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NiMo/Al₂O₃ Promoted Hybrid Catalysts of Nanosized Alumina and Beta Zeolite for Hydrocracking with Isomerization

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An efficient catalyst is desired to produce lighter isoparaffins from heavy *n*-paraffins by isomerization and hydrocracking, which are environmentally friendly processes for producing high-octane fuel. This paper assesses the suitability of a catalyst consisting of beta zeolite and nanosized (*i.e.*, 5–50 nm; hereafter *ns*) alumina particles for isomerization and hydrocracking of large *n*-paraffins. The catalytic performances of three catalysts, namely an alumina-supported metal catalyst (NiMo/ γ -Al₂O₃), a two-component catalyst (*ns* Al₂O₃–beta zeolite), and a three-component catalyst (NiMo/ γ -Al₂O₃–*ns* Al₂O₃–beta zeolite) for an isothermal reaction with *n*-hexadecane were evaluated. The results reveal that the conversion and selectivity are improved by increasing the number of components in a catalyst. Specifically, the three-component catalyst exhibits superior catalytic performance between 225 and 350 °C due to concerted effect of the three components. We investigated the effect of the SiO₂/Al₂O₃ molar ratio of beta zeolite on the performance of three-component catalysts and found that beta zeolite with a SiO₂/Al₂O₃ molar ratio of 25 has a higher activity and cracking selectivity with high isoparaffin selectivity of the cracked products (hereafter *iso*-selectivity) than three-component catalysts with SiO₂/Al₂O₃ molar ratios of 16, 50, and 150; this indicates that there is an optimum SiO₂/Al₂O₃ molar ratio of zeolite in the three-component catalyst. The three-component catalyst composed of NiMo/ γ -Al₂O₃, *ns* Al₂O₃, and dealuminated beta zeolite had a high conversion and *iso*-selectivity. Its catalytic performance is more suitable for producing isoparaffins of gasoline fraction than these of three three-component catalysts composed of *ns* Al₂O₃ and non-dealuminated beta zeolite, *ns* SiO₂ and non-dealuminated beta zeolite, or *ns* SiO₂ and dealuminated beta zeolite. Acid treating was found to remove extra-framework aluminum and amorphous alumina from the beta zeolite surface to make Si–OH. It produced reformed acid sites between the Si–OH of the external zeolite surface and *ns* Al₂O₃ surfaces, which consequently improved the isomerization and cracking activities due to the acid sites existing at nanopores.

Keywords

Hydrocracking, Isoparaffin, Beta zeolite, Nanosized oxide, Three-component catalyst, Dealumination

1. Introduction

Recently, gasoline has been produced by reforming naphtha and/or fluidized-bed catalytic cracking of hydrotreated vacuum gas oil. The oil produced by these processes contains a large amount of aromatic and olefin components that give it a high octane value. However, recent fuel quality regulations reduce the permissible levels of aromatics and olefin. Consequently, an efficient catalyst is desired to produce lighter isoparaffins from heavy paraffins by isomerization and hydrocracking to produce high-octane gasoline.

Catalysts that have been developed for hydrocracking can be broadly grouped into amorphous (*i.e.*, non-crystalline) and zeolite (*i.e.*, crystalline) catalysts. Amorphous catalysts are composite oxides made from

amorphous substances such as silica–alumina, alumina, and silica–titania, which exhibit solid acidity and have a controlled pore structure. Mild hydrocracking activities can be achieved by including a non-zeolitic promoter such as boron or supporting metals such as Ni–Mo (hereafter, NiMo)^{1)–3)}. The hydrocracking activity of amorphous catalysts in cracking and isomerization can be enhanced by incorporating a strong non-zeolitic acid such as heteropolyacids, tungsta-sulfate, and zirconia^{4)–7)}. Hydrogenation and dehydrogenation can be achieved and modified by using noble metals such as Pt and Pd^{8)–13)}. On the other hand, zeolite catalysts are composed of H-type zeolite as solid acid. They have a high cracking ability since they have a high degree of acidity and their activity is higher without any enhancement than that of amorphous catalysts. The hydrogenation and dehydrogenation function of zeolite catalysts is imparted and modified by NiMo or noble metals such as Pt and Pd^{14)–21)}. Some hybrid catalysts that are a

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mixture of amorphous and zeolite catalysts have been developed^{22)~24)}. Furthermore, hydrocracking and isomerization have been investigated in the mechanism^{25)~27)}.

