

Research Article

Conversion of Isoprenoid Oil by Catalytic Cracking and Hydrocracking over Nanoporous Hybrid Catalysts

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In order to produce petroleum alternatives from biomass, a significant amount of research has been focused on oils from microalgae due to their origin, which would not affect food availability. Nanoporous hybrid catalysts composed of $\text{ns Al}_2\text{O}_3$ and zeolites have been proven to be very useful compared to traditional catalysts in hydrotreating (HT), hydrocracking (HC), and catalytic cracking (CC) of large molecules. To evaluate the reaction scheme and products from model isoprenoid compounds of microalgae oil, nanoporous hybrid catalyst technologies (CC: $\text{ns Al}_2\text{O}_3/\text{H-USY}$ and $\text{ns Al}_2\text{O}_3/\text{H-GaAlMFI}$; HC: $[\text{Ni-Mo}/\gamma\text{-Al}_2\text{O}_3]/\text{ns Al}_2\text{O}_3/\text{H-beta}$) were studied. The major product from CC on $\text{ns Al}_2\text{O}_3/\text{H-USY}$ was highly aromatic gasoline, while the product from HC was half-isoparaffinic/olefinic kerosene. Although more than 50 wt% of the products from HT/CC on the USY catalyst was liquefied petroleum gas due to overcracking, the product from HT/CC on the MFI catalyst was high-octane-number gasoline. Delightfully, the product from HT/HC was kerosene and its average number was 11, with more than 80 wt% being isoparaffinic. As a result, it was demonstrated that hydrotreating may convert isoprenoid oil from microalgae over nanoporous hybrid catalysts into a variety of products.

1. Introduction

For more than three centuries, fossil fuels have been used in various aspects of our lives; however, these fuels are not renewable and will eventually be depleted. In fact, over 80% of the energy we use comes from petroleum, coal, and natural gas. About 98% of carbon emissions are due to fossil fuel combustion, resulting in large amounts of carbon dioxide being discharged into the atmosphere [1]. It is possible to reduce carbon dioxide emissions by reducing the amount of fossil fuels used. Biomass is one of the most potentially energetic organic resources to replace fossil fuels, because it is renewable and neutral with regard to carbon dioxide emissions. Recently, many researchers have studied synthetic hydrocarbon fuels from various biomass sources, for example, wheat, soy beans, sugar cane, corn, rapeseed and palm oils [2–9], or woody cellulose [10–12]. However, biomass has

become a problem since it may affect food availability. Therefore, attention has turned to microalgae oil as a new renewable energy source. Production of biofuels from microalgae consists of culturing microalgae and producing hydrocarbon fuels from the resulting oil. This paper will focus on the latter stage of fuel production from microalgae. Recently, microalgae oil has been used to produce hydrocarbon fuels and gas or other related products [13–19].

Microalgae oil can be divided into two types: a triglyceride series and an isoprenoid series. The triglyceride series is produced by *Euglena* and others, and the isoprenoid series is produced by *Botryococcus braunii* and others. Conversion of triglyceride fatty oil to fuels has generally been performed by transesterification using an alkali catalyst to produce biodiesel fuels (BDF) [20–22]. The main component in BDF is fatty acid methyl ester (FAME). FAME can be used directly in diesel engines, but it cannot replace gasoline and jet

fuels. In practice, BDF is used by mixing about 3% BDF with gasoline and jet fuels. Because BDF tends to contain some impurities, for example, oxygen and nitrogen, it causes damage to engines. Additionally, FAME is costly because it requires a large amount of methanol, and this must be separated from the final product. Thus, some problems still remain in using BDF as a renewable new energy source to replace gasoline and jet fuels.

In contrast, the microalgae oil produced by *Botryococcus braunii* is botryococcene, an isoprenoid hydrocarbon of 27–34 carbon atoms with a relatively high melting point, which is easy to handle and does not corrode equipment. The coauthor previously studied the catalytic cracking of isoprenoid oil extracted from *Botryococcus braunii* using the traditional catalytic cracking catalyst [23]. The main products were gasoline, light cycle oil, and heavy cycle oil. It was confirmed that the reactivity and products correlated with the catalytic cracking of squalene. Recently, studies on the fuel synthesis process and catalyst from botryococcene and/or squalene have been reported [24–27].

Our current research has been intentionally focused on composites containing unimodal nanoporous nanosized (defined as 5–50 nm, and hereafter referred to as **ns**) oxides with pore sizes ranging from about 5 nm to several tens of nanometers [28]. This research yielded some advances in catalysis, including hydrodesulfurization [29, 30], hydrocracking [31–35], reforming [36–38], and catalytic cracking [39, 40]. Various **ns** alumina matrices with different properties were studied for catalytic cracking catalysts. The activity was found to be dependent on the pore size of the matrix because precracking proceeds independently from the zeolite component. An inverse relationship was also demonstrated between the activity and the rate of degradation by coking, both of which were analyzed as a function of the pore diameter of the matrix. For hydrocracking and isomerization catalysts, a tricomponent catalyst consisting of beta zeolite, **ns** oxide, and metal/ γ -Al₂O₃ was studied. This catalyst has relatively high selectivity for hydrotreating large *n*-paraffins to lighter isoparaffins. The enhanced catalytic performance is due to the combined effects of zeolite, **ns** oxide, and metal/ γ -Al₂O₃. Catalysts containing dealuminated beta zeolite with **ns** Al₂O₃ have high conversion and isoselectivity; their catalytic performances are suitable for producing isoparaffins for gasoline. Therefore, the conversions of squalene and squalane, selected as models of microalgae oil and its hydrotreated version, respectively, were studied by catalytic cracking and hydrocracking on our own catalysts.

