[Regular Paper]

Dehydrogenation of Methylcyclohexane over Zinc-containing Platinum/Alumina Catalysts

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(Received June 4, 2018)

The catalytic performance of Pt supported on Al_2O_3 , TiO_2 , SiO_2 and activated carbon (AC) was investigated for the dehydrogenation of methylcyclohexane (MCH). The additive effects of Ce, Ga, Mn, Sn, and Zn on the Pt catalysts were also studied. Pt was highly dispersed on Al_2O_3 as an effective support, and was active for the dehydrogenation reaction. Sequential impregnation of Zn and Pt into Al_2O_3 in this order resulted in greatly increased MCH dehydrogenation activity and decreased methane selectivity, which were dependent on the amount of the loaded Zn. FT-IR of adsorbed CO, TEM, and XRD measurements revealed that dispersion of Pt on Al_2O_3 was little changed by loading Zn, and electron donation from Zn to Pt occurred. Therefore, the high dispersion and electron-donating ability of Pt in Zn-Pt/ Al_2O_3 are responsible for the excellent catalytic performance. In contrast, addition of Zn to AC-supported Pt catalyst reduced the catalytic activity probably due to the formation of aggregated PtZn alloy particles on the support.

Keywords

Dehydrogenation, Methylcyclohexane, Platinum catalyst, Zinc addition

1. Introduction

Hydrogen has high potential for use as a clean next-generation fuel for more sustainable development of society. In particular, efficient and safe storage and transportation of hydrogen may be achieved using a liquid organic hydride method based on cycloalkanes as the hydrogen carrier^{1)–5)}. Methylcyclohexane (MCH) is a potential candidate that can be obtained by hydrogenation of toluene (TOL) at a H_2 -producing facility. The resultant MCH and TOL are easy to store and transport in the liquid state under normal temperature and pressure using existing fuel infrastructure. After transportation, MCH will be treated for dehydrogenation at fueling stations to yield hydrogen and TOL. The construction of such hydrogen stations is currently in progress^{5),6)}.

Both hydrogenation of TOL and dehydrogenation of MCH proceed catalytically. Dehydrogenation of MCH is highly endothermic (**Scheme 1**), so the reaction is generally operated at high temperatures and side reactions are likely to occur. Therefore, development of a catalyst that is highly active and selective for the dehydrogenation of MCH is essential for practical

applications of H_2 station systems using organic hydrides.

Numerous efforts have been devoted to the development of dehydrogenation catalysts for organic hydrides, especially active metals^{7)–19)} that act as catalysts and promoters, as well as suitable supports^{7)–9),15)–17),20)–23)}. Investigations have assessed Pt, Rh, Re, Pd, Ir, W, Mn, Mo, Ni, Sn, etc., and supports including metal oxides, silica, carbon and so on. Consequently, mono- and bi-metallic Pt catalysts are well known to be effective. However, optimization of the catalysts by combination of metals and supports is needed.

The present study examined the behavior of various supported Pt catalysts for the dehydrogenation of MCH and modification of Pt catalysts by the addition of second metal components. In addition, the relationship between catalytic performance and physicochemical properties of Pt catalysts was evaluated.

2. Experimental**2.1. Preparation of Catalyst**

The supported Pt catalysts were prepared by impregnating Al_2O_3 (Nippon Aerosil Co., Ltd., Alu C), TiO_2

DOI: doi.org/10.1627/jpi.61.350

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Scheme 1 Dehydrogenation of Methylcyclohexane

(Nippon Aerosil Co., Ltd., P25), SiO₂ (Fuji Silysia Chemical Ltd., Q-10) and activated carbon (AC: Mitsubishi Chemical Corp., coconut charcoal, Diasorb-G) into an aqueous solution of H₂PtCl₆·6H₂O (Kanto Chemical Co., Inc.). The Pt loading was 1 wt%. Then, the catalyst precursors were dried at 110 °C for 24 h, followed by heat treatment at 450 °C for 3 h in a N₂ stream (200 mL/min) to decompose the Pt salt. Next, the samples were pressed into disks, crushed and sieved to 30-42 mesh granules, then calcined at 500 °C for 4 h in air. The prepared Pt catalysts are labeled as Pt(1)/support.

