

## [Research Note]

Selective Hydroconversion of *n*-Heptane over Pd-supported Zeolites and Pd-containing Hybrid CatalystXiaohong LI<sup>†1)\*</sup>, Jiani YANG<sup>†1)</sup>, Zhong-Wen LIU<sup>†1), †2)</sup>, Kenji ASAMI<sup>†1)</sup>, and Kaoru FUJIMOTO<sup>†1)</sup><sup>†1)</sup> Dept. of Chemical Processes and Environments, Faculty of Environmental Engineering, The University of Kitakyushu, Hibikino 1-1, Wakamatsu-ku, Kitakyushu 808-0135, JAPAN<sup>†2)</sup> College of Chemistry and Chemical Engineering, Nanjing University of Technology, Nanjing 210009, P. R. CHINA

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Hydroconversion of *n*-heptane was investigated over Pd-supported H-zeolite and hybrid catalyst consisting of Pd/SiO<sub>2</sub> and USY. Highly selective hydrocracking occurred over Pd/ZSM-5 whereas hydroisomerization dominated over Pd/USY and Pd/ $\beta$ . Skeletal isomerization occurred before the cracking reactions. The zeolite used and hydrogen spillover onto the zeolite were important in determining the isomerization selectivity. Experiments over hybrid catalysts suggested that close contact and the balance of metal and acidic sites are crucial in determining the activity and selectivity of isomerization and cracking. A reaction scheme based on the concept of hydrogen spillover was proposed.

**Keywords**

Hydrocracking, Hydroisomerization, Heptane, Bifunctional catalyst, Hydrogen spillover

**1. Introduction**

Upgrading of hydrocarbons through processes such as reforming, isomerization, cracking, etc., is very important in the hydrocarbon refinery industry. However, with increasing public concern about the environment, more and more stringent legislations are likely to be implemented to control the characteristics of gasoline. At present, isoparaffins appear to be more environmentally acceptable to increase the octane number of gasoline as high octane ratings can be achieved without the problems caused by current additives, such as tetraethyllead, aromatics and oxygenated compounds such as MTBE. Therefore, the skeletal isomerization of *n*-alkanes has received significant attention in recent years<sup>1)–6)</sup>.

The isomerization of pentane and hexane has been successfully carried out over noble metal catalysts supported on solid acids such as Pt/H-zeolite, Pt-superacid or Pt-hetero-polyacid. However, hydrocarbon chains longer than heptane are more difficult to isomerize because the cracking reaction becomes more favorable with increased carbon chain length<sup>7)</sup>. Although the hydroconversion of hydrocarbons has been intensively investigated, the reaction mechanism is still controversial. Hydroconversion of paraffins on Pt-supported

solid acids is widely believed to proceed through the following steps<sup>8)</sup>: Dehydrogenation of paraffin to olefin on the Pt surface; transfer of the olefin to an acidic site for protonation to carbenium ion; isomerization and/or cracking of the carbenium ion and de-protonation on an acidic site to olefin; and transfer of the product olefin to a Pt site for hydrogenation to the final paraffin.

Although this mechanism has been significantly developed, the key function of the noble metal in the bifunctional catalyst is to catalyze dehydrogenation of the reactant and hydrogenation of the intermediate olefin to the final product<sup>6),9)</sup>. Therefore, the high hydroconversion of isoparaffins at low temperature requires an extraordinarily high rate of dehydrogenation of the paraffins. Besides other challenges such as the very low equilibrium olefin content at the temperature of hydroconversion, palladium is well known to be a very poor catalyst for dehydrogenation, although it can effectively activate hydrogen<sup>10)</sup>. Furthermore, the distance between Pt particles and the acidic sites is important in determining the activity and selectivity of Pt/ $\beta$  for hexane hydroconversion<sup>11)</sup>, which cannot be satisfactorily explained based on the above bifunctional mechanism. Therefore, an alternative mechanism of hydrogen spillover has been developed based on the investigation of hydroisomerization of *n*-pentane and *n*-hexane over bifunctional catalysts<sup>2),3),12)–15)</sup>.

