1. Introduction

Hydrogenation and dehydrogenation reaction of aromatic compounds via homogeneous catalysts have been extensively researched for petrochemical processes and production of high octane fuels. Toluene (C7H8) hydrogenation for methylcyclohexane (MCH, C7H12) synthesis has also been gained much attention as a hydrogen carrier production technology in recent years. In comparison to compressed hydrogen, MCH has higher hydrogen gravimetric- and volumetric-density (6.1 wt% and 47.0 kg-H2 m–3 respectively). Furthermore, MCH has relatively higher transportability, superior storage characteristics and is not carcinogenic. Cyclohexane and decahydronaphthalene have also slightly higher hydrogen density (7.1 wt% and 7.2 wt% respectively) than MCH, however these two carriers have toxicities and carcinogenicity. Hydrogenation technologies for aromatic compounds in petrochemical processes are well established, so the infrastructures to synthesize and transport MCH are extensively developed. Therefore we consider that MCH is one of possible candidates for a hydrogen carrier.

Previous researches clarified that supported platinum-group metal catalyst and their bimetallic catalysts show higher activities against toluene hydrogenation and MCH dehydrogenation. Supported platinum catalysts showed higher activities in the order of Pt/Al2O3 > Pt/TiO2 (anatase-rutile mixture, AR) > Pt/TiO2 (anatase, A) > Pt/TiO2 (rutile, R) above 423 K, whereas Pt/TiO2 (anatase, A) showed remarkably higher activities at 393 K. To estimate the effects of support species, kinetic analysis using rate-based model was conducted. The correlation between adsorption behavior and catalytic activities was investigated using a Langmuir-Hinshelwood model. The kinetic constants for each catalyst were almost same. It was considered that only kinetic constants cannot explain the catalytic activities. Coverage of toluene and MCH were independent of the reaction rates, however the reaction rates increased as hydrogen coverage increased for all catalysts.

Keywords
Hydrogen carrier, Toluene hydrogenation, Methylcyclohexane, Titanium oxide support, Platinum catalyst, Kinetic analysis

DOI: doi.org/10.1627/jpi.62.28

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tuating power input\(^{21}\).

In order to develop novel hydrogenation catalysts for MCH synthesis from toluene and fluctuating hydrogen, systematic investigation are important to analyze effects of support species and their crystal structures on the catalytic activities of Pt. Furthermore, previous works about hydrogenation reaction of aromatic compounds pointed out that competitive adsorption of toluene and hydrogen are essential to understand kinetic behavior of catalysts\(^{9,15,16}\). As some previous works reported\(^{8,9,14}\), the toluene reaction order of toluene hydrogenation reaction indicated almost zero, whereas the hydrogen reaction rate indicates higher value than that of toluene (at ca. 2 to 3). Therefore, we consider that quantitative estimation of adsorption behavior of hydrogen and toluene is necessary to design robust hydrogenation systems for MCH synthesis against fluctuation of hydrogen, because drastic change of hydrogen and toluene partial pressure in a reactor could entail huge chemical potential change of the reactants and the products on the catalyst surface.

In this study, we prepared Pt/\(\gamma\)-Al\(_2\)O\(_3\) and Pt/TiO\(_2\) with different types of TiO\(_2\) structures to discuss the effects of support species and crystal structures on toluene hydrogenation reaction by means of rate-based model analysis.

