



## Kinetics of *n*-hexane cracking over ZSM-5 zeolites – Effect of crystal size on effectiveness factor and catalyst lifetime

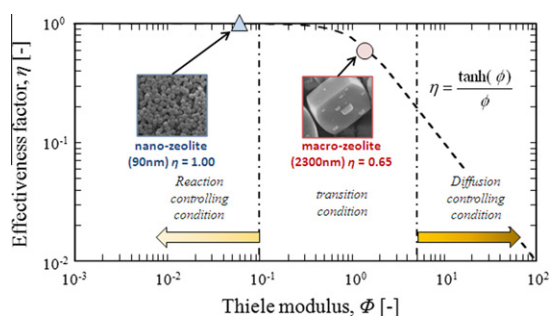
Hiroki Konno, Takuya Okamura, Takahito Kawahara, Yuta Nakasaka, Teruoki Tago\*, Takao Masuda

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

### HIGHLIGHTS

- ▶ The ZSM-5 zeolites with different crystal size were synthesized.
- ▶ *n*-Hexane cracking over ZSM-5 zeolites was carried out.
- ▶ Effect of crystal size was investigated using Thiele modulus.
- ▶ Cracking reaction over nano-zeolite proceeded under reaction limiting condition.
- ▶ The nano-zeolite effective in the stabilization of the catalytic activity.

### GRAPHICAL ABSTRACT



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### ABSTRACT

The catalytic cracking of *n*-hexane over ZSM-5 zeolite (MFI-type zeolite, Si/Al = 150 and 240) catalysts was examined at reaction temperatures ranging from 823 to 923 K under atmospheric pressure. The reaction rate constants and activation energies of *n*-hexane cracking over ZSM-5 zeolites with various crystal sizes and Si/Al ratios were evaluated. The catalytic cracking of *n*-hexane was first order with respect to the *n*-hexane concentration, and the activation energies of *n*-hexane cracking over ZSM-5 zeolites were found to be approximately 123–128 kJ mol<sup>-1</sup>. Compared with the macro-sized zeolite, the nano-sized zeolites exhibited high *n*-hexane conversion with stable activity for 50 h. This is because the cracking reaction with nano-sized zeolite proceeded under reaction-limiting conditions, whereas the reaction with macro-sized zeolite proceeded under transition conditions between reaction- and diffusion-limiting conditions. As a result, the application of nano-zeolite to the catalytic cracking of *n*-hexane was effective and gave light olefins with high yield and excellent stable activity.

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## 1. Introduction

Light olefins are important basic raw materials for the petrochemical industry, and demand for light olefins such as ethylene and propylene 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 naphtha cracking process is insufficient for the increased demand, because 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. In comparison with thermal cracking, because the catalytic cracking of naphtha over solid-acid catalysts can achieve a high propylene/ethylene ratio at low reaction temperatures via the carbenium ion/ $\beta$ -scission mechanism [6,7], using this process will reduce energy cost 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, which is a crystalline aluminosilicate material with various properties, such as strong acidity and high surface area, and studies

\* Corresponding author. Tel.: +81 117066551; fax: +81 117066552.  
E-mail address: [tago@eng.hokudai.ac.jp](mailto:tago@eng.hokudai.ac.jp) (T. Tago).

on the catalytic cracking of alkane over zeolite catalysts have been reported [8–10]. Because zeolites possess intracrystalline micropores and nanospaces close to the molecular diameters of light hydrocarbons, they exhibit a remarkable molecular-sieving effect for light hydrocarbons and have been widely used as shape-selective catalysts in various hydrocarbon processes (e.g., alkylation of aromatics [11,12], as well as olefin synthesis from alcohol [13] and acetone [14,15]). However, because the crystal sizes of zeolites are usually much larger than the sizes of the micropores, the rate-limiting step of the reaction tends to be the diffusion of the reactant/product molecules within the micropores. Moreover, carbon solid (coke) readily forms near the external surface of the crystal under diffusion-controlled conditions, thereby, rapidly plugging the pores, leading to a short catalyst lifetime. To achieve low diffusion resistance, nano-sized zeolites are effective because the diffusion length for reactant/product hydrocarbons, which depends on the zeolite crystal size, is reduced [16,17].

We have successfully prepared MFI-type and MOR-type zeolite nanocrystals via hydrothermal synthesis in a water/surfactant/organic solvent (emulsion method) [18–22]. The nano-crystalline zeolites are expected to be promising materials with low diffusion resistance as well as a large external surface area, which improves the catalytic activity and lifetime. In the present study, selective synthesis for light olefins by the catalytic cracking of *n*-hexane over ZSM-5 zeolite (MFI-type zeolite) was carried out as a model reaction for the catalytic cracking of naphtha. The effect of crystal size of the zeolite on catalyst lifetime was investigated using the Thiele modulus and an effectiveness factor.

