Development of Pt/Zeolite for Selective Conversion of \( n \)-Decane and \( n \)-Dodecane to \( i \)-C6-7 and \( i \)-C7-9

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Jet fuel production from long-chain \( n \)-paraffins obtained by hydrop processing of vegetable oils and animal fats has attracted immense interest. Isomerization and mild cracking are essential to transform long-chain \( n \)-paraffins with chain lengths of 16, 18, or 20 into bio-jet fuels consisting of isoparaffins with carbon numbers ranging from 9 to 15. Bifunctional catalysts consisting of noble metal and metal oxide support with solid acid, such as Pt loaded zeolite, are promising for hydroisomerization and cracking reactions. However, the effect of the specific properties of Pt loaded zeolite on the hydroisomerization and simultaneous mild cracking activity are not understood. We investigated the hydroisomerization and cracking of \( n \)-paraffins into isoparaffins with shorter chain length by 3-5 carbons over Pt loaded zeolite. \( n \)-Decane was first used as a reactant to simplify the reactions, and the effects of zeolite framework structure, solid acid sites, and Pt loading were investigated. 0.5 wt% Pt loaded MFI with Si/Al of 200 was found to maximize the targeted isoparaffin yield. Further modification of the optimized catalyst was performed for isoparaffin production from \( n \)-dodecane. Addition of MgO to the catalyst successfully suppressed overcracking and improved the desired isoparaffin yield.

Keywords
Hydroisomerization, Cracking, Platinum loaded zeolite, Long-chain \( n \)-paraffin, Isoparaffin, Magnesium addition

1. Introduction

Demand for aviation fuels continues to grow in contrast with the lower demand for other fuels to achieve reduction in greenhouse gas emissions, so the development of new production methods for jet fuel from non-petroleum raw materials has attracted immense interest\(^{1-4})\). Jet fuel mainly consists of isoparaffins with carbon numbers ranging from 9 to 15 to meet the jet fuel specifications, such as flash point, cold fluidity, and energy density.

Several processes have been proposed to obtain jet fuel from raw materials derived from biomass, such as hydrop processing of triglycerides\(^{5-7})\), alcohol polymerization\(^{8})\), and Fischer-Tropsch synthesis from synthesis gas (CO + H\(_2\))\(^{9})\). Hydrop processing of triglycerides derived from vegetable oils and animal fats is one of the most promising methods. In this process, triglycerides are first treated with H\(_2\) to convert glycerol and fatty acid moieties into propane and long-chain \( n \)-paraffins, respectively. Then, the long-chain \( n \)-paraffins are converted into jet fuel components. Most fatty acids in triglycerides contain 16, 18, or 20 carbon atoms. Therefore, isomerization and cracking reactions are required to convert the \( n \)-paraffins derived from vegetable oils and animal fats. In particular, control of the cracking reaction to adjust the number of carbon atoms and to suppress overcracking is essential to meet the jet fuel specification.

Transformation of \( n \)-paraffin to corresponding isoparaffin has been intensively studied\(^{10-13})\). The isomerization reaction is generally performed under hydrogen at pressures ranging from 0.1–8 MPa and temperature 280-350 °C over bifunctional catalyst containing metal and solid acids. Isomerization of \( n \)-paraffins over bifunctional catalysts is thought to undergo the following five steps\(^{11,13-16})\): (1) dehydrogenation on a metal site; (2) formation of carbenium ion on a solid acid site; (3) isomerization of the carbenium ion on the solid acid site; (4) desorption from the solid acid site as isoalkene; and (5) hydrogenation of isoalkene to isoparaffin on a...
metal site. Thus, noble metals, such as Pt, Pd, and Ru, and transition metals Ni and NiMo are used as the metal catalyst, and zeolites, SiO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3} and γ-Al\textsubscript{2}O\textsubscript{3}, are used as the solid acid catalyst and the support for the metal catalysts. Pt loaded zeolite has been intensively studied due to the high activity and selectivity. Zeolite with 1-dimensional pore structure consisting of 10-member ring pores is believed to be promising to enhance the isoparaffin yield because the cracking reaction is minimized\textsuperscript{20-23}. In addition, the addition of alkali metals, such as Mg, Ba and Ca, is reported to improve isomerization reaction selectivity as the additive metal reduces the solid acidity and amount\textsuperscript{17-19}.

