1. Introduction

1.1. Background

Light naphtha consists mainly of pentanes C5 and hexanes C6 which are both gasoline fractions, but the octane value of light naphtha has a low antiknock property index, so shipments for use in gasoline are restricted. Isomerization of light naphtha is intended to convert the n-pentane and n-hexane content to isopentane and isohexane with higher octane values, thus allowing the marketing of light naphtha as environmentally-friendly fuel oil with low sulfur and almost no aromatic contents. Several industrial processes have been developed for light naphtha isomerization and the UOP Penex and Par-isom processes are well known for C5/C6 isomerization1,2). These processes are carried out at high pressure of 2-3 MPa.

Our research has investigated low pressure catalysis to avoid the hydrocracking reaction, but high pressure can also be used. Catalyst based on high silica zeolite has relatively stable performance at low pressure. In addition, coke formation is suppressed by operating at low temperature. Our research with such reaction conditions seems to provide a relatively long life for the catalyst. Bicomponent catalysts consisting of platinum metal and acidic supports such as strong solid acid or zeolite can be applied for these industrial processes3,4). These catalysts do not include binders, so the mechanical strength of the catalyst is low and the metal dispersion is not so high.

Recent catalyst research has usually focused on nanoporous tri-component catalysts consisting of zeolites with various sub-nanometer order spaces and surfaces, or unimodally porous materials with tens-of-nanometer order spaces and surfaces, whereas one-nanometer order spaces and materials have not been so well studied catalysis in industrial applications5-9). Nanoporous tri-component catalysts can achieve active and selective performances because of the synergy between the components10). The hydrogenation and dehydrogenation functions for the catalyst are controlled and modified by noble metals such as Pt and Pd11-18). In our recent research on zeolite catalysts, we intentionally focused on composites containing unimodal nanoporous nano-sized (defined as 5-50 nm, and here called ns) oxides, to improve the state of metal species for isomerization into multi-branched isoparaffins. 

Nano-technology was applied to form composites of zeolites and nano-sized (defined as 5-50 nm, and here called ns) oxides, to improve the state of metal species for isomerization into multi-branched isoparaffins. Skeletal isomerization of n-hexane was advanced, based on catalyst optimization with 0.1-2 wt% Pt or Pd on 35 wt% ns Al2O3 or ns SiO2 and 65 wt% H-BEA zeolite (SiO2/Al2O3 × 16-39). The presence of ns Al2O3 in the catalyst increased the mechanical strength of the shaped zeolite catalyst and reformed the surface acidity of the zeolite to milder acid suitable for skeletal isomerization without cracking. X-ray photoelectron spectroscopy showed that the nano-alumina dispersed and combined to the anisotropic surface of BEA zeolite to form an ionic and highly developed surface for palladium dispersion to improve the catalyst activity and selectivity.

Keywords
Isomerization, Nano-sized oxide, Boundary, Acidity, Palladium species
This finding has advanced research in the \(n\)-C\(_6\)H\(_{14}\) isomerization reaction.

This study describes the applicability of such tri-component catalysts to \(C_5/C_6\) isomerization. The tri-component catalysts consist of Pd or Pt, \(ns\) oxide and nano-crystalline zeolite. \(n\)-C\(_6\)H\(_{14}\) is used as a model component for evaluation of the catalysts.

1.2. Reaction Mechanism of Isomerization and Role of Metal

Two types of solid catalysts are active for isomerization, solid acid catalyst and noble metal supported on solid acid catalyst. The nature of the carbenium ion decisively affects the rate and selectivity of isomerization. The reaction mechanism of isomerization has the following steps\(^{26} - ^{28}\): Alkane is converted to alkene by dehydrogenation at the metal surface, alkene is converted to carbenium ion by \(H^+\) addition at the acid site of the solid acid catalyst, carbenium ion skeletonally isomerizes at the acid site, isomerized carbenium ion forms isomerized alkene by deprotonating, and isomerized alkene is converted to iso-type alkane by hydrogenation at metal.

On the bicomponent catalyst, the carbenium ion is generated by \(H^+\) addition to the alkene, so no strong acid site is required for generation of carbenium ion. The nature of the acid decisively affects the isomerization process of carbenium ion as the rate-determining step. Alkene is usually not observed, since the alkene is an intermediate of the isomerization reaction mechanism and is converted to the corresponding isoalkane.

