



Effectiveness of nano-scale ZSM-5 zeolite and its deactivation mechanism on catalytic cracking of representative hydrocarbons of naphtha

Hiroki Konno, Teruoki Tago*, Yuta Nakasaka, Ryota Ohnaka, Jun-ichi Nishimura, Takao Masuda

Division of Chemical Process Engineering, Faculty of Engineering, Hokkaido University, N13 W8, Kita-ku, Sapporo, Hokkaido 060-8628, Japan

ARTICLE INFO

Article history:

Received 29 September 2012

Received in revised form 7 January 2013

Accepted 5 March 2013

Available online 26 March 2013

Keywords:

Catalytic cracking

Naphtha

Naphthenes

Nano-zeolite

ZSM-5

ABSTRACT

The catalytic cracking of representative hydrocarbons of naphtha (*n*-hexane, cyclohexane, and methyl-cyclohexane) over ZSM-5 zeolite catalysts was examined at reaction temperatures ranging from 823 K to 923 K under atmospheric pressure. It was found that the Si/Al ratio of the zeolite affected the product selectivity and conversion. In order to investigate the effects of the crystal size of the ZSM-5 zeolites on catalyst lifetime, macro- and nano-scale ZSM-5 (Si/Al = 150) with crystal sizes of 2300 nm and 90 nm, respectively, were used for the cracking of representative naphtha hydrocarbons. In the cracking of naphthenes (cyclohexane and methyl-cyclohexane), coke was readily formed from the beginning of the reaction leading to significant deactivation of the catalyst for the macro-scale ZSM-5. In contrast, the nano-scale ZSM-5 exhibited a high conversion and high light olefins yield with stable activity, regardless of the type of reactant. As a result, the application of nano-scale ZSM-5 zeolites to the catalytic cracking of naphtha was effective and gave light olefins with high yield and excellent stable activity.

© 2013 Elsevier Inc. All rights reserved.

1. Introduction

Light olefins, such as ethylene and propylene, are important basic raw materials for the petrochemical industry, and demand for light olefins is increasing every year [1,2]. Light olefins have been mainly produced by thermal cracking of naphtha, which gives yields of ethylene and propylene of approximately 25% and 13%, respectively [3–5]. However, the capacity of the naphtha cracking process is not large enough to satisfy the increase in demand, because in this process, it is difficult to control the selectivity for specific light olefins. Moreover, because this process consumes more than 30% of the total amount of energy required in petrochemical refinement, developing efficient processes for the production of light olefins is indispensable. Unlike thermal cracking, catalytic cracking of naphtha over solid acid catalysts can be achieved at a high propylene/ethylene ratio at low reaction temperatures [6,7], and thus using this process will reduce energy costs and provide selective production of propylene. Accordingly, the catalytic cracking of naphtha is expected to be an effective alternative to the thermal cracking process.

A promising catalyst for the catalytic cracking of naphtha is zeolite, a crystalline aluminosilicate material with various properties, such as strong acidity and a high surface area, and studies on the catalytic cracking of alkanes over zeolite catalysts have been reported [8–16]. We have also studied the catalytic cracking of *n*-hexane over a ZSM-5 zeolite catalyst [17–19], in which it was

revealed that ZSM-5 was effective for *n*-hexane cracking to light olefins synthesis. On the other hand, although naphthenes are important constituents of naphtha and affect the products generated from cracking [20], few studies have been published concerning the cracking of naphthenes [21–26] as compared to those of alkane cracking over zeolite catalysts. It is believed that not only alkane cracking, but also naphthene cracking, are indispensable in naphtha cracking, and thus both need to be investigated in order to gain a better understanding of naphtha cracking.

In the present study, the effect of the crystal size of a ZSM-5 (MFI-type) zeolite on the catalytic activity and light olefins yield in the catalytic cracking of representative hydrocarbons of naphtha was investigated. First, in order to optimize the reaction conditions for light olefins synthesis, the effects of reaction temperature and the Si/Al ratio of the ZSM-5 zeolite on *n*-hexane cracking were investigated. Next, the effect of the type of reactant on the catalyst lifetime and light olefins yield was examined using *n*-hexane, cyclohexane, and methyl-cyclohexane. Finally, the difference in the product selectivity and catalyst stability during alkane (*n*-hexane) and naphthene (methyl-cyclohexane) cracking were investigated from the viewpoint of coke formation using nano- and macro-scale ZSM-5 zeolites.

