[Review Paper]

Catalytic Cracking of Light-naphtha Fraction over Zeolite-based Composites for On-purpose Propylene Production

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Catalytic cracking of light-naphtha fraction over zeolite-based composites in fixed-bed mode was investigated to establish an efficient method for on-purpose propylene production. The composite catalysts, consisting of MFI-type zeolites containing iron, gallium and aluminum species (Fe-Ga-Al-MFI) and metal-oxide binder (*e.g.*, silicon oxide, aluminum oxide), were employed for cracking of light-naphtha fraction. Fe-Ga-Al-MFI zeolites as matrix, containing each heteroatom at adequate ratio in the zeolite framework, exhibited both overall acid strength suitable for selective formation of light olefins and enhanced activity for dehydrogenation of light alkanes to alkenes, so that high overall yields of light olefins (ethylene, propylene and butenes) were attained by suppressing aromatics formation compared to cracking of light-naphtha fraction using conventional Al-MFI zeolite (ZSM-5). The unique acidity of the Fe-Ga-Al-MFI zeolite was maintained in the extruded form by using neutral and inactive silicon-oxide binder, which was selected to enhance mechanical strength and/or reduce pressure drop during reaction. The zeolite-based composite (Fe-Ga-Al-MFI/SiO₂) selectively converted light-naphtha fraction (*n*-hexane) into light olefins including propylene with catalyst lifetime longer than 2000 h, suitable for fixed-bed operation, due to its excellent resistance to coke formation. Furthermore, the cracking reactions proceeded in the absence of steam at moderate temperatures below 650 °C, so catalytic cracking using the present zeolite-based composite saved considerable thermal energy required in the reaction unit, and the total amount of hydrocarbon feedstock was reduced by *ca.* 15 %, compared to conventional thermal cracking at 850 °C. The present review discusses the excellent properties of these zeolite-based catalysts and catalytic cracking of light-naphtha fraction emphasizing the catalytic chemistry and reaction engineering of the catalytic process.

Keywords

Zeolite based composite, Modified MFI zeolite, Silicon oxide binder, Catalytic cracking,
On-purpose propylene production, Fixed bed operation

1. Introduction

Light olefins such as ethylene and propylene are important basic chemicals as building blocks for producing polymers and chemicals, so demand for these chemicals continues to grow at annual rates of 3-4 %¹⁾. Thermal cracking of light-naphtha feedstock has been widely adopted for producing ethylene, propylene, butenes, butadiene and BTX (benzene, toluene and xylenes)²⁾ and most propylene is currently obtained as a byproduct from thermal light-naphtha cracking with weight ratio of propylene to ethylene in the range of 0.5-0.6. However, ethylene production through thermal cracking of ethane feedstock, which generates little propylene, is becoming common, especially in the United States where a large amount of ethane are available from shale gas at competitive cost³⁾. Consequently, it

is difficult to meet the increasing demand for propylene based on the current conventional thermal-cracking process. In addition to the potential shortage of propylene, savings of energy consumption and reduction of carbon dioxide emissions are now important in chemical processes⁴⁾. The thermal light-naphtha cracking requires temperatures higher than 800 °C in the presence of steam for pyrolysis, so this cracking technology is the most energy-consuming process in the chemical industry⁵⁾. Therefore, new technologies for producing propylene efficiently from light naphtha, a widely available feedstock, should be developed to meet the increasing demand for propylene and reduce energy consumption simultaneously.

Catalytic cracking of the light-naphtha fraction over zeolite catalysts such as ZSM-5 is considered promising for on-purpose propylene production based on the following advantages^{6,7)}: (1) high cracking activity; (2) high selectivity to light olefins (high weight ratio of propylene to ethylene in the range of 1.0-2.0); (3) ener-

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gy-saving due to moderate operation temperatures below 650 °C. Catalytic cracking of various hydrocarbons over modified ZSM-5 zeolites using the fixed-bed reactor has been actively investigated to form light olefins selectively^{6,7)}. However, catalytic cracking processes have not been commercialized because stable catalysts suitable for use in the fixed-bed reactor at the industrial level have not yet been developed.

New zeolite-based composite catalysts for on-purpose propylene production from light-naphtha fraction, consisting of MFI-type zeolites and metal-oxide binder (*e.g.*, SiO₂, Al₂O₃), have been developed by our group^{8)~12)} as proprietary catalysts for cracking of the light-naphtha fraction in fixed-bed mode. MFI-type zeolites containing iron, gallium and aluminum species at specific ratios (Fe-Ga-Al-MFI), acting as a matrix component, exhibited higher selectivity to light olefins (ethylene, propylene and butenes) than conventional ZSM-5 (Al-MFI zeolite) by suppressing aromatization of light olefins in the cracking reactions due to its adequate acidity. Fe-Ga-Al-MFI-based composites combined with metal-oxide binder (*e.g.*, Al₂O₃, SiO₂) were also developed as cracking catalysts in the extruded form for practical use, providing both high selectivity to light olefins and excellent catalytic stability. In particular, the catalytic performance of the Fe-Ga-Al-MFI/SiO₂ composite was maintained for longer than 2000 h in *n*-hexane cracking under practical conditions¹¹⁾, due to its excellent resistance to coke formation. Energy consumption in the reaction unit during catalytic cracking of the light-naphtha fraction over the present zeolite-based composite catalysts was superior to the conventional thermal-cracking process, as catalytic cracking proceeded in the absence of steam at lower than 650 °C. Consequently, the amount of naphtha feedstock required for producing unit amount of valuable products (ethylene, propylene, butenes and BTX) was remarkably reduced in the catalytic cracking process compared to the thermal-cracking process¹¹⁾.

The present review presents excellent properties of the Fe-Ga-Al-MFI-based composites as cracking catalysts for on-purpose propylene production on the experimental basis. Furthermore, the catalytic naphtha-cracking process over the composite catalysts in the fixed-bed reactor is compared with the conventional thermal naphtha-cracking process in terms of chemical process engineering.

2. Preparation and Characterization of Zeolite-based Catalysts

2.1. Synthesis and Characterization of MFI-type Zeolites

The MFI-type zeolites containing iron, gallium and aluminum species (Fe-Ga-Al-MFI) and the MFI-type zeolite containing iron and aluminum species (Fe-Al-

MFI) were synthesized by the conventional hydrothermal method^{8),9)}. Aqueous solution containing silicon, iron, gallium and aluminum sources and tetrapropylammonium bromide as an organic structure-directing agent were prepared as the mother gel with the following molar compositions: (1) Si/T = 25, 50, 75, 90, 150, 200 and 500, Fe/T = 0.4, Ga/T = 0.2, Al/T = 0.4, T = Fe + Ga + Al; (2) Si/T = 25, Fe/T = 0.4, Al/T = 0.6, T = Fe + Al. The mother gel was charged into autoclave and then heated at 150 °C for 72 h under specific stirring conditions. The obtained sodium-type zeolite was converted into the proton-type zeolite by ion-exchange with ammonium nitrate aqueous solution, dried at 120 °C for 3 h and finally calcined at 550 °C for 3 h under air stream. The MFI-type zeolite containing aluminum species (Al-MFI, molar ratio in mother gel: Si/Al = 25) was similarly synthesized as the reference sample.

The crystallinity and the molar compositions of silicon, aluminum, iron and gallium species in the bulk phase of all samples were examined by powder the X-ray diffraction (XRD; SmartLab, Rigaku Corp.) and the X-ray fluorescence technique (XRF; PW2400/00, Philips), respectively. The surface area of the Al-MFI (Si/Al = 25 [mol/mol]), the Fe-Al-MFI (Si/(Fe + Al) = 25 [mol/mol]) and the Fe-Ga-Al-MFI zeolites (Si/(Fe + Ga + Al) = 25 [mol/mol]) were measured by the BET method on the basis of nitrogen adsorption isotherms (Belsorp mini II, MicrotracBEL Corp.). The chemical bonds of aluminum and gallium species in these samples were characterized by the ²⁷Al-MAS-NMR and the ⁷¹Ga-MAS-NMR measurements (AVANCE300, Bruker Corp.), respectively. The chemical structure of iron species in the Fe-Al-MFI (Si/(Fe + Al) = 25 [mol/mol]) and the Fe-Ga-Al-MFI (Si/(Fe + Ga + Al) = 25 [mol/mol]) zeolites were examined by the UV-Vis/DRS (diffuse reflectance spectroscopy) measurement in the wavelength range from 200 to 700 nm with the V-660 spectrometer equipped with the diffuse reflectance accessory (JASCO Corp.). The acidic properties of these samples were investigated by the temperature-programmed desorption technique using an ammonium probe (NH₃-TPD; JMS-QIO50GC/Ultra Quad GC/MS, JEOL Ltd.)⁹⁾.

