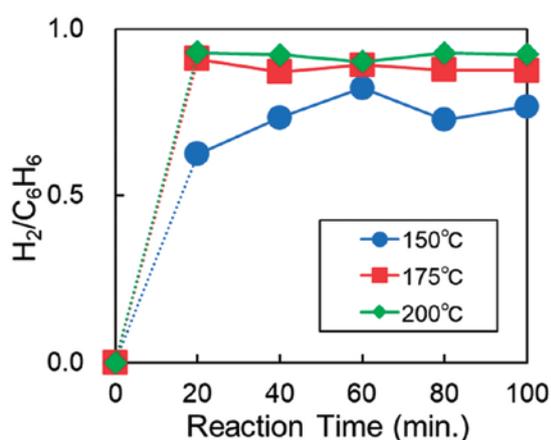


Fig. 6 Ratio of hydrogen vs. benzene on the steady state CH dehydrogenation reactivity over Pt(Cl)/ α -Al₂O₃ (presented in Fig. 5).

of Pt(Sil)/boehmite), it was assumed that even if ideal Pt fine particles were formed, it would be thermally unstable, which was reflected in the activity.

Based on these results, we are now immobilizing thermally stable and highly dispersed active Pt species on alumina, aiming at high and durable activity at low temperature below 200 °C.

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