Isoparaffins with smaller carbon chain length used in jet fuel are also obtained during the isomerization of long-chain \textit{n}-paraffins via the cracking reaction. Therefore, cracking has the potential to produce jet fuel from long-chain \textit{n}-paraffins. Hydroisomerization and simultaneous mild cracking of \textit{n}-paraffin was recently investigated over metal loaded zeolite catalysts\textsuperscript{13,20-23} using long-chain \textit{n}-paraffins with chain length ranging from 15 to 18. The reaction was conducted using similar catalysts and hydrogen pressure to isomerization at 290-400 °C. The yield of jet fuel fraction was only 20-30% due to the wide carbon number distribution caused by overcracking. The detailed effects of metal loading, solid acid sites and zeolite structure on product selectivity are not yet fully understood because various products were simultaneously formed which caused poor quantification of the reaction products, suggesting that suppression of overcracking was not adequate.

This study examined the effect of zeolite framework structure and acid-metal balance of Pt loaded zeolite on selective conversion of long-chain \textit{n}-paraffin to iso-paraffin with carbon chain length 3-5 carbons shorter than the reactant via hydroisomerization and mild cracking. The hydroisomerization and cracking reaction mechanism of \textit{n}-paraffin is generally considered to be independent of the carbon chain length whereas the reaction rate is affected by the carbon chain length\textsuperscript{4,16,24}. Therefore, first we selected \textit{n}-decane (\textit{n}-C10) as the reactant for optimization of the Pt loaded zeolite to simplify the expected reactions. Next, the optimized catalyst was applied to hydroisomerization and mild cracking of \textit{n}-dodecane (\textit{n}-C12) to examine whether the desired isoparaffins were formed. Finally, the catalyst was further modified to suppress overcracking of the desired isoparaffins. The catalyst investigated could be suitable for jet fuel production by adjusting the reaction conditions, such as reaction temperature and contact time, to utilize the same reaction mechanism.

2. Experimental

2.1. Catalyst Preparation

8 wt% H\textsubscript{2}PtCl\textsubscript{6} aqueous solution, 40 % colloidal silica (LUDOX\textsuperscript{®} HS-40), and triethylmethylammonium chloride (MTEACl, 97 % purity), were purchased from Sigma-Aldrich Japan. Tetraethyl orthosilicate (TEOS, 95 % purity), 10 % tetrapropylammonium hydroxide (TPAOH) aqueous solution, aluminum isopropoxide (98 % purity), sodium aluminate (Na\textsubscript{2}O/Al\textsubscript{2}O\textsubscript{3}=0.77 g/g), sodium hydroxide (97 % purity), sodium chloride (NaCl, 99 % purity), magnesium nitrate (Mg(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O, 99 % purity), distilled water, isopropanol (98 % purity), ammonium nitrate (NH\textsubscript{4}NO\textsubscript{3}, 98 % purity), \textit{n}-decane (\textit{n}-C10, 99.5 % purity), and \textit{n}-dodecane (\textit{n}-C12, 99.5 % purity) were purchased from FUJIFILM Wako Pure Chemical Corp., Japan. All chemicals were used without further purification.

Six types of zeolite structure, MFI, MTW, MOR, BEA, FAU, and FER, were used in this study. MOR (HSZ-640HOA; Si/Al = 9), BEA (HSZ-940HOA; Si/Al = 20), FAU (HSZ-371NHA; Si/Al = 12.5), and FER (HSZ-720NHA; Si/Al = 9) zeolites were purchased from Tosoh Corp., Japan. MFI and MTW zeolites were prepared by conventional hydrothermal synthesis\textsuperscript{25-29}. For MFI zeolite synthesis\textsuperscript{25,26}, aqueous solution was prepared by mixing TEOS, aluminum isopropoxide, TPAOH, and sodium chloride, transferred into a Teflon-sealed autoclave and treated at 150 °C for 3 days with rotation at 10 rpm. The Si/Al ratio ranged from 50-200. MTW zeolite was synthesized as reported\textsuperscript{27-29}. The synthetic gel was prepared by adding colloidal silica and sodium aluminate to sodium hydroxide aqueous solution containing MTEACl with vigorous stirring. After 24 h of mixing, the synthetic gel was transferred into a Teflon-sealed autoclave, and hydrothermal synthesis was performed at 150 °C for 7 days under the static condition. For both prepared zeolites, the sample was collected with a centrifuge, washed with isopropanol, dried overnight in an oven at 110 °C, and calcined at 550 °C for 12 h. The Na\textsuperscript{+} type zeolites were treated in NH\textsubscript{4}NO\textsubscript{3} aqueous solution to exchange Na\textsuperscript{+} ions on the solid acid sites of the zeolites to NH\textsubscript{4}\textsuperscript{+} ions. All zeolites were pretreated in a muffle furnace at 550 °C for 3 h to remove the adsorbed water and ammonia before the following treatments and analyses.