2.2. Preparation and Characterization of MFI Zeolite-based Composites

Fe-Ga-Al-MFI/Al₂O₃ composite catalysts, consisting of Fe-Ga-Al-MFI zeolites and aluminum-oxide binder, were prepared according to the following steps^{8),9)}. Sodium-type Fe-Ga-Al-MFI zeolites with the following molar ratios in mother gel: Si/T = 25, 50, 75, 90, 150, 200 and 500, Fe/T = 0.4, Ga/T = 0.2, Al/T = 0.4, T = Fe + Ga + Al, were synthesized as described in section 2.1. Then, the Fe-Ga-Al-MFI zeolite and alumina sol (Cataloid AP-1, JGC Catalysts and Chemicals Ltd.¹³⁾) were mixed at weight ratio of zeolite to aluminum oxide

[Sample] Al-MFI (molar composition: Si/Al = 19.4), Fe-Al-MFI (molar composition: Si/T = 19.4, Fe/T = 0.5, Al/T = 0.5, T = Fe + Al), Fe-Ga-Al-MFI (molar composition: Si/T = 19.4, Fe/T = 0.4, Ga/T = 0.3, Al/T = 0.3, T = Fe + Ga + Al).

Fig. 1 Characterization of Synthesized MFI-type Zeolites by Instrumental Analysis: (A) XRD pattern, (B) ^{27}Al -MAS-NMR spectrum, (C) ^{71}Ga -MAS-NMR spectrum

of 75/25, and the powdery mixture was molded in the extruded form (1.0 mm ϕ). Finally, the extruded sample was converted into the protonated-type zeolite with ammonium nitrate aqueous solution, dried at 120 °C for 3 h and then calcined at 550 °C for 3 h under air stream. The Fe-Ga-Al-MFI/ Al_2O_3 composite catalyst (molar ratio in mother gel: Si/T = 200, Fe/T = 0.4, Ga/T = 0.2, Al/T = 0.4, T = Fe + Ga + Al, weight ratio of Fe-Ga-Al-MFI/ Al_2O_3 : 85/15) was also prepared in the same manner.

The Fe-Ga-Al-MFI/ SiO_2 composite catalyst, consisting of the Fe-Ga-Al-MFI zeolite and silicon-oxide binder, was prepared as follows¹¹⁾. Sodium-type Fe-Ga-Al-MFI zeolite (molar ratio in mother gel: Si/T = 200, Fe/T = 0.4, Ga/T = 0.2, Al/T = 0.4, T = Fe + Ga + Al) was hydrothermally synthesized as described in section 2. 1. The Fe-Ga-Al-MFI zeolite and silica sol (AERO-SIL200, Evonik Industries AG) were mixed at weight ratio of zeolite to silicon oxide of 85/15, and the powdery mixture was molded in the extruded form (1.0 mm ϕ). Finally, the extruded sample was converted into the protonated-type zeolite with ammonium nitrate aqueous solution, it was dried at 120 °C for 3 h and then calcined at 550 °C for 3 h under air stream. The composite catalyst of nano-sized Fe-Ga-Al-MFI and silicon-oxide binder (molar ratio in mother gel: Si/T = 200, Fe/T = 0.4, Ga/T = 0.2, Al/T = 0.4, T = Fe + Ga + Al, weight ratio of Fe-Ga-Al-MFI/ SiO_2 : 60/40) was prepared in the same manner¹¹⁾.

The weight ratios of zeolite to binder in the composite catalysts were measured by the XRF technique (XRF; PW2400/00, Philips). The morphology and the elemental analysis of silicon and aluminum atoms of the Fe-Ga-Al-MFI/ Al_2O_3 composite catalyst (molar

ratio in mother gel: Si/T = 25, Fe/T = 0.4, Ga/T = 0.2, Al/T = 0.4, T = Fe + Ga + Al, weight ratio of Fe-Ga-Al-MFI/ Al_2O_3 : 75/25), was examined by the scanning electron microscopy equipped with an energy-dispersive fluorescence X-ray spectrometer (SEM-EDX; Hitachi, Ltd.)⁹⁾. The morphology of the Fe-Ga-Al-MFI/ SiO_2 and the Fe-Ga-Al-MFI/ Al_2O_3 composite catalysts (molar ratio in mother gel: Si/T = 200, Fe/T = 0.4, Ga/T = 0.2, Al/T = 0.4, T = Fe + Ga + Al, weight ratio of Fe-Ga-Al-MFI/ Al_2O_3 or Fe-Ga-Al-MFI/ SiO_2 : 85/15) were examined by the field emission scanning electron microscopy (FE-SEM; Ultra55, ZEISS) using an energy-dispersive fluorescence X-ray spectrometer (EDX; NSS-312E, Thermo Fischer Scientific K.K.)¹¹⁾. The acidic properties of these composites were investigated by the NH_3 -TPD (JMS-QIO50GC/Ultra, JEOL Ltd.)¹¹⁾ as described in section 2. 1.

3. Properties of MFI Zeolite-based Composites and Their Application to Catalytic Cracking of Light-naphtha Fraction

3.1. Characterization and Catalytic Properties of MFI-type Zeolites

Figure 1(A) presents the XRD patterns of three types of protonated MFI-type zeolites (Al-MFI (molar ratio in mother gel: Si/Al = 25), Fe-Al-MFI (molar ratio in mother gel: Si/T = 25, Fe/T = 0.4, Al/T = 0.6, T = Fe + Al) and Fe-Ga-Al-MFI (molar ratio in mother gel: Si/T = 25, Fe/T = 0.4, Ga/T = 0.2, Al/T = 0.4, T = Fe + Ga + Al). All three types displayed the diffraction patterns corresponding to the MFI-type framework. Table 1 gives the chemical composition of the bulk phase measured by the XRF technique and the BET

Table 1 Chemical Composition and BET Surface Area of Synthesized MFI-type Zeolites⁹⁾

Zeolite sample (Si/T ratio ^{a)})	Si/T ratio ^{b)} [mol/mol]	Ratio of each heteroatom ^{c)} [mol/mol]			BET Surface area [m ² /g]
		Fe/(Fe + Ga + Al)	Ga/(Fe + Ga + Al)	Al/(Fe + Ga + Al)	
Al-MFI (25.0)	20.0	0.0	0.0	1.0	330
Fe-Al-MFI (25.0)	19.4	0.5	0.0	0.5	330
Fe-Ga-Al-MFI (25.0)	19.4	0.4	0.3	0.3	320

a) Si/T molar ratio in mother gel (T = Al, Fe + Al, Fe + Ga + Al).

b) Si/T molar ratio of resultant zeolites measured by XRF technique (T = Al, Fe + Al, Fe + Ga + Al).

c) These values were calculated on the basis of results of XRF measurement.

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surface area⁹⁾. The molar ratios of silicon atoms to heteroatoms (Si/Al, Si/(Fe + Al) and Si/(Fe + Ga + Al)) and the BET surface area were nearly the same. In addition, the actual molar ratios of each heteroatom to total heteroatoms in the Fe-Al-MFI and the Fe-Ga-Al-MFI zeolites were calculated as follows: Fe-Al-MFI; Fe/T = 0.5, Al/T = 0.5, T = Fe + Al, Fe-Ga-Al-MFI; Fe/T = 0.4, Ga/T = 0.3, Al/T = 0.3, T = Fe + Ga + Al.

