



## Research paper

# Preferential dealumination of Zn/H-ZSM-5 and its high and stable activity for ethane dehydroaromatization



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## ARTICLE INFO

## Keywords:

Ethane dehydroaromatization  
Zeolite catalyst  
Coke deposition  
Preferential dealumination

## ABSTRACT

The effect of steam treatment on Zn/H-ZSM-5 catalysts prepared by an ion-exchange method for non-oxidative ethane dehydroaromatization was investigated. Steam treatment of Zn/H-ZSM-5 after Zn loading improved its catalytic stability on aromatic hydrocarbon formation including benzene, toluene and xylene. Temperature programmed oxidation measurements demonstrated that the steam treatment brought suppression of coke formation and it contributed to the improvement in the catalytic stability. Characterization of the local structure of the zeolites by <sup>27</sup>Al and <sup>29</sup>Si magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy revealed that dealumination of the framework Al in the MFI structure proceeded by steam treatment. Results of temperature programmed desorption of ammonia indicate the decrease in the amount of acid sites by the steam treatment. The slight changes in Zn content and its electronic state indicated that bared Al related with H<sup>+</sup>, not with Zn<sup>2+</sup>, in the MFI structure was preferentially dealuminated by steam treatment. The preferential dealumination led to suppression of coke formation by the selective removal of undesirable Brønsted acid sites.

## 1. Introduction

Converting natural gas to aromatic hydrocarbons is attractive because of the vast abundance and low cost of natural gas. Benzene, toluene, and xylene, called BTX, are extremely important as fundamental raw chemicals used in the petrochemical industry. Many studies have reported dehydroaromatization of methane which is abundant and cheap feedstock, conducted at temperatures higher than 973 K because of thermodynamic limitations [1,2]. The use of ethane instead of methane enables the reaction temperature to be lower than 873 K [3] leading to more feasible processes in terms of heat transfer, heat tolerance of the reactor, and catalysts. Nowadays, ethane is converted to ethylene using an ethane cracker, so direct BTX production from ethane is anticipated for an effective option.

To form BTX selectively, MFI type zeolite (ZSM-5) in H-form supported metal cations or oxides including Zn, Ga, Re [4–6] is effective because ZSM-5 has a three-dimensional 10-ring channel system with micropores of about 0.55 nm [7,8], which is close to the kinetic diameter of BTX. The active metals play a role in promoting the dehydrogenation of ethane to ethylene. Brønsted acid sites within the zeolite are involved in the oligomerization of ethylene to form aromatic hydrocarbons [3,5]. The formed alkenes were also converted to aromatic

hydrocarbons on active metal sites [9]. Especially, Zn is cost-effective. It exhibits high catalytic performance in all the reactions described above. However, the Zn/H-ZSM-5 catalyst is rapidly deactivated over time on stream because of coke deposition, which prevents reactants from approaching the active sites because of blocking of the micropores of the support. The carbon deposition on the external and internal surfaces of zeolites also decreases the catalytic activity and benzene selectivity in cases of the conversion of methane to benzene, as described in the literature [10,11]. Weckhuysen et al. reported that carbon species of three types were formed on the Mo/H-ZSM-5 surface [12]. In addition to the carbon derived from Mo carbide, graphite-like carbon on the internal surface and sp-hybridized carbon on the external surface were observed by XPS investigation. Ma et al. inferred that the coke formed on Mo/MCM-22 zeolite catalyst was associated with Brønsted acid sites [13], based on the results of temperature-programmed techniques.

The use of H-ZSM-5 with higher Si/Al molar ratios in this type of reaction is expected to suppress the coke formation because of a low number of Brønsted acid sites. However, low catalytic activity in initial dehydrogenation might occur because of the lower cation-exchange capacity for loading the active metal species. Therefore, dealumination of the framework Al by post-synthetic treatment [14–20] after loading

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of active metal species on H-ZSM-5 with low Si/Al ratios is expected to be an effective means of realizing tuning of the Brønsted acidity of zeolite with high content active metal species within the zeolite.