2. Experimental

2.1. Catalyst Preparation

The supported Pt catalysts were prepared by means of wet-impregnation method with a nominal Pt loading of 1.0 wt\%. The support materials were \(\gamma\)-Al\(_2\)O\(_3\) (99.9 \% of purification, Kojundo Chemical Laboratory Co., Ltd.) and TiO\(_2\) with different types of crystal structures: anatase (95 \% of purification, SSP-M, Sakai Kagaku Co., Ltd.), rutile and anatase–rutile mixture (99.5 \% of purification, P25, Nippon Aerosil Co., Ltd.). The rutile form TiO\(_2\) were obtained by calcining the anatase form TiO\(_2\) at 1173 K for 6 h in an electric heater with air flow. Hexachloroplatinic (IV) acid (\(\text{H}_2\text{PtCl}_6\), 99.9 \% of purification, FUJIFILM Wako Pure Chemical Corp.) was used as a Pt-precursor. \(\text{H}_2\text{PtCl}_6\) was dissolved with deionized water, and the support material was immersed into the Pt-precursor solution. Then the sample was evaporated at 353 K prior to calcination in a quartz tube at 773 K for 1 h under nitrogen atmosphere. The catalysts were reduced in the quartz tube with 100 \% of hydrogen at 773 K for 2 h.

2.2. Catalyst Preparation

Surface area and mean pore diameter of as-prepared catalysts were characterized by means of BET measurements (BELCAT II, MicrotacBEL Corp.\(^{28}\)). Nitrogen at 77 K was used as an adsorption gas. Prior to the measurement, the samples were dried at 573 K for 1 h under 100 \% helium gas flow.

2.3. Catalyst Test

We tested the catalyst prepared in the previous section using a continuous-flow fixed bed reactor at ambient pressure. Figure 1 shows the scheme of the experimental setup. As shown this figure, the catalyst 0.1 g was placed in a half inches SUS 304 tube, and the catalyst bed was supported with quartz wool. We used an electric heater and a K-type thermocouple inserted
into the catalyst bed to control reaction temperatures. Float meters were used to control flow rates of hydrogen and nitrogen gases into the reactor. Toluene or MCH was supplied to the catalyst bed by passing the hydrogen gas flow through a glass bottle containing the substrate. Temperature of the two glass bottles were maintained at 343 K by a thermostatic water bath to maintain the toluene and MCH partial pressures of the provided mixture gases into the bed. Partial pressure of hydrogen, toluene and MCH were 60-91, 9-23, 9-17 kPa respectively.

After the catalyst bed was flushed with 100 mL min^{-1} of nitrogen for 15 min, the catalyst bed was heated to 473 K in flowing hydrogen at a flow rate of 25 mL min^{-1}. Reaction temperature was varied from 398 to 473 K. During the catalyst tests, outlet gases from the bed was analyzed by a gas-chromatograph (Agilent 490 micro-GC, Agilent Technologies Japan Ltd.) to estimate conversion of toluene.

3. Results and Discussion

3.1. Catalytic Activities

Figure 2 shows the catalytic activities of Pt/Al2O3 and Pt/TiO2 with different crystal structures: anatase, rutile and their mixtures (described as Pt/TiO2(A), Pt/TiO2(R) and Pt/TiO2(AR) respectively). Toluene and hydrogen partial pressure were 23 kPa and 77 kPa respectively. Toluene hydrogenation reaction rate was calculated by the Eq. (1):

\[ r = \frac{F_{\text{toluene,0}} - (F_{\text{MCH}} - F_{\text{MCH,0}})}{V_{\text{cat}}} \]  

where \( F_{\text{MCH,0}} \) and \( F_{\text{toluene,0}} \) are the flow rates [mol s^{-1}] of MCH and toluene in the inlet gases respectively. \( F_{\text{MCH}} \) is the flow rate of MCH in the outlet gases and \( V_{\text{cat}} \) is the catalyst bed volume [m^3]. Flow rate of toluene or MCH was determined by outlet gas concentration analyzed by a gas chromatograph. From this figure, we found that, above 423 K, catalytic activities were higher in the order of Pt/Al2O3 > Pt/TiO2(A) > Pt/TiO2(AR) = Pt/TiO2(R). On the other hand, Pt/TiO2(A) shows remarkably higher activity than other catalysts at 393 K.

In order to investigate correlation between catalytic activities and surface morphology of the catalysts, BET surface area and mean pore diameters of each catalyst were summarized in Table 1. Form this table it was clear that surface area of the each catalyst was larger in the order of Pt/Al2O3 > Pt/TiO2(AR) = Pt/TiO2(A) > Pt/TiO2(R), and mean pore diameters were smaller in the order of Pt/Al2O3 > Pt/TiO2(AR) = Pt/TiO2(A) = Pt/TiO2(R). We considered that Pt/Al2O3 showed higher activities above 423 K because of larger surface area, however surface morphology on Pt/TiO2 catalysts can not explain the order of catalytic activities.