2. Experimental

2.1. Catalyst Preparation. Three types of catalysts for catalytic cracking were prepared using the following reagents [37–40]. Two kinds of zeolites, the commercial USY zeolite (SiO₂/Al₂O₃ molar ratio = 12) (JGC Catalysts and Chemicals, LTD.) and lab-made H-GaAlMFI zeolite (SiO₂/Al₂O₃ molar ratio = 30) were chosen as the zeolite catalyst component. The H-GaAlMFI zeolite was synthesized using sodium silicate, aluminum sulfate 14–18 hydrate (Al₂(SO₄)₃·14–18H₂O), gallium nitrate *n* hydrate (Ga(NO₃)₃·*n*H₂O),

tetrapropylammonium bromide (TPABr), sodium chloride, sulfuric acid, and deionized water. These reagents were mixed sequentially. The mixture was aged overnight at room temperature, then the zeolite was hydrothermally synthesized at 150°C for 24 h. The synthesized zeolite was washed with H₂O until the pH reached 7, then dried overnight at room temperature. Further drying was conducted at 120°C for 3 h, followed by calcination in air at 550°C for 3 h. A moderate developed kind of dry unimodal boehmite sol powder was prepared by the hydrothermal aging method. The powder can be converted to a type of **ns** Al₂O₃ matrix material with a unimodal pore diameter of 14 nm by calcination, as reported previously [39, 40]. Two of these solid powders were mixed with water to form a thick paste and this paste was mechanically kneaded. After kneading, the catalysts were extruded into pellets, then dried overnight at room temperature and heated at 120°C for 3 h. Finally, they were calcinated at 550°C for 3 h. The **ns** Al₂O₃/GaAlMFI catalyst pellets were converted into H-type zeolites by a conventional ion exchange method with an aqueous solution of 2.2 mol/L NH₄NO₃. The catalysts were made from **ns** Al₂O₃ and zeolite (dry weight ratio: 70 : 30).

[NiMo/ γ -Al₂O₃]/**ns** Al₂O₃/H-beta zeolite catalyst was prepared for hydrocracking with isomerization [31–35]. The NiMo/ γ -Al₂O₃ catalyst was prepared by coimpregnation using the incipient wetness method. Two catalysts were loaded with 0.39 g/g-(γ -Al₂O₃) and 0.36 g/g-(γ -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 Ni-Mo 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: 15 μ m) was obtained by grinding the catalyst. Cataloid AP-1 (JGC Catalyst and Chemical, LTD.) was used as the **ns** Al₂O₃ precursor for the hydrocracking catalyst. The precursor 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. H-beta zeolite (SiO₂/Al₂O₃ molar ratio = 25) is a commercial zeolite (Sud-Chemie Catalysts Japan, Inc.). [NiMo/ γ -Al₂O₃]/**ns** Al₂O₃/H-beta zeolite catalyst was synthesized by wet mixing followed by calcination. Three of these solid powders were mixed with water to form a thick paste and this paste was mechanically kneaded. After kneading, the catalysts were extruded into pellets. They were then dried overnight at room temperature and heated at 120°C for 3 h. Finally, they were calcined in air at 550°C for 3 h.

The tri-component catalysts were made from NiMo/ γ -Al₂O₃, **ns** Al₂O₃, and H-beta zeolite (dry weight ratio of 2:1:2).

2.2. Reaction Test and Catalyst Evaluation. The performances of the catalysts were evaluated using a feedstock of squalene (iso-C₃₀H₅₀) and its hydrotreated form, squalane (iso-C₃₀H₆₂), which have normal boiling points of 285°C and 350°C, respectively. These were selected as model compounds of microalgae oil.

A continuous-flow reactor with a down flow-type fixed bed catalyst (volume: 0.5 mL) was used for the reaction tests. Reaction conditions were as follows: temperature, 250~550°C; liquid hourly space velocity (LHSV), 7.2~40 h⁻¹(contact time (1/LHSV), 0.025~0.50 h); pressure, 0.12 MPa under nitrogen or hydrogen atmosphere; molar ratio of iso-C₃₀H₅₀ or iso-C₃₀H₆₂:N₂ or H₂, 1:15.

The acid amount was measured by the NH₃-TPD method [33]. Mesoporosity was measured using nitrogen adsorption-desorption isotherms [40]. Elemental composition of the catalyst surface layer was determined 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 with narrow scans using 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, Ga 2p, O 1s, and C 1s regions.

3. Results and Discussion

3.1. Catalytic Cracking of Nonhydrotreated Oil. The **ns** Al₂O₃/USY zeolite catalyst was developed as a fluid catalytic cracking catalyst in our previous research [39, 40]. It was confirmed that a catalyst with a middle pore size of around 14 nm made from two different pore sizes of **ns** Al₂O₃ of 7 nm and 35 nm exhibited higher cracking activity and a lower rate of degradation by coking. The properties of the catalyst are shown in Table 1. Catalytic cracking of nonhydrotreated oil, squalene, was investigated over the **ns** Al₂O₃/USY zeolite catalyst at temperatures in the range 400 to 500°C. The results are shown in Figures 1 and 2.