Incipient wetness impregnation was employed for loading Pt and Mg on the zeolites. In this study, H\textsubscript{2}PtCl\textsubscript{6} solution was used as the Pt precursor because it was more cost-effective and conventionally available than other Pt sources. First, the metal solution at the predetermined concentration and volume was added dropwise to the zeolite. The metal added zeolite was then stirred with a glass rod, dried at 20 kPa and 80 °C with a rotary evaporator, and calcined in a muffle furnace at 550 °C for 3 h. The prepared catalyst was labeled as MgO(x)/Pt(y)/zeolite(z), where x and y indicate loading of MgO and Pt [wt%], and z represents the Si/Al ratio [mol/mol] of the zeolite, respectively.
2.2. Characterization of the Catalyst

The porosity of the catalysts was evaluated by nitrogen adsorption at −196 °C using a Belsorp-mini high precision volumetric gas adsorption analyzer (MicrotracBEL Japan, Inc.). The amount of acid sites was measured by an ammonia temperature-programmed desorption technique (ac-NH$_3$-TPD) using a thermogravimetric analyzer (TGA-50, Shimadzu Corp., Japan). About 10 mg of the sample was put in a quartz pan and the pan was placed in an electric furnace. The sample was first heated in a helium stream to 550 °C to remove adsorbed water in the zeolite and ammonia on the acid sites. Next, the sample was cooled to 100 °C and the gas stream was changed from helium to 1 % NH$_3$ in helium to adsorb NH$_3$ on the zeolite acid sites. After the weight of the sample had stabilized, the sample was heated from 100 to 550 °C in 1 % NH$_3$ in helium. The effluent gas was passed through a condenser at 0 °C to collect liquid product and the remaining gas was collected in a gas bag. The liquid product was analyzed with a gas chromatograph (GC-2014, Shimadzu Corp., Japan) equipped with a flame ionization detector and a DB-WAX capillary column and a gas chromatograph-mass spectrometry (GC-MS). The gas product was quantified using a gas chromatograph (GC-2014) equipped with a flame ionization detector and a Porapak Q column. The undetectable products, labelled as “undetectable” in the figures, were components collected but not detected by GC, which were calculated by the carbon balance.

This study focused on the isomerization and cracking of long chain n-paraffins into isoparaffins of specific carbon number so the products were classified into 4 groups (Table 1) based on the reaction scheme shown in Fig. 1; (a) “Desired product”: isoparaffins with carbon number of 6 and 7 for n-C10 and 7-9 for n-C12; (b) “Isomerized intermediate”: isoparaffins with the same carbon number as the reactant; (c) “Cracked intermediate”: n-paraffin with the same carbon number as the desired product; and (d) “Lighter byproduct”: product with lower carbon number than the intermediates.

2.3. Reaction Test

Hydroisomerization and mild cracking of n-paraffins were carried out by using a fixed-bed flow reactor at ambient pressure. 0.24-2.4 g of the pelletized catalyst of 300-850 μm was placed in a quartz tube reactor with 10 mm diameter, pretreated with 10 % hydrogen containing nitrogen stream at 450 °C for 1 h, and then cooled to the reaction temperature ranging from 200 to 250 °C. The reactant (either n-C10 or n-C12) was fed to a preheater at 150 °C by a microsyringe pump at the selected flow rate to achieve the predetermined contact time (W/F), vaporized in the preheater, and supplied to the reactor with hydrogen and nitrogen streams. The W/F ranged from 0.3 to 3 g-cat. h/g-reactant and H$_2$/reactant molar ratio was fixed at 9 for n-C10 as reactant and at 13 for n-C12 as reactant to achieve the molar ratio of H$_2$ to carbon atoms in reactant at 1. The effluent of the reactor was passed through a condenser at 0 °C to collect liquid product and the remaining gas was collected in a gas bag. The liquid product was analyzed with a gas chromatograph (GC-2014, Shimadzu Corp., Japan) equipped with a flame ionization detector and a DB-WAX capillary column and a gas chromatograph-mass spectrometry (GC-MS). The gas product was quantified using a gas chromatograph (GC-2014) equipped with a flame ionization detector and a Porapak Q column. The undetectable products, labelled as “undetectable” in the figures, were components collected but not detected by GC, which were calculated by the carbon balance.