Addition of the second metals (M) was also carried out by a similar sequential impregnation procedure. The used metal precursors were MnCl₂·4H₂O, SnCl₂·2H₂O, Ce(NO₃)₂·6H₂O and Zn(NO₃)₂·6H₂O, supplied by Kanto Chemical Co., Inc., as well as Ga(NO₃)₂·9H₂O supplied by Sigma-Aldrich Co. The catalyst containing M(x wt% loading) and Pt sequentially impregnated into Al₂O₃ in this order is represented as M(x)-Pt(1)/Al₂O₃. In addition, Pt(1)-M(x)/Al₂O₃ denotes the catalyst in which Pt was first impregnated, then M was added. Furthermore, the catalyst prepared by co-impregnation is named as Pt(1)M(x)/Al₂O₃.

2. 2. Dehydrogenation of Methylcyclohexane

Dehydrogenation of MCH (Sigma-Aldrich Co., >99.9 %) was carried out using a fixed bed flow reactor under 0.1 MPa. The required amount of catalysts was charged into the reactor and reduced using H₂ at 350 °C for 1 h before reaction. The carrier gas (N₂) was passed at a rate of 32.8 mL/min. The MCH flow rate was 0.043 mL/min, and reaction temperature was 270-350 °C. The liquid products were collected by an ethanol trap at -50 °C and analyzed using a Shimadzu GC-2025 chromatograph equipped with a flame ionization detector. The gas products collected by a gas bag were analyzed using a Shimadzu GC-8A chromatograph equipped with a thermal conductivity detector. The MCH conversion, hydrocarbon selectivity and CH₄ concentration in H₂ were calculated using the equations as shown below.

$$\text{MCH conversion [\%]} = \frac{\text{Reacted MCH [mol]}}{\text{Fed MCH [mol]}} \times 100$$

$$\begin{aligned} \text{Hydrocarbon selectivity [\%]} \\ = \frac{\text{Produced hydrocarbon [mol]}}{\text{Total produced hydrocarbons [mol]}} \times 100 \end{aligned}$$

$$\text{CH}_4 \in \text{H}_2 \text{ [ppm]} = \frac{\text{CH}_4 \text{ [mol]}}{\text{CH}_4 \text{ [mol]} + \text{H}_2 \text{ [mol]}} \times 10^6$$

2. 3. Characterization of Catalysts

X-ray diffraction (XRD) patterns of the catalysts were measured using a Rigaku Ultima IV X-ray diffractometer with CuK α radiation source operated at 40 kV and 40 mA. XRD analysis was carried out at 30 °C in a He atmosphere after *in-situ* H₂ reduction of the cata-

lyst at 350 °C for 1 h. The crystallite size of Pt was calculated from Scherrer's equation using the full width at half maximum of the peak at 39.7°.

Transmission electron microscope (TEM) images were taken using a JEOL JEM-2100F with acceleration voltage of 200 kV. The particle size distribution of Pt was determined from the measurements of at least 1000 particles in the TEM images.

Adsorbed CO was analyzed using a JASCO FT/IR 4200. A disk of the catalyst with a diameter of 20 mm was loaded into an *in-situ* cell. Then, the catalyst was reduced using H₂ at 350 °C for 1 h, followed by cooling to room temperature in a He stream. CO chemisorption was carried out by maintaining the Pt catalyst in a stream of 1 vol% CO/He mixed gas at room temperature for 5 min. Finally, the Fourier transform infrared (FT-IR) adsorption spectrum was measured in a He stream from room temperature to 250 °C at intervals of approximately 20 °C.