In our recent research on catalysts, we have intentionally focused on zeolite catalysts containing various subnanometer pores and unimodal nanoporous oxides with pore sizes ranging from about 1 nm to several tens of nanometers. This research has resulted in some advances in catalyst designing in various industrial applications, including hydrodesulfurization^{28),29)}, N₂O decomposition³⁰⁾, hydrocracking^{31),32)}, and catalytic cracking^{33)~35)}. As hydrocracking catalysts, we studied efficient hydro-reform catalysts that have a high selectivity for producing lower isoparaffins from higher *n*-paraffin; this promises to produce an environmentally friendly gasoline³²⁾. We studied the catalytic performance of these catalysts in converting *n*-hexadecane (*n*-C₁₆H₃₄) into isoparaffins with carbon numbers in the range 6 to 12. Three-component nanoporous and *ns* catalysts composed of NiMo/ γ -Al₂O₃, *ns* oxide, and crystalline zeolite (several tens of nanometers in size) had relatively high activities and selectivities due to cooperation between NiMo/ γ -Al₂O₃ and the *ns* oxide and zeolite composite. The NiMo/ γ -Al₂O₃ component, which is responsible for the skeletal isomerization activity, enhances the cracking activity of the composite of *ns* Al₂O₃ and ultrastable Y (USY) zeolite; this yields isoparaffins with carbon numbers in the range 6 to 12 since isomerization of *n*-hexadecane follows cracking. A catalyst composed of USY zeolite (molar ratio of SiO₂ to Al₂O₃ = 12) could not be activated by *ns* SiO₂, but it could be activated by *ns* Al₂O₃. This activation depends on the SiO₂/Al₂O₃ molar ratio of USY zeolite. The catalytic properties of the three components partially depend on active sites that form at interfaces between *ns* oxides and the zeolite. These active sites play a major role in isomerization and cracking as moderate and strong acids. They are generated when Si-OH in the nanopores of the USY zeolite produced by dealumination traps Al-OH in the *ns* Al₂O₃ precursor. On the other hand, we found that catalysts composed of beta zeolite or ZSM-5 (hereafter, MFI) zeolite are activated more by *ns* SiO₂ than *ns* Al₂O₃ and that they have higher activities than a catalyst composed of USY zeolite³²⁾. Overcracking that produced a gaseous component was observed when a catalyst composed of MFI zeolite was used. Therefore, with the aim of obtaining a more efficient catalyst of hydrocracking and isomerization for producing isoparaffins in this study, three-component catalysts composed of NiMo/ γ -Al₂O₃, *ns* oxide, and beta zeolite were investigated. The effect of cooperation between the *ns* oxide and the beta zeolite on catalysis of hydrocracking and isomerization for heavier paraffins was also studied.

2. Experimental

2.1. Materials and Catalyst Preparation

Three catalysts, namely (a) a metal-supported alumina catalyst (NiMo/ γ -Al₂O₃), (b) a two-component catalyst (beta zeolite and *ns* Al₂O₃), and (c) a three-component catalyst (metal, beta zeolite, and *ns* Al₂O₃), were prepared to bring out the combined effects of the three catalyst components on catalysis.

The NiMo/ γ -Al₂O₃ catalyst was prepared by co-impregnation using the incipient wetness method. Two catalysts were loaded with 0.39 and 0.36 g/g-Al₂O₃ of Ni(NO₃)₂·6H₂O and (NH₄)₆Mo₇O₂₄·4H₂O in the following manner. A laboratory-produced Al₂O₃ extrudate with 11-nm unimodal pores and a high surface area of 225 m²/g was used as the metal carrier. 100 g of the alumina extrudate was impregnated with the NiMo metal solution. A solution of 39 g of nickel nitrate hexahydrate [Ni(NO₃)₂·6H₂O] was prepared in 40 mL of water. Similarly, 36 g of hexaammonium heptamolybdate tetrahydrate [(NH₄)₆Mo₇O₂₄·4H₂O] was dissolved in 40 mL of water and heated at 40-50 °C to dissolve the solid. The two solutions were mixed and quickly added to the extrudates. They were then mixed well to ensure that the alumina was homogeneously impregnated by the solution. The mixing and impregnation were performed quickly to avoid complex formation between the two solutions. The impregnated extrudate was aged overnight in a sealed container at room temperature. It was then dried at 120 °C for 5 h and calcined at 550 °C for 2 h.

A metal-impregnated alumina (NiMo/ γ -Al₂O₃) powder (particle size: 150 μ m) was obtained by grinding catalyst (a).

Cataloid AP-1 (JGC Catalysts and Chemicals Ltd.) was used as the *ns* Al₂O₃ precursor. It consists of 71.0 wt% alumina, 11.0 wt% acetic acid, and 18.0 wt% water and has an average particle size of 5.4 nm. For comparison with *ns* Al₂O₃, an *ns* silica gel (Aerosil 200, Nippon Aerosil Co., Ltd.) was used as *ns* SiO₂. It has an average primary particle size of *ca.* 12 nm.

