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

Shinya Hodoshima*, Azusa Motomiya, Shuhei Wakamatsu, and Fuyuki Yagi
Research & Development Center, Chiyoda Corporation
3-13 Moriya-cho, Kanagawa-ku, Yokohama, Kanagawa 221-0022, Japan

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 SiO_2 or Al_2O_3 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., SiO_2, Al_2O_3), have been developed to demonstrate efficient propylene production from light hydrocarbons at moderate temperatures (< 600^{o}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^{o}C for 24 h under adequate stirring conditions and then calcined at 550^{o}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%/SiO_2-10 wt%; Fe-Ga-Al-MFI(Si/(Fe+Ga+Al)=31.3)-75 wt%/Al_2O_3-25 wt%.

2. Catalytic reaction test

Catalytic cracking of *n*-hexane without dilution over the Fe-Ga-Al-MFI/SiO_2 was performed in a fixed-bed reactor under the following conditions: 565^{o}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/Al_2O_3 was also performed under the following conditions: 565^{o}C; 0.1 MPa; LHSV of n-C_6 at 1.0 h^{-1}. In addition, a long-term reaction with the Fe-Ga-Al-MFI/SiO_2 catalyst was carried out to evaluate its catalytic stability under the following conditions: 565-595^{o}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.

* Corresponding author, E-mail: shinya.hodoshima@chiyodacorp.com

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 (SiO_2 or Al_2O_3), 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/SiO_2. **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 SiO_2. The composites prepared for improving mechanical strength were found to exhibit both high propylene yield and excellent stability.

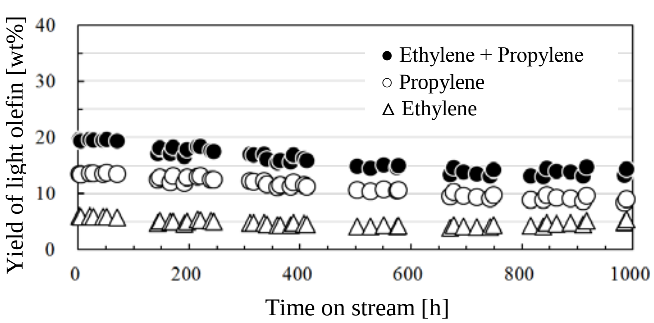
2. Energetic evaluation of the present cracking-catalysis

In order to evaluate the present cracking catalysis from

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

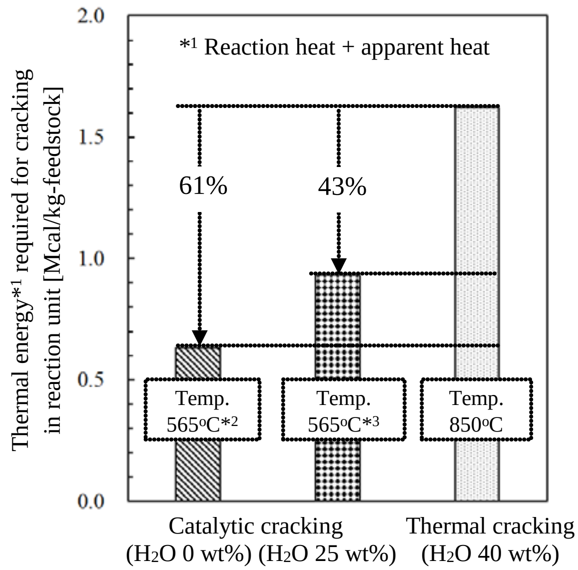
Production method	Temp. [°C]	H_2O conc. [wt%]	$C_3^=$ yield [wt%] One-pass	Overall
Thermal cracking	850	40	17.1	17.1
Catalytic cracking*	565	0	13.3	22.6
Catalytic cracking**	565	25	18.8	29.4

* Cat. Fe-Ga-Al-MFI(90 wt%)/SiO_2(10 wt%), Press. 0.1 MPa, Feedstock *n*-C_6H_{14} only, LHSV of *n*-C_6 6.0 h^{-1}
** Cat. Fe-Ga-Al-MFI(75 wt%)/Al_2O_3(25 wt%), Press. 0.1 MPa, Feedstock *n*-C_6H_{14}(75 wt%)/H_2O(25 wt%), LHSV of *n*-C_6 1.0 h^{-1}



Cat. Fe-Ga-Al-MFI/SiO_2, Temp. 565-595°C, Press. 0.1 MPa, Feedstock *n*-C_6H_{14}, LHSV of *n*-C_6H_{14} 4.5-7.0 h^{-1}

Figure 1 *Time courses of n-hexane cracking without dilution over Fe-Ga-Al-MFI/SiO_2 composite catalyst*



*2 FeGaAl-MFI(90 wt%)/SiO_2(10 wt%) cat., Press. 0.1 MPa, Feedstock *n*-C_6 only, LHSV of *n*-C_6 6.0 h^{-1}
*3 FeGaAl-MFI(75 wt%)/Al_2O_3(25 wt%) cat., Press. 0.1 MPa, Feedstock *n*-C_6/H_2O, LHSV of *n*-C_6 1.0 h^{-1}

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

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/Al_2O_3 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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