The function of the metal component of the bicomponent catalyst is to hydrogenate the intermediate alkene and to restrict the production of alkene. The ideal state is that dehydrogenation and hydrogenation quickly achieve equilibrium. As a result, hydrogenation under high pressure restricts the formation of both alkene and its dimer. In addition, the formation of coke is also restrained as hydrogen spilling over from the metal surface hydrogenates the coke precursor. Accordingly, the catalyst life is extended and byproduct production is suppressed. The functions of the metal and hydrogen are to prevent the degradation of activity and to improve the selectivity.

Clearly, dispersion of metal on the catalyst is expected to affect the catalytic performance. Tri-component catalysts consisting of zeolites with metal and \(ns\) oxide should be more effective in the suitable dispersion of metal than the bicomponent catalyst.

2. Experimental

2.1. Catalyst Preparation

Tri-component catalysts (platinum metal, \(ns\) oxide and zeolite) were prepared using the following reagents. Three types of zeolite, H-BEA zeolite (SiO\(_2\)/Al\(_2\)O\(_3\) molar ratio = 16-39), USY zeolite (SiO\(_2\)/Al\(_2\)O\(_3\) molar ratio = 12) and H-MFI zeolite (SiO\(_2\)/Al\(_2\)O\(_3\) molar ratio = 90) were chosen as the zeolite components. Cataloid AP-1 (JGC Catalysts and Chemicals Ltd.) was used as the \(ns\) Al\(_2\)O\(_3\) precursor, which consists of 71.0 wt% alumina (boehmite), 11.0 wt% acetic acid, and 18.0 wt% water, and has an average particle size of 5.4 nm. Aerosil 200 (Nippon Aerosil Co., Ltd.) was used as the \(ns\) SiO\(_2\) precursor and has an average primary particle size of 10 nm. The metal component, Pd or Pt, was dispersed on the \(ns\) oxide bound to zeolite.

Two of these solid powders (zeolite and \(ns\) oxide) were mixed with water to form a thick paste and mechanically kneaded then extrudated into pellets, which were dried in air overnight at room temperature and heating at 120°C for 3 h. Finally, the pellets were calcined in air at 550°C for 3 h. The composites were impregnated by the incipient wetness method with PtCl\(_6\)6H\(_2\)O or HCl-acidic PdCl\(_2\) aqueous solution.

After aging in a sealed vessel at room temperature for one night, the impregnated extrudates were dried in air at 120°C for 3 h and calcined in air at 550°C for 3 h. The final non-reduced tri-component catalysts were 0.1-2 wt% Pd or Pt on 35 wt% \(ns\) Al\(_2\)O\(_3\) or \(ns\) SiO\(_2\) and 65 wt% H-BEA or USY or H-MFI. Bicomponent catalysts, metal on zeolite were prepared by high pressure pelletizing in air. Dealuminated H-BEA zeolites were prepared as follows. At first, zeolite was calcined at from 550 to 850°C for 3 h. The zeolite was stirred for two hours in 0.1 N HCl solution of 50 mL/g-zeolite at room temperature, washed until pH 7, then dried by leaving overnight at room temperature and for 3 h at 120°C.

2.2. Reaction Test and Analysis

The catalytic reaction performances were examined using \(n\)-hexane feedstock in a continuous-flow reactor with a fixed catalyst bed of 0.5 mL at 250-350°C under hydrogen pressure. Reaction conditions were as follows. Reaction temperature: 250-350°C; liquid hourly space velocity (LHSV): 1.8-11.0 h\(^{-1}\); pressure: 0.12 MPa; molar ratio of \(n\)-C\(_6\)H\(_{14}\) : \(H_2\) = 1 : 15. Prior to the reaction test, all catalysts were reduced under hydrogen flow (GHSV: 5000 h\(^{-1}\); 450°C; 3 h). Gas chromatography was used to measure the composition of reactants with a Capillary TC-1 60 m column, FID detector, and Chromato-pack C-R8A for data processing. As shown in Fig. 1, chemical equilibrium is reached in the isomerization of \(n\)-hexane. In this study, approach conversion to chemical equilibrium was adopted.

Conversion to equilibrium [%] = (produced amount of each isomer/equilibrium value of each isomer) × 100

2.3. Catalyst Characterization

Acid amount was measured by the NH\(_3\)-TPD method\(^{29}\). Mesoporosity was measured using nitrogen adsorption-desorption isotherms\(^{29}\). Elemental compo-

sitions of the catalyst surface layer were measured by X-ray photoelectron spectroscopy (XPS) using a KRATOS equipped with a mono Al source operating at 450 W. The spectra were acquired at room temperature and narrow scans with rather high 40 eV pass energy for the samples. The spectrometer energy scale was calibrated with Ag 3d5/2. The binding energies and atomic concentrations of the catalysts were calculated from the XPS results using the total integrated peak areas of the Al 2p, Si 2p, Pd 3p, O 1s, and C 1s regions.