We synthesized beta zeolites with various SiO₂/Al₂O₃ molar ratios from parent gels with different compositions by using tetraethyl ammonium hydroxide as a structure-directing agent at 165 °C. These zeolite powders were converted into H zeolites by conventional ion exchange with an aqueous solution of NH₄Cl. The beta zeolite had a typical SiO₂/Al₂O₃ molar ratio of 25 and it had a crystalline size of 40 nm. Surface Al species of this beta zeolite was dealuminated by acid treatment. 10 g of the beta zeolite powder was stirred in 500 mL of 0.2 M (1 M = 1 mol·dm⁻³) HCl solution at room temperature for 2 h.

ns Al₂O₃-beta zeolite catalyst (b) and NiMo/ γ -Al₂O₃-*ns* Al₂O₃-beta zeolite catalyst (c) were synthesized by wet mixing followed by calcination. Two or three of

these solid powders were mixed with water to form a thick paste and this paste was mechanically kneaded. After kneading, catalysts were extruded into pellets. They were then dried by leaving overnight at room temperature and heating at 120 °C for 12 h. Finally, they were calcinated at 550 °C for 3 h. The two- and three-component catalysts were made from *ns* Al₂O₃ and beta zeolite (dry weight ratio of 1 : 2) and with NiMo/ γ -Al₂O₃, *ns* Al₂O₃, and beta zeolite (dry weight ratio of 2 : 1 : 2), respectively.

2.2. Reaction Test and Catalyst Evaluation

The catalytic performances of the catalysts were evaluated using a feedstock, *n*-hexadecane (*n*-C₁₆H₃₄), which has a normal boiling point of 287 °C. This compound was selected as a model paraffin that contains gas and heavy oils. The light gas oil and the vacuum gas oil had boiling points in the range 232–566 °C. *n*-Hexadecane is easy to handle since it is the heaviest *n*-paraffin that is a liquid at room temperature and is difficult to crack.

A continuous-flow reactor with a fixed bed catalyst volume of 1.0 mL was used for reaction tests at temperatures in the range 200–350 °C under hydrogen pressure. Typical reaction conditions were: gaseous hourly space velocity (GHSV): 5000 h⁻¹; pressure: 0.12 MPa; molar ratio of C₁₆H₃₄ : H₂ = 1 : 15. Prior to the reaction test, all the catalysts were reduced by H₂ flow (GHSV: 5000 h⁻¹; 550 °C; 3 h).

2.3. Catalyst Characterization

We measured the SiO₂/Al₂O₃ molar ratio of the surface layer and framework of beta zeolites by X-ray photoelectron spectroscopy with Ar etching. We also studied the zeolite structures by ²⁹Si- and ²⁷Al-magic angle spinning nuclear magnetic resonance (MAS NMR). NH₃ temperature-programmed desorption (TPD) profiles of three-component catalysts (NiMo/ γ -Al₂O₃-*ns* Al₂O₃-beta zeolite, NiMo/ γ -Al₂O₃-*ns* Al₂O₃-dealuminated beta zeolite, NiMo/ γ -Al₂O₃-*ns* SiO₂-beta zeolite, and NiMo/ γ -Al₂O₃-*ns* SiO₂-dealuminated beta zeolite) were obtained under the following conditions. Catalyst weight: 50.0 mg, pretreatment conditions: 600 °C, 3 h, 50 mL/min He, NH₃ adsorption conditions: 13.3 kPa, 100 °C, 30 min, and measurement in He with 0.1 % Ar: 50 mL/min, heating rate: 10 °C/min.

3. Results and Discussion

3.1. Combined Effect of Catalyst Components on Activity and Selectivity

In this study, we investigated three catalysts: metal-supported alumina catalyst (NiMo/ γ -Al₂O₃), a two-component catalyst (*ns* Al₂O₃-beta zeolite) and a three-component catalyst (NiMo/ γ -Al₂O₃-*ns* Al₂O₃-beta zeolite). The three-component catalyst, whose components have different functions, reveals the combined

GHSV: 5000 h⁻¹, pressure: 0.12 MPa, molar ratio of C₁₆H₃₄/H₂: 1/15. □: metal-supported alumina catalyst (NiMo/ γ -Al₂O₃), △: two-component catalyst (*ns* Al₂O₃-beta zeolite), ●: three-component catalyst (NiMo/ γ -Al₂O₃-*ns* Al₂O₃-beta zeolite), ○: conversion estimated by interpolating weight.

Fig. 1 *n*-Hexadecane Conversion (hydrocracking and isomerization) Rates

effect of the three components. Comparing the catalytic performances of these three catalysts will reveal the function of *ns* Al₂O₃. Figure 1 shows the conversions for *n*-hexadecane at temperatures in the range 200 to 350 °C of the three catalysts and Fig. 2 shows their product distribution selectivities at 300 °C.

These catalytic performances are considered to be due to individual or combined functions that follow the reaction paths below:

where, “isoparaffins (C₄–C₁₂)” means isoparaffins with carbon numbers in the range 4 to 12. Hereafter, the authors defined the expression of paraffins “with carbon numbers in the range *n* to *m*” as “(C_{*n*}–C_{*m*})” for the simplification of the expression in this paper, *e.g.* cracked products (C₃–C₁₃): cracked products with the carbon numbers in the range 3 to 13; *n*-paraffins (C₁–C₁₆): normal paraffins with the carbon numbers in the range 1 to 16.