Table 1 Classification of the Products Obtained by Hydroisomerization and Mild Cracking of Long-chain n-Paraffins

| Reactant | (a) Desired product | (b) Isomerized intermediate | (c) Cracked intermediate | (d) Lighter byproduct |
|----------|---------------------|-----------------------------|--------------------------|----------------------|
| n-C10    | i-C6 and i-C7       | i-C10                       | n-C6 and n-C7            | C1-C5                |
| n-C12    | i-C7, i-C8, and i-C9| i-C12                       | n-C7, n-C8, and n-C9     | C1-C6                |

3. Results and Discussion

3.1. Hydroisomerization and Mild Cracking of n-Decane (n-C10)

3.1.1. Effect of Zeolite Framework Structure

Table 2 lists the properties of prepared Pt(0.5)/zeolite catalysts. The kinetic diameter of isoparaffins is above 0.5 nm$^{30,31}$, and larger than the pore diameter of the 8-member ring$^{32}$, so the 8-member ring pores of FER and MOR did not contribute to the reaction. Therefore, FER(9) and MOR(9) were regarded as 1-dimensional pore structures in Table 2. The amount of solid acid sites increased with lower Si/Al ratio but the Pt particle size was not dependent on the Si/Al ratio, suggesting that a small amount of Pt atoms was located on the solid acid sites and most Pt atoms did not occupy the solid acid sites. Also, the average Pt particle size was larger than the pore diameter of the zeolites. Thus, the main content of Pt was considered to be located on the external surfaces of the zeolite particles.

Catalytic activity for hydroisomerization and cracking of n-C10 over Pt(0.5)/zeolite catalysts with different zeolite framework structures was evaluated at 200 °C and WIF of 1.0 h for 1 h. The carbon distribution at the outlet of the reactor is shown in Fig. 2. Isomers of the reactant, i-C10, and both linear and branched hydrocarbons with shorter carbon chains than the reactant were observed for all catalysts tested, indicating that the isomerization and cracking reactions proceeded. However, different zeolites gave different product yields and distributions, indicating that the zeolite framework structure affected the activity of both hydroisomerization and cracking. The zeolites with 3-dimensional pore structures, MFI, *BEA, and FAU, exhibited higher...
conversions than zeolites with 1-dimensional pore structures, FER, MOR, and MTW, possibly because the reactant molecule can access inside the zeolite micropores with 3-dimensional structure more easily than those with 1-dimensional structure. Zeolites with the same dimensional pore structure showed variable product selectivity. Zeolites with 12-member ring pores had lower selectivity for the desired and intermediate products and higher selectivity for the lighter byproducts than zeolites with 10-member ring pores except for MTW(100), possibly because contact frequency of the reactant with solid acid sites was higher and stereoselectivity was lower for 12-member ring pores. The diffusible distance in 12-member ring pores was longer than that in 10-member ring pores, so the reactant could access more acid sites in the 12-member ring pore zeolite. In addition, the 12-member ring pore was large enough for the reactant to form aromatic compounds and multibranched isoparaffins, which are more likely to decompose to smaller paraffins. MTW(100) showed higher selectivity for i-C10 than MOR(9), despite the 1-dimensional 12-member ring pore structure. This difference of selectivity between MOR(9) and MTW(100) could be attributed to the amount of acid sites. MTW(100) had a much smaller amount of acid sites than the other zeolites as listed in Table 2, so the cracking reaction proceeded more slowly than over MOR(9). Therefore, hydroisomerization and cracking activities of the Pt/zeolite were affected by both the zeolite pore structure and the solid acid site amount. The 3-dimensional pore zeolite structure was favorable for higher activity and the smaller zeolite pores and smaller acid site amount were favorable for higher selectivity of the hydroisomeriza-

Table 2  Properties of Prepared Pt(0.5)/Zeolite Catalysts

| Catalyst name    | Zeolite pore size<sup>a)</sup> | Nominal Si/Al ratio [mol/mol] | Solid acid amount<sup>b)</sup> [mmol/g] | Pt particle size<sup>c)</sup> [nm] |
|------------------|-------------------------------|--------------------------------|----------------------------------------|-------------------------------|
| Pt(0.5)/FER(9)   | 1-dimensional 5.4 Å x 4.2 Å | 9                              | 0.804                                  | 10.4                          |
| Pt(0.5)/MTW(100) | 1-dimensional 6.0 Å x 5.6 Å | 100                            | 0.136                                  | 10.1                          |
| Pt(0.5)/MOR(9)   | 1-dimensional 7.0 Å x 6.5 Å | 9                              | 0.754                                  | 13.4                          |
| Pt(0.5)/MFI(100) | 3-dimensional 5.5 Å x 5.1 Å | 100                            | 0.173                                  | 11.2                          |
| Pt(0.5)/FAU(12.5) | 3-dimensional 7.4 Å x 7.4 Å | 12.5                           | 0.552                                  | 6.3                           |
| Pt(0.5)/BEA(20)  | 3-dimensional 7.7 Å x 6.6 Å | 20                             | 0.475                                  | 6.8                           |

<sup>a)</sup> Pores with 8-member rings are excluded.  
<sup>b)</sup> Measured by ac-NH<sub>3</sub> TPD.  
<sup>c)</sup> Estimated from H<sub>2</sub> pulsed chemisorption.

