



## Effect of desilication of H-ZSM-5 by alkali treatment on catalytic performance in hexane cracking



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### ARTICLE INFO

#### Article history:

Received 22 July 2012

Received in revised form 6 October 2012

Accepted 10 October 2012

Available online 22 October 2012

#### Keywords:

ZSM-5

Alkali treatment

Mesoporous zeolite

Hexane cracking

Lewis acid site

### ABSTRACT

The effects of external surface and acid properties of desilicated H-type ZSM-5 zeolites (H-ZSM-5) on their catalytic performance in hexane cracking were investigated. H-ZSM-5 with two different crystallite sizes of 100 nm and 1  $\mu\text{m}$  were treated with NaOH solution of different concentrations. The external surface area ( $S_{\text{EXT}}$ ) was increased with an increase in the NaOH concentration, because of the formation of mesopores inside the H-ZSM-5 crystallites as a result of desilication. The increase in the  $S_{\text{EXT}}$  of the H-ZSM-5 catalysts contributed to mitigating the catalyst deactivation during the hexane cracking. Although the amount of coke deposited on the alkali-treated H-ZSM-5 was larger than that on the parent H-ZSM-5, the micropore volume of the alkali-treated H-ZSM-5 decreased less due to coke deposition than that of the parent. The deactivation rate and the decrease in the micropore volume of the small-sized H-ZSM-5 catalysts were smaller than those of the large-sized catalysts, because they had shorter average diffusion path lengths. Thus the activity of the alkali-treated H-ZSM-5, especially small-sized one is less sensitive to coke deposition. Lewis acid sites (LASs) were generated by treating with NaOH of high concentrations. The selectivities to benzene, toluene and xylene (BTX) in the hexane cracking were increased with an increase in the LASs amount at high reaction temperatures ( $\geq 873$  K). The LASs on the alkali-treated H-ZSM-5 were selectively removed by acid treatment. The resultant H-ZSM-5 exhibited a slightly lower hexane conversion and a lower selectivity to BTX but a small amount of coke compared to the parent and alkali-treated H-ZSM-5 catalysts, suggesting that LASs on alkali-treated H-ZSM-5 accelerated the dehydrogenation including hydride transfer and aromatization, forming BTX, which would be precursors of coke.

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### 1. Introduction

Light olefins such as ethylene and propylene have been mainly produced by thermal cracking of naphtha. The thermal cracking process needs a high reaction temperature ( $>1073$  K) and gives a low propylene/ethylene ratio ( $<0.6$ ), whereas the demand for propylene is growing faster than that for ethylene [1,2]. Therefore, there is an increasing demand for processes capable of controlling the composition of olefins under energy-saving and environmentally benign mild reaction conditions.

The catalytic cracking of naphtha over acidic zeolite catalysts gives a high propylene/ethylene ratio at lower temperatures [2,3], since the transformation of long-chain paraffins to short-chain olefins occurs at least partly via the carbenium ion/ $\beta$ -scission mechanism [4]. Therefore, this process may be a promising alternative to produce the light olefins. Among various zeolites, ZSM-5

with the **MFI** structure has been recognized as a prime candidate for the practical catalytic cracking, because of its high thermal and hydrothermal stabilities and its considerably high resistance to deactivation by coking as well as its strong acidity [2,3,5–8]. However, zeolites are generally subject to deactivation mainly due to pore blocking by coke formed during the cracking. Recently, we have reported that reduction in the crystallite size of ZSM-5 is highly effective in improving the catalytic lifetime in the hexane cracking owing to large external surface area and short diffusion path lengths [9]. Therefore, it is expected that the enlargement of external surfaces of H-ZSM-5 makes the catalyst life longer.

It has been reported that mesoporous zeolites can be prepared by various direct synthesis methods using carbon [10–12], organosilane surfactants [13] and cationic polymers [14]. Moreover, the desilication to form mesopores inside zeolite crystallites by the post treatment with NaOH solution have been reported [15,16]. Ogura et al. have reported that the NaOH treatment improves the conversion and activity per Al in the cumene cracking over alkali treated H-ZSM-5 [15]. They have claimed that alkali post-treatment does not lead to stronger acidity but leads to a

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**Table 1**  
Physicochemical properties and acid amount of parent, alkali-treated and alkali-acid-treated H-ZSM-5 catalysts.

Catalyst	Treatment time		Recovery yields (%)	Si/Al <sup>a</sup>	$S_{BET}$ <sup>b</sup> (m <sup>2</sup> g <sup>-1</sup> )	$S_{EXT}$ <sup>c</sup> (m <sup>2</sup> g <sup>-1</sup> )	$V_{micro}$ <sup>d</sup> (cm <sup>3</sup> g <sup>-1</sup> )	Acid amount <sup>e</sup> (mmol g <sup>-1</sup> )	Al content <sup>f</sup> (mmol g <sup>-1</sup> )
	NaOH	HNO <sub>3</sub>							
Parent L	–	–	–	53	387	12	0.18	0.288	0.309
AT-0.05L	5	–	66	36	442	88	0.16	0.410	0.450
AT-0.1L	3	–	60	37	452	134	0.14	0.371	0.439
AT-0.2L	1	–	55	33	443	152	0.12	0.310	0.490
AAT-1L	1	2	–	43	451	155	0.12	0.257	0.379
AAT-2L	1	2	–	55	435	148	0.11	0.198	0.298
Parent S	–	–	–	51	410	65	0.17	0.291	0.321
AT-0.05S	5	–	63	34	447	123	0.15	0.430	0.476
AT-0.1S	3	–	52	35	500	180	0.14	0.358	0.463
AT-0.2S	1	–	56	34	520	215	0.14	0.344	0.476