The metal-supported alumina catalyst (NiMo/ γ -Al₂O₃; □ in Fig. 1) has the lowest conversion of the three catalysts over the whole temperature range; its conversion increases monotonically from below 1 % at 200 °C to *ca.* 10 % at 350 °C with increasing temperature. The isomerization reaction of path (1) is thought to occur when the NiMo/ γ -Al₂O₃ catalyst is used since *i*-hexadecane is the main product. The NiMo/ γ -Al₂O₃ catalyst is considered to work as a dual function cata-

Reaction temperature: 300 °C, GHSV: 5000 h⁻¹, pressure: 0.12 MPa, molar ratio of C₁₆H₃₄/H₂: 1/15. Shaded region: isoparaffins, white region: *n*-paraffins.

Fig. 2 Product Distributions of (a) Metal-supported Alumina Catalyst (NiMo/ γ -Al₂O₃), (b) Two-component Catalyst (*ns* Al₂O₃-beta zeolite), and (c) Three-component Catalyst (NiMo/ γ -Al₂O₃-*ns* Al₂O₃-beta zeolite)

lyst of Ni metal and acidic molybdena-alumina, of which acidity is known to be controlled for different extents of reduction³⁶. The two-component catalyst (*ns* Al₂O₃-beta zeolite; $\triangle$) gives a higher conversion than the NiMo/ γ -Al₂O₃ catalyst. The cracked products are *n*- and isoparaffins (C₃-C₁₃), indicating that the hydrocracking reaction of path (2) and (3) consecutively proceed. The three-component catalyst (NiMo/ γ -Al₂O₃-*ns* Al₂O₃-beta zeolite; $\bullet$) gives a similar conversion to that of the two-component catalyst. The conversion on the three-component catalyst ($\circ$) was estimated by interpolating the weight compositions with the conversions for the metal-supported alumina and two-component catalysts based on first-order kinetics, which was confirmed by varying the liquid hourly space velocity. The actual conversion for the three-component catalyst is higher than the estimated conversion. Furthermore, in the actual three-component catalyst case, the main products are not *n*-paraffins but isoparaffins (C₆-C₁₂). The NiMo/ γ -Al₂O₃ component, which is responsible with acidic components for the skeletal isomerization activity, not only enhances the cracking activity of the composite of *ns* Al₂O₃ and beta zeolite but also controls the carbon numbers of cracked products: this mainly yields isoparaffins (C₄-C₁₂) since cracking occurred after isomerization of *n*-hexadecane and cracked positions were shifted to inner C-C bonds.

GHSV: 5000 h⁻¹, pressure: 0.12 MPa, molar ratio of C₁₆H₃₄/H₂: 1/15. $\square$: metal-supported alumina catalyst (NiMo/ γ -Al₂O₃), $\triangle$: two-component catalyst (*ns* Al₂O₃-beta zeolite), $\bullet$: three-component catalyst (NiMo/ γ -Al₂O₃-*ns* Al₂O₃-beta zeolite), $\circ$: conversion estimated by interpolating weight.

Fig. 3 Cracking Selectivity of *n*-Hexadecane for Catalysts

Therefore, the isomerization reaction of path (1) and the hydrocracking reaction of path (4) are thought to mainly proceed for the three-component catalyst. It is considered that in this case the path (4) includes consecutive path (3) to result a dominance of isoparaffins in the products.

The cracking selectivity [cracked products (C₁-C₁₅)/products (C₁-C₁₆) excepting *n*-C₁₆], and the *iso*-selectivity of the cracked products [isoparaffins (C₄-C₁₅)/cracked products (C₁-C₁₅)] were obtained from product yield data. For the three catalysts in the temperature range 275 to 350 °C, Fig. 3 shows the relationships between the conversion of *n*-hexadecane and the cracking selectivity and Fig. 4 shows the relationship between the conversion of *n*-hexadecane and the *iso*-selectivity. The conversion and the selectivity are increased by using catalysts containing more components. Although the estimated data for the three-component catalyst are intermediate between the data for the NiMo/ γ -Al₂O₃ catalyst and the data for the two-component catalyst, the actual data for the three-component catalyst has higher conversions and selectivities. This indicates that a concerted reaction occurs on the three-component catalyst. Just like for a three-component catalyst containing USY zeolite (NiMo/ γ -Al₂O₃-*ns* Al₂O₃-USY zeolite)³², a combined effect was confirmed for a three-component catalyst containing beta zeolite (NiMo/ γ -Al₂O₃-*ns* Al₂O₃-beta zeolite). Moreover, the three-component catalyst containing beta zeolite has a higher cracking activity and a higher selectivity despite beta zeolite having a higher SiO₂/Al₂O₃ molar ratio (approximately 25) than USY zeolite (about 12).

3.2. Effect of Reaction Temperature on Product Distribution

Figure 5 shows the product distributions on three-component catalyst (NiMo/ γ -Al₂O₃-*ns* Al₂O₃-beta zeolite) at six different reaction temperatures in the range 225–350 °C. The product distributions at any temperature between 225 and 350 °C consist of isomerized

C₁₆H₃₄, cracked products consisting mainly of isoparaffins (C₄–C₁₂), and minor *n*-paraffins (C₃–C₈). The ratio of cracked to converted products (*i.e.*, the cracking selectivity) varies with the temperature. Lower *n*-paraffins (C₃–C₆) were produced more at 325 and 350 °C. At the higher temperatures the path (2) proceeds even on the three-component catalyst.