Fig. 1  Reaction Scheme of Hydroisomerization and Cracking of Long-chain n-Paraffin
tion and mild cracking of \( n \)-paraffins. From these results, MFI(100), which showed the highest yield of the desired product, and FER(9) and MTW(100), which exhibited high selectivity for the intermediate, were considered to be suitable catalysts for the hydroisomerization and cracking of \( n \)-C10.

To further investigate the effect of the zeolite framework structure at similar \( n \)-C10 conversion, hydroisomerization and cracking of \( n \)-C10 over Pt(0.5)/MTW(100) and Pt(0.5)/FER(9) were performed at 250 °C. Figure 3(a) shows the carbon yield of the reaction over Pt(0.5)/MFI(100), Pt(0.5)/MTW(100) and Pt(0.5)/FER(9) at \( n \)-C10 conversion around 50-70 C-mol%.

The desired products were formed over Pt(0.5)/MTW(100) and Pt(0.5)/FER(9) at 250 °C, but Pt(0.5)/MFI(100) exhibited higher product yield than the other catalysts. To examine whether overcracking proceeded, the carbon number distribution was investigated. Figure 3(b) shows the carbon number distribution curve was nearly symmetrical for Pt(0.5)/MFI(100) and Pt(0.5)/MTW(100), suggesting that overcracking proceeded slowly. On the other hand, the peak of the carbon number distribution curve for Pt(0.5)/FER(9) appeared at 4, suggesting overcracking as cracking of C7 and C8 to C3 and C4, obviously proceeded.

In summary, MFI structure was most preferable to yield moderately-cracked branch hydrocarbons among the zeolite structures tested because of its 3-dimensional 10-member ring pores. Therefore, MFI type zeolite was used for further experiments.

3.1.2. Effect of Solid Acid Site Amount on Hydroisomerization and Cracking of \( n \)-C10

Cracking of long-chain \( n \)-paraffins into isoparaffins with specific carbon numbers is believed to proceed mainly on solid acid sites, so the amount and strength of the solid acid sites are considered to be one of the important parameters to control the catalytic activity. First, we focused on the effect of the amount of the solid acid sites in the hydroisomerization and cracking of \( n \)-C10 over Pt(0.5)/MFI with different solid acid

Reaction temperature: 200 °C or 250 °C. Reaction time: 1 h, \( W/F = 1.0 \) (g-cat. h)/\( g \)-\( n \)-C10, \( H_2/n \)-C10 = 9.

Fig. 3 (a) Product Selectivity and (b) Carbon Number Distribution of \( n \)-C10 Hydroisomerization and Cracking over Pt(0.5)/MFI(100), Pt(0.5)/MTW(100), and Pt(0.5)/FER(9) at \( n \)-C10 Conversion around 50-70 C-mol%.
amounts. The effect of the solid acid strength is investigated in Section 3.2, using n-C12 as reactant because overcracking of the desired isoparaffin proceeded more obviously for n-C12 conversion than for n-C10 conversion. Table 3 summarizes the properties of the catalysts used. The prepared catalysts possessed similar characteristics except for the solid acid amount. The solid acid amount monotonically decreased with higher Si/Al ratio.

Figure 4(a) shows the product selectivity for the hydroisomerization and cracking of n-C10 over Pt(0.5)/MFI with different solid acid sites at 200 °C. The reaction was sequential, so W/F was set at 3.0, 1.0, and 0.3 for MFI-type zeolite with Si/Al ratios of 200, 100, and 50, respectively, to adjust the conversion around 65 C-mol%. W/F value increased with lower amount of solid acid, so the solid acid site was presumably dominant in the reaction rate. Lower solid acid amount resulted in higher selectivity of i-C10 with coincident decrease of selectivity for the lighter by-product. The selectivity of the desired product increased from 16 to 29 C-mol% as the solid acid amount decreased from 0.31 to 0.17 mmol/g but decreased from 29 to 23 C-mol% as the solid acid amount decreased from 0.17 to 0.08 mmol/g. Figure 4(b) shows the carbon number distribution, indicating that the fractions of C3 and C4 increased with simultaneous decrease of C7 and C8 fractions with higher amount of solid acid. Pt(0.5)/MFI(50) and Pt(0.5)/MFI(100) had asymmetric carbon number distribution curves, indicating that overcracking proceeded on the catalysts with large amounts of solid acid. In contrast, Pt(0.5)/MFI(200) showed near symmetric carbon number distribution curve, as reported previously.23 The difference in the product selectivity may be ascribed to the contact frequency of the reactant with the solid acid. For Pt/MFI with large solid acid amount, the contact frequency of the reactant with the solid acid sites was high and the desired isoparaffins formed could access other solid acid sites where the overcracking proceeded. On the other hand, for Pt/MFI with small solid acid amount, the contact frequency of the reactant with the solid acid sites was low, so the desired isoparaffin had low possibility to access other acid sites. The highest selectivity of the sum of desired and intermediate products was obtained using Pt(0.5)/MFI(200) in this study. Therefore, catalyst with fewer solid acid sites was preferable to suppress overcracking of the desired products and MFI(200) was used for the following experiments.