<sup>a</sup> Si/Al: atomic ratio of Si/Al in the sample.<sup>b</sup>  $S_{BET}$ : BET surface area.<sup>c</sup>  $S_{EXT}$ : external surface area.<sup>d</sup>  $V_{micro}$ : micropore volume.<sup>e</sup> Acid amount: estimated by the NH<sub>3</sub>-TPD.<sup>f</sup> Al content: content of Al in the sample determined by ICP.

greater degree of diffusivity inside the zeolite crystal, providing easier access to the microporous entrance via the mesopores created by the treatment. Groen et al. have reported a change in properties of ZSM-5 by the alkali treatment in detail [16]. They have examined the effect of treatment conditions such as the Si/Al ratio of zeolite, treatment time and temperature and claimed that the alkaline treatment selectively removes silicon atoms from the framework, leaving the catalytically important Al sites unaffected. On the other hand, some papers reported on the formation not only of mesopores but of LASs with NaOH treatment. Bjørngen et al. have reported that product distribution and lifetime in methanol to gasoline reaction (MTG) are altered dramatically with desilication of H-ZSM-5, as a result of formation of Lewis acid sites (LASs) [17]. There are only a few reports on the catalytic performance of alkali-treated H-ZSM-5 in paraffin cracking [18]. Therefore, the influence of LASs on the lifetime of H-ZSM-5 in paraffin cracking is still unclear.

In this study we have investigated the effects of alkali treatment of H-ZSM-5 zeolites on the external surface area ( $S_{EXT}$ ) and acidic and catalytic properties. The alkali-treated ZSM-5 catalysts with different  $S_{EXT}$ s and Lewis acidities were prepared and examined to clarify the effect of their physicochemical properties on the activity, selectivity and lifetime in the cracking of hexane as a model compound of naphtha.

## 2. Experimental

### 2.1. Synthesis of different-sized ZSM-5 catalysts

Two H-ZSM-5 catalysts with a Si/Al ratio of ca. 50 and crystallite sizes of ca. 1  $\mu$ m and 100 nm were synthesized according to our method [9]. The gels with two different compositions of 1 SiO<sub>2</sub>:0.01 Al<sub>2</sub>O<sub>3</sub>: 0.25 TPAOH:0.05 Na<sub>2</sub>O:8.3 or 100 H<sub>2</sub>O were prepared from tetraethyl orthosilicate (TEOS), tetrapropylammonium hydroxide (TPAOH), aluminum nitrate and NaOH. The pre-aging was carried out at 353 K for 24 h before crystallization. Crystallization was carried out at 443 K for 24 h. The Na-type ZSM-5 (Na-ZSM-5) samples were obtained by calcination of the as-synthesized sample in an oven at 823 K to remove TPA cations. The calcined Na-ZSM-5 samples were treated with 1 M NH<sub>4</sub>NO<sub>3</sub> aq. at 353 K for 3 h twice followed by calcination at 823 K for 10 h to exchange Na<sup>+</sup> ions for H<sup>+</sup>. The larger and smaller sized H-ZSM-5 were denoted by “Parent L” and “Parent S”, respectively.

### 2.2. Alkali treatment of ZSM-5 zeolite with NaOH solutions

An alkali treatment of the ZSM-5 zeolite was performed with aqueous solutions of 0.05, 0.1, and 0.2 M NaOH. To 100 ml of the NaOH aqueous solution was added 1 g of calcined Na-ZSM-5. The solution was stirred at 353 K for 1–5 h. In order to adjust the Si/Al atomic ratio to ca. 35, the treatment time was controlled; the time for the alkali treatment with 0.05, 0.1 and 0.2 M NaOH were 5, 3 and 1 h, respectively. The yields of alkali-treated samples were ca. 50–70% (Table 1).

The alkali-treated zeolites were washed with deionized water to remove remaining NaOH. Then Na<sup>+</sup> ions in the Na-ZSM-5 were exchanged for H<sup>+</sup> by the conventional cation-exchange procedure described in Section 2.1. The samples thus prepared were denoted by AT-, NaOH concentration and crystallite sizes (L or S), e.g. “AT-0.1L”.

### 2.3. Acid treatment of alkali-treated ZSM-5 zeolite using HNO<sub>3</sub> solutions

The acid treatment of the alkali-treated ZSM-5 zeolite was performed with 1.0 or 2.0 M HNO<sub>3</sub> aqueous solution. To 100 ml of the HNO<sub>3</sub> aqueous solution was added 1 g of the large-sized Na-ZSM-5 treated with 0.2 M NaOH to provide Na type AT-0.2L. The solution was stirred at 353 K for 2 h. After washed with deionized water followed by drying at 383 K overnight, the sample was calcined. Thus obtained products were denoted by AAT-1L and AAT-2L, respectively.

### 2.4. Characterizations

XRD patterns were collected on a Rint-Ultima III (Rigaku) using a Cu K $\alpha$  X-ray source (40 kV, 20 mA). Nitrogen adsorption measurements to determine the BET surface area ( $S_{BET}$ ),  $S_{EXT}$ , and micropore volume ( $V_{micro}$ ) were conducted at 77 K on a Belsorp-mini II (Bel Japan).  $S_{EXT}$  and  $V_{micro}$  were estimated by the *t*-plot method. Field-emission scanning electron microscopic (FE-SEM) images of the powder samples were obtained on an S-5200 microscope (Hitachi) operating at 1–30 kV. The sample was mounted on a carbon-coated microgrid (Okenshoji Co.) without any metal coating. Transmission electron microscopic (TEM) images of the powder samples were obtained on a JEM-1400 microscope (JOEL) operating at 100 kV. Si/Al ratios of the samples were determined by using an inductively coupled plasma-atomic emission spectrometer

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