



Dealumination of organic structure-directing agent (OSDA) free beta zeolite for enhancing its catalytic performance in n-hexane cracking



Yong Wang, Ryoichi Otomo, Takashi Tatsumi, Toshiyuki Yokoi*

Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

ARTICLE INFO

Article history:

Received 22 June 2015

Received in revised form

8 August 2015

Accepted 7 September 2015

Available online 15 September 2015

Keywords:

n-Hexane cracking

Propylene

OSDA free beta

Dealumination

Lewis acid sites

ABSTRACT

This work deals with the dealumination of organic structure-directing agent (OSDA) free beta (OFB) zeolite by different methods to change its acid amount and enhance its catalytic performance in n-hexane cracking. The OFB zeolite was pre-treated with ammonium hexafluorosilicate (AHFS) solution, steaming, or concentrated NH_4NO_3 (ca. 10 M) followed by calcination at high temperature. Then, thus pre-treated OFB samples can be effectively dealuminated by acid treatment with the structure retained. The H-form OFB (HOFB) and dealuminated OFB (DOFB) catalysts were characterized by using X-ray diffraction, N_2 adsorption–desorption, SEM, ICP, NH_3 -TPD, ^{29}Si and ^{27}Al MAS NMR, and pyridine adsorption FT-IR. In the catalytic cracking of n-hexane, the DOFB catalysts showed a higher propylene selectivity and a longer catalytic life than the parent Al-rich HOFB catalyst. This would be attributed to the lower amount of acid sites, especially the Lewis acid sites, which suppressed the secondary reaction of propylene and butenes and the hydride transfer to form coke.

© 2015 Elsevier Inc. All rights reserved.

1. Introduction

Light alkenes, especially propylene, which is mainly supplied as a by-product of ethylene production through a thermal cracking of naphtha, are obtaining more and more significance in chemical industry. It is known that the thermal cracking is an energy intensive process, where the product distribution, especially propylene/ethylene ratio, is hard to control. Therefore, catalytic cracking of naphtha has been drawing increasing attention [1]. The catalytic cracking of alkanes over acidic zeolite catalysts gives a high propylene/ethylene ratio, since the transformation of long-chain alkanes to short-chain alkenes occurs at least partly via the carbenium ion/ β -scission mechanism, *i.e.* the classical bimolecular cracking [2].

Up to now, zeolites with various type structures such as FAU [3], *BEA [4], MOR [5], MWW [6], MFI [7] and MSE [8] have been extensively investigated as cracking catalysts. However, most of reports focus on the discussion on the cracking mechanism and/or the effects of structure of zeolites. In our recent works, ZSM-5 and MCM-22 catalysts have been investigated in the catalytic cracking of n-hexane to produce propylene as a model reaction of naphtha

cracking. We found that nano-sized ZSM-5 with medium Al content ($\text{Si}/\text{Al} \approx 50$) showed a good catalytic life however poor propylene selectivity at high n-hexane conversions [9]. However, we also found MCM-22 dealuminated by ammonium hexafluorosilicate (AHFS) ($\text{Si}/\text{Al} = 62$) showed a comparable catalytic life and higher propylene selectivity at high n-hexane conversions than nano-sized ZSM-5 with similar acid amount [10]. This may be due to its specific structure and lower amount of Lewis acid sites that accelerate the hydride transfer and resultant coke formation.

*BEA-type (beta) zeolite, an important catalyst in petrochemical industry, especially in the alkylation process of benzene for the production of ethylbenzene and cumene [11,12], possesses a three-dimensional 12-ring system of intersecting channels with pore openings with size of 6.6–6.7 Å [13]. Additionally, beta zeolite also shows an excellent catalytic performance in the FCC processes [14]. Although beta zeolite exhibits excellent properties in catalytic reactions, its wide applications are limited by the use of tetraethylammoniumhydroxide (TEAOH) as organic structure-directing agent (OSDA) in the synthesis, because the use of OSDA not only increases the cost but also results in consumption of energy and pollution for environments by the removal of OSDA at high temperature calcination. Therefore, it is strongly desirable to synthesize beta zeolite in the absence of any OSDAs.