3.1.3 Effect of Pt Content on Hydroisomerization and Cracking of n-C10
The effect of Pt loading on the hydroisomerization and cracking was examined using Pt/MFI(200) with Pt loading of 0.1-1 wt% as shown in Table 4. Pt particle size increased with higher Pt loading due to sintering of the metal particles during preparation and the largest Pt surface area estimated by H2 pulsed chemisorption was observed for Pt(0.5)/MFI(200).

Figure 5(a) shows the product selectivity of the hydroisomerization and cracking of n-C10 over Pt/MFI(200) at 200 °C and W/F of 1.0 h for 1 h. n-C10 conversion was 10-20 C-mol% for all catalysts at the same W/F, suggesting that the amount of Pt had a small effect on the conversion compared with that of the solid acid amount. Pt(0.1)/MFI(200) showed lower n-C10 conversion and i-C10 selectivity than the catalysts with higher Pt loading, possibly because few active sites for dehydrogenation, believed to be the initial step of isomerization41,11),(3~16), were present. n-C10 conversion over Pt(0.5)/MFI(200) was comparable to that over Pt(1.0)/MFI(200). The turnover frequency (TOF) of n-C10 conversion, estimated by dividing moles of the reacted n-C10 by moles of surface Pt atoms in the catalyst bed measured by H2 pulsed chemisorption, is shown in Fig. 5(a). The TOF of Pt(0.1)/MFI(200) was almost the same as that of Pt(0.5)/MFI(200) but lower than that of Pt(1.0)/MFI(200). On the other hand, the average Pt particle size of Pt(1.0)/MFI(200) was much larger than that of Pt(0.1)/MFI(200) and Pt(0.5)/MFI(200) as shown in Table 4, which implied that the catalytic activity of Pt(1.0)/MFI(200) would be lower than other catalysts due to the large particle size. The reason for the higher TOF of Pt(1.0)/MFI(200) was not fully understood. However, one of the possible reasons was that the long-chain n-paraffin conversion mainly proceeded near the external surface of the zeolite due to the high diffusion resistance of the reactant and products, so that Pt atoms located inside the zeolite pores did not participate in the n-C10 conversion. In contrast, H2 could access deep inside the zeolite pores.

### Table 3 Catalyst Properties of the Prepared Pt(0.5)/MFI with Different Si/Al Ratios

| Catalyst name | Nominal Si/Al ratio | Solid acid amount$^a$ | BET surface area$^b$ | Pt particle size$^c$ |
|---------------|---------------------|-----------------------|----------------------|---------------------|
| Pt(0.5)/MFI(50)| 50                  | 0.309                 | 405                  | 6.9                 |
| Pt(0.5)/MFI(100)| 100                 | 0.173                 | 431                  | 11.2                |
| Pt(0.5)/MFI(200)| 200                 | 0.083                 | 434                  | 11.2                |

$^a$ Measured by $\text{NH}_3$ TPD.
$^b$ Measured by $\text{N}_2$ adsorption.
$^c$ Estimated from H2 pulsed chemisorption.
Therefore, the number of Pt surface atoms estimated by H₂ pulsed chemisorption did not indicate the actual number of Pt atoms contributing to the reaction. Long-chain n-paraffin conversion did not change linearly with Pt loading as previously reported. The selectivity of the desired product for Pt(1.0)/MFI(200) was slightly higher than that for Pt(0.5)/MFI(200). Figure 5(b) shows the carbon number distribution in the products of n-C₁₀. Pt(0.1)/MFI(200) showed high C₃ fraction and low C₆ fraction, indicating that overcracking proceeded. Pt(0.5)/MFI(200) and Pt(1.0)/MFI(200) showed near symmetric carbon number distribution. Therefore, 0.5 wt% of Pt loading was sufficient to decrease the overcracking rate. The higher selectivity of the desired product over Pt(1.0)/MFI(200) than Pt(0.5)/MFI(200) was then due to the more rapid reaction progress of i-C₁₀ cracking. However, the selectivity for the desired product was small. Therefore, Pt in Pt(0.5)/MFI(200) effectively catalyzed hydrosomerization and mild cracking of n-C₁₀ because of the sufficient amount of Pt active sites. We concluded that the Pt/MFI catalyst with Pt loading of 0.5 wt% and Si/Al ratio of 200 was optimal to maximize i-C₆ and i-C₇ yield from n-C₁₀ in this study.