As shown in Figure 1, conversions were almost 100% and olefins were produced at about 50% selectivity at all temperatures. Aromatics were produced at about 40% selectivity at 500°C. As shown in Figure 2, the product distribution of carbon number peaked at nine with the main products being aromatics. It is considered that C₈ and C₉ olefins caused cyclization and aromatization reactions, resulting in hydrogenation of the highly unsaturated olefins by hydrogen transfer. The equilibrium between the hydrogenation and dehydrogenation reactions was balanced such that hydrogen gas was not used substantially in the reaction system.

3.2. Hydrocracking of Nonhydrotreated Oil. In our previous research, it was confirmed that the tri-component catalyst consisting of NiMo/ γ -Al₂O₃, **ns** Al₂O₃, and H-beta zeolite

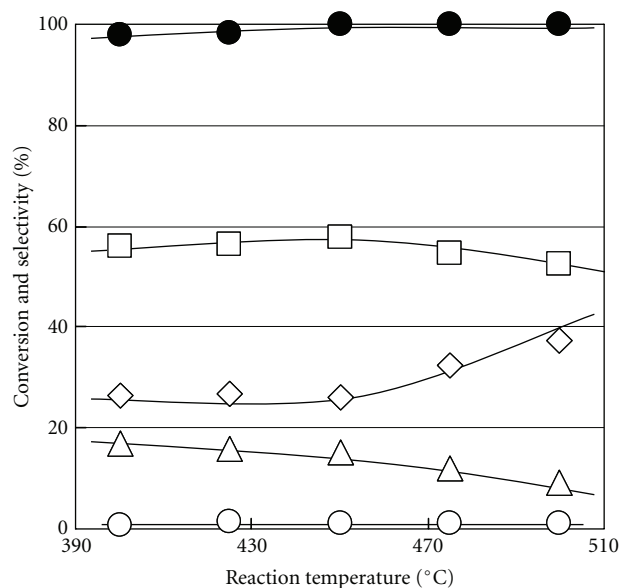


FIGURE 1: Conversion and product selectivity of catalytic cracking of nonhydrotreated oil over **ns** Al₂O₃/USY catalyst depending on reaction temperature. ●: Conversion; selectivity: ○: normal paraffins; △: isoparaffins; □: olefins; ◇: aromatics.

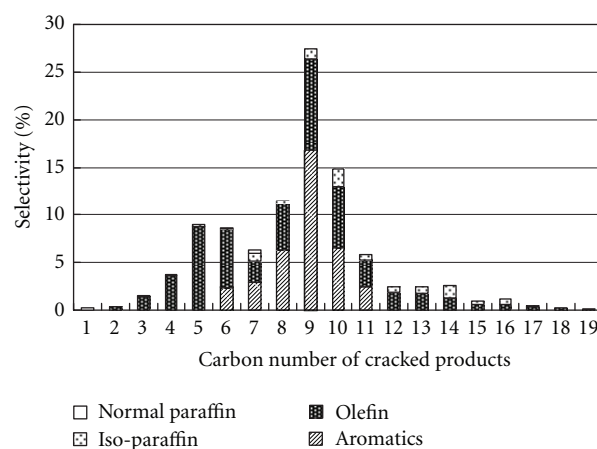


FIGURE 2: Product distribution over **ns** Al₂O₃/USY zeolite catalyst at 500°C.

TABLE 1: Basic physical properties of **ns** Al₂O₃/USY zeolite catalysts.

Catalysts	Surface area (m ² /g)	Pore volume (mL/g)	Average pore diameter (nm)
ns Al ₂ O ₃	200	0.44	14.1
USY	650	0.17	3.0
ns Al ₂ O ₃ /USY	480	0.42	9.2
ns Al ₂ O ₃ /USY*	515	0.25	6.3

* Theoretical addition by composition.

had relatively high selectivity for hydrotreating large n-paraffins to lighter isoparaffins [35]. As shown in Figure 3, H-beta zeolite bound with **ns** Al₂O₃ had more acid content

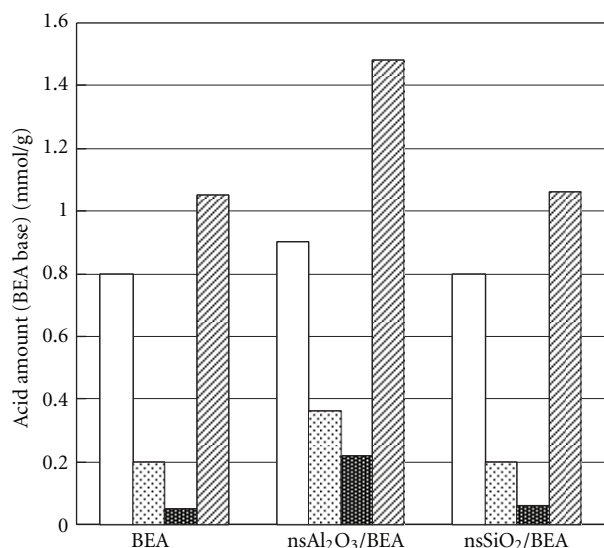


FIGURE 3: Generated acid sites at the boundary between **ns** Al₂O₃ and H-beta Zeolite. White region: weak acid sites*1; dotted region: mild moderate acid sites*2; black region: mild strong acid sites; shaded region: total acid sites*3*1: 200°C peak; *2: 310°C peak; *3: 410°C peak.

than only H-beta zeolite, and the increased acids consist of mild-moderate acid and mild-strong acid. On the other hand, H-beta zeolite bound with **ns** SiO₂ had almost the same acid content of only H-beta zeolite. It is considered that the generated acid sites at the boundary between **ns** Al₂O₃ and nanoporous zeolite were derived from pseudoboehmite and H-beta zeolite. Hydrocracking of nonhydrotreated squalene was investigated over [NiMo/ γ -Al₂O₃]/**ns** Al₂O₃/H-beta zeolite catalyst at temperatures in the range 250 to 350°C. The results are shown in Figures 4 and 5.