Figures 1(B) and **1(C)** shows the ²⁷Al-MAS-NMR spectrum of the Al-MFI, the Fe-Al-MFI and the Fe-Ga-Al-MFI zeolites and the ⁷¹Ga-MAS-NMR spectrum of the Fe-Ga-Al-MFI zeolite. The ²⁷Al-MAS-NMR spectrum included signals at around 50 ppm and around 0 ppm are assigned to the tetrahedral aluminum species located in the zeolite framework and the octahedral aluminum species located in the external framework, respectively. **Figure 1(B)** confirmed that most of aluminum species were incorporated in the MFI-type zeolite framework. The ⁷¹Ga-MAS-NMR spectrum included signals at around 160 ppm and around 0 ppm are assigned to the tetrahedral gallium species located in the framework and the octahedral gallium species located in the extra framework, respectively. The ⁷¹Ga-MAS-NMR spectrum of the Fe-Ga-Al-MFI zeolite (**Fig. 1(C)**) only detected the tetrahedral gallium species, indicating that most of gallium species were incorporated in the zeolite framework.

Iron species in the Fe-Al-MFI and Fe-Ga-Al-MFI zeolites were characterized by the UV/Vis-DRS measurement^{14)~18)}. As shown in **Figs. 2(A)** and **2(B)**, the UV/Vis spectrum detected the bands at 200-300 nm, smaller bands at 300-400 nm and small peaks at above 400 nm. The bands observed in the range of 200-300 nm are typically attributed to isolated Fe³⁺ species, either tetrahedrally coordinated in the zeolite framework or with higher coordination¹⁷⁾. The broad bands observed in the range of 300-450 nm and above 400 nm are characteristic of octahedral Fe³⁺ ions in small oligonuclear Fe_x³⁺O_y complexes and Fe³⁺ ions in large aggregated iron oxides, respectively¹⁷⁾. **Figures 2(A)** and **2(B)** thus indicates that most of iron species were well isolated in either the Fe-Al-MFI or the Fe-Ga-Al-MFI zeolites. The observed UV/Vis bands (solid line in blue) can be divided into three subbands by deconvolution¹⁵⁾, where line (*I*₁) is a single charge-transfer (Fe³⁺ ← O) band at 240 nm derived from the tetrahedral isolated iron species incorporated in the zeolite framework, line (*I*₂) is a single charge-transfer (Fe³⁺ ← O) band at 273 nm derived from isolated Fe³⁺ species in octahedral coordination, line (*I*₃) is the band derived from larger Fe₂O₃ particles and the baseline (in black). In addition, deconvolution provided that the relative percentage of tetrahedral isolated iron species incorporated in the zeolite framework, isolated Fe³⁺ species in octahedral coordination in zeolite and larger Fe₂O₃ particles in zeolite were 57 % : 37 % : 6 % for the Fe-Al-MFI and 45 % : 45 % : 10 % for the Fe-Ga-Al-MFI (**Figs. 2(A)** and **2(B)**).

Figure 3 shows the NH₃-TPD profiles of the Al-MFI, the Fe-Al-MFI and the Fe-Ga-Al-MFI zeolites. Two desorption peaks of ammonium molecules were observed at around 450 K and 620 K, respectively. The peak at around 450 K is the desorption peak derived from NH₃ molecules physically adsorbed on zeolites, whereas the peak at around 620 K is definitely associated with ammonium molecules chemically adsorbed on acid sites. **Table 2** presents the overall acidic properties of these zeolites estimated by analyzing the desorption peaks at high temperatures. Both acid amount and overall acid strength were estimated as the peak area and the activation energy required for desorption of ammonium molecules according to the method by Niwa and Katada *et al.*^{19)~22)}. The acid amount was nearly the same for all zeolites, whereas the desorption peaks of the Fe-Al-MFI and the Fe-Ga-Al-MFI zeolites, closely related to the acid strength, were shifted to lower temperatures compared to that of the Al-MFI zeolite (**Fig. 3**). The activation energy required for ammonium desorption from the Fe-Al-MFI and the Fe-Ga-Al-MFI were thus smaller than that of the Al-MFI zeolite (**Table 2**), indicating that the overall acid strength of the Fe-Al-MFI and the Fe-Ga-Al-MFI zeolites were reduced compared to the Al-MFI zeolite. The acid strength of isomorphous ZSM-5 zeolites is recognized to become stronger in the following order: Fe-MFI < Ga-MFI < Al-MFI (ZSM-5)^{6),11),18),23)}. The present results agree with this tendency.

These results confirmed that most of iron, gallium

[Sample] Fe-Al-MFI (molar composition: Si/T = 19.4, Fe/T = 0.5, Al/T = 0.5, T = Fe + Al), Fe-Ga-Al-MFI (molar composition: Si/T = 19.4, Fe/T = 0.4, Ga/T = 0.3, Al/T = 0.3, T = Fe + Ga + Al).

Fig. 2 UV-Vis/DRS Spectra of Synthesized MFI-type Zeolites: (A) Fe-Al-MFI, (B) Fe-Ga-Al-MFI

[Sample] Al-MFI (molar composition: Si/Al = 19.4), Fe-Al-MFI (molar composition: Si/T = 19.4, Fe/T = 0.5, Al/T = 0.5, T = Fe + Al), Fe-Ga-Al-MFI (molar composition: Si/T = 19.4, Fe/T = 0.4, Ga/T = 0.3, Al/T = 0.3, T = Fe + Ga + Al).

Fig. 3 NH_3 -TPD Profiles of Synthesized MFI-type Zeolites⁹⁾
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Table 2 Acidic Properties of Synthesized MFI-type Zeolites⁹⁾

Zeolite sample (Si/T ratio ^{a)})	Si/T ratio ^{b)} [mol/mol]	Acid amount ^{c)} [mmol/g]	Acid strength ^{c)} [kJ/mol]
Al-MFI (25.0)	20.0	0.57	143.0
Fe-Al-MFI (25.0)	19.4	0.51	138.6
Fe-Ga-Al-MFI (25.0)	19.4	0.52	137.1

a) Si/T molar ratio in mother gel (T = Al, Fe + Al, Fe + Ga + Al).
 b) Si/T molar ratio measured by XRF technique (T = Al, Fe + Al, Fe + Ga + Al).
 c) Acid amount and acid strength of zeolite samples and composite samples measured by NH_3 -TPD technique⁹⁾.
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and aluminum species in the Al-MFI, the Fe-Al-MFI and the Fe-Ga-Al-MFI zeolites were incorporated in the zeolite framework. The amount of acid sites was nearly the same, but the Fe-Al-MFI and Fe-Ga-Al-MFI zeolites, synthesized by introducing iron, gallium and aluminum species at specific ratios into the zeolite framework, exhibited weaker overall acid strength than the conventional ZSM-5 (Al-MFI zeolite).

Catalytic cracking of *n*-hexane diluted with nitrogen (molar ratio of nitrogen to *n*-hexane: 15/1) over the Al-MFI, the Fe-Al-MFI and the Fe-Ga-Al-MFI zeolites in the pellet form was performed under the same reaction conditions (550 °C, 0.1 MPa, LHSV of *n*-hexane:

[Catalyst] Al-MFI (molar composition: Si/Al = 19.4), Fe-Al-MFI (molar composition: Si/T = 19.4, Fe/T = 0.5, Al/T = 0.5, T = Fe + Al), Fe-Ga-Al-MFI (molar composition: Si/T = 19.4, Fe/T = 0.4, Ga/T = 0.3, Al/T = 0.3, T = Fe + Ga + Al).

[Reaction conditions] Temperature: 550 °C, Pressure: 0.1 MPa, Charged volume of catalyst: 1.0 mL, Feedstock: *n*-hexane diluted with nitrogen (molar ratio of *n*-hexane to nitrogen: 1/15, *1/5), LHSV of *n*-hexane: 1.0 h⁻¹.