3. Results and Discussion

3.1. Zeolite Component Selection by Comparison with BEA, USY and MFI Zeolite

*n*-Hexane was isomerized to four structural isomers, i.e. 2-methylpentane, 3-methylpentane, 2,2-dimethylbutane and 2,3-dimethylbutane. Lighter compounds were also produced by the cracking reaction.

The selection of the most suitable zeolite component for Pt/n-Al2O3/zeolite catalysts assessed three tri-component catalysts based on BEA zeolite (SiO2/Al2O3 = 25), USY zeolite (SiO2/Al2O3 = 12) and MFI zeolite (SiO2/Al2O3 = 90) as shown in Figs. 2, 3, 4 and 5. Figure 2 shows the *n*-hexane conversion to equilibrium, Fig. 3 shows the selectivity for mono-branched isoparaffins, Fig. 4 shows the selectivity for di-branched isoparaffins and Fig. 5 shows the selectivity for cracked products, at temperatures in the range of 250 to 350°C over the three catalysts. The MFI zeolite catalyst showed the highest conversion because of the rapid cracking reaction. On the other hand, the BEA zeolite catalyst had the high conversion and the highest isoparaffin selectivity because of the rapid cracking reaction. Therefore, zeolite with high acid strength seems to promote cracking reactions, so that BEA zeolite is more suitable than USY and MFI zeolite for *n*-hexane isomerization.

3.2. Effect of SiO2/Al2O3 Ratio of BEA Zeolite

The SiO2/Al2O3 ratio of the zeolite component was examined on the skeletal isomerization on *n*-hexane over 1.0 wt% Pd/n-Al2O3/BEA catalyst. The molar ratios of SiO2/Al2O3 investigated ranged from 16.2 to

**Fig. 1** Chemical Equilibrium Composition of *n*-Hexane Isomerization

**Fig. 2** Conversion to Equilibrium Depending on Reaction Temperature over 0.5 wt% Pt/n-Al2O3/BEA or USY or MFI Catalysts

**Fig. 3** Mono-branched Isoparaffins Selectivity Depending on Reaction Temperature over 0.5 wt% Pt/n-Al2O3/BEA or USY or MFI Catalysts

**Fig. 4** Conversion to Equilibrium Depending on Reaction Temperature over 0.5 wt% Pt/n-Al2O3/BEA or USY or MFI Catalysts

**Fig. 5** Mono-branched Isoparaffins Selectivity Depending on Reaction Temperature over 0.5 wt% Pt/n-Al2O3/BEA or USY or MFI Catalysts
39 as shown in Fig. 6. The relationship between the yield and the SiO$_2$/Al$_2$O$_3$ peaked from 25 to 30 of SiO$_2$/Al$_2$O$_3$ for both conversion and multi-branched isoparaffin selectivity. The optimum SiO$_2$/Al$_2$O$_3$ molar ratio was about 25, which implies that the formation of active isomerization sites depends on the SiO$_2$/Al$_2$O$_3$ molar ratio of beta zeolite. The observed dependencies of the activity and the selectivity on the SiO$_2$/Al$_2$O$_3$ molar ratio suggest that the aluminum species in the surface layer of the zeolite particles are controlling factor. Therefore, the optimum SiO$_2$/Al$_2$O$_3$ molar ratio of the zeolite for a multiple component catalyst would depend on the structure of the zeolite component.