Shawn et al.\(^6\)-\(^8\) carried out catalysts tests of toluene hydrogenation over Pt-loaded catalysts and reported turnover frequency was higher in the order of Pt/Al2O3 > Pt/SiO2 > Pt/TiO2(AR) > Pt/Al2O3 = Pt/SiO2 at 333-373 K and ca. 900 kPa using a micro reactor. Results in this study did not show agreement with their works, however we considered that catalyst preparation procedure and reaction condition especially pressure could change the order of activities. We will conduct optimization of the catalysts preparation procedure against toluene hydrogenation reaction at ambient pressure as our future work.

3.2. Kinetic Analysis

Obtained kinetics data from catalyst tests were analyzed using the Langmuir-Hinselwood model. Toluene hydrogenation reaction rate, \( r \) [mol s^{-1} m^{-3}] was described by the Eq. (2):

\[ r = k \theta_{\text{toluene}} \theta_{\text{H}}^{0} - k' \theta_{\text{MCH}} \]  

where \( k \) [mol s^{-1} m^{-3}] is the kinetic constant of the forward reaction, \( \theta_{i} \) [-] is the coverage on a catalyst surface of the component \( i \) (\( i = \) chemisorbed hydrogen atom, toluene or MCH) and \( k' \) [mol s^{-1} m^{-3}] is a kinetic constant of a reverse reaction. We note that the reverse reaction means MCH dehydrogenation reaction, and then we assumed that \( k' \) can be calculated from \( k \) and a thermodynamic equilibrium constant for toluene hydro-

\[ \text{Table 1 BET Surface Area and Mean Pore Diameter of Pt/Al2O3 and Pt/TiO2 at 398-473 K} \]

| Catalysts          | BET surface area [m^2 g^{-1}] | Mean pore diameter [nm] |
|--------------------|-------------------------------|-------------------------|
| Pt/Al2O3           | 207                           | 5                       |
| Pt/TiO2(A)         | 73                            | 20                      |
| Pt/TiO2(R)         | 49                            | 22                      |
| Pt/TiO2(AR)        | 75                            | 19                      |

J. Jpn. Petrol. Inst., Vol. 62, No. 1, 2019
generation reaction, $K_{eq}$:

$$k' = k K_{eq}$$  (3)

$K_{eq}$ was determined by the van’t Hoff equation, and thermodynamic constants for hydrogen, toluene and MCH were obtained from Ref. 29. Coverage of component $j$ ($j =$ toluene or MCH) was given by the Eq. (4):

$$\theta_j = K_j P_j / \left[1 + \left(K_H P_H\right)^{0.5} + \sum_j K_j P_j\right]$$  (4)

where $K_j$ [kPa$^{-1}$] and $P_j$ [kPa] are the adsorption equilibrium constant and partial pressure of component $j$ respectively. Hydrogen coverage on the catalyst surface can be described by the following equation, because of the dissociative adsorption of hydrogen molecules:

$$\theta_H = \left(K_H P_H\right)^{0.5} / \left[1 + \left(K_H P_H\right)^{0.5} + \sum_j K_j P_j\right]$$  (5)

Using Eq. (2), we conducted parameter-fitting by generalized reduced gradient method to determine $k$ and $K_j$ from the observed reaction rates. The kinetic parameters were determined as to minimize normalized error as defined by the Eq. (6):

$$\varepsilon = \sum_i \left[\left(r_{obs.} - r_{est.}\right)^{0.5} / r_{obs.}\right]$$  (6)

where $r_{obs.}$ and $r_{est.}$ were observed and estimated reaction rate respectively.