2. Experimental

2.1. Preparation of ZSM-5 zeolites with different crystal sizes

The nano-scale ZSM-5 zeolite was prepared via hydrothermal synthesis using a water/surfactant/organic solvent (emulsion

* Corresponding author. Tel.: +81 117066551; fax: +81 117066552.

E-mail address: tago@eng.hokudai.ac.jp (T. Tago).

method [27–32]). An aqueous solution containing the Si and Al source materials was obtained by hydrolyzing each metal alkoxide in a dilute tetrapropyl ammonium hydroxide (TPAOH)/water solution. The water solution (10 ml) thus obtained was added to the surfactant/organic solvent (70 ml, surfactant concentration of 0.5 mol/l). Polyoxyethylene-(15)-oleylether and cyclohexane were employed as the surfactant and organic solvent, respectively. The water/surfactant/organic solvent thus obtained was poured into a Teflon-sealed stainless steel bottle and heated to 423 K for 72 h. In order to obtain the macro-scale ZSM-5, a hydrothermal synthesis was also carried out, but without the surfactant/organic solvent (conventional method). The molar compositions of the aqueous solution for the macro-scale ZSM-5 and the nano-scale ZSM-5 synthesis were SiO_2 : $0.0033\text{Al}_2\text{O}_3$: 0.038NaOH : 0.10TPA : $355\text{H}_2\text{O}$ and SiO_2 : 0.0017 – $0.01\text{Al}_2\text{O}_3$: 0.01 – 0.06NaOH : 0.33TPA : $33\text{H}_2\text{O}$, respectively. The precipitates obtained from both methods were washed with alcohol, dried at 373 K for 12 h, and then calcined at 823 K for 3 h in an air stream. Physically adsorbed and/or ion-exchanged sodium ions on the zeolite surfaces were removed and exchanged with NH_4^+ using a conventional ion exchange technique with a 10% NH_4NO_3 aqueous solution, and then the zeolites were heated to 923 K to yield H-ZSM-5 zeolites. The powdered zeolites described above were pelletized, crushed, and sieved to yield samples ca. 0.3 mm in diameter for use in the catalytic cracking reactions.

2.2. Characterization

The morphology and crystallinity of the samples were analyzed using field emission scanning electron microscopy (FE-SEM; JSM-6500F, JEOL Co. Ltd.) and X-ray diffraction (XRD; JDX-8020, JEOL Co. Ltd.), respectively. The micropore volumes and the total and external surface areas of the samples were calculated using the BET- and the t -methods based on N_2 adsorption isotherms (Belsorp mini, BEL JAPAN Co. Ltd.). The Si/Al ratios of the samples were determined by X-ray fluorescence measurements (XRF; Supermini, Rigaku Co. Ltd.), and the acidity of the samples was evaluated via the ac-NH_3 -TPD method [33] using TG. In the TPD experiment, samples were first calcined under N_2 stream at 823 K, then cooled to 373 K. The gas was shifted from N_2 to 1.0% NH_3 (balance He), and NH_3 molecules were adsorbed on the acid sites of the sample. After reaching adsorption/desorption equilibrium condition at 373 K, a temperature of the reactor was increased from 373 K to 823 K at a heating rate of 5 K min^{-1} . The desorption of NH_3 molecules from the acid sites of the zeolite was measured under a 1.0% NH_3 -He atmosphere so that the TPD profile could be measured under complete adsorption equilibrium conditions, which is referred to as the ac-NH_3 -TPD method. In this method, the amount of NH_3 molecules desorbed from the sample above approximately 600 K were referred to the amount of strong acid sites on the sample.