The present study found that either selective isomerization or cracking occurred during the hydroconversion

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Table 1 Hydroisomerization of *n*-Heptane over Different Catalysts<sup>a)</sup>

Catalysts	Conversion [%]	Isoheptane selectivity [%]	<i>I/C</i> ratio
Pd/ZSM-5	45.83	2.24	0.02
Pd/ $\beta$	53.06	90.3	9.31
Pd/USY	44.11	91.40	10.62
Hybrid catalyst <sup>b)</sup>	14.35	71.55	2.52
Pd/Mordenite	35.79	26.64	0.36

a) Reaction conditions:  $T = 523$  K,  $P = 0.5$  MPa,  $W/F = 1.8$  g<sub>cat</sub> · h/mol,  $H_2/n$ -heptane = 12, time on stream = 4 h, catalyst loading = 0.33 g.

b) Hybrid catalyst containing 0.22 g of USY and 0.11 g of 1.5 wt% Pd/SiO<sub>2</sub>.

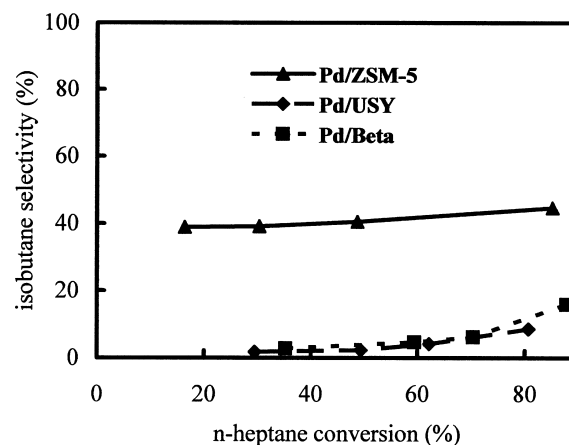
of *n*-heptane over Pd-catalyst supported on different zeolites. Some new concepts for the hydrogen spillover mechanism of the alkane hydroconversion are proposed.

## 2. Catalyst Preparation and Experimental Procedure

The palladium loading of the catalysts used in this study was fixed at 0.5 wt%. Pd-supported H-zeolite catalysts were prepared by ion exchange of ZSM-5 (Si/Al = 20),  $\beta$  (Si/Al = 18.5), USY (Si/Al = 5) and mordenite (Si/Al = 8.5) with an aqueous solution of [Pd(NH<sub>3</sub>)<sub>4</sub>]Cl<sub>2</sub>. These Pd/H-zeolite catalysts were activated as described previously<sup>10</sup>. Pd/SiO<sub>2</sub> catalyst with Pd loadings of 0.5 wt% and 1.5 wt% was prepared by incipient wetness impregnation of commercial SiO<sub>2</sub> with an aqueous solution of [Pd(NH<sub>3</sub>)<sub>4</sub>](NO<sub>3</sub>)<sub>2</sub>. Hybrid catalyst was prepared by cogrinding and pressure molding of the mixture of USY and Pd/SiO<sub>2</sub>. The reaction was carried out in a continuous flow fixed-bed reactor. Prior to reaction, 330 mg of each catalyst (20-40 mesh) diluted with 1.0 g quartz particles was loaded and reduced in a hydrogen flow at 673 K at atmospheric pressure for 2 h. The *n*-heptane was introduced to the reactor using a pump. To test the deactivation of the catalyst, standard operating conditions of  $T = 523$  K,  $P = 0.5$  MPa,  $H_2$  to *n*-heptane molar ratio = 12, and  $W/F = 1.8$  g<sub>cat</sub> · h/mol were applied before and after each run. To change the conversion level of *n*-heptane,  $W/F$  was adjusted from 0.9 to 5.4 g<sub>cat</sub> · h/mol. The reaction products were analyzed with an on-line GC equipped with an NB-1 capillary column (GL Sciences Inc.).

