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Effects of dealumination and desilication of H-ZSM-5 on xylose dehydration

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ABSTRACT

The continuous liquid-phase dehydration of D-xylose into furfural was examined over various zeolites (H-ferrierite, H-ZSM-5, H-mordenite, H-β, and H-Y) having a similar surface area, external surface area, and amount of acid sites to determine the effects of zeolite structure on catalytic performance. Xylose conversion was proportional to the zeolite channel size, whereas the H-ZSM-5 zeolite showed the highest furfural selectivity due to shape-selectivity. In order to improve the catalytic activity, H-ZSM-5 zeolite was dealuminated or desilicated using an aqueous solution of HCl or NaOH, respectively. The prepared catalysts were characterized using N_2 physisorption, X-ray diffraction (XRD), solid-state ^{27}Al and ^{29}Si magic-angle spinning nuclear magnetic resonance (MAS/NMR) spectroscopy, temperature-programmed desorption of ammonia (NH_3-TPD) and isopropylamine (IPA-TPD). Dealumination of H-ZSM-5 appeared to remove extra-framework Al species without a collapse of the crystalline zeolite framework, while desilication generated extra-framework Al species accompanied by destruction of the zeolite framework. Among the tested catalysts, dealuminated H-ZSM-5 showed the highest furfural selectivity.

1. Introduction

Global warming because of an increase in CO_2 concentration in the atmosphere has become one of the most important issues facing human beings today. Since lignocellulosic biomass consumes CO_2 for growth, it is a promising substitute for fossil energy sources and could thus help mitigate the effects of climate change. Further, it can be converted into a variety of other chemicals through biological and/or chemical transformations [1–3]. Lignocellulosic biomass is mainly composed of cellulose (40–50%), hemicellulose (25–30%), and lignin (15–20%). Among these, hemicellulose is a polysaccharide comprising xylose, arabinose, galactose, mannose, and glucose. The most abundant compound of hemicellulose is xylan that is a polymer made from units of xylose.

Xylose can be converted into a wide variety of products such as ethanol, xylitol, furfuryl alcohol, furan and furfural. Among these derivatives, furfural is a key component for the preparation of fine chemicals, pharmaceuticals, and furan-based polymers. Moreover, furfural was reported to be a potential platform for biofuels [4]. Furfural is currently produced from xylose using homogeneous mineral acid catalysts, causing severe environmental problems. Therefore, to overcome the drawbacks of the current process, heterogeneous catalytic processes have been actively investigated [5–21]. There are several solid acid catalysts, such as microporous zeolites and related materials [5–8], modified mesoporous silica [9–12], Amberlyst [13], Keggin-type heteropolyacids [14,15], titanates and niobates [16], and metal oxides (TiO_2, ZrO_2, Zr-WO_x, VPO_x, SnO_2, SiO_2–Al_2O_3) [17–21]. Although it is well-documented that a correlation exists between the concentration of acid sites and dehydration activity of xylose, further efforts to increase the furfural yield by considering the nature of reactants and the catalyst structure are required.

Zeolite, a representative solid acid, is a crystalline aluminosilicate that has a high thermal stability, strong intrinsic acidity, and a high surface area with uniform micropore channels. Owing to these advantages, zeolites have been successfully applied to various industrial fields [22,23]. One of the major drawbacks of zeolites is a diffusion limitation due to the presence of micro-sized channels. To overcome this limitation, dealumination or desilication, where the framework Al or Si atoms are removed, respectively, has been used to form mesopores [24–27]. Zeolite can be dealuminated by various methods including steaming and pretreatment with chemicals such as HCl, oxalic acid, $SiCl_4$, and ammonium hexafluorosilicate [24–26]. Although it is well-known that dealumination of zeolites can generate intracrystalline mesopores and modify its acidic property, it was reported that only extra-framework Al species (EFAl) could be extracted in dealuminated ZSM-5 zeolite prepared through a treatment in aqueous acidic solution because of the narrow channel size of ZSM-5 zeolite [25,26]. On the other hand, desilication of ZSM-5 zeolite was reported to be carried out easily in an aqueous alkaline solution and found to be

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dependent on treatment temperature, time, and alkaline solution concentration [27]. This desilication process can be used to control the mesoporosity without affecting the micropore size or the surface acidity noticeably.

