EFFICIENT PROPYLENE PRODUCTION FROM LIGHT HYDROCARBONS WITH MFI-ZEOLITE/METAL-OXIDE COMPOSITE CATALYSTS

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Abstract
Catalytic cracking of light hydrocarbons over zeolite-based catalysts were investigated to establish the efficient propylene production technology. The Fe-Ga-Al-MFI zeolites combined with SiO₂ or Al₂O₃ showed excellent properties (e.g., high propylene yield, long lifetime and low energy-consumption), indicating that the cracking is superior to conventional thermal-cracking in terms of reaction engineering.

Keywords
On-purpose propylene production, Fe-Ga-Al-MFI/metal-oxide composite, Energy-saving cracking

Introduction
Catalytic cracking of light hydrocarbons (e.g., light-naphtha) as an alternative method for on-purpose propylene production to conventional thermal-cracking is strongly desired to meet the increasing propylene demand and save energy in petrochemical processes. Catalytic cracking of naphtha over zeolites (e.g., ZSM-5) have been actively investigated for these reasons [1]. It is necessary to develop zeolite catalysts with high activity and stability to commercialize the cracking process in fixed-bed mode.

In the present research, unique composite catalysts [2], consisting of Fe-Ga-Al-MFI zeolites and metal-oxides (e.g., SiO₂, Al₂O₃), have been developed to demonstrate efficient propylene production from light hydrocarbons at moderate temperatures (< 600°C). This paper presents excellent properties of the proprietary catalysts from the viewpoint of reaction engineering in cracking catalysis.

Experimental
1. Preparation of zeolite-based catalysts
Fe-Ga-Al-MFI zeolites (molar ratios: Si/T=31.3 and 121.3, Fe/T=0.4, Ga/T=0.3, Al/T=0.3, T=Fe+Ga+Al) [2] were hydrothermally synthesized in autoclave at 150°C for 24 h under adequate stirring conditions and then calcined at 550°C. Cylindrical composite catalysts with diameter of 1.0 mm, consisting of protonated zeolites and metal oxides, were prepared by extrusion to improve mechanical strength.

Mixed ratios of these composites were as follows: Fe-Ga-Al-MFI(Si/(Fe+Ga+Al)=121.3)-90 wt% SiO₂-10 wt%; Fe-Ga-Al-MFI(Si/(Fe+Ga+Al)=31.3)-75 wt% Al₂O₃-25 wt%.

2. Catalytic reaction test
Catalytic cracking of n-hexane without dilution over the Fe-Ga-Al-MFI/SiO₂ was performed in a fixed-bed reactor under the following conditions: 565°C; 0.1 MPa; LHSV at 6.0 h⁻¹. Catalytic cracking of n-hexane diluted with steam of 25 wt% over the Fe-Ga-Al-MFI/Al₂O₃ was also performed under the following conditions: 565°C; 0.1 MPa; LHSV of n-C₆ at 1.0 h⁻¹. In addition, a long-term reaction with the Fe-Ga-Al-MFI/SiO₂ catalyst was carried out to evaluate its catalytic stability under the following conditions: 565-595°C; 0.1 MPa; LHSV at 4.5-7.0 h⁻¹. Both catalytic conversion and yield of each product were estimated by gas-chromatographic analysis.

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Results and discussion

1. High propylene productivity and excellent stability

Catalytic cracking of n-hexane, representing light-naphtha, over the Fe-Ga-Al-MFI-based composites were performed to evaluate their cracking abilities. Table 1 compares propylene productivities of these catalysts to conventional thermal-cracking. It has been confirmed that the MFI zeolites containing Fe, Ga and Al at the optimized ratio gives high propylene selectivity in catalytic cracking of paraffin [2]. The composite catalysts, consisting of Fe-Ga-Al-MFI and metal oxides (SiO2 or Al2O3), were also found exhibit higher overall yields than non-catalytic thermal-cracking in spite of low temperature (Table 1).

Durability of the present composite was examined by performing n-hexane cracking without dilution over the Fe-Ga-Al-MFI/SiO2. Fig. 1 presents time courses of one-pass yields of ethylene and propylene. Catalytic stability was maintained for ca. 1,000 h in spite of severe conditions to cause coke formation easily. This long lifetime, being applicable to cracking process in fixed-bed mode, was achieved by its excellent resistance to coking due to a kind of interaction between zeolite and SiO2. The composites prepared for improving mechanical strength were found to exhibit both high propylene yield and excellent stability.

2. Energetic evaluation of the present cracking-catalysis

In order to evaluate the present cracking catalysis from the energetic viewpoints, thermal energy required for cracking was estimated on the experimental basis. Fig. 2 provides thermal energy required for cracking hydrocarbon feedstock of 1 kg in reaction unit. As shown in Fig. 2, energy consumption in steam-cracking over the Fe-Ga-Al-MFI/Al2O3 was reduced by ca. 43% compared to the thermal-cracking because of reducing apparent heat for heating steam as well as its low reaction temperature. In the n-hexane cracking without dilution, its energy-consumption was further improved (43%→61%) because of no apparent heat for diluent. The supply of hydrocarbon feedstock without dilution or diluted with steam at low concentration (25 wt%) was thus confirmed to be advantageous in terms of energy consumption.

Conclusions

The Fe-Ga-Al-MFI/metal-oxide catalysts for light-hydrocarbon cracking were developed. These catalysts gave high propylene productivity, excellent stability that is applicable to cracking process in simplified fixed-bed mode and low energy-consumption. It was suggested on the experimental basis that the energy-saving cracking of light hydrocarbons as an on-purpose propylene-production technology is feasible by using the present catalysts.

References


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**Table 1** Comparison of propylene productivity between thermal cracking and catalytic cracking

<table>
<thead>
<tr>
<th>Production method</th>
<th>Temp. [°C]</th>
<th>H2O conc. [wt%]</th>
<th>C2 yield [wt%]</th>
<th>One-pass</th>
<th>Overall</th>
</tr>
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<tbody>
<tr>
<td>Thermal cracking</td>
<td>850</td>
<td>40</td>
<td>17.1</td>
<td>17.1</td>
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<tr>
<td>Catalytic cracking*</td>
<td>565</td>
<td>0</td>
<td>13.3</td>
<td>22.6</td>
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<tr>
<td>Catalytic cracking**</td>
<td>565</td>
<td>25</td>
<td>18.8</td>
<td>29.4</td>
<td></td>
</tr>
</tbody>
</table>

* Cat. Fe-Ga-Al-MFI(90 wt%)/SiO2(10 wt%), Press. 0.1 MPa, Feedstock n-C6H14 only, LHSV of n-C6 6.0 h⁻¹
** Cat. Fe-Ga-Al-MFI(75 wt%)/Al2O3(25 wt%), Press. 0.1 MPa, Feedstock n-C6H14(75 wt%)/H2O(25 wt%), LHSV of n-C6 1.0 h⁻¹

**Figure 1** Time courses of n-hexane cracking without dilution over Fe-Ga-Al-MFI/SiO2 composite catalyst

**Figure 2** Comparison of thermal energy required in reaction unit between thermal and catalytic cracking