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Controlling naphtha cracking using nanosized TON zeolite synthesized in the presence of polyoxyethylene surfactant

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ABSTRACT

Valorization of naphtha, a derived intermediate from crude oil is still a crucial subject. Here we report an effort to control catalytic cracking of naphtha using nanosized TON zeolite, which was synthesized by microwave assisted hydrothermal synthesis (MAHyS) in the presence of polyoxyethylene-based surfactant. The effects polyoxyethylene (POE) surfactant on the crystal size, morphology and the crystal aspect-ratio were studied. The crystals with lengths in the range of 90–300 nm were obtained. The addition of polyoxyethylene surfactant reduced the agglomeration rate of ZSM-22 zeolite crystals. The polyoxyethylene surfactant was added with POE/Al from 2.5 to 10. Effect of Si/Al in the presence of POE surfactant was studied by changing the Si/Al ratio from 45 to 80. Naphtha was simulated using a model compound, *n*-hexane. Excellent selectivity toward propylene was obtained over ZSM-22 zeolite crystals in *n*-hexane cracking. High selectivity to propylene was maintained over different size of ZSM-22 zeolite crystals. Decreasing crystal length from 300 to 90 nm considerably increased the catalytic activity of ZSM-22 crystals.

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1. Introduction

Catalytic cracking of naphtha is a promising route for 'on-purpose propylene' as a source for the increasing demand on propylene [1]. Development of a catalyst which efficiently converts crude oil to olefins is highly needed. Abrevaya [2] reported that one-dimensional pore zeolites are potential catalysts to increase propylene/ethylene ratio. Conventional zeolite crystals (micron size), especially with one-dimensional pore system, suffer from serious diffusion limitation that hampers the reaction rate. In one-dimensional pore zeolites like ZSM-22, reducing the crystals' size leads to reduce pore length and subsequently shorter diffusion length [3]. In addition to that, reducing the crystals' size will also improve the catalyst activity via preventing pore blocking and coke deposition [4]. Tuning the crystal size from micron to nanoscale affects the product selectivity. Shorter diffusion length allows better access to acid sites, while longer diffusion length gives the chance for larger products to form. Hence, the shorter diffusion length by either reducing the crystal size or the aspect ratio (length/diameter) is very essential to obtain better catalytic activity against deactivation in catalytic cracking reactions.

Recently, many zeolites have been synthesized using microwave assisted hydrothermal synthesis (MAHyS) such as ZSM-5 (MFI) [5], Beta (BEA) [6], zeolite-Y (FAU) [5,7], and zeolite-L (LTL) [5]. The as-synthesized ZSM-22 crystals by MAHyS were small and uniform, nevertheless they were severely agglomerated which reflect the high agglomeration rate of ZSM-22 crystals. One of the effective techniques used to reduce the agglomeration rate is using non-ionic surfactants [8]. In this work, we investigated the effect of polyoxyethylene with oxyethylene chain length of 10 under microwave irradiation. Over the last two decades, an increasing interest can be observed for using non-ionic surfactants in the zeolites synthesis such as in ZSM-5 (MFI) [8] for inducing crystallinity enhancements as well as controlling of zeolite crystals' size and morphology [8–10].

Conventional ZSM-22 crystals look like needle-shaped crystals with one-dimensional channels (ca. 0.46–0.57 nm aperture) oriented along the [0 0 1] direction [11,12], and with the crystals size in the range of 0.5–2 μm [13–15]. The performance of ZSM-22 crystals as shape-selective catalysis in the oil refinery and petrochemical industries depends mainly on their crystal size and morphology (length/diameter). Conventional ZSM-22 crystals have a severe diffusion resistance and in order to overcome this problem, both

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crystal length and aspect ratio should be decreased. The required crystallization time for conventional hydrothermal synthesis of ZSM-22 will be more than 48 h [14,16–18]. Fast synthesis can be achieved by using microwave as a heating source for the crystallization of ZSM-22 zeolite. As reported by Hayasaka et al. [19], the synthesis of ZSM-22 can be divided into two steps as nucleation followed by crystallization, and then the thus formed crystals are aggregated together as time progressed. In order to produce small uniform crystal length, the aging time should be prolonged to increase the number of produced nuclei. Meanwhile, crystallization time should be shortened to reduce the severity of agglomeration. Prolonging aging times in zeolite synthesis decreases the crystal length of the produced zeolite as a consequence of the increase in nuclei amount created in the synthesis of gel solution [20]. Alfaro et al. [20] reported that the extension of aging times decreased crystals' lengths of LTA zeolites, which was in agreement with other findings for zeolite Y [21] and ZSM-5 [22]. On the other hand, increasing crystallization time is undesired, since it gives the chance for the crystals to grow as well as stimulate the appearance of impurity phases.

In this work, we used non-ionic surfactant as agglomeration inhibitor for zeolite nanocrystals.

This research is devoted to synthesizing the nanosized ZSM-22 zeolites with less agglomeration as a catalyst in mass-transfer limited reactions like the catalytic cracking of naphtha (represented by *n*-hexane as model component). Investigating the catalytic performance advantage of reducing agglomeration rates of the nanosized ZSM-22 crystals is an essential part of this research. To achieve this goal, we reduced the agglomeration of ZSM-22 zeolite crystals. We report a surfactant-microwave method as a powerful technique to synthesize ZSM-22 nano-crystals with uniform size and less aggregation. The non-ionic surfactant used in this study was polyoxyethylene with a chain length of 10 with a HLB value of ca.12.