In this work, we found that Zn/H-ZSM-5 showed high initial activity for the conversion of ethane to BTX, so we investigated the effects of steam treatment on the catalytic performance of the Zn/H-ZSM-5 catalysts for non-oxidative ethane dehydroaromatization. Various characterizations were conducted for elucidating the influence of steam treatment on the catalysts.

## 2. Experimental

### 2.1. Catalyst preparation and activity tests

Zeolite H-ZSM-5 was obtained by calcination of NH<sub>4</sub>-ZSM-5 (HSZ-820NHA, Tosoh) at 773 K for 5 h. The loading of Zn on the zeolite support was carried out by an ion-exchange method. First, H-ZSM-5 was soaked and stirred in the 0.02 M aqueous solution of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Kanto Chemical Co., Inc.) at 353 K for 24 h. The suspension contained 1 g of the zeolite in 100 mL of the aqueous solution. Next, the powder was separated by suction filtration, washed with distilled water and dried in air with an oven at 393 K for 24 h. Finally, the dried powder was calcined at 823 K for 5 h.

Steam treatment of H-ZSM-5 and Zn/H-ZSM-5 was conducted in a fixed bed reactor. The catalyst (ca. 0.9 g) was charged into a quartz tube and then temperature was raised to 823 K under Ar flow. After that, steam treatment was conducted at 823 K for 1 h under H<sub>2</sub>O/Ar flow at a constant partial pressure of water (38 kPa). The water vapor was introduced to the reactor by Ar flow through a bubbler heated at 348 K. The partial pressure of water was controlled by the bubbler temperature calculated from the Antoine equation. The catalyst was subsequently purged at 823 K for 30 min under Ar flow. The steam-treated samples are denoted as H-ZSM-5 ST and Zn/H-ZSM-5 ST. Zn loading was also conducted by the ion-exchange method using the H-ZSM-5 ST support. The catalyst exchanged with Zn<sup>2+</sup> after steam treatment of H-ZSM-5 is denoted as Zn/H-ZSM-5 ST bef. IE.

Catalytic activity tests were carried out in a fixed bed reactor at atmospheric pressure for 4 h. The catalyst (0.2 g) was charged into a quartz tube (i.d. 6 mm) and then temperature was raised to 873 K under Ar flow. The feed gas of 80 vol% ethane and balanced nitrogen was supplied at a flow rate of 25 mL min<sup>-1</sup> (SATP). Products were analyzed by a gas chromatography (GC-8A, Shimadzu) equipped with a thermal conductivity detector (TCD) using a Shincarbon ST packed column (3 mm × 4 m, Shinwa Chemical Industries Ltd.) to detect H<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>, and an on-line gas chromatography (GC-8A, Shimadzu) equipped with a flame ionization detector (FID) using a HP-PLOT/Q capillary column (0.53 mm × 30 m, Agilent) to detect CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub> hydrocarbons, C<sub>4</sub> hydrocarbons, benzene, toluene, ethylbenzene and xylene. Ethane conversion and products selectivity were calculated as follows:

$$\text{Ethane conversion(\%, C-based)} = \frac{\sum_{n=1}^8 n \times f_{C_n}^{\text{out}} / 2 - f_{C_2H_6}^{\text{out}}}{f_{C_2H_6}^{\text{in}}} \times 100 \quad (1)$$

$$\text{Selectivity(\%, C-based)} = \frac{n \times f_{C_n}^{\text{out}}}{2 \times (\sum_{n=1}^8 n \times f_{C_n}^{\text{out}} / 2 - f_{C_2H_6}^{\text{out}})} \times 100 \quad (2)$$

Here, the description of  $f$ ,  $n$  means the formation rate of a detected hydrocarbon shown as the subscript and the number of carbon atoms of the hydrocarbon respectively. The superscripts of “in” and “out” also express the inlet and outlet gas.

Catalyst regeneration was performed continuously at 873 K for 1 h under 20 vol% O<sub>2</sub>/Ar flow at a rate of 25 mL min<sup>-1</sup> (SATP) after the catalytic activity test, and the reactant was supplied again to evaluate the catalytic performance.

### 2.2. Characterization

The BET specific surface area was calculated from nitrogen adsorption–desorption isotherm obtained by nitrogen physisorption at 77 K, measured by a surface area gas sorption analyzer (Autosorb iQ, Quantachrome Instruments). The external surface area and micropore volume were estimated by the  $t$ -plot method. Prior to the measurement, the sample (ca. 80 mg) was heated *in vacuo* to 673 K for 12 h to remove adsorbed water.