**Figure 3** shows the correlation between observed and evaluated reaction rates for each catalysts. From this figure, we considered that good linearity was obtained because $R^2$ values are over 0.9 for the catalysts. **Figures 4 and 5** show temperature dependencies of $k$ and $K_j$. The former is an Arrhenius plot, and then we calculated apparent activation energy, $E_a$ for each catalysts from gradients of a $k$ vs. $T^{-1}$ plot (see **Table 2**). $E_a$ varied from 29.2 to 48.1 kJ mol$^{-1}$. Though $K_{toluene}$ and $K_{MCH}$ for each catalyst are almost same, $K_{H2}$ for Pt/TiO$_2$(A) was indicated higher value than other catalysts.

Though **Fig. 3** shows good linearity, we note that the kinetics model described by Eq. (2) does not indicates true chemical reaction behavior on the Pt surface. Some preceding researches have adopted various kinetic models assuming rate determining steps (RDS)$^{9,14}$, and RDS could be determined by method such as parameter fitting, spectroscopic analysis of catalyst surface and first principle calculation. For instance, Thybaut et al.$^9$ reported 40-50 kJ mol$^{-1}$ of $E_a$ on a Pt/ZSM-22 catalyst, whereas our data showed 29.2-48.1 kJ mol$^{-1}$ (see **Fig. 4 and Table 2**). Therefore, we considered that...
our data showed good agreement with previous work. However, we note that reaction rate and coverage of hydrogen, toluene and MCH were discussed as apparent values in this study.

Kinetic constants, $k$ for each catalyst were almost the same as shown in Fig. 4, however $k$ for Pt/Al$_2$O$_3$ and Pt/TiO$_2$(AR) at 398 K were slightly lower than for other catalysts. Therefore, from Figs. 2 and 4, it is clear that only the order of kinetic constants cannot explain the catalytic activities. As described in Eq. (2), it is clear that not only kinetic constant but also the coverage of the reactants and product are essential for the hydrogenation reaction. Therefore, we considered that competitive adsorption of reactants are as well as essential for catalytic activities as pointed out in previous works$^{6-9,14}$.

3.3. Effects of Toluene and MCH Coverage on Catalytic Activities

In the previous section, we found that the order of kinetic constants cannot explain the order of catalytic activities. Therefore, we estimated the correlation between coverage of the reactants and reaction rates. Correlation between toluene coverage, $\theta_{\text{toluene}}$, and reaction rates for each catalysts are shown in Fig. 6. The horizontal axis in this figure shows $\theta_{\text{toluene}}$ calculated by Eq. (4) and adsorption equilibrium constants of toluene, hydrogen and MCH determined from Fig. 5, and the vertical axis means observed reaction rates. $R^2$ values for all data in Fig. 6 were also evaluated. Table 3 summarizes the $R^2$ of reaction rate vs. toluene coverage plots for each catalyst. Table 3 shows that reaction rates had weak correlation with toluene coverage. From Fig. 6, it is clear that $\theta_{\text{toluene}}$ on each catalyst surface is less dominant for reaction rates, as each $R^2$ value is below 0.15 in this study. Considering the correlation between $\theta_{\text{toluene}}$ and the reaction rates, we considered that reaction rates were almost independent of the chemical potential of toluene on catalysts surface for all

| Catalysts | Activation energy [kJ mol$^{-1}$] |
|-----------|----------------------------------|
| Pt/Al$_2$O$_3$ | 43.3 |
| Pt/TiO$_2$(A) | 34.5 |
| Pt/TiO$_2$(R) | 29.2 |
| Pt/TiO$_2$(AR) | 48.1 |
Previous works\(^8\),\(^9\),\(^{14}\) also conducted kinetic analysis using a power law model as shown in the Eq. (7):  
\[
r = k P_{H2}^m P_{toluene}^n
\]  
They reported that toluene reaction order of almost zero or drastically lower than that of hydrogen (e.g. \(\sim 0.2\) to \(0.3\) in Ref. 9)). This means that chemical potential of toluene in gas phase is independent with the catalytic activities, and also adsorption rate of toluene would be faster than that of hydrogen on Pt-loaded catalyst. Consequently, the mechanisms of the low dependency of \(\theta_{toluene}\) on reaction rates is derived from strong interaction between the metal surface and adsorbed toluene molecule because \(K_{toluene} \geq K_{hydrogen}\) for each catalyst.