2. Experimental

2.1. Synthesis of ZSM-22 zeolite using microwave assisted hydrothermal synthesis (MAHyS)

Aluminate solution was made by adding 0.9 g of aluminum sulfate octadecahydrate and 4.2 g of 1,6-diaminohexane (DAH) as template to 1.9 g KOH and 44.2 g deionized (DI) water. Silicate solution was prepared by adding 18 g silica colloidal solution to 31 g DI water. The gel solution was prepared by adding silicate to aluminate solution. The gel was heated to 50 °C under continuous stirring at 250 rpm for 5 min before adding Brij-76, a polyoxyethylene surfactant with chain length of 10, at 105 °C. The initial molar composition of the prepared gel was: 1 Al_2O_3:91.4 SiO_2:26.5 K_2O:27.4 DAH:3202 H_2O:*y* Brij-76 (where *y* = 0, 2.5, 5, 7.5 and 10). The gel was aged at 50 °C for 72 h. Synthesis was performed in a microwave lab station (MicroSYNTH, Milestone, 400 W) at 180 °C for 12 h. The resulted powder was centrifuged and dried for 12 h at 120 °C, and then the sample was calcined at 550 °C for 8 h under a flow of air with the heating rate of 1 K min^{-1}. The calcined zeolites (K-ZSM-22) were transformed to NH_4-ZSM-22 by ion-exchanging with NH_4NO_3 (under microwave irradiation) then calcined to obtain H-ZSM-22.

2.2. Characterization of ZSM-22 zeolite

ZSM-22 catalysts were characterized using powder X-ray diffraction (XRD), scanning electron microscopy (SEM), N_2 adsorption–desorption measurements (BET measurement), and temperature programmed desorption (TPD). Finally, the catalytic behavior of the resulted ZSM-22 crystals was investigated in a catalyst-packed bed reactor.

Crystallinity of the as-synthesized crystals was identified using X-ray diffraction using Rigaku X-ray diffractometer with a step size of 0.03°, with Bragg–Brentano geometry, position sensitive detector and CuK α radiation (λ = 1.5406 Å). XRD data were analyzed using EVA 8.0 (Rigaku).

The crystal size and morphology were investigated using scanning electron microscopy. The ZSM-22 crystals sample was spread on a sample holder using volatile solvents such as ethanol. Low acceleration voltage (15 kV) and spot size 3 were used for imaging. The equipment used was SEM-FIB Tescan Lyra. The ZSM-22 catalyst was suspended in ethanol, and a drop of the mixture was spread and dried on porous carbon film sample cell. The dried specimens were analyzed using electron microscope. The Si/Al ratios of the resulted ZSM-22 samples were determined by equipping energy dispersive X-ray spectrometry (EDX, Oxford Instruments).

The surface areas and micropore volume of ZSM-22 catalysts were measured by using nitrogen adsorption isotherm at a temperature of 77 K (Belsorp mini, BEL JAPAN Co. Ltd.). About 60 mg of the catalysts was pretreated by outgassing the catalysts at 80 °C for 1 h followed by heating at 300 °C for 4 h.

The acidity of the ZSM-22 zeolite crystals was investigated using ammonia temperature-programmed desorption (NH_3-TPD). The NH_3-TPD is helpful in showing the effect of changing crystal size and Si/Al ratio on the acidity of ZSM-22 zeolite. For each experiment, 150 mg of the catalyst sample was degassed using helium gas (30 ml min^{-1}) for 2 h at 300 °C; then the sample was cooled to 100 °C and saturated with ammonia gas which is then removed gradually by using helium gas. Temperature was then raised up till 500 °C. In the meantime, the adsorbed ammonia was starting to desorb. Different heating rates (10, 15 and 20 °C min^{-1}) were used to desorb ammonia from the catalyst sample. The NH_3-TPD experiments were done using AutoChem II Analyzer from Micrometrics.

2.3. Catalyst activity evaluation

The catalytic behavior of the resulted ZSM-22 crystals was evaluated for the catalytic cracking of *n*-hexane. The catalytic cracking of *n*-hexane was carried out over H-ZSM-22 catalysts in a packed bed reactor. The catalyst (100 mg) was pelletized and sieved in the range of 500–300 μm.

The reaction was carried out at 650 °C (923 K). To maintain a constant amount of aluminum atoms for each reaction, catalyst weights were changed in the packed bed, *W*/*F* (amount of catalyst (g)/feed rate (g h^{-1})) was (0.125 h for Si/Al = 46 and 0.167 h for Si/Al = 60). The reaction products were analyzed by connected online gas chromatographs (GC, Shimadzu GC-2014), more details about the *n*-hexane cracking reaction experiments and products analysis were described by Konno et al. [23].

3. Results and discussion

ZSM-22 crystals tend to grow as a bundle of needles with length normally taller by 1 μm and high aspect-ratio (length/diameter >10). Reducing crystal length of one dimensional pore system zeolites such as ZSM-22 leads to reduce pore length and subsequently shorter diffusion length and better catalyst activity via preventing pore blocking and coke deposition [8].

XRD patterns in Fig. 1 show the effect of aging time (2–84 h), and pure ZSM-22 zeolite was resulted regardless aging time. As shown in Fig. 2, the shortest ZSM-22 crystal length (ca.100 nm) was produced using prolonged aging time (72 h) and controlled growth under microwave irradiation for 12 h at 180 °C (453 K). However, the resulted ZSM-22 crystals were agglomerated as can be seen in Fig. 2.

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