3. Results and Discussion

3. 1. Dehydrogenation Properties of Various Pt Catalysts

Figure 1 shows MCH conversion with time on stream (TOS) over various supported Pt catalysts. Pt(1)/Al₂O₃ and Pt(1)/AC catalysts exhibited comparable high conversion for the dehydrogenation of MCH. In comparison, Pt(1)/TiO₂ showed a moderate dehydrogenation activity, whereas Pt(1)/SiO₂ was inactive. Therefore, the catalytic activity of Pt depended greatly on the supports used.

Table 1 summarizes the catalytic activity and product selectivity for the dehydrogenation of MCH, as well as the Pt particle size measured by TEM and XRD. Selectivity for TOL was as high as 99.4 % or more, except for Pt/SiO₂. Methylcyclohexenes, benzene and

Fig. 1 Dehydrogenation of MCH over Supported Pt Catalysts

Table 1 Properties of Supported Pt Catalysts for the Dehydrogenation of MCH and Pt Particle Size

Catalyst	Reaction temp. [°C]	W/F [g h/mol]	Conversion [mol%]	Hydrocarbon selectivity [mol%]				Methane in H ₂ [ppm]	Pt size [nm]	
				Toluene	Methylcyclohexenes	Benzene	Methane		TEM	XRD
Pt(1)/AC	300	2.47	69.6	99.92	0.06	0.01	n. d. ^{a)}	n. d. ^{a)}	3.5	4.1
	350	0.99	53.5	99.47	0.32	0.09	0.10	294		
Pt(1)/TiO ₂	300	2.47	47.5	99.84	0.13	0.02	n. d. ^{a)}	n. d. ^{a)}	1.4	n. d. ^{a)}
Pt(1)/SiO ₂	300	2.47	0.1	27.86	72.14	n. d. ^{a)}	n. d. ^{a)}	n. d. ^{a)}	14.6	21.1
Pt(1)/Al ₂ O ₃	270	2.47	43.3	99.89	0.08	0.01	n. d. ^{a)}	n. d. ^{a)}	1.0	n. d. ^{a)}
	300	2.47	74.0	99.91	0.03	0.03	0.02	63		
	350	2.47	87.8	99.72	0.05	0.11	0.11	338		
	350	1.48	80.8	99.71	0.07	0.11	0.10	292		
	350	0.99	53.6	99.43	0.27	0.16	0.15	425		

a) n. d.: not detected.

Fig. 2 Dehydrogenation of MCH over Pt(1)/Al₂O₃ Catalyst at Different Reaction Temperatures (a) and Contact Times (*W/F*) (b)

methane accounted for most of the by-products. Methylcyclohexenes, which were mainly formed over Pt(1)/SiO₂, were the intermediate products and were

further dehydrogenated to yield TOL as conversion increased. Benzene and methane were obtained in comparable yields, suggesting that demethylation of TOL and/or MCH occurred. Furthermore, Pt was highly dispersed on Al₂O₃, AC and TiO₂ and so was active for MCH dehydrogenation. On the other hand, Pt was present as large particles on SiO₂, greatly decreasing the catalytic activity of Pt/SiO₂.

Pt/Al₂O₃ catalyst showed high dehydrogenation activity, so was further studied in detail. **Figures 2(a) and 2(b)** show the time courses of MCH dehydrogenation over Pt(1)/Al₂O₃ at different reaction temperatures and contact times (*W/F*), respectively. The conversion of MCH increased with higher reaction temperature and longer contact time. However, the selectivities for benzene and CH₄ also increased at higher temperatures resulting from more demethylation (**Table 1**). Since the formation of by-products tended to lead to catalyst deactivation by coking²⁴⁾, a lower reaction temperature of 270 °C was optimal to obtain stable catalytic activity. The activity of the deactivated catalyst was restored by air oxidation.