Recently, Al-rich OSDA free beta (OFB) zeolite ($\text{Si}/\text{Al} \approx 5$) has been successfully synthesized by the seed-directed method

* Corresponding author. Fax: +81 45 924 5282.

E-mail address: yokoi@cat.res.titech.ac.jp (T. Yokoi).

[15–18]. Compared with conventional beta synthesized with OSDA, the OFB zeolite exhibits unprecedentedly high density of active sites, resulting in superior catalytic performance in the cracking of light vacuum gas oil [18]. More recently, the OFB zeolite has been successfully dealuminated by steaming followed by acid treatments while maintaining an intact framework. The dealuminated OFB zeolite exhibits better catalytic performance in different types of reactions such as the alkylation of benzene, the acylation of anisole, the hydroconversion of *n*-decane and the cracking of *n*-hexane [19–21].

In our recent unpublished work, we found that H-beta with Si/Al ratio of 12 showed a low propylene selectivity and a rapid deactivation in the cracking of *n*-hexane. However, dealuminated beta with high Si/Al ratio of *ca.* 160 showed a higher propylene selectivity than H-ZSM-5 and H-MCM-22 with similar acid amounts. This may be due to its specific structure, lower acid amount and higher Brønsted/Lewis acid ratio. Hence, the directly synthesized OFB zeolite with a high Al content should be dealuminated for using as the catalyst for the cracking of *n*-hexane cracking to selectively produce propylene.

In this study, the method for the dealumination of OFB zeolite was extensively investigated. The OFB zeolite was pre-treated with ammonium hexafluorosilicate (AHFS) solution, steaming, or concentrated NH_4NO_3 (*ca.* 10 M) followed by calcination at high temperature. Then, thus pre-treated OFB samples can be effectively dealuminated by acid treatment. The catalytic performances of H-form OFB (HOFB) and dealuminated OFB (DOFB) catalysts were also examined for the cracking of *n*-hexane as a model reaction of naphtha cracking. In addition, the relationship between the catalytic performance and the acidic properties of the catalysts was discussed.

2. Experimental

2.1. Catalyst preparation

The as-made OFB zeolite was synthesized according to the literature with slight modification [15]. Typically, colloidal silica (Ludox-HS-40) and $\text{Al}(\text{OH})_3$ were used as Si and Al sources, respectively, and sodium hydroxide was used to adjust the pH of the mother gel. The resulting mixture had a molar composition of 1 SiO_2 :0.04 Al_2O_3 :0.3 Na_2O :25 H_2O . The calcined Na-form Beta with Si/Al = 12 (JRC-Z-B25, from the Catalysis Society of Japan) (10% weight of SiO_2) was used as the seed. The hydrothermal treatment was carried out in static conditions under autogenous pressure at 413 K for 4 days. The sample was filtered, washed, dried at 373 K overnight to obtain the as-made OFB zeolite (Na-form). Then, it was converted to the H-form OFB (HOFB) zeolite by treating with 1 M NH_4NO_3 twice at 353 K for 2 h followed by the calcination in air at 773 K for 2 h.

Dealumination of OFB was carried out by three methods as follows. The HOFB zeolite was pre-treated with 0.5 M ammonium hexafluorosilicate (AHFS) solution at 363 K for 2 h. Then, AHFS-treated samples were treated with 1 M nitric acid treatment at 393 K for 6 h. Thus prepared catalyst was denoted by "HOFB-AHFS-AT". The HOFB zeolite was also pre-steamed at 873 K for 1 h, and then treated with 6 M nitric acid treatment at 393 K for 6 h. Thus prepared catalyst was denoted by "HOFB-ST-AT". Additionally, the as-made OFB zeolite was firstly ion-exchanged with concentrated NH_4NO_3 (*ca.* 10 M). The ion-exchanged sample was calcined at high temperature, *i.e.* 973 K for 2 h, and then treated with 1 M nitric acid treatment at 393 K for 1 h. Thus prepared catalyst was denoted by "OFB-IE-AT". As a control, HOFB was directly dealuminated by 1 M nitric acid solution at 393 K for 1 h (denoted by "HOFB-AT").