In this study, we reveal that the channel size of zeolite is an important factor in controlling the catalytic activity for the dehydration of D-xylose and that H-ZSM-5 is a promising catalyst to achieve a high selectivity of furfural. We also attempt to improve the catalytic activity of H-ZSM-5 by dealumination or desilication and find that dealuminated H-ZSM-5 shows a higher selectivity than the parent H-ZSM-5 owing to the removal of EFAl species.

2. Experimental

2.1. Catalyst preparation

2.1.1. Parent zeolites

Various zeolites, i.e., H-ferrierite (FER, Si/Al = 10, Zeolyst, CP914C, $S_{BET} = 390\ m^2/g$), NH_4-ZSM-5 (MFI, Si/Al = 12, Zeolyst, CBV2314, $S_{BET} = 315\ m^2/g$), H-β (BEA, Si/Al = 13, Zeolyst, CP814E, $S_{BET} = 508\ m^2/g$), NH_4-mordenite (MOR, Si/Al = 10, Zeolyst, CBV21A, $S_{BET} = 424\ m^2/g$), and H-Y (FAY, Si/Al = 2.5, Zeolyst, CBV400, $S_{BET} = 631\ m^2/g$), were purchased and utilized after calcination in air at 600 °C. Therefore, NH_4-form zeolite was transformed into H-form zeolite.

2.1.2. Acid treatment

Three different modified H-ZSM-5 samples were prepared from a calcined H-ZSM-5, through treatment with 1–3 M aqueous solution of HCl at 90 °C for 24 h. After filtration, washing and drying at 120 °C, the solid product was calcined in air at 600 °C before the reaction. The prepared samples were denoted as DeAl (*x*) H-ZSM-5, where *x* in the parentheses represents the molar concentration of HCl during the pretreatment.

2.1.3. Alkaline treatment

Three different modified H-ZSM-5 samples were prepared from a calcined H-ZSM-5 through treatment with 0.2–0.6 M aqueous solution of NaOH at 65 °C for 2 h. After filtration, washing and drying at 120 °C, the recovered solid in Na-form was converted into the H-form by ion-exchange in 0.1 M NH_4NO_3 solution and calcination in air at 600 °C before the reaction. The prepared samples were denoted as DeSi (*x*) H-ZSM-5, where *x* in the parentheses represents the molar concentration of NaOH during the pretreatment.

2.2. Catalyst characterization

The bulk Si/Al ratios for all of the prepared zeolites were analyzed using inductively coupled plasma-atomic emission spectroscopy (ICP-AES, JY-70Plus, Jobin–Yvon).

The bulk crystalline structures of the catalysts were determined using the X-ray diffraction (XRD) technique. The XRD patterns were obtained with a Rigaku D/MAC-III instrument operated at 50 kV and 30 mA using Cu Kα radiation. The assignment of the crystalline phases was carried out using the PCPDFWIN software (version 2.2) for the ICDD database.

The Brunauer–Emmett–Teller (BET) surface area was calculated based on N_2 adsorption–desorption data obtained using an ASAP 2020 apparatus (Micromeritics) at liquid N_2 temperature. Prior to the measurement, the sample was degassed under vacuum for 6 h at 200 °C. The *t*-plot method was applied to obtain the micropore surface area and volume.