3. 2. Dehydrogenation Properties of Pt Catalysts Containing Second Metals

Pt/Al₂O₃ was modified by adding second metal components to improve its catalytic performance. To clarify the modification effect, MCH dehydrogenation was carried out at 350 °C and *W/F* of 0.99 g h/mol, which corresponded to adverse reaction conditions to achieve high selectivity and stability. **Figure 3** shows the MCH conversion and CH₄ concentration in H₂ formed over various Pt(1)-M(0.3)/Al₂O₃ catalysts at TOS of 30-60 min. Addition of second metal components such as Ce, Ga, Zn, and Sn enhanced the MCH dehydrogenation activity of Pt(1)/Al₂O₃. Furthermore, the CH₄ concentration in H₂ obtained over the Pt catalyst was reduced by adding Mn, Ga, Zn, and Sn. The modification effect of Zn was particularly pronounced. Therefore, three Zn-containing Pt/Al₂O₃ catalysts were prepared by different impregnation procedures and tested. **Figure 3** shows sequential impregnation of Zn and Pt in this order was superior to the reverse order of im-

Fig. 3 Effect of Additives on the Dehydrogenation Performance of Pt(1)/Al₂O₃ Catalyst (second metal loading: 0.3 wt%)

Fig. 4 Dehydrogenation of MCH over Zn(x)-Pt(1)/Al₂O₃ Catalysts

pregnation and co-impregnation. In particular, Pt/ZnO showed no catalytic activity. **Figure 4** shows the effect of loading amounts of Zn on the catalytic activity and selectivity of Zn-Pt/Al₂O₃ for the dehydrogenation of MCH. Higher amounts of loaded Zn increased the MCH conversion to a maximum at 0.5 wt% loading (Zn/Pt molar ratio of 1.5). Further loading of Zn decreased the conversion. On the other hand, CH₄ selectivity was monotonously and greatly decreased by higher amounts of Zn loading. The CH₄ concentration (48 ppm) obtained over Zn(0.5)-Pt(1)/Al₂O₃ was one order of magnitude lower than that (425 ppm) over Zn-free Pt/Al₂O₃ catalyst. Furthermore, **Fig. 5** shows addition of Zn improved the stability of Pt/Al₂O₃ catalyst. In addition, the effect of Zn loading on the Zn-Pt/AC catalyst is shown. As mentioned already, the activity of Pt/AC for MCH dehydrogenation was almost the same as that of Pt/Al₂O₃. However, the catalytic activity of Zn-Pt/AC was much lower than that of Zn-free

Fig. 5 Dehydrogenation of MCH over Al₂O₃- and AC-supported Pt Catalysts with Zn Loading

(a) Al₂O₃, (b) Pt(1)/Al₂O₃, (c) Zn(0.5)-Pt(1)/Al₂O₃, (d) Zn(1.5)-Pt(1)/Al₂O₃, (e) AC, (f) Pt(1)/AC, (g) Zn(0.5)-Pt(1)/AC.

Fig. 6 XRD Patterns of Supported Al₂O₃- and AC-supported Pt Catalysts with Different Zn Loadings

Pt/AC catalyst. Therefore, no additive effect of Zn was observed on AC-supported Pt catalysts.

3.3. Characterizations of Catalysts

Differences between Al₂O₃- and AC-supported catalysts were investigated using XRD, TEM and FT-IR. Metal particle size and electronic state of the Pt catalysts can be considered as factors determining the effects of added Zn. First, the size effect was examined. **Figure 6** shows the XRD patterns of Al₂O₃- and AC-supported Pt catalysts with and without Zn. The peak at 39.7° was assigned to Pt(111) in the XRD patterns of Pt(1)/AC. After Zn loading, this peak disappeared and a new peak appeared at 41.0°, implying that PtZn alloy²⁵⁾ was formed in Zn(0.5)-Pt(1)/AC. Moreover, the Pt crystallite size of Zn(0.5)-Pt(1)/AC was determined as 14.6 nm, which is remarkably larger than