3.2. Modification of Pt/MFI Catalyst for Hydrosomerization and Mild Cracking of n-Dodecane (n-C₁₂)

Application of this reaction system to bio-jet fuel production from biomass-derived n-paraffin requires investigation of the reaction of n-paraffins with longer carbon chain lengths. Thus, we applied Pt(0.5)/MFI(200) to the hydrosomerization and cracking of n-C₁₂. Table 5 lists the product selectivity for the hydrosomerization and cracking of n-C₁₀ and n-C₁₂ over Pt(0.5)/MFI(200) at 200 °C and W/F of 0.8 h. Isoparaffins and n-paraffins were obtained, showing the hydrosomerization and cracking proceeded over Pt/MFI. Compared with the reaction of n-C₁₀, conversion of n-C₁₂ was comparable and the selectivity for the isomerized intermediate decreased with concomitant increase of the desired product and lighter byproduct. This result suggests that cracking of i-C₁₂ is more likely to occur than that of i-C₁₀. The increase in lighter byproduct selectivity was higher than that for the desired product and the cracked intermediate. This result suggests that the overcracking reaction proceeded for n-C₁₂ but not for n-C₁₀ under the same reaction conditions, which was confirmed in the following.

![Figure 4](image-url)  
(a) Product Selectivity and (b) Carbon Number Distribution of n-C₁₀ Hydrosomerization and Cracking over Pt(0.5)/MFI with Different Si/Al Ratios

| Catalyst name       | Nominal Pt loading [wt%] | Pt surface areaa [m²/g] | Pt particle sizea [nm] |
|---------------------|--------------------------|------------------------|-----------------------|
| Pt(0.1)/MFI(200)    | 0.1                      | 0.10                   | 2.7                   |
| Pt(0.5)/MFI(200)    | 0.5                      | 0.12                   | 11.2                  |
| Pt(1.0)/MFI(200)    | 1.0                      | 0.04                   | 68.4                  |

a) Estimated from H₂ pulsed chemisorption.
Further modification of Pt/MFI catalyst was therefore indispensable to inhibit overcracking in the n-C12 reaction. Addition of alkali metals to the catalyst is reported to decrease the amount of strong acid sites \(^{17,18}\) and suppress the cracking reactions. Addition of Mg moderately suppressed the cracking reaction, resulting in production of isoparaffins with shorter carbon chain length, whereas Ca and Ba completely suppressed the cracking reaction due to the stronger basicity compared with Mg. Therefore, we selected the addition of Mg to Pt/MFI to improve the desired product yield from n-C12 conversion. Figure 6 shows the NH\(_3\)-TPD profiles of MFI(200) and MgO(1)/MFI(200). The peak ranging from 300 to 450 °C corresponds to the desorption of NH\(_3\) adsorbed on the solid acid sites of the zeolite. The peak area represents the amount of solid acid sites and the desorption temperature related to the strength of the solid acid sites. The amount of the solid acid sites was decreased by the addition of Mg, presumably caused by loading of Mg on the solid acid sites.

Figure 7(a) shows the carbon yield in hydroisomerization and cracking of n-C12 over Pt(0.5)/MFI(200) with and without 1 wt% MgO loading at 200-250 °C and W/F of 0.8 h. At 200 °C, MgO(1)/Pt(0.5)/MFI(200) exhibited lower cracking activity as i-C12 was selectively produced, whereas Pt(0.5)/MFI(200) formed products with shorter carbon chain length. Therefore, MgO addition strongly suppressed the cracking reaction and almost no cracking proceeded at 200 °C. The reaction temperature was increased to obtain the cracking product over MgO(1)/Pt(0.5)/MFI(200). The desired products over MgO(1)/Pt(0.5)/MFI(200) were observed above 225 °C and the yield increased with higher reaction temperature. The yield of the desired product reached 35 C-mol% over MgO(1)/Pt(0.5)/MFI(200) at 250 °C, much higher than that obtained over MgO(1)/Pt(0.5)/MFI(200) at 225 °C (5.9 C-mol%) and Pt(0.5)/MFI(200) at 200 °C with W/F of 0.8 h (3.3 C-mol%).

