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Catalytic conversion of light hydrocarbons to propylene over zeolite-based composites.

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Highlights

- Fe-Ga-Al-MFI/SiO_2 composite with unique acidity was synthesized as novel catalyst.
- The present composite exhibited excellent performance for light-hydrocarbon cracking.
- Catalytic cracking in fixed-bed operation was attained at low energy consumption.

1. Introduction

Catalytic naphtha cracking as an alternative method for on-purpose propylene production to conventional thermal-cracking is strongly desired to meet the increasing propylene demand and reduce energy consumption in petrochemical processes. Though catalytic naphtha cracking over zeolites (e.g., ZSM-5) have been actively investigated, the processes in fixed-bed mode haven't been established due to the lack of stable catalysts. It is necessary to develop zeolite catalysts with high selectivity and stability to commercialize the cracking process using fixed-bed reactors. In present study, unique zeolite-based catalysts [1,2], consisting of Fe-Ga-Al-MFI zeolites and silicon-oxide binder, have been developed to demonstrate efficient propylene production from naphtha at moderate temperatures (565-635°C). This paper presents excellent properties of the proprietary catalyst from the viewpoints of catalytic chemistry and reaction engineering.

2. Methods

Both Al-MFI (Si/Al=122.9 [mol/mol]) and Fe-Ga-Al-MFI (Si/T=124.6, Fe/T=0.4, Ga/T=0.3, Al/T=0.3 [mol/mol], T=Fe+Ga+Al) zeolites were hydrothermally synthesized. Cylindrical composite with diameter of 1.0 mm, consisting of protonated MFI zeolites (85 wt%) and SiO_2 binder (15 wt%), was prepared by extrusion. All samples were characterized by XRD, XRF and NH_3-TPD techniques. In order to evaluate catalytic performance, cracking of *n*-hexane (*n*-C_6H_{14}) or mixed hydrocarbons (*n*-C_5H_{12}(65 wt%) + *n*-C_6H_{14}(35 wt%), *n*-C_6H_{14}(50 wt%) + *n*-C_7H_{16}(25 wt%) + *n*-C_8H_{18}(25 wt%)), were performed in a fixed-bed reactor under the following conditions: 565-635°C; 0.1 MPa; LHSV at 6.0 h^{-1}. Conversion and product selectivity were estimated on the basis of gas-chromatographic analysis. Additionally, cracking reactions of *n*-C_6 or the above-described mixture (*n*-C_6(50 wt%) + *n*-C_7(25 wt%) + *n*-C_8(25 wt%)) over the Fe-Ga-Al-MFI/SiO_2 catalyst were carried out for longer than 250 h to evaluate its catalytic stability under the following conditions: 565-595°C; 0.1 MPa; LHSV at 6.0 h^{-1}.

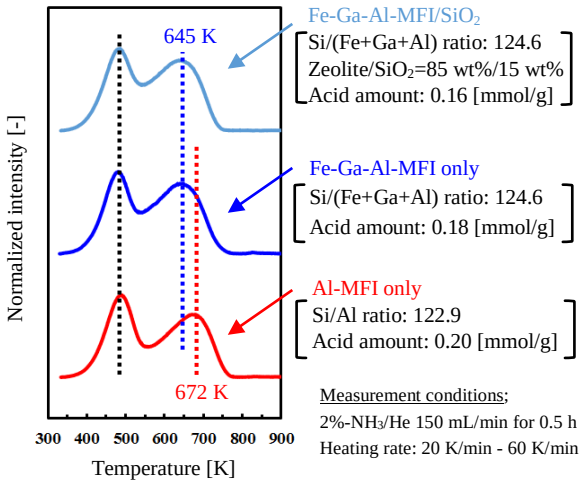


Figure 1. Profile of NH_3-TPD measurement of MFI-type zeolites and MFI-zeolite/SiO_2 composite

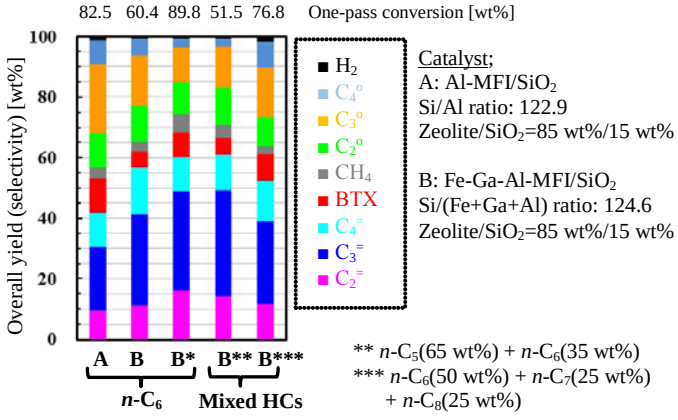
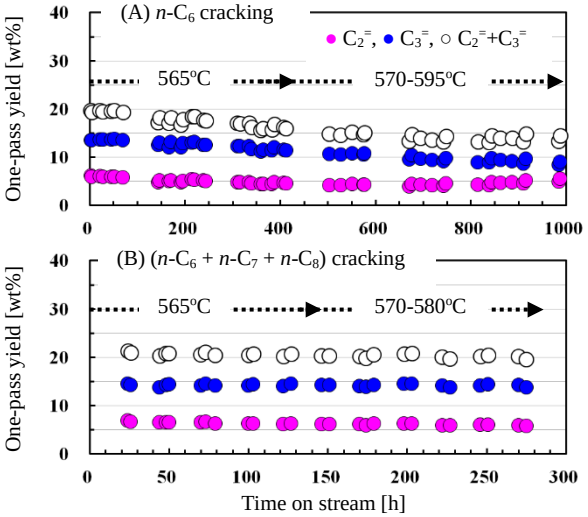