As shown in Figure 4, the selectivity for isoparaffins was about 35%, while aromatics selectivity was about 40% at 350°C. As shown in Figure 5, the product distribution of carbon number in hydrocracking also had a peak at nine, similar to catalytic cracking. The main aromatics were xylenes and trimethylbenzenes. Thus, large amounts of aromatics were produced despite the hydrocracking reaction. It was considered that the cracking reaction was suppressed because the reaction temperature of hydrocracking is lower than that of catalytic cracking. Therefore, aromatization progressed much further, resulting in highly unsaturated products of 8~9 carbon atoms. The reaction scheme of catalytic cracking and hydrocracking of nonhydrotreated oil based on Figures 2 and 5 is summarized in Figure 6.

As shown in Figure 6, in the case of catalytic cracking of nonhydrotreated oil, aromatics are produced by aromatization and transhydrogenation of cracked C₈~C₉ olefins with hydrogen transfer as a result of the high temperature and lack of hydrogen in the reaction system. In the case of hydrocracking, aromatics are similarly produced by aromatization of cracked C₈~C₉ olefins. In this reaction system, olefins were converted to paraffins, and hydrogen transfer proceeded more often than in catalytic cracking.

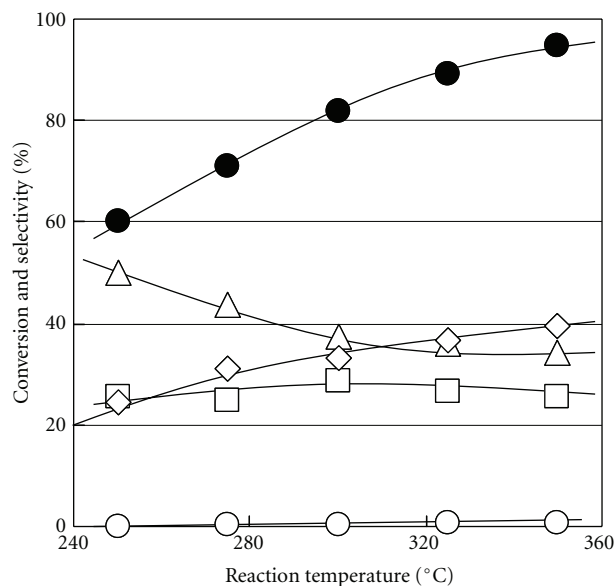


FIGURE 4: Conversion and pProduct selectivity of hydrocracking of nonhydrotreated oil over [NiMo/ γ -Al₂O₃]/**ns** Al₂O₃/H-beta zeolite catalyst depending on reaction temperature. ●: Conversion; selectivity: ○: normal paraffins; △: isoparaffins; □: olefins; ◇: aromatics.

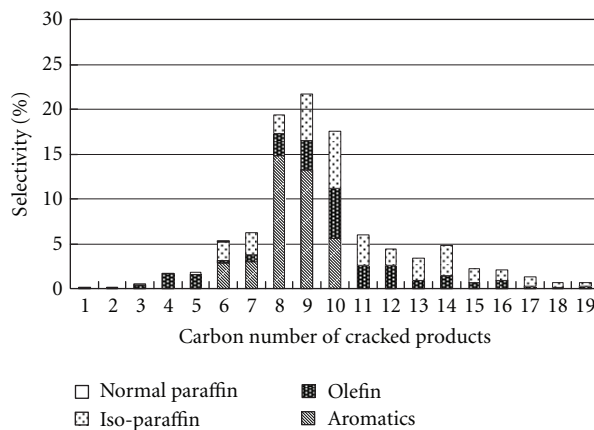


FIGURE 5: Product distribution from hydrocracking of nonhydrotreated oil over [NiMo/ γ -Al₂O₃]/**ns** Al₂O₃/H-beta zeolite catalyst at 350°C.

It was revealed that a large amount of olefins and aromatics was inevitably produced from nonhydrotreated oil of highly unsaturated olefins.

3.3. Catalytic Cracking of Hydrotreated Oil

3.3.1. ns Al₂O₃/H-USY Zeolite Catalyst. Catalytic cracking of hydrotreated oil, squalane, was investigated over **ns** Al₂O₃/USY zeolite catalyst at temperatures in the range 300 to 500°C. The results are shown in Figures 7 and 8.

As shown in Figure 7, this catalyst showed very high activity (more than 90% conversion at 350°C) and aromatics

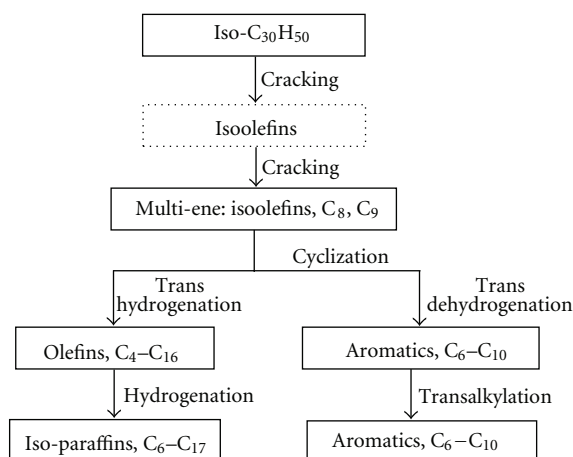


FIGURE 6: Reaction Scheme of Catalytic Cracking and Hydrocracking of Nonhydrotreated Oil Based on Figures 2 and 5.