Fig. 4 Product Distribution during the Initial Stage of Catalytic *n*-Hexane Cracking over Synthesized MFI-type Zeolites⁹⁾
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1.0 h⁻¹) using a fixed-bed-type reactor to compare catalytic performance of these zeolites⁹⁾. **Figure 4** shows the product selectivity at initial stage. The product distribution in *n*-hexane cracking over the Fe-Al-MFI or the Fe-Ga-Al-MFI zeolites was obviously changed compared to the Al-MFI zeolite. The Al-MFI zeolite exhibited comparatively high selectivity to light olefins, but it gave high selectivity to aromatics such as BTX (Benzene, Toluene and Xylenes). On the other hand, the Fe-Al-MFI and the Fe-Ga-Al-MFI zeolites showed remarkably enhanced selectivity to light olefins by suppressing aromatics formation, so that high propylene yields in the range of 24.7-27.0 wt% were obtained in spite of the low temperature of 550 °C. In addition, selectivity at the same level conversion was compared by *n*-hexane cracking over the Fe-Ga-Al-MFI zeolite at the molar ratio of nitrogen to *n*-hexane of 5/1, giving *n*-hexane conversion of 98.5 wt%. Selectivity to aromatics increased with conversion, but the Fe-Ga-Al-MFI zeolite still maintained higher selectivity to propylene than the Al-MFI zeolite, resulting in high propylene yield of 24.3 wt%. Catalytic cracking of light paraffinic hydrocarbons over zeolite catalysts consecutively proceeds *via* light olefins to generate aromatics^{24)~27)} and selectivity to light olefins strongly depends on the acid strength of the zeolites^{11),18)}. Overall acid strength of the Fe-Ga-Al-MFI, containing iron, gallium and aluminum species at the optimized ratio into the zeolite framework, was reduced compared to the parent Al-MFI, as clearly shown by the NH₃-TPD profiles (**Fig. 3**). Furthermore, gallium species contained in zeolites could accelerate dehydrogenation of light alkane to light alkenes^{25),28)}. Therefore, the Fe-

[Sample] Fe-Ga-Al-MFI/Al₂O₃ composite (molar composition of zeolite: Si/T = 19.4, Fe/T = 0.4, Ga/T = 0.3, Al/T = 0.3, T = Fe + Ga + Al, weight ratio of Fe-Ga-Al-MFI/Al₂O₃: 75/25 [wt%/wt%]).

Fig. 5 SEM Image of Fe-Ga-Al-MFI/Al₂O₃ Composite and Distribution of Silicon and Aluminum Atoms in Composite Form by SEM-EDX Analysis⁹⁾: (A) SEM image, (B) and (C) distribution of Si and Al atoms measured by SEM-EDX analysis

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Ga-Al-MFI zeolite catalytically converted *n*-hexane selectively into light olefins including propylene based on the suitable acid strength and enhanced dehydrogenation ability.

3. 2. Characterization and Catalytic Properties of Fe-Ga-Al-MFI/Al₂O₃ Composites

The use of zeolites as industrial catalysts requires molding of the powdery zeolites into the extruded form using a binder such as aluminum oxide¹³⁾. In the present study, the composite catalyst in the extruded form with diameter of 1.0 mm ϕ , consisting of the Fe-Ga-Al-MFI zeolite (Si/(Fe + Ga + Al) ratio: 19.4 [mol/mol]) and aluminum-oxide binder, was prepared to improve mechanical strength and/or reduce pressure drop during reaction^{8),9),13),29)}. **Figure 5(A)** shows the SEM image of the composite sample and **Figs. 5(B)** and **5(C)** illustrates the distribution of silicon and aluminum atoms in the composite sample measured by the SEM-EDX analysis⁹⁾. Clearly both silicon and aluminum atoms were uniformly distributed in the composite sample. **Table 3** compares catalytic activities for *n*-hexane cracking with respect to the Fe-Ga-Al-MFI-zeolite only and the Fe-Ga-Al-MFI/Al₂O₃ composite (weight ratio of zeolite to aluminum-oxide binder in resultant sample: 75/25 [wt%/wt%]). The composite catalyst exhibited higher *n*-hexane conversion and apparent yields of light olefins than the Fe-Ga-Al-MFI zeolite. The

Table 3 Comparison of Catalytic Performance for *n*-Hexane Cracking over Fe-Ga-Al-MFI and Fe-Ga-Al-MFI/Al₂O₃ Composite

Catalyst (Si/T ratio ^{a)})	Zeolite/Al ₂ O ₃ ratio [wt%/wt%]	Conv. [wt%]	Product yield [wt%]			Space time yield of light olefins [g-(C ₂ + C ₃)/g-zeolite h]
			Ethylene (C ₂)	Propylene (C ₃)	BTX	
Fe-Ga-Al-MFI (19.4) only	100/0	71.8	8.3	27.0	7.1	0.53
Fe-Ga-Al-MFI (19.4)/Al ₂ O ₃	75/25	80.9	10.0	28.3	10.8	0.62

a) Si/T molar ratio measured by XRF technique (T = Fe + Ga + Al).

Reaction conditions; Temperature 550 °C, Pressure 0.1 MPa, Charged volume of catalyst 1.0 mL, Feedstock: *n*-hexane diluted with nitrogen (molar ratio of *n*-hexane to nitrogen: 1/15), LHSV of *n*-hexane 1.0 h⁻¹.

Table 4 Initial Activity for Catalytic *n*-Hexane Cracking over Fe-Ga-Al-MFI/Al₂O₃ Composites with or without Nitrogen Dilution

Feedstock	Mixed ratio [mol/mol]	LHSV of <i>n</i> -C ₆ [h ⁻¹]	Conv. [wt%]	Ethylene yield [wt%]	Propylene yield [wt%]	Space time yield of light olefins [g-(C ₂ + C ₃)/g-zeolite h]
<i>n</i> -C ₆ H ₁₄ /N ₂	1/15	1.0	80.9	10.0	28.3	0.62
<i>n</i> -C ₆ H ₁₄ only	1/0	5.0	67.3	8.2	18.1	1.40

Catalyst; Fe-Ga-Al-MFI/Al₂O₃ composite for *n*-hexane cracking diluted with nitrogen (Si/T = 19.4, Fe/T = 0.4, Ga/T = 0.3, Al/T = 0.3, T = Fe + Ga + Al, mixed ratio of zeolite to aluminum oxide: 75/25 [wt%/wt%]), Fe-Ga-Al-MFI/Al₂O₃ composite for *n*-hexane cracking without dilution (Si/T = 121.3, Fe/T = 0.3, Ga/T = 0.2, Al/T = 0.5, T = Fe + Ga + Al, mixed ratio of zeolite to aluminum oxide: 75/25 [wt%/wt%]).

Reaction conditions: Temperature 550 °C (*n*-hexane/nitrogen), 565 °C (*n*-hexane only), Pressure 0.1 MPa.

amount of light olefins generated per hour per one gram of zeolite, *i.e.* space time yield of light olefins, was also enhanced by use of the composite catalyst, suggesting that the zeolite species combined with aluminum-oxide binder were well dispersed. The experimental findings thus confirmed that the present composite was suitable catalyst for industrial cracking.

The application of the present composite catalysts to the cracking process under practical conditions was investigated through *n*-hexane cracking without dilution over the Fe-Ga-Al-MFI/Al₂O₃ composites under the following conditions: 565 °C; 0.1 MPa; LHSV 5.0 h⁻¹. To feed hydrocarbon feedstock without dilution into the cracking catalyst is more advantageous than catalytic cracking of hydrocarbons diluted with nitrogen or steam, because the supply of hydrocarbon feedstock without dilution needs no apparent heat for heating the diluent as well as preventing irreversible catalyst deactivation caused by de-alumination of the zeolites^{8,9,11}. **Figure 6** presents the relationship between amount of acid sites (*i.e.* Si/(Fe + Ga + Al) ratio) of the Fe-Ga-Al-MFI/Al₂O₃ composites and catalytic activities for *n*-hexane cracking without dilution. In contrast to cracking of *n*-hexane diluted with nitrogen (**Fig. 4** and **Table 3**), the Fe-Ga-Al-MFI/Al₂O₃ catalysts with low Si/(Fe + Ga + Al) ratios (*e.g.*, 19.4 [mol/mol], 31.3 [mol/mol]) provided high yields of aromatics. Lower amount of acid sites (*i.e.*, higher the Si/(Fe + Ga + Al) ratio) resulted in higher selectivity to light olefins by suppressing aromatics formation and the highest propylene selectivity of *ca.* 27 wt% was obtained at the Si/(Fe + Ga + Al) ratio of 121.3 [mol/mol]. Higher Si/(Fe + Ga + Al) ratios than 150 [mol/mol] (*i.e.*, smaller amounts of acid sites) caused lower selectivity to light

[Catalyst] Fe-Ga-Al-MFI/Al₂O₃ composites (molar composition of zeolite: Si/T = 19.4-56.0 (Fe/T = 0.4, Ga/T = 0.3, Al/T = 0.3, T = Fe + Ga + Al), Si/T = 92.9-177.5 (Fe/T = 0.3, Ga/T = 0.2, Al/T = 0.5, T = Fe + Ga + Al), weight ratio of Fe-Ga-Al-MFI/Al₂O₃: 75/25 [wt%/wt%]).

