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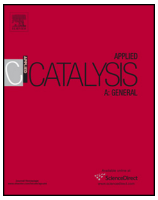

Recreation of Brønsted acid sites in phosphorus-modified HZSM-5(Ga) by modification with various metal cations

Nao Tsunoji, Takushi Sonoda, Yoshiyasu Furumoto, Masahiro Sadakane, Tsuneji Sano*

Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, Higashi-Hiroshima 739-8527, Japan

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ABSTRACT

To investigate the recreation of Brønsted acid sites in phosphorus-modified HZSM-5(Ga) zeolites by modification with various metal cations, we prepared several HZSM-5(Ga) zeolites co-modified with Mg, Ca, La or Zr and P (M/P/HZSM-5(Ga)). From FT-IR, ^{31}P MAS NMR, and NH_3-TPD measurements, it was found that the introduced metal cations (M) of Mg, Ca, La, and Zr react with the pre-introduced phosphorus to generate phosphorus species such as $M_x(PO_4)_y$, resulting in the recreation of some native Brønsted acid sites (Si(OH)Ga). The degree of recreation of the Brønsted acid sites was strongly dependent on the M/Ga ratio and doped metal valence. Modification with La and Zr that have higher valences more effectively recreated the Brønsted acid sites compared to Mg and Ca, which have di-valence. The conversion of ethanol to propylene was carried out over the M/P/HZSM-5(Ga). The propylene yield increased with increasing M/Ga ratio and reached maximum values of ca. 26 C-% for Zr/P/HZSM-5(Ga) with a Zr/Ga ratio of 0.25 and ca. 29 C-% for La/P/HZSM-5(Ga) with a La/Ga ratio of 0.4. The propylene yield hardly changed for the co-modified HZSM-5(Ga) zeolites during the 24 h of reaction time, indicating the suppression of both carbonaceous deposition and the release of gallium from the zeolite framework.

1. Introduction

Light olefins such as ethylene and propylene are basic raw materials used in the synthesis of various chemicals and are generally produced by steam cracking of naphtha. Owing to the increasing concerns in recent years about global warming and the exhaustion of petroleum resources, production of light olefins, especially propylene, from bio-ethanol obtained by the fermentation of biomass has attracted considerable attention. Many studies have investigated the production of hydrocarbons such as ethylene, gasoline, and aromatics from ethanol, aqueous ethanol, and bioethanol using solid catalysts such as zeolites [1–13]. However, there are few reports on the selective conversion of ethanol to propylene [14–21].

It is well known that the distribution of products obtained by the zeolitic ethanol conversion process is strongly dependent on the acidity (acid strength and number of acid sites) and channel structure of the zeolites. Significant efforts have been devoted to control the acidity of zeolites by modifying them with a variety of metal and non-metal cations, including Zr, La, Ca, and P [22–25]. Recently, we prepared isomorphously framework-substituted ZSM-5 zeolites (HZSM-5(M), M = Al, Ga, and Fe) with different acid strengths and investigated their catalytic performance in the conversion of ethanol to propylene. High propylene yields were obtained on HZSM-5(Ga) and HZSM-5(Al), and the hydrothermal stability of HZSM-5(Ga) was found to be higher than that of HZSM-5(Al) because of the weaker acid strength of HZSM-5(Ga) [26]. In addition, HZSM-5(Ga) co-modified with lanthanum and phosphorus (La/P/HZSM-5(Ga)) showed good catalytic activity and stability because of the suppression of both carbonaceous deposition and the release of gallium from the zeolite framework [27]. From FT-IR, NH_3-TPD, and ^{31}P and ^{71}Ga MAS NMR measurements, it was suggested that the introduced lanthanum reacts with the pre-introduced phosphorus to generate $LaPO_4$, resulting in the recreation of some of the native Brønsted acid sites (Si(OH)Ga). To obtain further information about the recreation of Brønsted acid sites, we prepared several co-modified HZSM-5(Ga), M/P/HZSM-5(Ga), from P/HZSM-5(Ga) by adding various metal cations and investigated their ethanol conversion efficiency.