Fig. 7 Particle Size Distributions of Pt(1)/Al₂O₃ and Zn(0.3)-Pt(1)/Al₂O₃ Catalysts Determined by TEM

4.1 nm of Pt(1)/AC. These results suggest that the low activity of Zn(0.5)-Pt(1)/AC catalyst was caused by the formation of aggregated PtZn alloy species. In contrast, the XRD patterns of Pt/Al₂O₃ and Zn-Pt/Al₂O₃ were the same as that of the pure Al₂O₃ support. No peak attributable to Pt was observed regardless of the presence or the absence of Zn. This means that Pt was present in the form of fine particles on Al₂O₃, even after Zn loading.

No observation of any great effect of Zn on Pt dispersion on Al₂O₃ was supported further by the TEM analysis. **Figure 7** shows the Pt particle size distributions for Pt/Al₂O₃ and Zn(0.3)-Pt/Al₂O₃ determined by TEM. The average Pt particle size was little changed by the addition of Zn, from 0.99 nm for Pt/Al₂O₃ to 1.04 nm for Zn(0.3)-Pt/Al₂O₃. Therefore, the added Zn was presumably present as ZnO or ZnAl₂O₄²⁶⁾. However, formation of Pt-Zn alloy species on Al₂O₃ support could not be excluded, especially in the catalysts containing excess amounts of Zn. Two types of Pt-Zn alloys, Pt₃Zn and PtZn, have been reported^{25),27)}, and the

Fig. 8 FT-IR Spectra of CO Adsorbed on Pt(1)/Al₂O₃ Catalyst at Room Temperature, Followed by Heating to Elevated Temperatures

former was active for dehydrogenation whereas the latter was inactive. Therefore, PtZn species might be likely to form in catalyst with a high Zn/Pt ratio.

Next, the electronic state of the catalyst surface was analyzed by CO chemisorption. **Figure 8** shows the FT-IR spectra of CO adsorbed on Pt(1)/Al₂O₃ at room temperature, followed by heating to elevated temperatures. Some peaks were observed for the CO stretching vibration in the spectrum measured at room temperature. The broad band around 1830 cm⁻¹ is attributed to bridged Pt⁰-CO-Pt⁰ species²⁸⁾, and peaks at 2055 cm⁻¹ and 2080 cm⁻¹ are assigned to linearly adsorbed CO on Pt⁰ and Pt²⁺, respectively. A peak at 2121 cm⁻¹ represents physically adsorbed CO. Metallic Pt can catalyze dehydrogenation, so the peak at 2055 cm⁻¹ for Pt⁰-CO was used to evaluate the catalytic activity. The peak for Pt⁰-CO shifted to low wavenumbers and its absorbance decreased at higher temperatures. The frequency of the CO stretching vibration was affected by interactions between the adsorbed CO species because many CO molecules are adsorbed at room temperature. However, such interactions decreased at elevated temperatures. Therefore, an absorption band that reflected the true electronic interaction between Pt⁰ and adsorbed CO was observed. The peak for Pt⁰-CO was detectable up to 170 °C, but was not evident at 190 °C. Based on these results, the FT-IR spectrum of adsorbed CO was measured at 170 °C.

Figure 9 shows the FT-IR spectra of CO adsorbed on Pt/Al₂O₃ and Zn-Pt/Al₂O₃ containing 0.5 wt% and 1.5 wt% of Zn. The Pt⁰-CO peak appeared at wavenumber of 2040 cm⁻¹ for Pt(1)/Al₂O₃ but at lower wavenumbers of 2035 cm⁻¹ and 2029 cm⁻¹ for Zn(0.5)-Pt(1)/Al₂O₃ and Zn(1.5)-Pt(1)/Al₂O₃, respectively, indicating that the electron-donating ability of Pt was enhanced by the addition of Zn²⁹⁾. The resultant electron-rich Pt