The cracking selectivity, the *iso*-selectivity, and the average carbon number of the cracked products (C₁–C₁₅) were obtained from the data in Fig. 5. Figure 6 shows the reaction temperature dependencies of the *n*-hexadecane conversion, the cracking selectivity, the *iso*-selectivity, and the average carbon number of cracked products. Except for the large increase in the cracking selectivity between 225 and 250 °C, the selectivities vary little with temperature. The conversion increases gradually as the temperature increases from 225 to 350 °C. Therefore, the ratio of the isomerization reaction of path (1) to the hydrocracking reaction of path (4) varies little at reaction temperatures above 250 °C. As Fig. 7 shows, the ratio of the selectivity of path (4) to path (1) increases monotonically with increasing conversion. As the *iso*-selectivity and the average carbon number of the cracked products remain almost constant, the selectivities are largely independent on the degree of the reaction progress, rather they substantially reflect the catalytic ability being effective to the reaction path.

GHSV: 5000 h⁻¹, pressure: 0.12 MPa, molar ratio of C₁₆H₃₄/H₂: 1/15.
□: metal-supported alumina catalyst (NiMo/ γ -Al₂O₃), △: two-component catalyst (*ns* Al₂O₃-beta zeolite), ●: three-component catalyst (NiMo/ γ -Al₂O₃-*ns* Al₂O₃-beta zeolite), ○: conversion estimated by interpolating weight.

Fig. 4 *iso*-Selectivity of *n*-Hexadecane Hydrocracking for Nanoporous Catalysts

GHSV: 5000 h⁻¹, pressure: 0.12 MPa, molar ratio of C₁₆H₃₄/H₂: 1/15.
Shaded regions: isoparaffins, white regions: *n*-paraffins.

Fig. 5 Product Distributions on Three-component Catalyst at Six Different Temperatures: (a) 225, (b) 250, (c) 275, (d) 300, (e) 325, and (f) 350 °C

GHSV: 5000 h⁻¹, pressure: 0.12 MPa, molar ratio of C₁₆H₃₄/H₂: 1/15, catalyst: NiMo/γ-Al₂O₃-*ns* Al₂O₃-beta zeolite.
●: conversion, ○: cracking selectivity, △: *iso*-selectivity, □: average carbon number of cracked products.

Fig. 6 Dependencies of Conversions and Selectivities of *n*-Hexadecane Hydrocracking over Three-component Catalyst on Reaction Temperature

GHSV: 5000 h⁻¹, pressure: 0.12 MPa, molar ratio of C₁₆H₃₄/H₂: 1/15, catalyst: NiMo/γ-Al₂O₃-*ns* Al₂O₃-beta zeolite.
○: cracking selectivity, △: *iso*-selectivity, □: average carbon number of cracked products.

Fig. 7 Dependencies of Selectivities of *n*-Hexadecane Hydrocracking over Three-component Catalyst on Conversion

3.3. Effect of SiO₂/Al₂O₃ Ratio of Beta Zeolite in Three-component Catalyst on Activity and Selectivity

As for a three-component catalyst consisting of NiMo/γ-Al₂O₃, *ns* Al₂O₃ and beta zeolite with a weight ratio of 2 : 1 : 2, we investigated how the kind of zeolite in this catalyst affects the reaction performance by using beta zeolites with SiO₂/Al₂O₃ molar ratios of 16, 25, 50, and 150. In a previous study³²⁾, we measured the *n*-hexadecane conversion and the C₁-C₁₆ selectivity of three-component catalysts containing USY zeolite with SiO₂/Al₂O₃ molar ratios of 6 and 12; however, it was

GHSV: 5000 h⁻¹, pressure: 0.12 MPa, molar ratio of C₁₆H₃₄/H₂: 1/15, catalyst: NiMo/γ-Al₂O₃-*ns* Al₂O₃-beta zeolite.
SiO₂/Al₂O₃ molar ratios: 16 (○), 25 (△), 50 (□), 150 (◇).

Fig. 8 Combined Effect on SiO₂/Al₂O₃ Molar Ratio of Beta Zeolite in Three-component Catalyst

not possible to determine whether there is an optimum SiO₂/Al₂O₃ molar ratio in that study since only two SiO₂/Al₂O₃ molar ratios were used.