3.3. Effect of Metal Species and Metal Ratio of Catalyst

The involvement of the metal species was investigated by comparing skeletal isomerization of n-hexane over 1.0 wt% Pt/ns Al$_2$O$_3$/BEA catalyst and 1.0 wt% Pd/ns Al$_2$O$_3$/BEA catalyst. Figure 7 shows the catalytic performance of these catalysts, as expressed by multi-branched isoparaffin, mono-branched isoparaffin and
cracked product yields. The total of these yields is the conversion. Conversion over the Pd catalyst was higher than over the Pt catalyst, although the yields of cracked product were almost the same. Generally, Pt catalyst is more active than Pd catalyst. However, most of these catalysts do not use binder such as Al₂O₃ and so the state of the metal precursor is different. Platinum metals are aggregated in the oxidized state, for example, in the case of using Pd nitrate. This catalyst was produced with Pd chloride in HCl, so Pd was dispersed as PdCl₄²⁻ on the support. Therefore, Pd was aggregated in the form of perchlorate. In addition, this catalyst included Al₂O₃, so Pd was more easily dispersed than Pt. The dispersion of Pd is further discussed in section 3.7. Pd catalyst causes more effective isomerization to both mono-branched and multi-branched isomers. The metal component promotes dehydrogenation and hydrogenation reactions cause generation of the carbenium ion precursor and successive quenching. The excess of metal means that the rate-determining step changes from generation of carbenium ion to isomerization. Therefore, the effect of Pd amount was investigated. Figure 8 shows the effect of Pd amount from 0 to 2 wt% of Al₂O₃/H-BEA catalyst showed no activity without Pd because of the absence of hydrogenation and dehydrogenation functions. Saturation of Pd is the upper limit to effective isomerization, which is 1.0 wt% for this catalyst. Therefore, higher amounts of Pd cause the rate-determining step to change to isomerization controlled by zeolite acidity.

3.4. Effect of Nano-sized Oxides of Tri-component Catalyst

Four different types of oxides, none, SiO₂, Al₂O₃ and TiO₂ were examined for the tricomponent catalyst. Figure 9 shows that the Pd/Al₂O₃/BEA catalyst demonstrated superior catalytic performance for isomerization compared to catalysts with none, SiO₂ and TiO₂. In particular, the multi-branched isoparaffin yield was the highest. We previously found that the acid sites were formed at the boundary between zeolite and Al₂O₃. Pd/Al₂O₃/H-BEA catalyst was considered to have a different structure at the boundary between Al₂O₃ and zeolite. For example, Pd/SiO₂/BEA catalyst without oxide has some strong acid sites at the zeolite surface, which promote the cracking reaction. On the other hand, the Pd/Al₂O₃/BEA catalyst can form meso-porous spaces and mild moderate or mild strong acid sites at the boundary between Al₂O₃ and zeolite. Pd can be also dispersed at the boundary acid sites, so the catalyst has high dispersion of Pd. Such acid sites can not be formed on the Pd/SiO₂/BEA and Pd/TiO₂/BEA catalysts because of the valence balanced Si-O-Si and Si-O-Ti at the boundary. Therefore, the catalytic performance of these catalysts is almost the same as the Pd/BEA catalyst without oxide. Therefore, Al₂O₃ is more suitable as the oxide component than SiO₂ and TiO₂ for isomerization of n-hexane, especially to multi-branched isoparaffins. Nanoporous space and mild acid sites formed at the boundary between Al₂O₃ and zeolite are the most important characteristics for this catalyst and the Al₂O₃ component in the reforming catalyst is active.
ly involved in the catalysis.

Subsequently, the effect of \( \text{ns Al}_2\text{O}_3 \) content on the catalytic performances was investigated. Figure 9 shows that \( \text{ns Al}_2\text{O}_3 \) can reform di-branched isoparaffin depending on the zeolite. Therefore, the content of \( \text{ns Al}_2\text{O}_3 \) should affect the reforming activity. Figure 10 shows that conversion and di-branched isoparaffin yield over Pd/\( \text{ns Al}_2\text{O}_3 \)/H-BEA zeolite catalyst is the highest at 35 % \( \text{ns Al}_2\text{O}_3 \) content, resulting in the most effective reforming because the maximum of catalytic acid sites can be formed with the \( \text{ns Al}_2\text{O}_3 \) content of 35 % based on our previous research\(^{22,23}\). To clarify the effect of \( \text{ns Al}_2\text{O}_3 \) on the zeolite component, rate constants for the catalytic activities were normalized to the relative activities by zeolite content as shown in Fig. 11. Pd/\( \text{ns Al}_2\text{O}_3 \)/H-BEA zeolite catalyst maintained the mesoporous spaces and mild acid sites at the boundary between the zeolite and \( \text{ns Al}_2\text{O}_3 \), so that the \( \text{ns Al}_2\text{O}_3 \) was highly dispersed onto the zeolite surface. Therefore, Pd could be highly dispersed at the acid sites of the catalyst. \( \text{ns Al}_2\text{O}_3 \) content of 35 wt% was considered to be optimum in terms of catalytic performance and cost performance.