Figure 2. Initial product distribution in cracking of hydrocarbons over MFI-zeolite/SiO_2 composites

3. Results and discussion

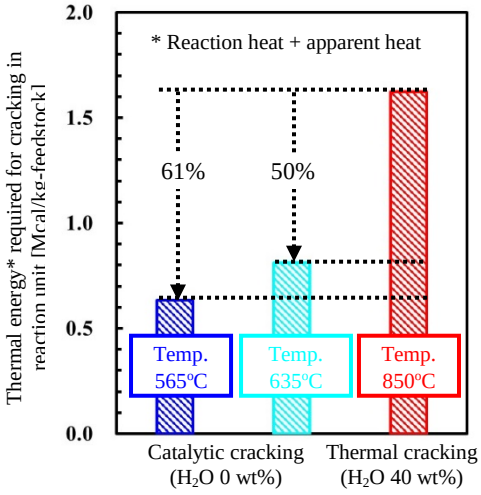
The Fe-Ga-Al-MFI zeolite [1,2], containing Fe and Ga species at optimized ratio, exhibited unique acidity compared to the conventional Al-MFI as a reference, as shown in the NH_3-TPD profiles (**Fig. 1**). Though acid amount was nearly the same, the peak top of the Fe-Ga-Al-MFI in high-temperature region, closely related to acid strength, was shifted to lower temperatures (672 K → 645 K), suggesting that acid strength was reduced by introducing Fe and Ga species. The peak-top temperature of Fe-Ga-Al-MFI in composite sample combined with silicon oxide binder was unchanged.

Cracking of *n*-hexane over zeolite-based composites were performed to evaluate their cracking abilities (**Fig. 2**). The Fe-Ga-Al-MFI/SiO_2 composite gave much higher propylene selectivity than the Al-MFI/SiO_2 by suppressing aromatics formation either under the same conditions or at the same level conversion (Cats. A, B and B* in **Fig. 2**), due to its adequate acidity. Moreover, the Fe-Ga-Al-MFI/SiO_2 exhibited high overall yields (27-35 wt%) in cracking of mixed hydrocarbons as model naphtha, being much higher than conventional thermal-cracking ($C_3^=$ yield: 15 wt%). Long-term reactions were carried out to examine its durability. **Fig. 3** presents time courses of one-pass yields of ethylene and propylene in both reactions. Catalytic stability was maintained for 280-1,000 h in spite of severe conditions to cause coke formation easily. This long lifetime, applicable to fixed-bed operation, was achieved due to its excellent resistance to coking. The zeolite-based composite prepared for industrial use was thus found to exhibit both excellent productivity and stability. **Fig. 4** compares energy consumption between the catalytic cracking and conventional thermal-cracking. Thermal energy required for cracking feedstock of 1 kg in reaction unit was estimated on the experimental basis. Energy consumption in the catalytic cracking was reduced by 50-61% compared to the thermal cracking because of no apparent heat for heating steam as well as its moderate reaction temperature (< 650ºC). The present catalytic cracking was thus confirmed to be advantageous in terms of energy consumption.



Reaction conditions; Cat.: Fe-Ga-Al-MFI(85 wt%)/SiO_2(15 wt%), Temp.: 565-595ºC, Press.: 0.1 MPa, LHSV: 6.0 h^{-1}, Feedstock: *n*-C_6, *n*-C_6(50 wt%) + *n*-C_7(25 wt%) + *n*-C_8(25 wt%)

Figure 3. Time courses of one-pass yield of light olefins in cracking reactions over Fe-Ga-Al-MFI/SiO_2 catalyst



Reaction conditions; Cat.: Fe-Ga-Al-MFI/SiO_2 composite (Si/(Fe+Ga+Al) ratio: 124.6, Zeolite/SiO_2 = 85 wt%/15 wt%) Temp.: 565ºC, Press.: 0.1 MPa, LHSV: 6.0 h^{-1}, Feedstock: *n*-C_6

Figure 4. Comparison of thermal energy required for cracking in reaction unit between catalytic and thermal cracking

4. Conclusions

The Fe-Ga-Al-MFI-based composite catalyst was developed to produce propylene from light hydrocarbons quite efficiently in the present study. Due to its excellent acidity (e.g., high propylene selectivity and resistance to coking), the present catalyst gave high propylene overall yield, long lifetime that is applicable to fixed-bed operation, and low energy-consumption. It was confirmed on these experimental basis that the energy-saving naphtha cracking is feasible as an alternative technology for on-purpose propylene production by use of this composite catalyst.

References

[1] S. Hodoshima, A. Motomiya, S. Wakamatsu, R. Kanai, F. Yagi, Res. Chem. Intermed. 41(12) (2015) 9615-9626.
[2] S. Hodoshima, A. Motomiya, S. Wakamatsu, R. Kanai, F. Yagi, Micropor. Mesopor. Mater. 233 (2016) 125-132.

Keywords: "Fe-Ga-Al-MFI zeolite"; "MFI/SiO_2 composite"; "Catalytic naphtha cracking"; "Low energy consumption"