Figure 8 shows that the *n*-hexadecane conversion on three-component catalysts containing beta zeolite depends on both reaction temperature and the SiO₂/Al₂O₃ molar ratio of beta zeolite. The conversions decrease similarly at each reaction temperature in the order of the SiO₂/Al₂O₃ molar ratio: 25 > 50 > 150 > 16. **Figure 9** shows that the C₁-C₁₆ selectivity at 300 °C on three-component catalysts containing beta zeolite depends on the SiO₂/Al₂O₃ molar ratio of beta zeolite. The C₁-C₁₆ selectivity changed from skeletal isomerized product (C₁₆) to cracked products (C₃-C₁₂) with increase of the SiO₂/Al₂O₃ molar ratio and the distribution of the cracked products (C₃-C₁₂) also changed from wide to narrow (mainly C₆-C₉). **Figure 10** shows that the conversion, the cracking selectivity, the *iso*-selectivity, and the average carbon number of the cracked products at 300 °C depend on the SiO₂/Al₂O₃ molar ratios of beta zeolite. Of the catalysts containing beta zeolite with SiO₂/Al₂O₃ molar ratios of 16, 25, 50, and 150, the catalyst containing beta zeolite with a SiO₂/Al₂O₃ molar ratio of 25 has the highest conversion with the higher cracking and *iso*-selectivities.

Figure 11 shows the dependence of the relationship between the conversion and the selectivities on the SiO₂/Al₂O₃ molar ratio of beta zeolite. They have similar reaction performances in terms of both conversion and selectivity. Except for the changes in the conversion and the cracking selectivity between SiO₂/Al₂O₃ molar ratios of 16 and 25, no large differences were observed for catalysts containing beta zeolite with different SiO₂/Al₂O₃ molar ratios. The optimum SiO₂/Al₂O₃ molar ratio was found to be about 25, which

Reaction temperature: 300 °C, GHSV: 5000 h⁻¹, pressure: 0.12 MPa, molar ratio of C₁₆H₃₄/H₂: 1/15, catalyst: NiMo/ γ -Al₂O₃-*ns* Al₂O₃-beta zeolite.

Shaded region: isoparaffins, white region: *n*-paraffins.

Fig. 9 Product Distributions of Three-component Catalysts with SiO₂/Al₂O₃ Molar Ratios for Beta Zeolite of (a) 16, (b) 25, (c) 50, and (d) 150

implies that the formation of active cracking sites depends on the SiO₂/Al₂O₃ molar ratio of beta zeolite.

Regarding active cracking sites, based on the observed dependencies of the activity and the selectivity on the SiO₂/Al₂O₃ molar ratio, the activity and the selectivity are considered to depend on the aluminum species in the surface layer of the zeolite particles. Because, it is expected that the optimum SiO₂/Al₂O₃ molar in case of plural-component catalyst would be developed by the existence of surrounds of the zeolite component. Therefore, beta zeolite dealuminated by acid treating was used in this study to clarify the role of the aluminum species in the zeolite in the three-component catalyst.

3. 4. Effect of Dealumination of Beta Zeolite on Concerted Reaction with *ns* Oxide

Figure 12 compares *n*-hexadecane conversion using three-component catalysts containing non-dealuminated or dealuminated beta zeolite and *ns* Al₂O₃. The catalyst containing dealuminated zeolite has a higher *n*-hexadecane conversion than the catalyst containing

Reaction temperature: 300 °C, GHSV: 5000 h⁻¹, pressure: 0.12 MPa, molar ratio of C₁₆H₃₄/H₂: 1/15, catalyst: NiMo/ γ -Al₂O₃-*ns* Al₂O₃-beta zeolite (SiO₂/Al₂O₃ ratio: 16-150).

●: conversion, ○: cracking selectivity, △: *iso*-selectivity, □: average carbon number of cracked products.

Fig. 10 Dependencies of Cracking and *iso*-Selectivity of *n*-Hexadecane Hydrocracking of a Three-component Catalyst on SiO₂/Al₂O₃ Ratio

Reaction temperature: 300 °C, GHSV: 5000 h⁻¹, pressure: 0.12 MPa, molar ratio of C₁₆H₃₄/H₂: 1/15, catalyst: NiMo/ γ -Al₂O₃-*ns* Al₂O₃-beta zeolite (SiO₂/Al₂O₃ molar ratio: 16-150).

○: cracking selectivity, △: *iso*-selectivity, □: average carbon number of cracked products.

Fig. 11 Dependencies of Cracking and *iso*-Selectivity of *n*-Hexadecane Hydrocracking over Three-component Catalyst on Conversion

non-dealuminated zeolite. Figure 13 shows a similar comparison for catalysts containing non-dealuminated and dealuminated beta zeolite with *ns* SiO₂; it shows that the catalyst with dealuminated zeolite is less active than that with non-dealuminated zeolite. Furthermore, of the catalysts containing non-dealuminated zeolite, the one with *ns* SiO₂ is more active than the one with *ns* Al₂O₃ (see Fig. 13). Therefore, the *n*-hexadecane conversions of the four three-component decrease in the order: *ns* Al₂O₃/dealuminated $\approx$ *ns* SiO₂/non-dealuminated > *ns* Al₂O₃/non-dealuminated $\approx$ *ns* SiO₂/dealuminated.

GHSV: 5000 h⁻¹, pressure: 0.12 MPa, molar ratio of C₁₆H₃₄/H₂: 1/15.
○: NiMo/γ-Al₂O₃-*ns* Al₂O₃-beta zeolite, ●: NiMo/γ-Al₂O₃-*ns* Al₂O₃-dealuminated beta zeolite.