Reaction rates correlated with MCH coverage on the catalysts are shown in Fig. 7, and the \(R^2\) values in this figure are summarized in Table 3. From this figure it

| Catalysts   | Temperature [K] | \(r\) vs. \(\theta_H\) | \(r\) vs. \(\theta_{toluene}\) | \(r\) vs. \(\theta_{MCH}\) |
|-------------|-----------------|------------------------|-----------------------------|--------------------------|
| Pt/Al\(_2\)O\(_3\) | 398             | 0.771                  | 0.004                       | 0.132                    |
|             | 423             | 0.783                  | 0.008                       | 0.000                    |
|             | 448             | 0.613                  | 0.003                       | 0.039                    |
|             | 473             | 0.633                  | 0.005                       | 0.054                    |
| Pt/Ti\(_2\)O\(_2\)(A) | 398             | 0.732                  | 0.002                       | 0.082                    |
|             | 423             | 0.854                  | 0.045                       | 0.066                    |
|             | 448             | 0.819                  | 0.007                       | 0.024                    |
|             | 473             | 0.655                  | 0.004                       | 0.155                    |
| Pt/Ti\(_2\)O\(_2\)(R) | 398             | 0.828                  | 0.001                       | 0.002                    |
|             | 423             | 0.844                  | 0.015                       | 0.064                    |
|             | 448             | 0.780                  | 0.005                       | 0.003                    |
|             | 473             | 0.689                  | 0.006                       | 0.016                    |
| Pt/Ti\(_2\)O\(_2\)(AR) | 398             | 0.787                  | 0.154                       | 0.032                    |
|             | 423             | 0.927                  | 0.010                       | 0.081                    |
|             | 448             | 0.960                  | 0.020                       | 0.071                    |
|             | 473             | 0.836                  | 0.146                       | 0.024                    |
was found that coverage of the product did not affect catalytic activities in the MCH partial pressure ranged from 9 to 17 kPa. Therefore, we considered that the reverse reaction rates were not dominant in the relatively lower temperature as ranged from 398 to 473 K because MCH coverage for each catalyst were lower than toluene and hydrogen. However, in a case of a practical reactor which almost perfectly converts toluene into MCH, catalysts in a later position of the reactor could be exposed to higher MCH partial pressure. Moreover temperatures of the hydrogenation reactor could increase through reaction heat because the toluene hydrogenation reaction is an exothermic reaction. Therefore, we will estimate the effects of MCH coverage on reverse reaction rates and competitive adsorption behavior as our future work.

3.4. Effects of Hydrogen Coverage on Catalytic Activities

Dependences of catalytic activities on hydrogen coverage were also analyzed as shown in Fig. 6. In contrast to Fig. 6, this result indicates that the hydrogenation reaction rates for each catalysts increased with higher $\theta_{\text{hydrogen}}$ because $R^2$ for each catalyst was obviously higher than that in Fig. 6 and Table 3. From this figure and table, it is also found that hydrogen coverage at 398 K was higher in the order of Pt/TiO$_2$(A) > Pt/Al$_2$O$_3$ > Pt/TiO$_2$(R) = Pt/TiO$_2$(AR). This order is as same as the order of catalytic activities at 398 K (see Fig. 2). Therefore we considered that $\theta_{\text{hydrogen}}$ is the most dominant factor for the hydrogenation reaction. In the previous works$^{[9]}$, the reaction order of hydrogen was 0.6-1.8, and that is higher than that of toluene, in which Eq. (7) was used to determine the order. Therefore, we considered that our data about correlations between reaction rates and coverage of reactants showed good agreement with the preceding research.