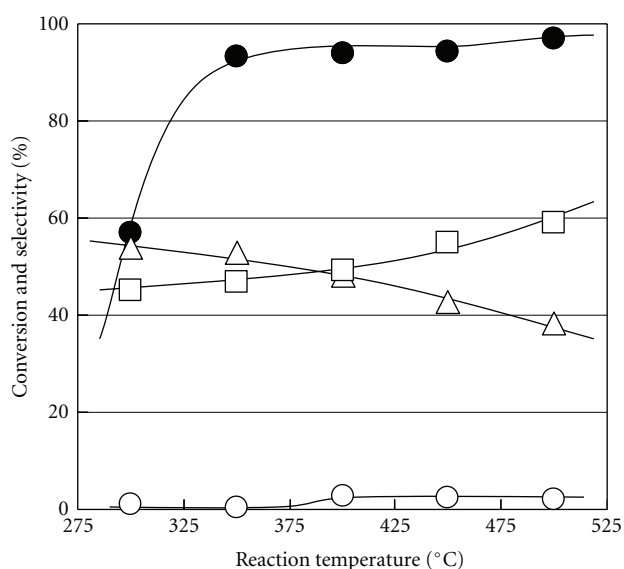


FIGURE 7: Conversion and product selectivity of catalytic cracking of hydrotreated oil over **ns** Al₂O₃/USY catalyst depending on reaction temperature. ●: Conversion; selectivity: ○: normal paraffins; △: isoparaffins; □: olefins.

were not produced at any of the reaction temperatures. It was revealed that isoparaffins used as feedstock were easier to decompose at low temperatures. In addition, olefins were produced by the cracking reaction without aromatization because there were enough paraffins in the reaction system to keep the equilibrium far from highly unsaturated olefins.

As shown in Figure 8, the product distribution of carbon number in catalytic cracking of hydrotreated oil at 350°C still had a peak at nine. On the other hand, overcracking occurred at the higher temperature. The product distribution of carbon number at 550°C had a peak at three (data not shown). It was demonstrated that the optimum reaction temperature to obtain useful products in catalytic cracking of hydrotreated oil on **ns** Al₂O₃/USY catalyst was 350°C.

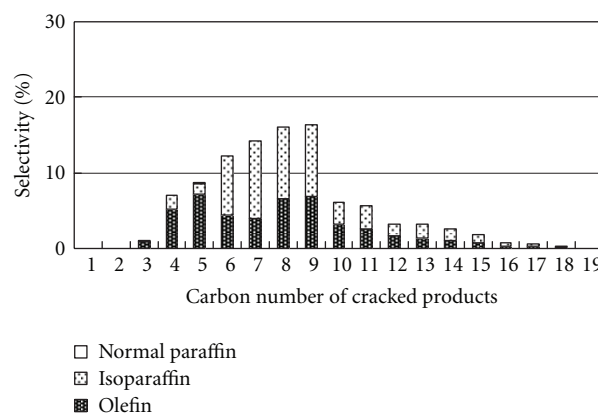


FIGURE 8: Product distribution from catalytic cracking of hydrotreated oil over **ns** Al₂O₃/USY catalyst at 350°C.

TABLE 2: Basic physical properties of **ns** Al₂O₃/GaAlMFI zeolite catalysts.

Catalysts	Surface area (m ² /g)	Pore volume (mL/g)	Average pore diameter (nm)
H-GaAlMFI	333	0.29	3.5
ns Al ₂ O ₃	313	0.44	5.7
ns Al ₂ O ₃ /H-GaAlMFI	216	0.41	7.6
ns Al ₂ O ₃ +H-GaAlMFI*	319	0.39	5.0

* Theoretical addition by composition.

3.3.2. ns Al₂O₃/H-GaAlMFI Zeolite Catalyst. **ns** Al₂O₃/H-GaAlMFI zeolite catalyst was developed for cracking reforming of heavier *n*-paraffins [37]. The properties of the catalyst are shown in Table 2. The catalyst generated new acid sites at the boundary between **ns** Al₂O₃ and GaAlMFI zeolite. In addition, as shown in Figure 9, the Ga species can be extracted to the surface layer by calcination, protonation, and composition. The extracted Ga species has a relatively high activity for aromatization.

Catalytic cracking of hydrotreated oil was investigated over **ns** Al₂O₃/H-GaAlMFI zeolite catalyst with contact times in the range 0.025 to 0.1 h and at temperatures in the range 400 to 500°C. The results are shown in Figures 10, 11, and 12.

As shown in Figure 10, at the longer contact time, the aromatics yield was increased and many polycyclic aromatics were produced in 0.1 h. *n*-paraffins also increased due to hydrogen transfer reactions. Therefore, 0.05 h was selected as the optimum contact time.