[Reaction conditions] Temperature: 565 °C, Pressure: 0.1 MPa, Charged volume of catalyst: 2.0 mL, Feedstock: *n*-hexane (100 wt%), LHSV: 5.0 h⁻¹.

Fig. 6 Initial Activity for Catalytic Cracking of *n*-Hexane without Dilution of Fe-Ga-Al-MFI/Al₂O₃ with Various Si/(Fe + Ga + Al) Ratios⁸⁾

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olefins (ethylene and propylene) because of lower *n*-hexane conversions. **Table 4** shows the catalytic performance of the Fe-Ga-Al-MFI/Al₂O₃ catalysts in the *n*-hexane cracking with or without dilution. The space time yield of light olefins was *ca.* 1.4 [g-(ethylene + propylene)/g-zeolite h], more than twice the value in the case of diluting with nitrogen. Aromatization proceeds much easier in the cracking of *n*-hexane without

dilution than diluted with nitrogen due to re-adsorption of light olefins on acid sites, indicating that aromatics would be generated quite selectively using zeolites with low Si/(Fe + Ga + Al) ratios. In other words, zeolites with high Si/(Fe + Ga + Al) ratios would provide high selectivity to light olefins by suppressing aromatics formation.

Catalytic cracking of the light-naphtha fraction without dilution is favorable from these aspects, but cracking catalysts require excellent stability because it is

[Catalyst] Fe-Ga-Al-MFI/Al₂O₃ composites (molar composition of zeolite: Si/T = 121.3, Fe/T = 0.3, Ga/T = 0.2, Al/T = 0.5, T = Fe + Ga + Al, weight ratio of Fe-Ga-Al-MFI/Al₂O₃ 75/25 [wt%/wt%]).
[Reaction conditions] Temperature: 565 °C, Pressure: 0.1 MPa, Charged volume of catalyst: 2.0 mL, Feedstock: *n*-hexane (100 wt%), LHSV: 5.0 h⁻¹.

Fig. 7 Time Course of One-pass Conversions for Catalytic Cracking of *n*-Hexane without Dilution over Fe-Ga-Al-MFI/Al₂O₃ Composite

easy to cause coke formation if hydrocarbons without diluent are supplied into the catalyst. The *n*-hexane cracking without dilution at 565 °C was continued for a long time to examine the lifetime of the Fe-Ga-Al-MFI/Al₂O₃ composite catalyst with Si/(Fe + Ga + Al) ratio of 121.3 [mol/mol]. **Figure 7** shows that one-pass conversions of *n*-hexane obtained at the initial stage were maintained for *ca.* 80 h despite the quite severe conditions, indicating that this composite catalyst is highly resistant to coke formation⁹⁾.

3.3. Characterization and Catalytic Properties of Fe-Ga-Al-MFI/SiO₂ Composites

The Fe-Ga-Al-MFI/Al₂O₃ composite catalyst achieved both high selectivity to light olefins and excellent stability (lifetime of *ca.* 80 h) in cracking of *n*-hexane without dilution, but further improvement in the catalytic stability is necessary to apply the present composites to catalytic cracking processes in the industrial fixed-bed mode. To improve the lifetime, the Fe-Ga-Al-MFI zeolite combined with silicon-oxide binder (Fe-Ga-Al-MFI/SiO₂) was evaluated as a cracking catalyst.

Figures 8(A), 8(B) and **8(C)** shows the FE-SEM images of the Fe-Ga-Al-MFI (Si/(Fe + Ga + Al) ratio: 121.3 [mol/mol]) and the Fe-Ga-Al-MFI/SiO₂ and the Fe-Ga-Al-MFI/Al₂O₃ composites (Si/(Fe + Ga + Al) ratio: 121.3 [mol/mol], with weight ratio of zeolite to binder: 85/15 [wt%/wt%]), respectively. The Fe-Ga-Al-MFI/SiO₂ consisted of zeolite particles with uniform diameter well dispersed in the composite and most of

[Sample] Fe-Ga-Al-MFI (molar composition of zeolite: Si/T = 121.3, Fe/T = 0.3, Ga/T = 0.2, Al/T = 0.5, T = Fe + Ga + Al), Fe-Ga-Al-MFI/SiO₂ composite (weight ratio of Fe-Ga-Al-MFI/SiO₂: 85/15 [wt%/wt%]), Fe-Ga-Al-MFI/Al₂O₃ composite (weight ratio of Fe-Ga-Al-MFI/Al₂O₃: 85/15 [wt%/wt%]).

Fig. 8 FE-SEM Images of Fe-Ga-Al-MFI Zeolite, Fe-Ga-Al-MFI/SiO₂ Composite and Fe-Ga-Al-MFI/Al₂O₃ Composite: (A) Fe-Ga-Al-MFI, (B) Fe-Ga-Al-MFI/SiO₂, (C) Fe-Ga-Al-MFI/Al₂O₃

Table 5 Acidic Properties of Synthesized MFI-type Zeolites and Composites

Sample	Si/T ratio ^{a)} [mol/mol]	Fe/T ratio ^{a)} [mol/mol]	Ga/T ratio ^{a)} [mol/mol]	Al/T ratio ^{a)} [mol/mol]	Zeolite/binder ratio ^{b)} [wt%/wt%]	Acid amount ^{c)} [mmol/g]
Fe-Ga-Al-MFI only	121.3	0.3	0.2	0.5	100/0	0.18
Fe-Ga-Al-MFI/SiO ₂	121.3	0.3	0.2	0.5	85/15	0.16
Fe-Ga-Al-MFI/Al ₂ O ₃	121.3	0.3	0.2	0.5	85/15	0.20

a) Molar ratios (Si/T, Al/T, Ga/T, Fe/T, T = Fe + Ga + Al) of zeolite samples measured by XRF technique.

b) Weight ratio of composite samples by XRF technique.

c) Acid amount of zeolite samples and composite samples measured by NH₃-TPD technique¹¹⁾.

powdery SiO₂ binder was present in space between the zeolite particles (**Fig. 8(B)**). The Fe-Ga-Al-MFI particle sizes in the composite form were in the range of 1-2 μm , smaller than the zeolite particle size (*ca.* 5 μm , **Fig. 8(A)**) before molding. The Fe-Ga-Al-MFI/Al₂O₃ (**Fig. 8(C)**) consisted of zeolite particles combined with the Al₂O₃ binder which were well dispersed in the composite form and the average size (*ca.* 2-3 μm) was smaller than the zeolite particle size before molding. However, some zeolite particles were connected with the Al₂O₃ binder in the plate form unlike in the Fe-Ga-Al-MFI/SiO₂.

Figure 9 shows the NH₃-TPD profiles of the Fe-Ga-Al-MFI zeolite and the Fe-Ga-Al-MFI/SiO₂ and the Fe-Ga-Al-MFI/Al₂O₃ composites¹¹⁾. As described in section 3.1., the overall acidic properties of these samples were estimated on the basis of the NH₃-TPD measurements (**Table 5**). The Fe-Ga-Al-MFI/SiO₂ composite gave two desorption peaks, similar to the Fe-Ga-Al-MFI zeolite, at lower than 550 K and in the range of 550-750 K. The amount of acid sites was reduced by *ca.* 85 %, corresponding to the content of zeolite species (*ca.* 85 wt%), compared to the Fe-Ga-Al-MFI-zeolite (**Table 5**). Both the peak shape and the peak-top positions in the profile of composite were the same as the zeolite, suggesting that the overall acid strength of the zeolite was unchanged in the composite form were (**Fig. 9**). Therefore, the SiO₂ species purely acted as a binder without affecting the overall acid strength of the zeolite species due to its neutral and inactive nature.