400-MHz solid-state ^{27}Al and ^{29}Si magic-angle spinning nuclear magnetic resonance (MAS/NMR) spectra were recorded using an Avance-II+ Bruker solid-state NMR system at ^{27}Al and ^{29}Si radio frequencies of 104.26 and 79.49 MHz, respectively. The ^{27}Al and ^{29}Si spectra were calibrated using tetramethylsilane (TMS) and $AlCl_3$ solution, respectively. All detected peaks for ^{27}Al-MAS and ^{29}Si-MAS spectra were deconvoluted at different positions using the Peakfit 4.01 program, with a Gaussian–Lorentzian function for peak fitting, from which the peak area was calculated.

The acid properties of the prepared zeolites were characterized by the temperature-programmed desorption of ammonia (NH_3-TPD) and isopropylamine (IPA-TPD) in an AutoChem 2910 unit (Micromeritics) equipped with a thermal conductivity detector (TCD) and on-line mass spectrometer signals (QMS 200, Pfeiffer Vacuum). A quartz U-tube reactor was loaded with 0.10 g of sample, and the catalysts were pretreated in He at 600 °C to eliminate any adsorbed water and organic species. For NH_3-TPD, the charged sample was exposed to 3 vol.% NH_3/He at 150 °C, whereas for IPA-TPD it was exposed to IPA (2 mL/pulse, 15 pulses, 1 min/pulse) at 100 °C. The catalyst was then flushed with He for 1 h. The TPD process was performed using 30 mL/min of He by heating the sample at a heating rate of 5 °C/min while monitoring the TCD signals and mass spectrometer signals NH_3 ($m/z = 17$), H_2O ($m/z = 18$), C_3H_6 ($m/z = 41$), IPA ($m/z = 44$). The total acid sites and Brønsted acid sites were quantified from the NH_3-TPD profile based on the TPD peak area and from the IPA-TPD profile based on the peak area of the decomposed propylene, respectively.

Temperature-programmed oxidation (TPO) was conducted over 0.05 g of each sample in a 2% O_2/He stream by heating the sample along the temperature range 30–750 °C at a heating rate of 10 °C/min while monitoring the TCD signals (Autochem 2910 unit, Micromeritics) and on-line mass spectrometer signals H_2O (m/z = 18), CO (m/z = 28), and CO_2 (m/z = 44) (QMS 200, Pfeiffer Vacuum), after the samples were purged with He at RT for 1 h.

2.3. Catalytic performance tests

2.3.1. Continuous flow reaction

Fig. 1 depicts the continuous tubular reactor used for the liquid-phase dehydration of D-xylose. The tubular stainless steel reactor (I.D. = 5.5 mm and $L = 15$ cm) was used in a split type tube furnace. A K-type thermocouple (Eutech instruments) was installed inside the reactor to measure the fluid temperature, which was controlled with a PID temperature controller (Ilhae). For the dehydration of D-xylose, 0.2 M aqueous D-xylose (Sigma-Aldrich) solution was fed at 0.032 mL/min into the reactor with a HPLC pump (LabAlliance, Series 1500), in which 0.10 g of the catalyst was brought into contact with the reactant solution. The reaction pressure was maintained at 3.0 MPa using a back-pressure regulator (TESCOM). A pre-heater was installed to heat the feed to 80 °C using heating tape and the reactor's effluent was cooled to ambient temperature.

2.3.2. Batch reaction

The liquid-phase dehydration of D-xylose was also carried out in a batch reactor. 0.2 M D-xylose (Sigma–Aldrich) solution and the catalyst were mixed and the resulting mixture was introduced into a 100 mL autoclave. The reactor was filled with nitrogen for 15 min. The slurry was stirred with a magnetic stirrer at 500 rpm. The reaction temperature was attained after 0.5 h. The zero reaction time was regarded as the time at which the measured temperature reached the set temperature. The reaction vessel was pressurized due to the vapor pressure of the solution at the defined reaction temperature. A dip tube was inserted into the reaction mixture for sampling purposes. Samples were immediately quenched with ice.

2.3.3. Product analysis

Samples were filtered with a 0.2 μm syringe filter and analyzed using a high-performance liquid chromatograph (Waters 1525 Binary HPLC pumps, YL 9110 quaternary pump) equipped with a