## 2. Experimental

### 2.1. Preparation of ZSM-5 zeolite with different crystal size

Nano-crystalline ZSM-5 zeolite (below 200 nm) was prepared via hydrothermal synthesis using a water/surfactant/organic solvent (emulsion method) [19]. An aqueous solution containing a Si and Al source material was obtained by hydrolyzing each metal alkoxide in a dilute tetra-propyl-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). Poly-oxyethylene-(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 macro-crystalline ZSM-5 zeolite (above 2000 nm), hydrothermal synthesis was also carried out without the surfactant/organic solvent (conventional method). The precipitates thus obtained were washed with alcohol, dried at 373 K for 12 h, and calcined at 823 K for 3 h in an air stream. Physically adsorbed and/or ion-exchanged sodium ions on the zeolite surface were removed and exchanged with  $\text{NH}_4^+$  by a conventional ion exchange technique with a 10%  $\text{NH}_4\text{NO}_3$  aqueous solution, and then heated to 923 K to yield H-ZSM-5 zeolite. The powdered zeolite described above was pelletized, crushed and sieved to yield samples ca. 0.3 mm in diameter for the catalytic cracking reaction.

### 2.2. Characterization

The morphology and crystallinity of the obtained samples were analyzed by field emission scanning electron microscopy (FE-SEM; JSM-6500F, JEOL Co. Ltd.) and X-ray diffraction (XRD; JDX-8020, JEOL Co. Ltd.), respectively. The total and external surface areas of the obtained samples were calculated by BET- and *t*-methods, respectively, using an  $\text{N}_2$  adsorption isotherm (Belsorp mini, BEL JAPAN Co. Ltd.). The Si/Al ratios of the samples were measured

by X-ray fluorescence measurements (XRF; Supermini, Rigaku Co. Ltd.).

The acidity of the obtained samples (Si/Al = 150) were determined after adsorption of pyridine using FT-IR spectroscopy (FT/IR-4100, Jasco Co. Ltd.) [23,24]. Because the analysis of high-silica zeolite encountered a difficulty due to a small amount of acid site, this procedure slightly differs from some preliminary experiments. The samples were activated in situ at 573 K for 1 h before IR analysis. After cooling to room temperature, the reference spectra of the activated samples were collected. The pyridine was adsorbed to the samples with the pyridine vapor pressure for 30 min at room temperature, followed by desorption of physically-adsorbed pyridine at room temperature for 20 min, and the spectrum was collected at room temperature. Additionally, the acidity of the obtained samples was also evaluated by the  $\text{NH}_3$ -TPD method [25]. In the TPD experiment, the carrier gas was 1.0%  $\text{NH}_3$  (balance He), the heating rate was  $5 \text{ K min}^{-1}$ , and the temperature range was 373–823 K. The desorption of  $\text{NH}_3$  molecules from the acid sites of the zeolite was measured under a 1.0%  $\text{NH}_3$ -He atmosphere so that the TPD profile could be measured under complete adsorption equilibrium conditions, referred to as the *ac*- $\text{NH}_3$ -TPD method.

### 2.3. Catalytic cracking of *n*-hexane over ZSM-5 zeolites

Catalytic cracking of *n*-hexane over ZSM-5 zeolite catalysts was carried out using a fixed-bed reactor at a reaction temperature of 823–923 K under  $\text{N}_2$  at atmospheric pressure. A schematic of the reaction setup is shown in Fig. 1. The ZSM-5 zeolite catalyst was placed in a quartz tube reactor and activated in flowing  $\text{N}_2$  at a reaction temperature for 1 h before each run. The quartz tube reactors with inner diameters of 4 and 10 mm were employed for the kinetic analysis and the investigation on the catalyst lifetime, respectively. *W/F* (*W*: amount of catalyst/g, *F*: feed rate/ $\text{g h}^{-1}$ )

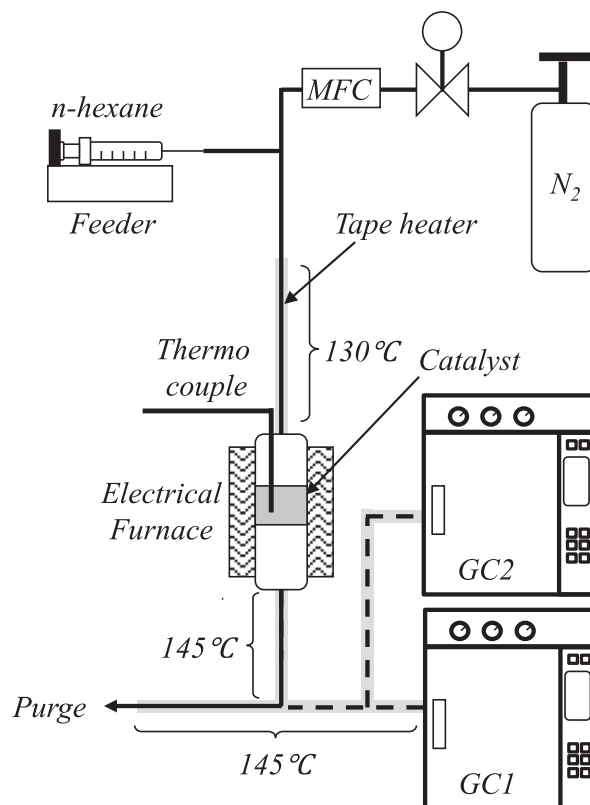


Fig. 1. Experimental setup of the fixed-bed flow reactor.

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