XRD patterns were measured using an X-ray diffractometer (SmartLab 3, Rigaku) using CuK $\alpha$  radiation at 40 kV and 40 mA in the 2 $\theta$  range from 5 to 60° at a scan rate of 5° min<sup>-1</sup>.

Temperature programmed oxidation (TPO) was performed to determine the amount of carbon deposition on the spent catalysts using a thermogravimetry (TGA-50, Shimadzu). The samples (ca. 15 mg) were firstly heated to 873 K for 30 min under Ar flow to remove adsorbed water and volatile hydrocarbons. After cooling to 323 K, the temperature was raised at a ramping rate of 10 K min<sup>-1</sup> under 20 vol% O<sub>2</sub>/Ar flow. The weight loss of the sample was regarded as the weight of coke formed on the catalysts. The amount of carbon deposition was calculated as follows:

$$\text{The amount of carbon deposition(mg g}_{\text{cat}}^{-1}) = \frac{W_i - W_f}{W_f} \quad (3)$$

The description of  $W_i$  and  $W_f$  means initial and final weight of the sample respectively.

Temperature programmed desorption of ammonia (NH<sub>3</sub>-TPD) was also carried out to estimate the amount of adsorbed ammonia corresponded to acid sites. The desorbed ammonia was detected by a catalyst analyzer (BELCAT II, MicrotracBEL) equipped with a TCD. Prior to measurements, the samples (ca. 50 mg) were heated to 773 K for 1 h under He flow and cooled to 373 K. After that, 5 vol% NH<sub>3</sub>/He was introduced to the sample for 30 min and purged under He flow for 15 min. After the pre-treatment, NH<sub>3</sub>-TPD profile was obtained at a ramping rate of 10 K min<sup>-1</sup> in the temperature range from 373 to 873 K.

Al and Zn contents in the catalysts were measured by elemental analyses using an ICP emission spectrometer (iCAP-6500, Thermo Scientific). The samples (ca. 10 mg) were dissolved in HF to prepare the aqueous solution of the sample for the measurement.

UV–vis diffuse reflectance spectra were obtained using a UV–vis spectrometer (Lambda 650, PerkinElmer) equipped with an integrating sphere coated by BaSO<sub>4</sub>. BaSO<sub>4</sub> was used as a reference material and then relative reflectance of the catalysts was measured. The range of wave length was from 190 to 800 nm at a scan rate of 96 nm min<sup>-1</sup>. The obtained reflectance was converted by Kubelka-Munk (KM) function given in the following equation.

$$F(R_{\infty}) = \frac{(1 - R_{\infty})^2}{2R_{\infty}} \quad (4)$$

Here,  $R_{\infty}$  is relative reflectance and  $F(R_{\infty})$  is KM function that is proportional to the absorption coefficient.

The solid-state MAS NMR measurements were performed on an ADVANCEIII-600 (600 MHz (<sup>1</sup>H), Bruker Biospin) with a 4 mm diameter ZrO<sub>2</sub> rotor. The loading amount of sample powder was ca. 60–80 mg. The <sup>27</sup>Al direct-excitation (DE) MAS NMR spectra (156.4 MHz) were recorded at 0.5 s of the contact time for 1024 times at a spinning rate of 13.0 kHz. The <sup>27</sup>Al chemical shifts were determined using aqueous Al(NO<sub>3</sub>)<sub>3</sub> solution, the resonance peak of which was adjusted to 0 ppm. The <sup>29</sup>Si dipolar decoupling (DD) MAS NMR spectra (119.2 MHz) were recorded at 30 s of the contact time for 1024 times at a spinning rate of 10.0 kHz. The <sup>29</sup>Si cross polarization (CP)/MAS NMR spectra were also recorded at 4 s of the contact time for 4096 times at a spinning rate of 10 kHz. The reference of <sup>29</sup>Si chemical shifts was determined with reference to the <sup>29</sup>Si signal of hexamethylcyclotrisiloxane (HMCS) at –9.66 ppm.

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