In contrast to the Fe-Ga-Al-MFI/SiO₂, the Fe-Ga-Al-MFI/Al₂O₃ composite exhibited different behaviors in the NH₃-TPD profile¹¹⁾. Firstly, the acid amount was a little larger than that of the zeolite (0.18 $\rightarrow$ 0.20 mmol/g, **Table 5**). Secondly, the peak-top positions of the Fe-Ga-Al-MFI/Al₂O₃ composite were nearly the same as those of the Fe-Ga-Al-MFI/SiO₂ composite, but obvious broadening of the desorption peak in the high-temperature region (550-825 K) was seen, as shown in **Fig. 9**. Furthermore, a shoulder peak was detected in the range of 700-825 K, suggesting that stronger acid sites were also formed at the interface between the Fe-Ga-Al-MFI zeolite and the Al₂O₃ binder (*vide infra*). The Al₂O₃ species thus functioned not only as a binder but also affected the acidity of the zeolite species.

[Sample] Fe-Ga-Al-MFI (molar composition of zeolite: Si/T = 121.3, Fe/T = 0.3, Ga/T = 0.2, Al/T = 0.5, T = Fe + Ga + Al), Fe-Ga-Al-MFI/SiO₂ composite (weight ratio of Fe-Ga-Al-MFI/SiO₂: 85/15 [wt%/wt%]), Fe-Ga-Al-MFI/Al₂O₃ composite (weight ratio of Fe-Ga-Al-MFI/Al₂O₃: 85/15 [wt%/wt%]).

Fig. 9 NH₃-TPD Profiles of Fe-Ga-Al-MFI Zeolite, Fe-Ga-Al-MFI/SiO₂ Composite and Fe-Ga-Al-MFI/Al₂O₃ Composite

Catalytic cracking of *n*-hexane without dilution over the Fe-Ga-Al-MFI/SiO₂ composite was performed under the following conditions: 565 $^{\circ}\text{C}$; 0.1 MPa; LHSV 6.0 h^{-1} to estimate its catalytic performance. In addition to *n*-hexane, cracking of two mixed hydrocarbons (*n*-C₅H₁₂ (65 wt%) + *n*-C₆H₁₄ (35 wt%), *n*-C₆H₁₄ (50 wt%) + *n*-C₇H₁₆ (25 wt%) + *n*-C₈H₁₈ (25 wt%)) were conducted over the Fe-Ga-Al-MFI/SiO₂ under the same conditions¹¹⁾. **Figure 10** shows the overall yield (refer to section 3.4.) of each product from the cracking reactions. Overall yields of propylene higher than 30 wt% were achieved in the cracking of *n*-hexane or mixed hydrocarbons of *n*-C₅H₁₂ and *n*-C₆H₁₄, representing light naphtha. One-pass conversion higher than 77 wt% was attained in the cracking of mixed hydrocarbons of *n*-C₆H₁₄, *n*-C₇H₁₆ and *n*-C₈H₁₈, representing heavy naphtha, but overall yields of propylene and light olefins were lower than other cases. Product selectivity and catalytic stability of the Fe-Ga-Al-MFI/Al₂O₃ was compared by cracking of mixed hydrocarbons of *n*-C₆H₁₄, *n*-C₇H₁₆ and *n*-C₈H₁₈ under the same condi-

[Catalyst] Fe-Ga-Al-MFI/SiO₂ composite (molar composition of zeolite: Si/T = 121.3, Fe/T = 0.3, Ga/T = 0.2, Al/T = 0.5, T = Fe + Ga + Al, weight ratio of Fe-Ga-Al-MFI/SiO₂: 85/15 [wt%/wt%]), Fe-Ga-Al-MFI/Al₂O₃ composite (molar composition of zeolite: Si/T = 121.3, Fe/T = 0.3, Ga/T = 0.2, Al/T = 0.5, T = Fe + Ga + Al, weight ratio of Fe-Ga-Al-MFI/Al₂O₃: 85/15 [wt%/wt%]).

[Reaction conditions] Temperature: 565 °C, Pressure: 0.1 MPa, Charged volume of catalyst: 2.0 mL, Feedstock: *n*-hexane (100 wt%), *n*-pentane (65 wt%) + *n*-hexane (35 wt%), *n*-hexane (50 wt%) + *n*-heptane (25 wt%) + *n*-octane (25 wt%), LHSV: 6.0 h⁻¹.

Fig. 10 Overall Product Distribution during the Initial Stage of Catalytic Cracking of Light Hydrocarbons over Fe-Ga-Al-MFI/SiO₂ Composite and Fe-Ga-Al-MFI/Al₂O₃ Composite¹¹⁾

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tions. The Fe-Ga-Al-MFI/Al₂O₃ gave slightly higher one-pass conversion and overall yields of aromatics (BTX) than the Fe-Ga-Al-MFI/SiO₂, but the product distribution showed no apparent difference.

The effect of binder species on catalytic stability was examined in the cracking of mixed hydrocarbons (*n*-C₆H₁₄ (50 wt%) + *n*-C₇H₁₆ (25 wt%) + *n*-C₈H₁₈ (25 wt%))¹¹⁾. Aromatic hydrocarbons generated in cracking are precursor of carbonaceous deposits formed by polymerization, so are likely to cause coke formation on the catalyst. Consequently, suppression of aromatics formation is important to maintain stable catalytic activity stably during cracking in the fixed-bed mode. Therefore, cracking of C₆-C₈ hydrocarbons with higher selectivity to aromatics (Fig. 10) will evaluate catalytic stability under accelerated conditions. Figure 11 shows the time courses of one-pass conversions in the catalytic cracking of C₆-C₈ hydrocarbons over the Fe-Ga-Al-MFI/SiO₂ and the Fe-Ga-Al-MFI/Al₂O₃ for 55 h under the same reaction conditions (565 °C, 0.1 MPa, LHSV 6 h⁻¹). Catalytic activity of the Fe-Ga-Al-MFI/Al₂O₃ was rapidly decreased after 35 h and apparent deactivation was observed within 50 h, whereas catalytic activity of the Fe-Ga-Al-MFI/SiO₂ gradually decreased with elapsed time, but deterioration was much lower than for the Fe-Ga-Al-MFI/Al₂O₃. The amount of coke deposited on the Fe-Ga-Al-MFI/Al₂O₃ and the Fe-Ga-Al-MFI/SiO₂ was 17.7 wt% for 55 h and 7.0 wt% for 55 h, respectively. These results confirmed that catalytic stability was re-

[Catalyst] Fe-Ga-Al-MFI/SiO₂ composite (molar composition of zeolite: Si/T = 121.3, Fe/T = 0.3, Ga/T = 0.2, Al/T = 0.5, T = Fe + Ga + Al, weight ratio of Fe-Ga-Al-MFI/SiO₂: 85/15 [wt%/wt%]), Fe-Ga-Al-MFI/Al₂O₃ composite (molar composition of zeolite: Si/T = 121.3, Fe/T = 0.3, Ga/T = 0.2, Al/T = 0.5, T = Fe + Ga + Al, weight ratio of Fe-Ga-Al-MFI/Al₂O₃: 85/15 [wt%/wt%]).

[Reaction conditions] Temperature: 565 °C, Pressure: 0.1 MPa, Charged volume of catalyst: 2.0 mL, Feedstock: *n*-hexane (50 wt%) + *n*-heptane (25 wt%) + *n*-octane (25 wt%), LHSV: 6.0 h⁻¹.

Fig. 11 Time Courses of One-pass Conversions for Catalytic Cracking of C₆-C₈ Hydrocarbons without Dilution over Fe-Ga-Al-MFI/Al₂O₃ Composite and Fe-Ga-Al-MFI/SiO₂ Composite¹¹⁾

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markably improved by use of the Fe-Ga-Al-MFI/SiO₂ with excellent resistance to coke formation.