In this study we estimated the effects of reactants coverage on the catalytic activities as shown in Figs. 6 and 8. We considered that hydrogen coverage increased the reaction rate, and decrease in toluene coverage on Pt/Al$_2$O$_3$ and Pt/TiO$_2$(A) could lead increase in hydrogen coverage due to competitive adsorption of the reactants. However, we cannot explain the detailed effects of the competitive adsorption of reactants on reaction rates here. Applying kinetics data as shown in Figs. 4 and 5, we intend to perform a quantitative analysis of the competitive adsorption using a zero-dimensional simulation$^{[31]}$.

From Fig. 8, we found that hydrogen coverage on Pt/TiO$_2$(A) indicated notably higher values at 398 K, so that $\theta_{\text{hydrogen}}$ was varied from ca. 0.4 to 0.6 under this condition, as $K_{H_2}$ for Pt/TiO$_2$(A) increased drastically as increase in 1/T. Though we considered that this catalyst exhibited higher catalytic activities derived from
higher hydrogen coverage, we could not discuss the detailed mechanisms in this study. For our future work, we will conduct a zero-dimension simulation to clarify the correlation between coverage and catalytic activities quantitatively. In addition we also cannot discuss the mechanisms of hydrogen adsorption behavior against support species from our data. We estimated that strong support-metal interaction (SMSI) could be a possible mechanism of higher hydrogen coverage of Pt/TiO2(A). We will also figure out this phenomena as our future work.

4. Conclusion

In order to estimate effects of support materials and their crystal structures, we prepared Pt-loaded Al2O3 and TiO2 with different crystal structures. Catalytic activities on the catalysts were higher in the order of Pt/Al2O3 > Pt/TiO2(A) > Pt/TiO2(AR) = Pt/TiO2(R) above 423 K, whereas Pt/TiO2(A) showed remarkably higher activities at 398 K.

Catalytic reaction rates were analyzed by an apparent Langmuir-Hinshelwood model to evaluate the macroscopic catalysis behavior and support effects. From kinetic analysis, we found that kinetic constants for each catalysts were almost the same. Therefore, we concluded that only the kinetics constants cannot explain catalytic activities of hydrogenation reaction on the catalysts. Toluene and MCH coverage on Pt-loaded catalysts had weak correlations with catalytic activities, reaction rates increased as hydrogen coverage increased for each catalyst. Therefore we considered that hydrogen adsorption is the dominant factor for the hydrogenation reaction.

Though we estimated the apparent correlation between catalytic activities and coverage of the reactants and the product over Pt/TiO2 with different crystal structures, we could not figure out the effects of TiO2 crystal structures on the Pt surface. In order to determine the true, not apparent reaction orders of hydrogen, toluene and MCH, we will carry out surface analysis of the catalysts in order to clarify the mechanism of support effects as our future work.

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要 旨

Pt担持トルエン水素化触媒反応における担体効果の反応速度論解析

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固定層反応器内に充填したPt担持Al₂O₃またはTiO₂触媒を用い、トルエン水素化反応試験を常圧 398 ～ 473 K の条件で実施した。トルエン、水素、MCH 分圧はそれぞれ 60 ～ 91、9 ～ 23、9 ～ 17 kPa で変化させた。反応温度 423 K 上において、Pt担持触媒はPt/Al₂O₃、Pt/TiO₂（アナターゼ、A）、Pt/TiO₂（アナターゼ/ローチル混合物、AR）、Pt/TiO₂（ルチル、R）の順に高い活性を示したが、398 K ではPt/TiO₂（A）が特筆して高い活性を示した。担体化学種がPt触媒活性に及ぼす影響を評価するために、速度論解析を行った。吸着挙動が触媒活性に及ぼす影響を議論するために、Langmuir-Hinshelwood型の反応速度式を適用した。速度論解析から、反応速度定数の大きさだけでは、観測した触媒活性の序列を説明できないことが分かった。このことから、速度定数だけでは反応速度の大きさを説明できないと考えた。また、吸着平衡定数から算出した被覆率と反応速度の相関から、トルエン・MCH 被覆率が反応速度とほとんど相関がないのに対し、水素被覆率と反応速度には比較的強い相関があることが分かった。