## 3. Results and Discussion

The results for the Pd/H-zeolite catalysts are given in **Table 1**. Pd/ $\beta$  showed the highest activity for the conversion of *n*-heptane whereas Pd/mordenite had the lowest activity. Moreover, *n*-heptane conversion over Pd/mordenite decreased gradually during the experiment, whereas the other catalysts showed no decreases (not shown). However, a different pattern was seen in the selectivity to branched heptanes. The Pd/ $\beta$  and Pd/

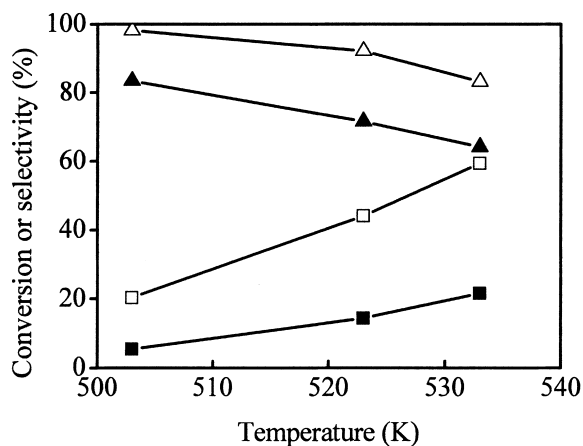


Reaction conditions:  $T = 523$  K,  $P = 0.5$  MPa,  $H_2/n$ -C<sub>7</sub> = 12.

Fig. 1 Relationship between *n*-Heptane Conversion and Isobutane Selectivity over Different Catalysts

USY catalysts showed very high isomerization selectivities of over 90%. In contrast, the selectivity of Pd/ZSM-5 for branched heptanes was very low and most converted *n*-heptane was cracked as shown in the data of isomerization to cracking (*I/C*) ratios in **Table 1**.

Isobutane is one of the main products of the cracking reaction, so the selectivity for isobutane is closely related to the reaction mechanism. Therefore, isobutane selectivity at different conversions of *n*-heptane was calculated as shown in **Fig. 1**. Over Pd/ $\beta$  and Pd/USY, isobutane selectivity increased continuously with increased *n*-heptane conversion, suggesting that at least part of the isobutane is not a primary product of *n*-heptane cracking. However, in the case of Pd/ZSM-5, the isobutane selectivity remained almost constant despite the change in *n*-heptane conversion, which indicates that the isobutane is a primary product of *n*-heptane cracking. These results suggest that hydroisomerization or hydrocracking of *n*-heptane is strongly affected by the zeolite support as the Pd loading was the same. ZSM-5 mainly favored the cracking of *n*-heptane whereas  $\beta$  and USY favored isomerization. A previous study of the hydroconversion of *n*-heptane over different solid acids loaded with Pt showed that porosity



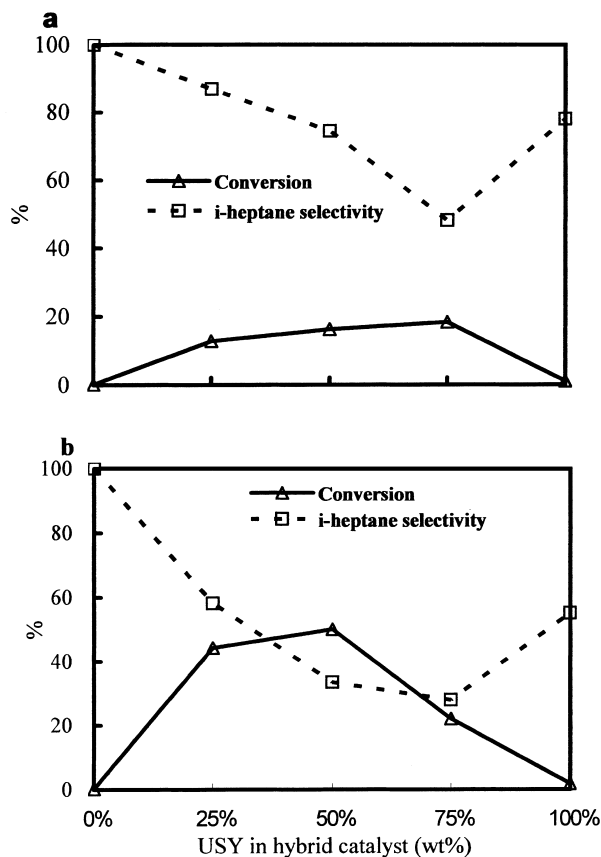
Reaction conditions:  $P = 0.5$  MPa,  $W/F = 1.8$  g<sub>cat</sub> h/mol,  $H_2/n-C_7 = 12$ .