2.2. Catalysts characterization

The catalysts were characterized by various techniques. The Si/Al ratios were determined by inductively coupled plasma-atomic emission spectrometer (ICP-AES) on a Shimadzu ICPE-9000. The X-ray diffraction (XRD) patterns were recorded on a Rint-Ultima III (Rigaku) diffractometer using a $\text{Cu K}\alpha$ X-ray source. The N_2 adsorption measurements were carried out at 77 K on a Belsorp-mini II (BEL Japan) apparatus. The crystal morphology and size were examined with a Hitachi S-5200 field-emission scanning electron microscope (FE-SEM). Solid-state ^{27}Al and ^{29}Si magic-angle spinning (MAS) NMR spectra were obtained on a JEOL ECA-600 spectrometer. Temperature-programmed desorption profile of ammonia (NH_3 -TPD) were recorded on a Japan BEL Multitrack TPD equipment. IR spectra were collected on a Jasco FT-IR 6100 spectrometer. The IR spectra of pyridine adsorbed were recorded as follows. A self-supported wafer (9.6 mg cm^{-2} thickness and $\varnothing 2 \text{ cm}$) was set in a quartz IR cell sealed with CaF_2 windows, where it was evacuated at 723 K for 2 h before pyridine adsorption. The adsorption was carried out by exposing the wafer to pyridine vapor (1.3 kPa) at 423 K for 0.5 h. Physisorbed pyridine was then removed by evacuation at 423 K for 1 h. Then IR spectra were collected at 423 K. Thermogravimetric analyses (TGA) were conducted on a thermogravimetric differential thermal analyzer (RigakuThermo plus EVO II) in air atmosphere.

2.3. Catalytic cracking of *n*-hexane

The catalytic cracking of *n*-hexane was carried out with a fixed-bed flow reactor under atmospheric pressure. Typically, 0.1 g of catalyst (18–30 mesh size) was put into a tubular reactor (6 mm in i. d.) and activated in an air flow of 20 ml min^{-1} at 923 K for 1 h. Then, *n*-hexane vapor diluted in the helium was fed into the reactor. The initial partial pressure of *n*-hexane was set at 6 kPa. To investigate the effect of contact time on the cracking of *n*-hexane, the ratio of the catalyst weight to the *n*-hexane flow rate ($W/F_{n\text{-hexane}}$) was varied from 6.4 to 64 g-cat h/mol-*n*-hexane. The reaction products were analyzed with an on-line gas chromatograph (Shimadzu, GC-14B) with an FID detector and a HP-AL/S column ($50 \text{ m} \times 0.32 \text{ mm} \times 8 \mu\text{m}$). The selectivities to the products were calculated based on the carbon numbers. The coke amount was calculated by thermogravimetric analysis (TGA). The weight loss from 673 to 1073 K in each TG profile was defined as the contents of coke on the used catalyst.

3. Results and discussion

3.1. A summary of catalysts characterization

The XRD patterns of the products are shown in Fig. 1. The as-made OFB exhibited the diffraction peaks attributed to the *BEA structure with very weak peaks attributed to the MOR structure (Fig. 1a). When the as-made OFB zeolite was transformed to HOFB, the crystallinity was slightly decreased (Fig. 1b). However, the structure was completely destroyed after the direct acid treatment using 1 M nitric acid at 393 K for 1 h (Fig. 1c), which means the structure of the Al-rich HOFB zeolite was instable to acid leaching. Obviously, the dealumination of the Al-rich HOFB zeolite by direct acid treatment resulted in the formation of high lattice defect concentrations and diminished the stability of the crystal structure. Similarly, it was reported that the structure of the FAU-type zeolites completely collapsed upon strong mineral acid treatment [22].

In contrast, the *BEA structure almost remained after the AHFS followed by the acid treatments (Fig. 1d), the steaming followed by the acid treatment (Fig. 1e), and the ion-exchange with

Download English Version:

<https://daneshyari.com/en/article/72261>

Download Persian Version:

<https://daneshyari.com/article/72261>

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