As shown in Figure 11, comparing the conversions among reaction temperatures, the maximum value was about 80% at 500°C. Typically, conversion increases with increasing reaction temperature. However, the conversion decreased at 550°C. A large amount of polycyclic aromatics were observed in the product oil at high temperatures, especially at 550°C. Therefore, it was considered that a large amount of coke was produced, which caused rapid

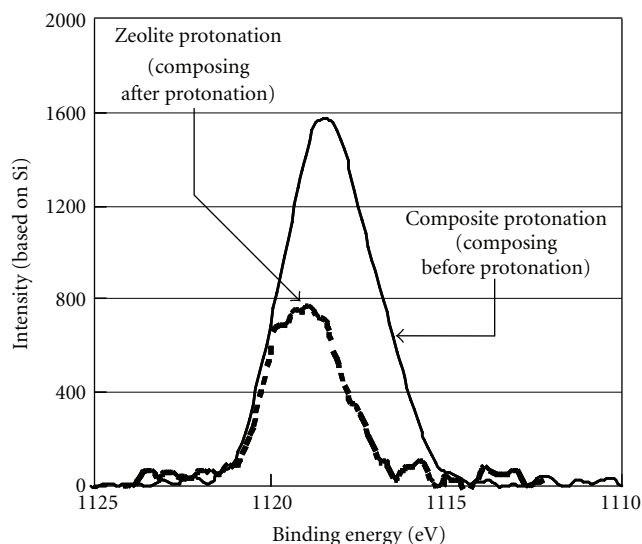


FIGURE 9: Ga 2p XPS spectra of **ns** Al₂O₃/GaAlMFI zeolite catalyst.

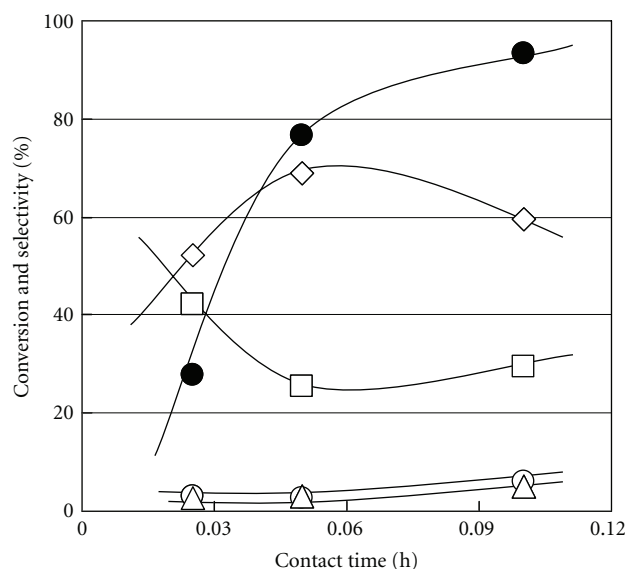


FIGURE 10: Conversion and product selectivity of catalytic cracking of hydrotreated oil over **ns** Al₂O₃/H-GaAlMFI catalyst depending on contact time. ●: Conversion; selectivity: ○: normal paraffins; △: isoparaffins; □: olefins; ◇: aromatics.

degradation of the catalyst. It was demonstrated that the optimum reaction temperature for the catalyst was 500°C.

As shown in Figure 12, the main aromatic products were toluene, xylenes, and benzene. The reaction scheme of catalytic cracking of hydrotreated oil based on Figures 8 and 12 is summarized in Figure 13. As shown in Figure 13, aromatics were produced by oligomerization and aromatization of cracked olefins. **ns** Al₂O₃/USY zeolite catalyst does not cause aromatization, whereas MFI-type zeolite does and Ga promotes dehydrogenation. Therefore, **ns** Al₂O₃/H-GaAlMFI could have produced most of the aromatics in this study.

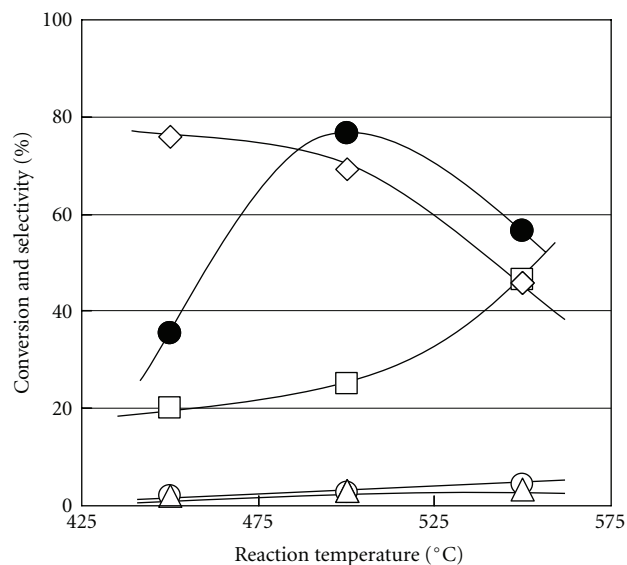


FIGURE 11: Conversion and product selectivity of catalytic cracking of hydrotreated oil over **ns** Al₂O₃/H-GaAlMFI catalyst depending on reaction temperature. ●: Conversion; selectivity: ○: normal paraffins; △: isoparaffins; □: olefins; ◇: aromatics.