2. Experimental

2.1. Synthesis of gallium-substituted ZSM-5 (HZSM-5(Ga))

Protonated ZSM-5(Ga) (HZSM-5(Ga)) was synthesized by adding gallium nitrate hexahydrate ($Ga(NO_3)_3{\cdot}6H_2O$, Soekawa

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* Corresponding author. Tel.: +81 82 424 7607; fax: +81 82 424 5494.
E-mail address: tsano@hiroshima-u.ac.jp (T. Sano).

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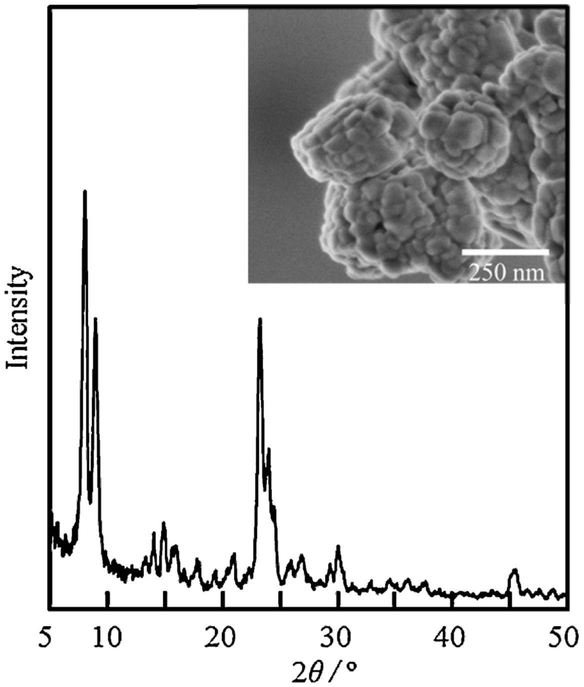

Fig. 1. XRD pattern and SEM image of prepared HZSM-5(Ga) zeolite.

Chemical Ind. Co. Ltd., Japan), colloidal silica (SiO_2 = 30.5 wt%, Na_2O = 0.4 wt%, H_2O = 69.1 wt%, Cataloid SI-30, JGC Catalysts and Chemicals Ltd., Japan), and tetrapropylammonium bromide (TPABr, Tokyo Chemical Ind. Co. Ltd., Japan) to a stirred solution of sodium hydroxide (Kanto Chemical Co Inc., Japan) in distilled water. The resultant hydrogel with a chemical composition of $SiO_2/Ga_2O_3 = 70$, $OH^-/SiO_2 = 0.2$, $TPABr/SiO_2 = 0.1$, and $H_2O/SiO_2 = 40$ was transferred into a 300 mL stainless-steel autoclave and stirred at 160 °C under autogenous pressure for 16 h. The precipitated solids obtained were washed with distilled water, dried at 120 °C for one night, and calcined in air at 500 °C for 10 h to remove the organic cations occluded in the zeolitic pores. The zeolite was protonated in a 0.6 M hydrochloric acid solution at 60 °C for 24 h, washed with distilled water and then calcined in air at 500 °C for 6 h. The prepared HZSM-5(Ga) with a SiO_2/Ga_2O_3 ratio of 70 had a well-defined ZSM-5 type zeolite structure, as demonstrated by the XRD pattern (Fig. 1). No diffraction peaks other than those of the ZSM-5 phase were observed. The SEM observations revealed a round morphology of the ZSM-5(Ga) crystals.

2.2. Preparation of phosphorus-modified HZSM-5(Ga) (P/HZSM-5(Ga)) and co-modified HZSM-5(Ga) (M/P/HZSM-5(Ga))

Phosphorus-modified HZSM-5(Ga) (P/HZSM-5(Ga)) was prepared by the impregnation method. First, 1 g of HZSM-5(Ga) was suspended in 5 mL of distilled water, and then the desired amount of an aqueous solution of 0.02 M $(NH_4)_2HPO_4$ (Wako Pure Chemical Ind. Ltd., Japan) was added. After stirring at 60 °C for 6 h, the residual water was removed under reduced pressure. The residue was dried at 60 °C and calcined at 500 °C for 6 h. Co-modified HZSM-5(Ga) (M/P/HZSM-5(Ga)) was prepared from P/HZSM-5(Ga) by the impregnation method using 0.02–0.06 M aqueous solutions of the corresponding metal nitrates (Mg, Ca, La, and Zr).