2.3. Catalytic cracking of hydrocarbons over the ZSM-5 zeolites

Catalytic cracking of hydrocarbons over ZSM-5 zeolite catalysts was carried out using a fixed-bed reactor at reaction temperatures ranging from 823 K to 923 K under atmospheric pressure [17,18]. The ZSM-5 zeolite catalyst was placed into a quartz tube reactor with inner diameter of 10 mm and calcined in flowing N_2 for 1 h at the reaction temperature before each run. In order to maintain the same volume of height in catalyst bed, the macro-scale ZSM-5 zeolite was mixed with quartz sand when catalytic reaction. Meanwhile, the nano-scale ZSM-5 was not added anything when catalytic reaction. The W/F (W : amount of catalyst (g), F : feed rate (g h^{-1})) was 0.125 h or 0.15 h. In order to maintain a constant amount of carbon feed to the reactor, the partial pressure of hydrocarbons as feedstock was 22.1 kPa in the C6 feedstock (n -hexane and cyclohexane) and 18.9 kPa in the C7 feedstock (methyl-cyclo-

hexane) at the inlet of the reactor. The feed rate of the hydrocarbons as feedstock was $8.22 \times 10^{-2} \text{ C-mol/h}$. The composition of the exit gas was measured using an on-line gas chromatograph (GC-2014, Shimadzu Co. Ltd.) with a Porapak-Q column for the thermal conductivity detector (TCD) and Gaskuropack-54 and SP-1700 columns for the flame ionization detectors (FIDs). The amount of coke deposited on the catalyst after the reaction was measured via thermogravimetric analysis (TG; TGA-50, Shimadzu Co. Ltd.). Although aromatics with high vaporization temperature such as benzene, toluene and xylene are formed during the reaction, all products were measured using on-line gas chromatograph through the pre-heater at 410 K. Total carbon yields of these products were approximately 90–98 C-mol% in each cracking reactions.

3. Results and discussion

3.1. Characterization of synthesized ZSM-5 zeolites with different crystal sizes

To investigate the effect of the Si/Al ratio of the ZSM-5 zeolites on the product selectivity and yield, nano-scale ZSM-5 with different Si/Al molar ratios (50, 150, and 300) were prepared via hydrothermal synthesis in a water/surfactant/organic solvent [27]. Figs. 1 and 2 show the X-ray diffraction patterns and FE-SEM micrographs of the samples, respectively. The X-ray diffraction patterns of the samples with different Si/Al ratios showed peaks corresponding to an MFI-type zeolite. Moreover, nano-scale zeolites with crystal sizes of approximately 90 nm were observed. The XRD pattern and FE-SEM micrograph of a macro-scale zeolite are also shown for comparison and to illustrate the macro-scale zeolite (Si/Al = 150) with a crystal size of approximately 2300 nm. As can be seen in Table 1, while the external surface area increased with decreasing crystal size, the micropore volume ($0.18 \text{ cm}^3/\text{g}$) and the BET surface area ($400 \text{ m}^2/\text{g}$) were nearly constant, regardless of the crystal size. Fig. 3 and Table 1 show the NH_3 -TPD profiles and Si/Al ratios as determined by XRF analysis of the zeolites with different crystal sizes and Si/Al ratios, respectively. The Si/Al values were nearly the same for each Si/Al ratio, which was calculated from the Si and Al concentrations in the corresponding synthetic solution, indicating that the Al atoms in the synthetic solutions were incorporated into the framework structures of the ZSM-5 zeolites during the hydrothermal synthesis.

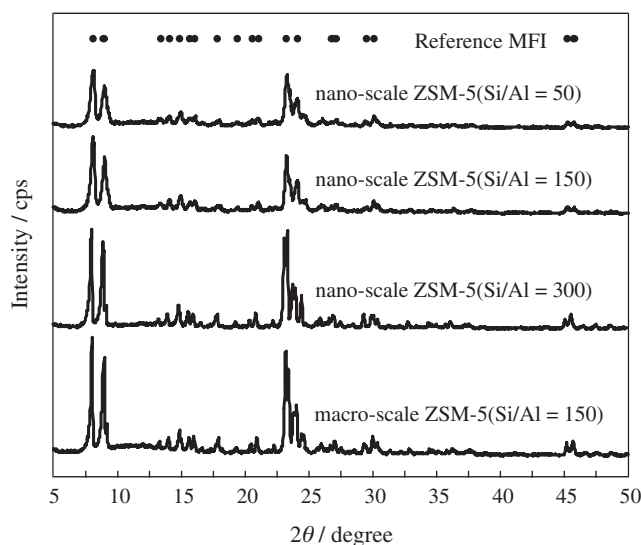


Fig. 1. XRD patterns of ZSM-5 zeolites with different Si/Al ratios and crystal sizes.

Download English Version:

<https://daneshyari.com/en/article/73435>

Download Persian Version:

<https://daneshyari.com/article/73435>

[Daneshyari.com](https://daneshyari.com)