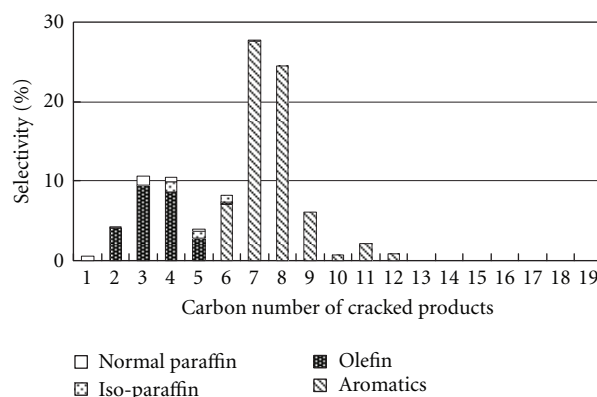


FIGURE 12: Product distribution of catalytic cracking of hydrotreated oil over **ns** Al₂O₃/H-GaAlMFI catalyst at 500°C (contact time: 0.05 h).

3.4. Hydrocracking of Hydrotreated Oil. Hydrocracking of hydrotreated oil was investigated over [NiMo/ γ -Al₂O₃]/**ns** Al₂O₃/H-beta zeolite catalyst at temperatures in the range 250 to 350°C. The results are shown in Figures 14 and 15.

As shown in Figure 14, the catalytic performance was very high. The conversion was over 90% and isoparaffins selectivity was about 90% at 300°C. As shown in Figure 15, the cracking reaction was suppressed and the product distribution of carbon number at 275°C had a peak at 10. At higher temperatures, the cracking reaction progressed and the product distribution of carbon number at 350°C had a peak at 7 (data not shown). Thus, the product distribution could be controlled by changing the reaction temperature on [NiMo/ γ -Al₂O₃]/**ns** Al₂O₃/H-beta zeolite catalyst. It was demonstrated that the optimum reaction temperature was 275~300°C.

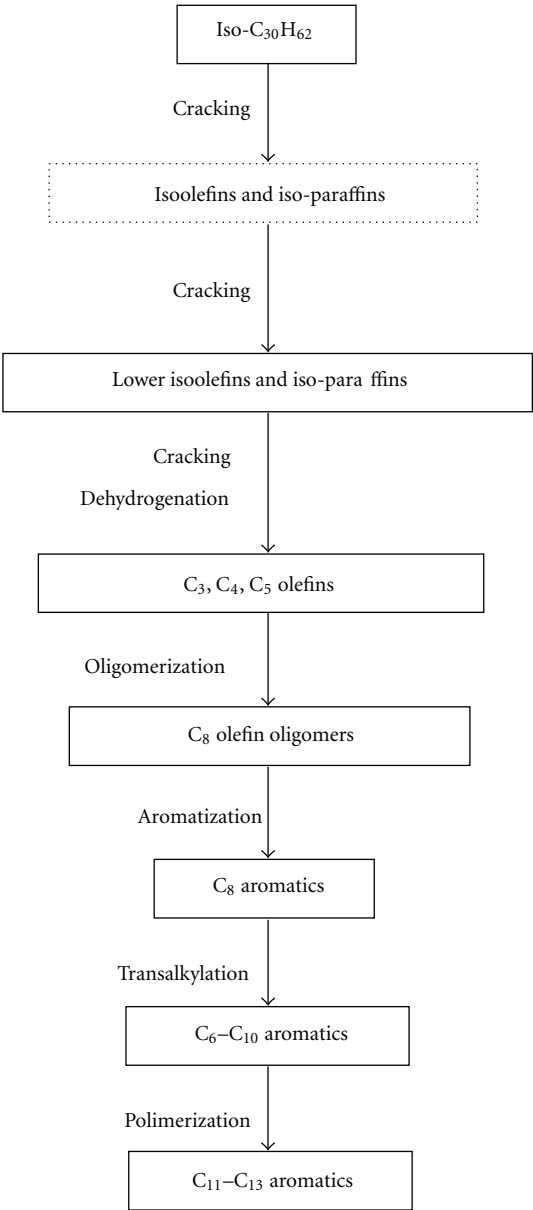


FIGURE 13: Reaction scheme of catalytic cracking of hydrotreated oil over **ns** Al₂O₃/USY and **ns** Al₂O₃/H-GaAlMFI zeolite catalyst based on Figures 8 and 12.

3.5. *Evaluation of Processes.* These four processes (CC: catalytic cracking; HC: hydrocracking; HT-CC: hydrotreating-catalytic cracking; HT-HC: hydrotreating hydrocracking) were compared in terms of conversion and product selectivities under optimum reaction conditions. The results are shown in Table 3. Comparison of the obtained fuel fraction and hydrogen consumption is shown in Table 4 and the evaluation summary of these processes is shown in Figure 16.

As shown in Table 3, the products of CC were olefinic because the material contains only a small amount of hydrogen. It was considered that hydrocracking used hydrogen in the carrier gas, but selectivity for olefins was still less than in CC. The products from HT-CC on **ns** Al₂O₃/USY

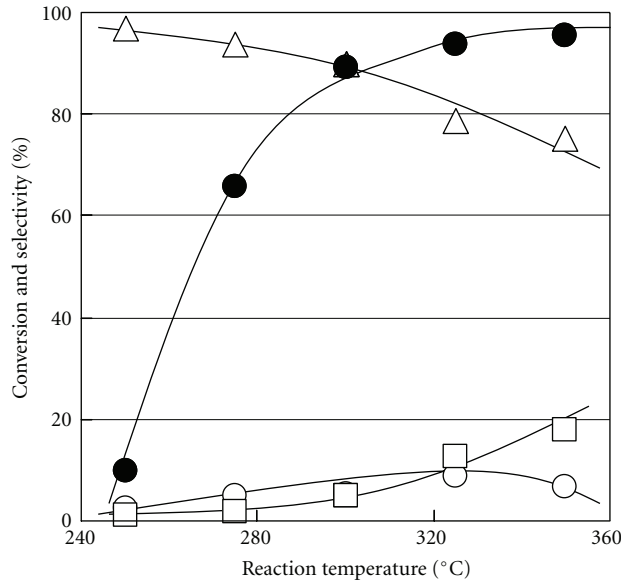


FIGURE 14: Conversion and product selectivity of hydrocracking of hydrotreated oil over [NiMo/ γ -Al₂O₃]/**ns** Al₂O₃/H-beta zeolite catalyst depending on reaction temperature. •: Conversion; selectivity: ○: normal paraffins; △: isoparaffins; □: olefins.