Finally, to examine the effect of MgO addition on the suppression of overcracking, the carbon number distribution of n-C12 conversion over Pt(0.5)/MFI(200) at 200 °C and over MgO(1)/Pt(0.5)/MFI(200) at 225 °C and 250 °C was investigated as shown in Fig. 7(b). For Pt(0.5)/MFI(200), the C7 fraction significantly decreased and the C3 and C4 fractions increased, resulting in an asymmetric distribution curve. This result clearly indicated that overcracking proceeded over Pt(0.5)/MFI(200). On the other hand, a symmetric distribution curve was observed for MgO(1)/Pt(0.5)/MFI(200) at 225 °C, indicating that MgO addition successfully suppressed overcracking. The C7-9 fraction was slightly decreased with simultaneous increase of the C3-5 fraction at 250 °C. The carbon number distribution for MgO(1)/Pt(0.5)/MFI(200) at 250 °C was still nearly symmetrical so the effect of overcracking on the product selectivity was limited. Thus, MgO addition could suppress overcracking at higher reaction temperature and higher n-C12 conversion.

Summarizing the results, we concluded that the addition of MgO was effective for the modification of the cracking activity of Pt/MFI catalyst and resulted in
higher yield of C3-5 isoparaffins. The detailed effects of MgO loading on the active site properties and the reaction mechanism remain unknown. In addition, the catalyst stability must be established for the application of the catalyst to bio-jet fuel production. We will focus on these further investigations next. Our finding that \(i\)-C12 was selectively obtained over MgO/Pt/MFI catalyst at 200 °C suggests that overcracking of isoparaffins with carbon numbers larger than 12 could be suppressed by further modification of the properties of MgO/Pt/MFI as well as the reaction conditions. Thus, the MgO/Pt/MFI catalyst has a potential to obtain isoparaffins with selected carbon number from long-chain \(n\)-paraffins with carbon numbers larger than the reactant used in this study.

### 4. Conclusion

Hydroisomerization and mild cracking of long-chain \(n\)-paraffins into isoparaffins with specific carbon numbers over Pt loaded zeolite was investigated for potential use in bio-jet fuel production from biomass-derived long-chain \(n\)-paraffins. Investigation of zeolite frame-
work structures suggested that the MFI structure was the most suitable among the zeolites tested because the 3-dimensional pore structure improved the conversion of n-C10 and smaller pores consisting of 10-member ring pores enhanced the selectivity for the desired products. Modification of the solid acid amount and Pt loading were assessed to improve the desired product yield from n-C10. Lower amount of solid acid sites and adequate Pt loading were preferable to yield the desired isoparaffins by decreasing the overcracking reaction rate. Pt/MFI catalyst with 0.5 wt% Pt loading and Si/Al of 200 was found to be the optimal catalyst for n-C10 conversion to i-C6 and i-C7 paraffins.

However, overcracking of the desired products proceeded during hydroisomerization and mild cracking of n-C12 over the optimized catalyst for n-C10, because the desired product for n-C12 had higher reactivity due to the larger carbon numbers than that for n-C10. Addition of Mg to Pt/MFI successfully suppressed overcracking of the desired products in n-C12 conversion by decreasing the amount and strength of the solid acid sites. The yield of the desired isoparaffins reached 35 C-mol% over MgO(1)/Pt(0.5)/MFI(200) at 250 °C and W/F of 0.8 h for 1 h. MgO/Pt/MFI clearly has the potential for selective production of isoparaffins with the selected carbon numbers. The reaction mechanism of hydroisomerization and cracking of n-paraffins with carbon number of 15 to 18 is generally accepted as the same as that of n-C10 and n-C12 but the reaction rates are different4,16,24. The MgO/Pt/MFI catalyst can be effective for jet fuel production from biomass-derived n-paraffins by suppressing the overcracking of the desired isoparaffins though adjustment of the reaction conditions, such as reaction temperature and contact time. The findings of this paper will help in the development of efficient bio-jet fuel production processes.

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要 旨

$n$-デカン、$n$-ドデカンから $i$-C6-7、$i$-C7-9選択合成のためのゼオライト担持 Pt触媒の開発

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近年、動植物性油脂から得られる長鎖直鎖パラフィンを原料としたジェット燃料製造が高い関心を集めている。炭素数16～20の直鎖パラフィンから炭素数9～15のイソパラフィンであるジェット燃料を得るには、異性化と過酸化分解反応が必要である。一般に水素化異性化および分解反応にはゼオライト担持 Pt等の二元機能触媒が有効である。しかし、その触媒性能が活性に及ぼす影響は解明されていない。そこで、ゼオライト担持 Pt触媒を用い、水素化異性化および分解反応による直鎖パラフィンからの炭素数3～5少ないイソパラフィンの合成実験を行った。$n$-デカンを原料とし、ゼオライト構造、酸点、白金担持量の影響を検討した。0.5 wt% Pt担持MFI（Si/Al比200）が最も高い目的イソパラフィン収率を示した。さらなる改良のため、$n$-デカンに対し選択分解した触媒を$n$-ドデカン原料に展開した。MgO担持により過分解反応が抑制され、目的イソパラフィン収率が向上することを見出した。