2.3. Characterization

X-ray diffraction (XRD) patterns of the solid products were obtained using a powder X-ray diffractometer (Bruker D8 Advance) with graphite monochromatized Cu Kα radiation at 40 kV and 30 mA. The SiO_2/Ga_2O_3 ratio was determined via X-ray fluorescence (XRF, Philips PW 2400). To make the samples of XRF, a fixed amount of the sample (0.5 g) was fused with 5 g of dilithium tetraborate ($Li_2B_4O_7$) at 1100 °C. The crystal morphology was observed using scanning electron microscopy (SEM, Hitachi S-4800). Thermal analyses were carried out using a TG/DTA apparatus (SSC/5200 Seiko Instruments). The sample (ca. 3 mg) was heated from room temperature to 800 °C at a rate of 10 °C/min under a flow of air (50 mL/min). ^{31}P MAS NMR and ^{71}Ga MAS NMR spectra were recorded at 600 MHz on a Varian 600 spectrometer using a 3.2 mm diameter zirconia rotor with spinning at 15 kHz. The spectra were obtained with 2.8 μs pulses, a 15 s recycle delay, and 10,000 scans for ^{31}P MAS NMR, and 2.8 μs pulses, a 0.1 s recycle delay, and 400,000 scans for ^{71}Ga MAS NMR. $NH_4H_2PO_4$ and $Ga(NO_3)_3{\cdot}6H_2O$ were used as the chemical shift references. Nitrogen adsorption isotherms were obtained at −196 °C using a conventional volumetric apparatus (BELSORP-max, Bel Japan). Prior to performing the adsorption measurements, the calcined samples (ca. 0.1 g) were evacuated at 400 °C for 10 h. IR spectra were recorded at room temperature on an FT-IR spectrometer (Nicolet 6700) with a resolution of 4 cm^{-1}. Measurements in the OH stretching region were carried out by pressing the sample into a self-supporting thin wafer (ca. 6.4 mg/cm^2), which was placed in a quartz IR cell with CaF_2 windows. Prior to carrying out the measurements, each sample was dehydrated under vacuum at 400 °C for 2 h. The distribution of the acidity of the zeolite samples was measured in the temperature range 150–700 °C by measuring the temperature-programmed desorption of ammonia (NH_3-TPD, CAT-B-82 NH_3-TPD, Bel Japan). Helium was used as a carrier gas. The samples (ca. 0.1 g) were pre-heated at 500 °C under a flow of helium (50 mL/min) and then ammonia (NH_3/He = 1/99 vol%) was adsorbed at 150 °C. After removing of the excess adsorbed ammonia by flushing with helium at 150 °C for 30 min, the samples were heated at a rate of 10 °C/min.

2.4. Ethanol conversion

Zeolitic ethanol conversion was carried out at a reaction temperature of 500 °C with a contact time (*W*/*F*) of 0.02 g_{cat}/mL/min in an atmospheric-pressure flow system. The required amount of zeolite (12–24 mesh) was retained by placing quartz wool at the center of a quartz reactor with a 10 mm inner diameter. A thermocouple inserted at the center of the catalyst bed was used to measure the temperature during the reaction. The catalyst was activated at 500 °C for 1 h under a flow of nitrogen prior to carrying out the reaction. Ethanol (>99.5%, Wako Pure Chemical Ind. Ltd., Japan) was pumped into the vaporizer and mixed with N_2 at a total flow rate of 20 mL/min (C_2H_5OH/N_2 = 50/50 mol%). The gaseous products were analyzed using on-time GC equipped with TCD- and FID-type detectors on a Shincarbon ST (Shinwa Chem. Ind. Ltd., Japan) column for N_2, H_2, and CO_2; on a Gaskropack54 (GL Sciences, Japan) column for ethanol; and on an RT-alumina PLOT (Restek, USA) column for C_1–C_4 hydrocarbons. The product yields were calculated using N_2 as an internal standard.

3. Results and discussion

3.1. Effect of M/Ga ratio on recreation of Brønsted acid sites

Fig. 1 shows the XRD pattern of the obtained HZSM-5(Ga). The characteristic peaks of a ZSM-5 phase were clearly observed. The SEM image of HZSM-5(Ga) revealed a spherical morphology with a particle size of 50–100 nm. We confirmed from the XRD and SEM measurements that there were no differences in the crystallinity and morphology among the HZSM-5(Ga), P/HZSM-5(Ga),