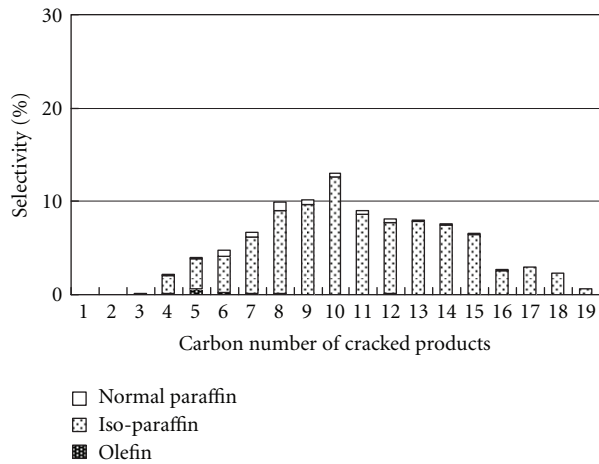


FIGURE 15: Product distribution of hydrocracking of hydrotreated oil over [NiMo/ γ -Al₂O₃]/**ns** Al₂O₃/H-beta Zeolite catalyst at 275 °C.

	Process	H ₂ consumption (NL/L)	Product fraction
CC	→ CC	→ -53	Gasoline
HC	→ HC	→ 130	Kerosene and gasoline
HT-CC (USY)	→ HT → CC	→ 253	Gasoline
HT-CC (MFI)	→ HT → CC	→ -19	Gasoline
HT-HC	→ HT → HC	→ 530	Kerosene

FIGURE 16: Evaluation of processes.

TABLE 3: Comparison of catalytic performance in various processes.

Process	CC	HC	HT-CC (USY)	HT-CC (MFI)	HT-HC
Conversion (%)	100.0	94.9	93.3	76.6	89.2
isopara. sel. (%)	15.2	34.3	52.8	3.1	89.7
olefins sel. (%)	57.6	25.6	46.9	25.0	5.0
aroma. sel. (%)	26.0	39.6	0.0	69.2	0
Ave. Carbon number of cracked	10.1	9.6	8.2	6.3	10.8

TABLE 4: Comparison of the obtained fuel fraction from various processes.

Process	CC	HC	HT-CC (USY)	HT-CC (MFI)	HT-HC
Conversion (%)	100.0	94.9	93.3	76.6	89.2
LPG sel. (%)	5.3	2.2	8.1	21.1	2.3
Gasoline sel. (%)	35.4	32.8	51.2	64.5	25.4
Kerosene sel. (%)	54.1	60.0	39.1	9.7	62.4
Diesel sel. (%)	2.0	4.7	1.7	0.0	9.9
Hydrogen consumption (NL/L)	−53.1	130.1	253.9	−19.1	530.0

zeolite catalyst were isoparaffins and olefins. Aromatics were not produced due to low temperatures and the mild cracking ability of this catalyst. The products from HT-CC on **ns** Al₂O₃/H-GaAlMFI zeolite catalyst were mostly aromatics because this catalyst has high aromatization and dehydrogenation abilities. On the other hand, the products of HT-HC were isoparaffins due to the relatively mild cracking ability of the catalyst.

As shown in Table 4 and Figure 16, the major fuel fractions from CC on **ns** Al₂O₃/H-USY were gasoline and kerosene, while those from HC were half-isoparaffinic/olefinic kerosene and gasoline. Although more than 50 wt% of the products from HT-CC on the USY catalyst were isoparaffinic/olefinic gasoline, the products from HT-CC on the MFI catalyst at ca. 500°C were high-octane-number gasoline including aromatics. Furthermore, an external hydrogen supply was not required in HT-CC on the MFI catalyst. Attractively, the carbon number distribution of the products from HT/HC at 275~300°C populated the kerosene region and its average carbon number was between 10 and 11, while more than 80 wt% was isoparaffinic. It was demonstrated that the fuel produced can be used as kerosene.

4. Conclusion

Various hybrid zeolite catalysts with **ns** Al₂O₃ had high performance for HT-CC and HT-HC from isoprenoid oil derived from microalgae to afford gasoline, aromatics, and kerosene, while required hydrogen consumption increased in the order CC<HT-CC(MFI)<HC<HT-CC(USY)<HT-HC. Isoparaffinic/olefinic gasoline could be produced by hydrotreating-catalytic cracking on **ns** Al₂O₃/H-USY catalyst; high-octane-number aromatics-rich gasoline could be produced without an external hydrogen supply by hydrotreating-catalytic cracking on **ns** Al₂O₃/H-GaAlMFI catalyst. While hydrotreating hydrocracking on [NiMo/γ-Al₂O₃]/**ns** Al₂O₃/H-beta catalysts required a good supply of

hydrogen, isoparaffins-rich kerosene could be produced at low temperatures.

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