Fig. 12 Effect of Zeolite Dealumination on Cracking Activity of Three-component Catalyst

GHSV: 5000 h⁻¹, pressure: 0.12 MPa, molar ratio of C₁₆H₃₄/H₂: 1/15.
○: NiMo/γ-Al₂O₃-*ns* Al₂O₃-beta zeolite, △: NiMo/γ-Al₂O₃-*ns* SiO₂-beta zeolite, ▲: NiMo/γ-Al₂O₃-*ns* SiO₂-dealuminated beta zeolite.

Fig. 13 Effect of Zeolite Dealumination on Activity of Three-component Catalyst of Beta Zeolite with *ns* SiO₂

As Fig. 14 shows, the four catalysts have different product distributions for C₅-C₁₂ but exhibit similar tendencies. The product distribution of the catalyst containing non-dealuminated zeolite and *ns* SiO₂ is shifted to a lower carbon number relative to those of the other three catalysts. This implies that the products of the catalyst consisting of *ns* SiO₂ and beta zeolite are more cracked than those of the catalyst consisting of *ns* Al₂O₃ and dealuminated beta zeolite. The product distributions of the other three catalysts have similar shapes and a peak at a carbon number of eight; consequently, they are preferable for the gasoline fraction.

Reaction temperature: 300 °C, GHSV: 5000 h⁻¹, pressure: 0.12 MPa, molar ratio of C₁₆H₃₄/H₂: 1/15, catalyst: NiMo/γ-Al₂O₃-*ns* oxide-beta zeolite without or with dealumination.
Shaded region: isoparaffins, white region: *n*-paraffins.

Fig. 14 Product Distributions of Three-component Catalysts NiMo/γ-Al₂O₃-*ns* Oxide-Beta Zeolite (a) *ns* Al₂O₃ /non-dealuminated, (b) *ns* Al₂O₃/dealuminated, (c) *ns* SiO₂/non-dealuminated, (d) *ns* SiO₂/dealuminated

Figure 15 shows that the cracking selectivities decrease in the order: *ns* Al₂O₃/dealuminated ≈ *ns* SiO₂/non-dealuminated > *ns* SiO₂/dealuminated > *ns* Al₂O₃/non-dealuminated. The cracking selectivities on the catalysts containing dealuminated zeolite increase with the conversion increase due to reaction temperature increase though the selectivities on the catalysts containing non-dealuminated zeolite decrease reversely. This result suggests that the cracking sites as moderate and strong acids may be generated at the surface layer of the dealuminated zeolite by the dealumination before composing with *ns* oxides, which make acid sites for isomerization with the dealuminated zeolite surface.

3.5. Characterization of Three-component Catalyst Consisting of *ns* Oxide and Non-dealuminated or Dealuminated Beta Zeolite

The results of X-ray photoelectron spectroscopy with Ar etching reveal that the surface layers of the non-dealuminated and dealuminated beta zeolites have SiO₂/Al₂O₃ molar ratios of 25 and 40, respectively. However, as the ²⁹Si-MAS NMR results in Fig. 16

show, the $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratios of the zeolite structures of the non-dealuminated and dealuminated beta zeolites are very similar, indicating that the zeolite structure is only slightly dealuminated. We conjecture that the aluminum species on the surface of beta zeolite are removed without greatly altering the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of the beta zeolite structure and that Si-OH groups form on the surface of beta zeolite through aluminum removal.

Figure 17 shows NH_3 TPD profiles of the four three-component catalysts. There are three broad kinds of

acid sites: weak, moderate and strong acid sites, of which acid amounts are summarized in Table 1. Catalysts with *ns* Al_2O_3 have more strong acid sites than catalysts with *ns* SiO_2 . For both *ns* oxides, the amount of strong acid sites increases and the amount of weak acid sites decreases after dealumination of the zeolite component. The activity of the three-component catalyst composing of *ns* SiO_2 and dealuminated beta zeolite reflects a reduction in the amount of weak and moderate acid sites rather than an increase in the amount of strong acid sites, which might explain the result for the cracking selectivity shown in Fig. 15.

GHSV: 5000 h^{-1} , pressure: 0.12 MPa, molar ratio of $\text{C}_{16}\text{H}_{34}/\text{H}_2$: 1/15.
○: NiMo/ γ - Al_2O_3 -*ns* Al_2O_3 -beta zeolite, ●: NiMo/ γ - Al_2O_3 -*ns* Al_2O_3 -dealuminated beta zeolite, △: NiMo/ γ - Al_2O_3 -*ns* SiO_2 -beta zeolite, ▲: NiMo/ γ - Al_2O_3 -*ns* SiO_2 -dealuminated beta zeolite.