Both catalysts showed nearly the same one-pass conversions and similar product distributions in the initial stage (Fig. 10). In addition, both the Al₂O₃ binder and the SiO₂ binder had no cracking activity. However, different catalytic stability was definitely found in both samples. The present result could be attributed to the interaction between the Fe-Ga-Al-MFI zeolite and the Al₂O₃ binder. Figure 9 shows the NH₃-TPD profile of the Fe-Ga-Al-MFI/Al₂O₃ was different from those of the Fe-Ga-Al-MFI zeolite or the Fe-Ga-Al-MFI/SiO₂, with the new shoulder peak in the temperature range of 700-825 K. Neither the Fe-Ga-Al-MFI zeolite or the Al₂O₃ binder had any desorption band in the range of 750-825 K, indicating that the overall acidic properties of the Fe-Ga-Al-MFI zeolite were apparently affected by the Al₂O₃ binder. Acid sites are formed at the boundary between zeolite and binder during preparation of composite catalyst, consisting of BEA zeolite and Al₂O₃ binder¹³⁾. One possible explanation is thus that stronger acid sites were formed at the interface between the external surface of the Fe-Ga-Al-MFI zeolite and the Al₂O₃ binder. The acid sites formed at the interface might accelerate polymerization of generated aromatics and result in rapid deactivation by coke formation. On the other hand, the overall acid strength of the Fe-Ga-Al-MFI zeolite combined with the SiO₂ binder was unchanged due to its neutral nature (Fig. 9). In particular, external acid sites unrestricted

Fig. 12 Simplified Process-flow-diagram of Catalytic Cracking of Light Hydrocarbons over the Fe-Ga-Al-MFI/SiO₂ Composite

by the porous structure easily cause coke formation, but are blocked by inactive silicon oxide. As a consequence, stable cracking activity was maintained for long time by preventing coke formation on the catalyst.

4. Evaluation of Catalytic Cracking of Light-naphtha Fraction over the Zeolite-based Composites from the Viewpoint of Chemical Process Engineering

From the viewpoint of chemical process engineering¹¹⁾, the further advantages of the Fe-Ga-Al-MFI/SiO₂ composites were evaluated by comparing the catalytic cracking of light-naphtha fraction as a promising method for on-purpose propylene production with the conventional thermal cracking of light-naphtha feedstock for producing light olefins including propylene. **Figure 12** shows a simplified block-flow diagram of the catalytic cracking process using the present zeolite-based composites. This process mainly consists of the hot section for cracking light-naphtha fraction and the cold section for separating and recovering products, where proven technologies developed for the thermal cracking can be applied. The hot section consists of the catalytic reactor, cooling unit for gas-liquid separation and extractive distillation unit for separating BTX. Both products and unconverted feedstock per pass are separated into gas and liquid components in the cooling unit. After separation of BTX from liquid components in the extractive distillation unit, both unconverted feedstock and higher olefinic hydrocarbons (C₅+), which are quite selectively converted into light olefins^{9),11),30)}, are recycled into the cracking reactor. The present catalytic cracking process was designed on the basis of

[Catalyst] Nano-Fe-Ga-Al-MFI/SiO₂ composite (molar composition of zeolite: Si/T = 124.6, Fe/T = 0.3, Ga/T = 0.2, Al/T = 0.5, T = Fe + Ga + Al, weight ratio of Fe-Ga-Al-MFI/SiO₂: 60/40 [wt%/wt%]).
[Reaction conditions] Temperature: 565 °C, Pressure: 0.15 MPa, Feedstock: *n*-hexane (100 wt%), LHSV: 6.0 h⁻¹ (Case 1), Temperature: 615 °C, Pressure: 0.15 MPa, Feedstock: *n*-hexane (100 wt%), LHSV: 6.0 h⁻¹ (Case 2), Temperature: 615 °C, Pressure: 0.15 MPa, Feedstock: *n*-pentane (32 wt%) + *n*-hexane (33 wt%) + *n*-heptane (35 wt%), LHSV: 6.0 h⁻¹ (Case 3).

Fig. 13 Comparison of Overall Product Distributions for Thermal Cracking and Catalytic Cracking over Fe-Ga-Al-MFI/SiO₂ Composite¹¹⁾

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recycling unconverted feedstock (incl. olefinic hydrocarbons)¹¹⁾, so the productivity of the cracking process was estimated as the overall yield, defined as the ratio of each product yield to fresh feedstock. **Figure 13** compares the overall yields of the catalytic cracking and the conventional thermal cracking. Experimental results for the catalytic cracking were obtained using a bench-scale reactor under the following conditions: Case 1 (565 °C, 0.15 MPa, *n*-C₆H₁₄ (100 wt%) feedstock, LHSV 6.0 h⁻¹); Case 2 (615 °C, 0.15 MPa,

[Catalyst] Nano-Fe-Ga-Al-MFI/SiO₂ composite (molar composition of zeolite: Si/T = 124.6, Fe/T = 0.3, Ga/T = 0.2, Al/T = 0.5, T = Fe + Ga + Al, weight ratio of Fe-Ga-Al-MFI/SiO₂: 60/40 [wt%/wt%]).

[Reaction conditions] Temperature: 565 °C, Pressure: 0.15 MPa, Feedstock: *n*-hexane (100 wt%), LHSV: 6.0 h⁻¹ (Case 1), Temperature: 615 °C, Pressure: 0.15 MPa, Feedstock: *n*-hexane (100 wt%), LHSV: 6.0 h⁻¹ (Case 2), Temperature: 615 °C, Pressure: 0.15 MPa, Feedstock: *n*-pentane (32 wt%) + *n*-hexane (33 wt%) + *n*-heptane (35 wt%), LHSV: 6.0 h⁻¹ (Case 3).

*Amount of hydrocarbon feedstock required for producing unit amount of valuable products (ethylene, propylene, butenes and BTX) (relative value to thermal cracking).

Fig. 14 Comparison of Amount of Hydrocarbon Feedstock Required for Producing Valuable Products* by Thermal Cracking and Catalytic Cracking over Fe-Ga-Al-MFI/SiO₂ Composite⁽¹¹⁾

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n-C₆H₁₄ (100 wt%) feedstock, LHSV 6.0 h⁻¹); Case 3 (615 °C, 0.15 MPa, mixed hydrocarbon feedstock (*n*-C₅H₁₂ (32 wt%) + *n*-C₆H₁₄ (33 wt%) + *n*-C₇H₁₆ (35 wt%)), LHSV 6.0 h⁻¹)⁽¹¹⁾. In Cases 1-3, the composite with excellent durability to coking were employed as the cracking catalyst, consisting of nano-sized Fe-Ga-Al-MFI zeolite (Si/T = 124.6 [mol/mol], Fe/T = 0.5 [mol/mol], Ga/T = 0.2 [mol/mol], Al/T = 0.3 [mol/mol], T = Fe + Ga + Al, average size: 200-300 nm)⁽¹¹⁾ of 60 wt% and silicon-oxide binder of 40 wt%. The *n*-hexane cracking (Cases 1 and 2) or the model-naphtha cracking (Case 3) under practical conditions achieved overall yields of propylene higher than 30 wt% by controlling one-pass conversions in the range of 40-50 wt% and the sum of valuable product yields (ethylene, propylene, butenes and BTX) reached *ca.* 70 wt% in all cases. The catalytic cracking was thus confirmed as superior to the thermal cracking in terms of productivity.

The energy efficiency was compared by estimating the amount of feedstock required for producing unit amount of valuable products (ethylene, propylene, butenes and BTX) was estimated (Fig. 14). The thermal naphtha cracking mainly utilizes byproducts such as methane as fuels for driving the endothermic cracking reactions, so external input of fuel is not needed in principle unlike natural gas reforming. As naphtha acts as both feedstock and fuel, lower amount of naphtha feedstock leads to reduced energy consumption in

the overall process. The amounts of hydrocarbon feedstock (*n*-hexane or C₅-C₇ hydrocarbons) required for producing unit amount of valuable products by catalytic cracking were calculated on the basis of testing results (Cases 1, 2 and 3) and the process flow diagram (Fig. 12). The amount of light-naphtha feedstock consumed in the thermal cracking was calculated according to the existing database (*e.g.*, feedstock compositions, product yields, operating conditions)⁽²⁾. Catalytic cracking required *ca.* 15 % less hydrocarbon feedstock compared to the thermal cracking, as shown in Fig. 14.