### 3.5. Dependency of Selectivity on Contact Time

The dependency of selectivity on contact time over Pd/\( \text{ns Al}_2\text{O}_3 \)/H-BEA catalyst was investigated. The reaction rates could be represented by the first-order model for reactant concentration. The result of conversion and selectivity with contact time are shown in Table 1. Product selectivities changed with contact time in the range 0.09 to 0.55 h. With longer contact time, the selectivity for multi-branched isoparaffins increased, and the selectivity for mono-branched isoparaffins decreased. Therefore, longer contact time resulted in higher selectivity for multi-branched isoparaffins. On the other hand, selectivity for cracking products changed with contact time in the range 0.09 to 0.55 h. With longer contact time, the selectivity for cracking products decreased. Therefore, longer contact time resulted in higher selectivity for multi-branched isoparaffins.

![Figure 10: Effect of \( \text{ns Al}_2\text{O}_3 \) Content in the Catalyst on Products Yields](image)

![Figure 11: Effect of \( \text{ns Al}_2\text{O}_3 \) Content in the Catalyst on Relative Activity per Zeolite](image)

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**Table 1** Conversion to Equilibrium, Yields and Selectivities in \( n \)-Hexane Isomerization at Various Contact Times

<table>
<thead>
<tr>
<th>Contact time [h]</th>
<th>0.09</th>
<th>0.14</th>
<th>0.18</th>
<th>0.27</th>
<th>0.55</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conversion to equilibrium [%]</td>
<td>56.6</td>
<td>72.9</td>
<td>82.8</td>
<td>93.7</td>
<td>98.4</td>
</tr>
<tr>
<td>Di-branched to equilibrium [%]</td>
<td>12.1</td>
<td>19.1</td>
<td>28.1</td>
<td>42.4</td>
<td>63.3</td>
</tr>
<tr>
<td>Yields (selectivities) [%]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Isoparaffins</td>
<td>53.6 (94.7)</td>
<td>69.6 (95.6)</td>
<td>79.6 (96.1)</td>
<td>90.6 (96.7)</td>
<td>95.3 (96.9)</td>
</tr>
<tr>
<td>Mono-branched</td>
<td>49.6 (87.7)</td>
<td>63.3 (87.0)</td>
<td>70.3 (84.9)</td>
<td>76.6 (81.7)</td>
<td>74.4 (75.6)</td>
</tr>
<tr>
<td>Di-branched</td>
<td>4.0 (7.0)</td>
<td>6.3 (8.6)</td>
<td>9.3 (11.2)</td>
<td>14.0 (15.0)</td>
<td>20.9 (21.3)</td>
</tr>
<tr>
<td>2-MP</td>
<td>30.3 (53.6)</td>
<td>39.4 (54.0)</td>
<td>43.3 (52.3)</td>
<td>46.6 (49.7)</td>
<td>45.7 (45.0)</td>
</tr>
<tr>
<td>3-MP</td>
<td>19.3 (34.1)</td>
<td>23.9 (33.0)</td>
<td>27.0 (32.6)</td>
<td>30.0 (32.0)</td>
<td>29.4 (29.9)</td>
</tr>
<tr>
<td>2,2-DMB</td>
<td>2.3 (4.0)</td>
<td>3.4 (4.7)</td>
<td>5.3 (6.4)</td>
<td>7.5 (8.0)</td>
<td>11.0 (11.2)</td>
</tr>
<tr>
<td>2,3-DMB</td>
<td>3.0 (5.3)</td>
<td>3.3 (4.5)</td>
<td>3.2 (3.8)</td>
<td>3.1 (3.3)</td>
<td>3.1 (3.1)</td>
</tr>
</tbody>
</table>

\( MP \): methylpentane; \( DMB \): dimethylbutane.

<table>
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<tr>
<th>Contact time [h]</th>
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<th>0.55</th>
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<tr>
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<tr>
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<td>39.4 (54.0)</td>
<td>43.3 (52.3)</td>
<td>46.6 (49.7)</td>
<td>45.7 (45.0)</td>
</tr>
<tr>
<td>3-MP</td>
<td>19.3 (34.1)</td>
<td>23.9 (33.0)</td>
<td>27.0 (32.6)</td>
<td>30.0 (32.0)</td>
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<td>5.3 (6.4)</td>
<td>7.5 (8.0)</td>
<td>11.0 (11.2)</td>
</tr>
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<td>2,3-DMB</td>
<td>3.0 (5.3)</td>
<td>3.3 (4.5)</td>
<td>3.2 (3.8)</td>
<td>3.1 (3.3)</td>
<td>3.1 (3.1)</td>
</tr>
</tbody>
</table>

\( MP \): methylpentane; \( DMB \): dimethylbutane.

Catalyst: 1.0 wt% Pd/\( \text{ns Al}_2\text{O}_3 \)/H-BEA (SiO\(_2\)/Al\(_2\text{O}_3\) = 25).