Fig. 15 Product Distributions for Non-dealuminated and Dealuminated NiMo/ γ - Al_2O_3 -*ns* Oxide-Beta Zeolite

Fig. 16 ^{29}Si -MAS NMR Spectra of (upper) Non-dealuminated and (lower) Dealuminated Beta Zeolite

○: NiMo/ γ - Al_2O_3 -*ns* Al_2O_3 -beta zeolite, ●: NiMo/ γ - Al_2O_3 -*ns* Al_2O_3 -dealuminated beta zeolite, △: NiMo/ γ - Al_2O_3 -*ns* SiO_2 -beta zeolite, ▲: NiMo/ γ - Al_2O_3 -*ns* SiO_2 -dealuminated beta zeolite.

Fig. 17 NH_3 TPD Profiles of Three-component Catalysts

Table 1 Acid Amount of Three-component Catalysts

Catalyst	Acid amount [mmol/g-cat]			
	Weak ^{a)}	Moderate ^{b)}	Strong ^{c)}	Total
NiMo/ γ -Al ₂ O ₃ - <i>ns</i> Al ₂ O ₃ -beta zeolite	0.63	0.07	0.12	0.82
NiMo/ γ -Al ₂ O ₃ - <i>ns</i> Al ₂ O ₃ -dealuminated beta zeolite	0.47	0.07	0.14	0.68
NiMo/ γ -Al ₂ O ₃ - <i>ns</i> SiO ₂ -beta zeolite	0.61	0.06	0.07	0.74
NiMo/ γ -Al ₂ O ₃ - <i>ns</i> SiO ₂ -dealuminated beta zeolite	0.43	0.03	0.10	0.56

a) 200 °C peak. b) 310 °C peak. c) 410 °C peak.

The four catalysts have different surface models for the interface between *ns* oxides and beta zeolite depending on whether they contain non-dealuminated or dealuminated beta zeolite with *ns* oxides. Acid sites like amorphous SiO₂-Al₂O₃ are generated between *ns* SiO₂ and the aluminum species on non-dealuminated beta zeolite surfaces. Dealumination of beta zeolite by acid treating is effective in removing the aluminum species on the beta zeolite surface; consequently, acid sites form between Si-OH of the dealuminated zeolite and *ns* Al₂O₃. The reformation of these acid sites observed in **Fig. 17** and **Table 1** enhances the conversion and the isomerization selectivity on the catalyst containing *ns* Al₂O₃ with dealuminated zeolite. The reformed acid sites on the zeolite surface function as active sites for isomerization and mild cracking.

4. Conclusion

A three-component catalyst consisting of beta zeolite, *ns* Al₂O₃, and NiMo/ γ -Al₂O₃ has a relatively high selectivity for hydro-reforming large *n*-paraffins to lighter isoparaffins. Its enhanced catalytic performance is due to the combined effects of zeolite, *ns* Al₂O₃, and NiMo/ γ -Al₂O₃. Its catalytic performance depends on the state of the zeolite; beta zeolite with *ns* SiO₂ is more active than that with *ns* Al₂O₃, whereas dealuminated beta zeolite with *ns* Al₂O₃ is even more active than that with *ns* SiO₂. A higher SiO₂/Al₂O₃ ratio of the zeolite enhances the cracking activity of the catalyst. Since acid treating removes unstable aluminum from the surface of beta zeolite, the SiO₂/Al₂O₃ ratio of the surface increases; in contrast, the SiO₂/Al₂O₃ ratio of framework remains almost constant. Catalysts containing dealuminated beta zeolite have a high cracking activity on their surfaces and retain a high isomerization activity within them. Catalysts containing dealuminated beta zeolite with *ns* Al₂O₃ have a high conversion and *iso*-selectivity; their catalytic performances are suitable for producing isoparaffins for gasoline fraction.

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要 旨

異性化・水素化分解用の NiMo/Al₂O₃ 促進ナノサイズアルミナ複合ベータゼオライト触媒

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重質な直鎖パラフィンを高オクタン価な軽質イソパラフィンへ転換するための水素化分解・異性化反応に有効な触媒開発を実施した。 γ -アルミナ担持 NiMo 触媒に、ナノサイズアルミナと BEA ゼオライトを組み合わせた触媒を *n*-C16 を原料とした反応系で触媒性能を検討した。単元系から多元系へと触媒を組み合わせることで転化率およびイソパラフィンへの選択性が向上した。BEA ゼオライトの骨格 SiO₂/Al₂O₃ 比の触媒性能に与える影響を検討したところ、SiO₂/Al₂O₃ 比 25 が転化率、選択性ともに最適値であった。BEA ゼオライトの USY 化には酸洗浄が有効であり、この脱アルミナ BEA ゼオライトとナノサイズ

アルミナを組み合わせた系は転化率、選択性ともにさらに向上した。しかし、この系のナノサイズアルミナの代わりにナノサイズシリカを組み合わせても転化率、選択率の向上は見られなかった。このことは、酸洗浄によってゼオライト表面に生成した 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が分解および異性化の活性点として作用し、*n*-パラフィン転化率、イソパラフィン選択率を向上させると推定できた。結果として、多元系に組み合わせることで触媒性能に与える相乗効果、すなわち分解性能と異性化選択性の向上が明確となった。