The cracking reactor consumes the major part of the energy required in the overall process of both the thermal cracking and the catalytic cracking⁽⁵⁾, so energy saving in the reaction unit might reduce total energy consumption. The catalytic cracking reactor can save 50-61 % thermal energy compared to the thermal cracking reactor⁽¹⁰⁾. The thermal cracking of light naphtha proceeds at higher than 800 °C with steam diluent in the range of 30-40 wt%, so the pyrolysis reactor requires a large input of thermal energy. In contrast, the catalytic cracking of *n*-hexane or model light-naphtha over the present zeolite-based composites proceeded at temperatures lower than 650 °C without steam dilution. Consequently, energy consumption in the reaction unit was considerably suppressed, due to the moderate reaction temperatures and no need for heating steam, so that the energy efficiency for the overall process was remarkably improved and the amount of hydrocarbon feedstock was reduced by *ca.* 15 %. The catalytic cracking was thus confirmed as superior to the thermal cracking in terms of total energy consumption.

Catalytic cracking of light hydrocarbons in the absence of steam also has advantages for preventing irreversible deactivation due to de-alumination of zeolites. However, cracking catalysts require excellent resistance to coke formation to maintain stable cracking reactions in the fixed-bed mode, as catalytic cracking without steam easily causes polymerization of aromatics, as described in section 3.2. The excellent catalytic stability under practical conditions was investigated in a long-term reaction at bench scale for the Case 1. Figure 15 presents the time courses of one-pass conversions together with the FE-SEM image of the nano-sized Fe-Ga-Al-MFI/SiO₂ sample. Catalytic cracking of *n*-hexane was performed under the following conditions: 565-620 °C; 0.15-0.18 MPa; LHSV 6 h⁻¹. Various modifications of ZSM-5 zeolites have been investigated to improve catalytic stability^{(6,31)~(35)}, but zeolites with catalyst lifetime longer than 100 h have not yet been developed. As a result, cost-competitive catalytic cracking processes in the fixed-bed mode have not been commercialized. However, the Fe-Ga-Al-MFI/SiO₂ catalyst exhibited excellent stability with the aid of temperature compensation during the reaction. One-

[Catalyst] Nano-Fe-Ga-Al-MFI/SiO₂ composite (molar composition of zeolite: Si/T = 124.6, Fe/T = 0.3, Ga/T = 0.2, Al/T = 0.5, T = Fe + Ga + Al, weight ratio of Fe-Ga-Al-MFI/SiO₂: 60/40 [wt%/wt%]). [Reaction conditions] Temperature: 565-620 °C, Pressure: 0.15-0.18 MPa, Feedstock: *n*-hexane (100 wt%), LHSV: 6.0 h⁻¹.

Fig. 15 Time Courses of One-pass Conversions for Catalytic *n*-Hexane Cracking over Fe-Ga-Al-MFI/SiO₂ Composite Using Bench-scale Equipment⁽¹⁾
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pass conversions were stably maintained for longer than 2000 h despite the quite severe conditions. The lifetime of the present zeolite-based catalyst is long enough for application to fixed-bed-type cracking reactors. Furthermore, spent catalysts could be regenerated by removing carbon deposits through combustion by diluted air³⁶⁾. These findings suggest catalytic cracking of light-naphtha fraction in the fixed-bed mode has potential as a practical choice for on-purpose propylene production.

5. Conclusions

The composite catalysts for on-purpose propylene production by cracking of the light-naphtha fraction, consisting of the Fe-Ga-Al-MFI zeolite and the silicon-oxide binder, were newly developed on the basis of original concepts. The MFI zeolites containing iron, gallium and aluminum atoms in zeolite framework at optimized ratio were employed as the matrix component. The Fe-Ga-Al-MFI zeolites showed overall acid strength suitable for selective generation of light olefins from light-naphtha fraction as well as enhanced activity for alkane dehydrogenation compared to conventional ZSM-5 zeolite, resulting in higher selectivity to light olefins including propylene. The Fe-Ga-Al-MFI zeolite-based catalyst combined with silicon-oxide binder (Fe-Ga-Al-MFI/SiO₂) was prepared for practical use and gave excellent performance for cracking of the light-naphtha fraction. The use of silicon-oxide binder with neutral and inactive nature maintained the original acidity of the Fe-Ga-Al-MFI zeolite in the composite form, resulting in both high selectivity to light olefins and excellent stability, unlike the composite catalyst

(Fe-Ga-Al-MFI/Al₂O₃) combined with aluminum-oxide binder.

Overall yields of propylene higher than 30 wt%, *ca.* twice of that in the conventional thermal cracking of light naphtha, were obtained in the catalytic cracking of light-naphtha fraction without dilution over the Fe-Ga-Al-MFI/SiO₂ composite using a fixed-bed-type reactor. Overall yields of valuable chemicals (ethylene, propylene, butenes and BTX) also reached 68.5-72.9 wt%, indicating that the catalytic cracking is advantageous in terms of productivity. Long-term reaction test for evaluating catalytic stability showed longer lifetime than 2000 h, suitable for the fixed-bed reactor, due to the excellent resistance to coke formation. The present zeolite-based composite thus exhibited both high selectivity to light olefins and excellent stability in catalytic cracking under practical conditions. On the basis of these experimental results, catalytic cracking of light-naphtha fraction over the present composite catalyst was compared to the conventional thermal cracking with respect to total energy consumption (*i.e.* amount of hydrocarbon feedstock consumed in the cracking process). Catalytic cracking of the light-naphtha fraction required 15 % less feedstock for producing unit amount of valuable products (ethylene, propylene, butenes and BTX) compared to the thermal cracking of light-naphtha feedstock. Catalytic cracking proceeds at lower temperatures than 650 °C in the absence of steam, so thermal energy required in the cracking reactor was remarkably reduced and total energy consumption was lower compared to the thermal cracking as a result. Catalytic cracking of light-naphtha fraction over the present composite catalyst in fixed-bed mode has high potential for on-purpose propylene production in terms of productivity, catalytic stability and energy consumption.

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要 旨

プロピレン製造のための複合型ゼオライトによるライトナフサ留分の接触分解

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千代田化工建設(株)ではライトナフサ留分からプロピレンを効率良く製造するための固定床型接触分解法を開発中であり、ゼオライトと金属酸化物からなる複合体を触媒として用いている。主成分の MFI 型ゼオライトはゼオライト骨格内に最適化された割合で Fe, Ga, Al 元素を含有し、全体として適度な酸強度とアルカンからアルケンへの脱水素能を併せ持つため、従来の ZSM-5 に比べて芳香族生成を抑制しつつライトナフサ留分から低級オレフィンを高選択的に生成可能である。さらに、機械的強度の向上や反応中の圧力損失の低減等の実用的観点から本ゼオライトをシリカバインダーと成形化した複合触媒を調製した。化学的に不活性なシリカバインダーを用いることで、Fe-Ga-Al-MFI ゼオライトの酸性質は複合体中においても維持

され、Fe-Ga-Al-MFI/SiO₂ 触媒はライトナフサ留分をプロピレン等の低級オレフィンへと高選択的に変換した。*n*-ヘキサン接触分解での触媒安定性に関しては、優れた耐コーク性により触媒性能は2000時間を超える長期間に渡り維持され、固定床反応器に十分に適用可能な優れた安定性を持つことが示された。また、本触媒を用いる接触分解法は650℃以下の比較的温和な温度域でスチーム希釈なしで進行するため、反応工程でのエネルギー削減効果が大きく、プロセス全体で消費される炭化水素原料量は既存の熱分解法(850℃)と比較して約15%削減可能と評価された。本論文では、開発触媒を用いるライトナフサ留分の接触分解法の優れた特性について、触媒化学および化学プロセス工学的観点から解説する。