Reaction temperature: 300 °C; LHSV: 1.7-11.1 h\(^{-1}\); Pressure: 0.12 MPa; Molar ratio of C\(_6\)H\(_{14}\)/H\(_2\): 1/15.
decreased with increased contact time. The cracking reaction is considered to proceed in parallel to isomerization. The isomers 2-methylpentane and 3-methylpentane are difficult to decompose despite containing a tertiary C–H bond. The β position C–C bonds of the cracked C–H bond are terminal or absent because of allyl resonance. Therefore, the cracking reaction can initiate only at the secondary C–H bond of the 2-position carbon. Therefore, n-hexane is less likely to undergo the cracking reaction.

### 3. 6. Effect of Acid Treatment on BEA Zeolite

To increase the selectivity for multi-branched isoparaffins, BEA zeolite was modified by acid treatment to form dealuminated nanoporous zeolite after heat treatment. The SiO2/Al2O3 molar ratio of BEA zeolite based on the basic components was modified by control of the calcination temperature as shown in Fig. 12. Calcination at 650 °C dealuminated the zeolite to change the SiO2/Al2O3 ratio from 25 to 38, and formed nanoporous space with pore diameter of ca. 5 nm at the boundary between the zeolite surface and ns Al2O3.

Table 2 shows the differences in catalytic performance between non-treated zeolite catalyst and nanoporous treated zeolite catalyst for 1.0 wt% Pd/ns Al2O3/BEA catalyst and 1.0 wt% Pd/ns SiO2/BEA catalyst. For Pd/ns Al2O3/BEA catalyst, temperatures of 250 °C and 280 °C resulted in 90% conversion at chemical equilibrium for the non-treated and nanoporous treated catalysts, respectively. The non-treated catalyst had slightly higher activity than the nanoporous treated catalyst. However, the nanoporous treated catalyst showed higher selectivity than the non-treated catalyst for both isoparaffins and di-branched isoparaffins and formed less cracked product. As shown in Fig. 1, the conversion at equilibrium was 83% at 280 °C, indicating a shift from the equilibrium value. However, di-branched isoparaffin yield had not reached the equilibrium value. On the other hand, for Pd/ns SiO2/BEA catalyst, as with Pd/ns Al2O3/BEA catalyst, the temperatures of 290 °C and 310 °C resulted in 90% conversion at chemical equilibrium for the non-treated and nanoporous treated catalysts, respectively. However, the nanoporous treated catalyst showed lower performance than the non-treated catalyst for isoparaffin selectivity and produced more cracked product. In addition, the Pd/ns SiO2/BEA catalyst had lower selectivity for di-branched isoparaffins than the Pd/ns Al2O3/BEA catalyst. At higher temperature, molecular motion is faster and the shape selectivity is increased in large pore zeolites. Therefore, formation of di-branched isoparaffins is unlikely. Thus, acid treatment of BEA zeolite has very different effects on the ns oxides species. These four catalysts are considered to have different surface models for the interface between ns oxides and BEA zeolite, depending on whether non-treated or nanoporous treated BEA zeolite with ns oxides. Strong acid sites like amorphous SiO2–Al2O3 are generated between ns SiO2 and aluminum species on non-treated BEA zeolite surfaces. Dealumination of BEA zeolite by acid treatment is effective for removing the aluminum species on the BEA zeolite surface, so that the acid sites form between the Si–OH of dealuminated zeolite and the Al–OH of ns Al2O3. The reformed acid sites on the zeolite surface function as active sites for isomerization. No acid site was formed between the Si–OH of dealuminated zeolite and the Si–OH of ns SiO2. In contrast, the higher strength of acid sites inside the zeolite promotes the cracking reactions. Acid treatment of BEA zeolite was effective only for the Pd/ns Al2O3/BEA catalyst.

### 3. 7. Characterization and Modeling of Optimized Tri-component Catalysts and Discussion of Active Sites

Design of an effective isomerization catalyst should ensure the presence of metal such as Pt or Pd at non-

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Table 2: Effect of Nanoporous Treatment of H-BEA Zeolite on Catalysis

<table>
<thead>
<tr>
<th></th>
<th>ns Al2O3</th>
<th>ns SiO2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature of 90% to equilibrium [°C]</td>
<td>250</td>
<td>280</td>
</tr>
<tr>
<td>Selectivity of total isoparaffins [%]</td>
<td>97.1</td>
<td>98.7</td>
</tr>
<tr>
<td>Selectivity of di-branched [%]</td>
<td>20.5</td>
<td>24.2</td>
</tr>
<tr>
<td>Selectivity of cracked [%]</td>
<td>2.9</td>
<td>1.3</td>
</tr>
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</table>