Fig. 2 *n*-Heptane Conversion and Isoheptane Selectivity over 0.5 wt% Pd/USY ( $\triangle$ : *n*-heptane conversion  $\blacksquare$ : isoheptane selectivity) and Hybrid Catalyst Containing 0.11 g of 1.5 wt% Pd/SiO<sub>2</sub> and 0.22 g of USY ( $\triangle$ : *n*-heptane conversion  $\blacksquare$ : isoheptane selectivity)

of the solid acid was more important than acidity for the isomerization of *n*-heptane<sup>16</sup>). We can tentatively say that the structure of zeolites is crucial in determining the selectivity of products (cracking or isomerization). Further characterization of the acid or other properties of zeolite is necessary. As mordenite contains only one-dimensional channels in the framework, deactivation was continuous during the hydroconversion of *n*-heptane.

As shown in **Table 1** and **Fig. 2**, Pd/SiO<sub>2</sub> and USY showed little catalytic activity, whereas the hybrid catalyst of the two components showed some activity for both *n*-heptane conversion and isoheptane selectivity, but less than Pd/USY. The difference in *n*-heptane conversion over Pd/USY and hybrid catalyst was greatly affected by temperature whereas the selectivity for isoheptane was less influenced by temperature (**Fig. 2**).

The amount of USY in the hybrid catalyst was less (2/3) than that in the Pd/USY catalyst although the metallic Pd content was the same. Therefore, the low activity and selectivity over the hybrid catalyst may derive from the longer distance between Pd and acidic sites in USY and the balance of Pd and acidic sites. To confirm this, experiments with different compositions of 0.5 wt% Pd/SiO<sub>2</sub> and USY were carried out at different temperatures as shown in **Fig. 3**. Both Pd/SiO<sub>2</sub> and USY showed negligible activity for the conversion of *n*-heptane. However, much higher activity was achieved over the hybrid catalyst irrespective of the reaction temperature, indicating that both Pd and acid are required for the hydroconversion of *n*-heptane. Moreover, both the *n*-heptane conversion and isoheptane selectivity were significantly influenced by the Pd to USY ratio, showing that an increase in Pd content



Reaction conditions:  $P = 0.5$  MPa,  $W/F = 1.8$  g<sub>cat</sub> h/mol,  $H_2/n-C_7 = 12$ .

Fig. 3 Effect of Composition of the Hybrid Catalyst on Hydroconversion of *n*-Heptane at a) 533 K, b) 573 K

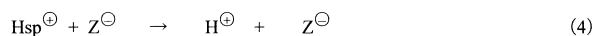
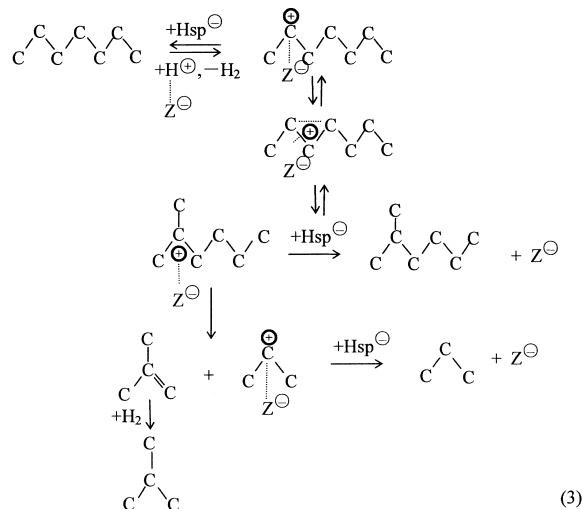
promoted isomerization, whereas an increase in USY promoted cracking. With an increase in reaction temperature from 533 K to 573 K, the selectivity for isoheptanes changed faster with the change in the catalyst composition. The catalyst composition corresponding to the maximum conversion of *n*-heptane had lower USY content at higher temperature, suggesting that the balance of metal and acid is an important parameter to achieve high activity for the hydroconversion of *n*-heptane. Therefore, close contact and balance of Pd and USY are important for determining the *n*-heptane conversion and isoheptane selectivity during the hydroconversion of *n*-heptane.