Fig. 9 FT-IR Spectra of CO Adsorbed on Pt(1)/Al₂O₃ Catalysts with Different Zn Loadings at Room Temperature, Followed by Heating to 170 °C

species on Zn(0.5)/Al₂O₃ seemed to activate the C–H bond of MCH by back donation of electrons from Pt into C–Hσ* anti-bonding orbital and to accelerate MCH dehydrogenation²³. Moreover, the presence of electron-rich Pt species on TiO₂ facilitates the desorption of the TOL formed⁹. A similar function could be expected with Zn–Pt/Al₂O₃ catalyst. Easy desorption of TOL from the Pt catalyst surface improved dehydrogenation selectivity and decreased demethylation selectivity. Such suppression of undesirable demethylation would lead to reduced coking.

The Zn(1.5)–Pt/Al₂O₃ catalyst also exhibited high electron-donating potential in CO adsorption, as well as the Zn(0.5) catalyst. However, no improvement in MCH dehydrogenation activity was observed in the former by the addition of Zn (Fig. 4). Probably the structure and composition of active Pt species differ depending on the amount of Zn added. Further studies are necessary for detailed discussion.

4. Conclusions

Pt catalyst supported on Al₂O₃ showed high activity for the dehydrogenation of MCH. The catalytic performance was improved by adding second metal components such as Zn, Ga, and Sn. Zn was most effective to enhance the dehydrogenation activity and to decrease the selectivity for by-products. Strong additive effects were obtained over Zn(0.5)–Pt(1)/Pt/Al₂O₃ catalyst prepared by sequential impregnation of Zn and Pt in this order. XRD and TEM measurements revealed that Pt was highly dispersed on Al₂O₃ and the dispersion was little changed by the addition of Zn. On the other hand, the electron-donating ability of Pt was enhanced by adding Zn, determined from FT-IR measurements of the chemisorbed CO, which seems to explain why the

catalytic performance was improved. Unlike the Al₂O₃-supported catalysts, addition of Zn to Pt/AC formed aggregated PtZn alloy species, so the Zn–Pt/AC catalyst showed lower activity than Pt/AC.

Acknowledgment

We would like to thank Nippon Aerosil Co., Ltd. for supplying Al₂O₃ and TiO₂, Fuji Silysia Chemical Ltd. for supplying SiO₂, and Mitsubishi Chemical Corp. for active carbon. We are also grateful to Mr. Akira Koikeda, Mr. Makoto Okuda, Mr. Masahiro Nagakane and Mr. Hidekazu Arikawa (Hrein Energy Co., Ltd.) for their helpful discussions.

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要 旨

Zn 添加 Pt/Al₂O₃ 触媒によるメチルシクロヘキサンの脱水素反応

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メチルシクロヘキサン (MCH) 脱水素触媒の高性能化を目的として, Pt 触媒の活性に対する担体 (Al₂O₃, TiO₂, SiO₂ および活性炭 (AC)) の影響と第二金属 (Ce, Ga, Mn, Sn および Zn) の添加効果について検討した。担体として Al₂O₃ を用いると, Pt は高分散担持され高い MCH 脱水素活性を示した。第二金属として添加した Zn の効果は添加量に依存するが, Al₂O₃ に Zn と Pt の順に逐次含浸すると活性が大きく向上し, 水素中メタン濃度が添加前の触媒よりも一桁ほど低くなった。

Zn 添加 Pt/Al₂O₃ 触媒の TEM, XRD および CO 吸着 FT-IR の測定結果より, Zn を添加しても Pt 分散度の変化は小さく, Pt の電子供与性が向上することが明らかとなった。したがって, Zn-Pt/Al₂O₃ が優れた触媒性能を示すのは Pt の高い分散性と電子供与能によるものと推測される。一方, Pt/AC に Zn を添加すると触媒活性は低下した。AC 上の Pt と Zn は凝集した PtZn 合金を形成していることが分かり, これが Pt/AC 系で Zn の添加効果が見られない要因と考えられる。