Catalyst: 1.0 wt% Pd/ns Al2O3/H-BEA.
zeolitic acid sites in the catalyst because the zeolite acid sites promote isomerization. Nanoporous Al₂O₃ is useful as a binder to improve the mechanical strength of the catalyst and is also effective to improve the catalytic activity. The acid strength of these catalysts was measured by NH₃-TPD, which identified weak, mild moderate and mild strong acid sites. Measurements were not made above 600 °C because strong acid was not observed on this catalyst. These types were determined from the peak top position of waveform separation. The desorption temperature was defined as follows.

Weak acid 200 °C peak, mild moderate acid 310 °C peak, mild strong acid peak 410 °C. As shown in Fig. 13, BEA zeolite bound with ns Al₂O₃ has more acid sites than BEA zeolite, and the increased acid sites are medium and strong acids. On the other hand, BEA zeolite bound with ns SiO₂ has almost the same acid sites of BEA zeolite. The acid sites generated at the boundary between ns Al₂O₃ and nanoporous BEA zeolite were derived from pseudo-boehmite and BEA zeolite.

In addition, the acid sites act as anionic sites desirable for metal dispersion. This acid site strength is weaker than zeolite acid sites, but is found as the basic site in ns Al₂O₃ which is preferable to act as the cationic site to fix the counter anion of Pd²⁺, i.e. Cl⁻. Therefore, the dispersed Pd can function effectively in the isomerization of n-hexane. The skeletal SiO₂/Al₂O₃ ratio of zeolite effect the catalytic performance of tricomponent catalyst as discussed in section 3.2., and the activity peaks at SiO₂/Al₂O₃ of 25 to 30. The acid sites are generated and arranged according to SiO₂/Al₂O₃. The acid sites are closely packed for zeolite of lower SiO₂/Al₂O₃ and widely dispersed for higher SiO₂/Al₂O₃. The most suitable dispersion of metal is produced with SiO₂/Al₂O₃ of 25 to 30. The surface model of the interaction between nano-(AlO)OH and the acid site of nanoporous BEA zeolite is described in Fig. 14. The acidity and anionic strength at the boundary between zeolite and ns Al₂O₃ may be improved with Al coordination of nano-(AlO)OH to O of Si-(OH⁻)-Al.

Pd dispersion and surface distributions of Pd/BEA and Pd/ns Al₂O₃/BEA catalyst were confirmed by X-ray photoelectron spectroscopy (XPS). These catalysts were non-reduced or reduced by hydrogen before measurements. Figure 15 shows the peak of Pd 3p with intensity on non-reduced Pd/BEA and Pd/ns Al₂O₃/BEA catalysts. These peaks were corrected to the same intensity of Si. As shown in Fig. 15, a peak of Pd 3p with intensity (based on Si) about 100 was observed on Pd/BEA catalyst. On the other hand, an intensity of about 300 was observed on Pd/ns Al₂O₃/BEA catalyst. Metal dispersion on the Pd/ns Al₂O₃/BEA catalyst was higher than that of Pd/BEA catalyst before reduction. Figure 16 shows the peak of Pd 3p with intensity (based on Si) for reduced Pd/BEA and Pd/ns Al₂O₃/BEA catalysts and Fig. 17 shows the peak of Pd 3p with intensity (based on Al) for reduced Pd/ns Al₂O₃ and Pd/ns Al₂O₃/BEA catalysts. Both Pd/BEA catalyst and Pd/ns Al₂O₃/BEA catalyst had higher dispersion of Pd than non-reduced catalysts. Therefore, aggregation of Pd occurred, but ns Al₂O₃ in both non-reduced catalyst and reduced catalyst was still effective for Pd dispersion. In addition, a peak of Pd 3p with intensity for Pd/ns Al₂O₃ catalyst was lower than for Pd/ns Al₂O₃/BEA zeolite catalyst. XPS showed that.
Al₂O₃ was highly dispersed onto the zeolite surface, and then formed acid sites at the boundary. Therefore, Pd could be dispersed on the acid sites at the boundary instead of the Al₂O₃ surface.