Based on the classic hydrogenation-dehydrogenation mechanism<sup>5),6),8),9)</sup>, the present results are difficult to explain because supported Pd shows little activity for dehydrogenation of paraffins. However, as Pd is active for the dissociation of H<sub>2</sub> under the present conditions, if hydrogen spillover is taken into account, all of the above experimental results can be explained. The H<sub>2</sub> molecule dissociates on Pd to H and presumably spills over to the acid surface as H<sup>+</sup> and H<sup>-</sup><sup>15),16)</sup>. The H<sup>+</sup> or existing H<sup>+</sup> or zeolite acts as an acid and abstracts H<sup>-</sup>

from *n*-heptane or attacks one of the carbon atoms in *n*-heptane to promote the reactions of carbenium ion (isomerization) or cracking determined by properties of the zeolite<sup>10,15</sup>. Accordingly, high activity for the hydroconversion of *n*-heptane can be achieved if the amount of spilt-over hydrogen dissociated on Pd matches the number of acidic sites for the formation of carbenium ions. As isobutane is always present in the primary product as discussed above, *n*-C<sub>7</sub><sup>+</sup> should be first isomerized to *i*-C<sub>7</sub><sup>+</sup>, and then either reacts with H<sup>-</sup> to form *i*-C<sub>7</sub> or cracks to C<sub>3</sub> + C<sub>4</sub>. Moreover, further cracking of *i*-C<sub>7</sub> cannot be ruled out based on the present results. This mechanism and the main reaction steps are shown in Eqs. (1) to (4). This mechanism can be more simply and clearly illustrated by a figure which has been claimed by our group<sup>2),3),17),18)</sup>. As there is either no active site for hydrogen dissociation or no acidic site on USY or Pd/SiO<sub>2</sub>, respectively, these catalysts showed negligible activity for the reaction. As Pd was directly loaded on USY for the Pd/USY catalyst, both high *n*-heptane conversion and isoheptane selectivity were achieved due to the effective spillover of hydrogen from Pd to USY. In comparison with Pd/USY, the hybrid catalyst showed lower activity and selectivity for isoheptane because the contact between Pd and USY in the hybrid catalyst was not as close as that in the directly loaded catalyst, which reduced the efficiency of hydrogen spillover. Isomerization or cracking was determined by the zeolite used as well as the degree of hydrogenation of carbenium ion. Hydrocracking was dominant over ZSM-5 whereas highly selective isomerization occurred over USY and β.

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where, H<sup>⊕</sup> is proton on Brønsted acid

Hsp<sup>⊕</sup> is proton supplied from gas phase by spillover

Hsp<sup>⊖</sup> is hydride ion supplied from gas phase by spillover

Z<sup>⊖</sup> is counter anion of Brønsted acid site on zeolite

## 要 旨

Pd 担持ゼオライトとハイブリッド触媒を用いる *n*-ヘプタンの選択的水素化転換黎 暁紅<sup>†1)</sup>, 楊 佳妮<sup>†1)</sup>, 劉 忠文<sup>†1), †2)</sup>, 朝見 賢二<sup>†1)</sup>, 藤元 薫<sup>†1)</sup><sup>†1)</sup> 北九州市立大学国際環境工学部環境化学プロセス工学科, 808-0135 北九州市若松区ひびきの1-1<sup>†2)</sup> 南京工業大学化学化工学院, 南京新模範馬路5号, 南京 210009, 中国

パラジウム担持ゼオライト (Pd/Zeolite) 触媒と Pd/SiO<sub>2</sub> + USY よりなるハイブリッド触媒を用いて *n*-ヘプタンの水素化転換反応を行った。ゼオライト上の水素移動が生成物の選択性に大きく影響を及ぼした。Pd 担持 ZSM-5 触媒上では水素化分解反応が主に進行したのに対し, Pd 担持 USY と Pd 担持 β 触媒上では異性化反応が主に進行した。生成物の中のイソブタンの定量により, *n*-ヘプタンの水素化分解では, 分解したフラクションが異性化するのではなく, *n*-ヘプタンは異性化して

分解することが分かった。Pd/SiO<sub>2</sub> と USY との物理混合よりなるハイブリッド触媒は, その構成成分単独では全く示さないにもかかわらず, 優れた異性化, 分解活性を示した。また, 金属サイトと酸点との量のバランスにより触媒の活性および生成物の選択性を制御し得ることが明らかとなった。この一連の触媒上での *n*-パラフィンの反応の挙動について, スピルオーバーの概念に基づく妥当な反応機構を提案した。

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