3.8. Performance of Optimum Catalyst

The optimum catalyst was compared to known technology catalyst as shown in Table 3. The known technology catalyst, Pd/H-BEA, was prepared by a conventional method. In this method, palladium nitrate was directly supported on BEA zeolite so that Pd dispersion was low due to aggregation at the oxide stage. As shown in Table 3, the optimum catalyst has higher activity and di-branched isoparaffin selectivity, primarily caused by the nanoporous space and mild acid sites formed at the boundary between Al₂O₃ and zeolite. Moreover, dealumination of BEA zeolite by acid treatment is effective in removing the aluminum species on the BEA zeolite surface, so the acid sites form between the Si-OH of dealuminated zeolite and the Al-OH of Al₂O₃. The reformed acid sites on the zeolite surface function as active sites for isomerization. Therefore, Al₂O₃ was highly dispersed onto the zeolite surface, and acid sites were formed at the boundary, so that Pd was dispersed on the acid sites.

4. Conclusion

The conversion of n-hexane to isohexanes was studied on various catalysts consisting of Pt group metal on nano-components. The composite Pd/Al₂O₃/H-BEA catalyst was selected. The composite showed selective product distribution for skeletal isomerization due to the metal dispersion at the boundary between Al₂O₃ and H-BEA zeolite. This catalyst contained mesoporous spaces at the boundary face. In addition, the acid sites were generated at the nano-interface by the combination of Al₂O₃ and H-BEA zeolite as desirable sites for metal dispersion. The catalytic site on the nano-zeolite surface was modified with Al₂O₃. The novel function of the nano-interface between oxide and nano-zeolite was revealed.

Acknowledgment

Financial support from CREST, Japan Science and Technology Agency for this work is acknowledged. Financial support of basic research for this work from JOGMEC is also acknowledged. The technical cooperation of Mr. Tetsuya Kaneko and Ms. Sowaka Sudo is highly appreciated.
Table 3 Performance of Optimum Catalyst

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Optimum catalyst</th>
<th>Known technology catalyst</th>
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</thead>
<tbody>
<tr>
<td>Conversion to equilibrium [%]</td>
<td>90.0</td>
<td>21.9</td>
</tr>
<tr>
<td>Yields (selectivities) [%]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>isoparaffins</td>
<td>88.8 (98.7)</td>
<td>21.6 (98.6)</td>
</tr>
<tr>
<td>mono-branched</td>
<td>67.1 (74.5)</td>
<td>17.2 (78.4)</td>
</tr>
<tr>
<td>di-branched</td>
<td>21.8 (24.2)</td>
<td>4.4 (20.3)</td>
</tr>
<tr>
<td>2-MP</td>
<td>40.3 (44.7)</td>
<td>10.7 (48.8)</td>
</tr>
<tr>
<td>3-MP</td>
<td>26.8 (29.8)</td>
<td>6.5 (29.6)</td>
</tr>
<tr>
<td>2,2-DMB</td>
<td>9.4 (10.4)</td>
<td>1.5 (6.8)</td>
</tr>
<tr>
<td>2,3-DMB</td>
<td>12.4 (13.8)</td>
<td>2.9 (13.2)</td>
</tr>
<tr>
<td>cracked</td>
<td>1.2 (1.3)</td>
<td>0.3 (1.4)</td>
</tr>
</tbody>
</table>

MP: methylpentane; DMB: dimethylbutane.
Optimum catalyst: Nanoporous treated 1.0 wt% Pd/35 wt% Al₂O₃/65 wt% H-BEA zeolite (SiO₂/Al₂O₃ = 25).
Known technology catalyst: 1.0 wt% Pd/H-BEA zeolite (SiO₂/Al₂O₃ = 25).
Reaction temperature: 280 °C; LHSV: 3.8 h⁻¹; Pressure: 0.12 MPa; Molar ratio of C₆H₁₄/H₂: 1/15.

References

要 旨
ノルマルヘキサン異性化用のナノサイズアルミナ複合ベータゼオライト担持パラジウム触媒

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ナノサイズアルミナの一種であるノルマルヘキサンから、イソパラフィン、特に多分解イソパラフィンを選択的に合成できる触媒の開発を行った。白金族／ナノ酸化物／ゼオライト複合触媒の最適化を行ったところ、1.0 wt% Pt/Na2O/Al2O3/H-BEA 触媒が最も高選択性であり、多分岐体の収率が増加したと考えられる。さらには、ゼオライト酸処理を行うことでも収率率や選択性が向上したことから、ゼオライト表面の Si-OH とナノサイズアルミナの Al-OH の間で形成される新たな酸点は、特に異性化の活性点として作用し、高選択性、イソパラフィン選択性を向上させることが示された。その活性点の近傍に高分散に存在するパラジウムによって、分解反応の抑制や高構造率・高選択性に繋がったと推測される。

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