Conversion of glycerol to aromatic hydrocarbons over Zn-promoted HZSM-5 catalysts

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ABSTRACT

Catalytic conversion of glycerol to BTX aromatics has been investigated over HZSM-5 and Zn-promoted HZSM-5 catalysts. The reaction pathway of glycerol to aromatics was proposed. Glycerol was first dehydrated to three main intermediates, propenal, acetaldehyde, and acetol. The combination of oxygenate pool and olefins formed heavy aromatics in the hydrocarbon pool via oligomerization and cyclization. The disproportion and cracking of the hydrocarbon pool generated aromatics and also short alkanes. The effects of zeolite acid properties to the aromatization of glycerol were investigated over HZSM-5 with various SiO_2/Al_2O_3 ratios i.e. 23, 30, 50, 80, and 280. In order to improve the aromatics selectivity, the dehydrogenation metal, Zn, was promoted on the HZSM-5 zeolites by both aqueous phase ion-exchange (IE) and incipient wetness impregnation (IWI) methods. XPS, EXAFS, H_2-TPR, NH_3–TPD and TPD-IPA (temperature programmed desorption of isopropylamine) were employed to investigate the active species of Zn in aromatization of glycerol. By using aqueous phase ion-exchange method, the appearance of Zn species was only in the form of bivalent Zn cations at exchange site. Due to the exchange of these species with strong Brönsted acid site, the formation of aromatics tended to increase by suppressing the hydrogen transfer reaction and formation of light paraffins. ZnO species, formed by incipient wetness impregnation method was found to be less active for the reaction.

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1. Introduction

Aromatics are in widespread used as feedstocks for numerous chemical industrial processes. The conventional processes, catalytic reforming of heavy naphtha and aromatization of light paraffins are the traditional routes for these aromatics production [1]. However, both processes relied on the nonrenewable resources of crude petroleum oil and coal. Due to the shortage of petroleum resources and the rising environmental concern, the use of renewable resources has gained more attention. As one of the biomass-derived oxygenated hydrocarbons, glycerol is obtained approximately 10 wt.% as by-product during the biodiesel production via transesterification reaction of vegetable oils and animal fats

[2–4]. The worldwide growth of biodiesel production is leading to a continued increase in the glycerol supply and also decrease in the glycerol price. For these reasons, recent studies have investigated ways to convert glycerol to more valuable chemicals such as 1-hydroxyacetone [5], formaldehyde [6], fuel additives [7], acrolein [8–10], acetol [6], and alkyl aromatics [11]. Several studies have investigated the reaction pathway for transformation of glycerol to olefins and aromatics [11–13]. However, the detailed intermediates have not been published.

Herein, we report the one-step transformation of glycerol to aromatics over various SiO_2/Al_2O_3 ratios of HZSM-5 catalysts. Due to its shape selectivity and suitable acid properties, HZSM-5 showed the superior catalytic performance in converting glycerol to aromatics [11,14,15]. To enhance the activity and selectivity to BTX aromatics, dehydrogenation promoter, Zn, is incorporated to the HZSM-5 zeolites [16]. Broadly speaking, HZSM-5 zeolites modified with Zn are active catalysts for the aromatization of light alkanes [17–20]. The modified Zn promotes the formation of aromatics by decrease the strong Brönsted acid sites, suppressed the paraffins

formation and play a key role in the dehydrogenation reaction for the formation of olefins [16] whereas the Brönsted acid sites of HZSM-5 are responsible for oligomerization and aromatization of the resulting olefins [21]. Although addition of Zn has been found very effective, the Zn species that enhanced aromatization reaction is still a matter of dispute.

The methods of Zn introduction had a strong influence to the formation of different Zn species [22]. By using the conventional incipient wetness impregnation (IWI) and ion exchange (IE) techniques, Zn/HZSM-5 was found to contain (i) isolated Zn^{2+} ions exchanged at the cation-exchange site of the zeolite, (ii) ZnO species [21,22] and (iii) $[ZnOZn]^{2+}$ resulting from the condensation of partially hydrolyzed $ZnOH^+$ [20,23]. Aleksandrov and co-workers used the linear combination of Gaussian-type orbitals fitting-functions density functional method (LCGTO-FF-DF) to study the structure and stability of different Zn species, Zn^{2+}, $ZnOH^+$, $Zn(H_2O)^{2+}$, and $ZnOZn^{2+}$ [24]. They concluded that the formation of $[ZnOZn]^{2+}$ from $ZnOH^+$ or $Zn(H_2O)^{2+}$ was energetically unfavorable which was accepted very well with the previous studies [25–27]. The activity of isolated Zn^{2+} ions at exchanged site of the zeolite and ZnO species was studied by Yu et al. [16,28]. They used pyridine-IR and UV–vis absorption spectra confirmed the generation of Zn cations at exchanged site and ZnO cluster. The Zn cations at exchanged site promoted the aromatization reaction by suppressing the multiple oligomerization cracking steps for C_3 formation and facilitating the dehydrogenation reactions for the formation of aromatics, where as the formation of large ZnO particle resulted in the decreasing of aromatics yield by blocking the pore of HZSM-5. However, from the theoretical calculations, the C—H activation by extra-framework O ligands of oxygenated Zn complexes is more favorable than the lattice oxygens of the zeolite due to its higher basicity and affinity towards H^+ [29]. The crucial role of ZnO species on HZSM-5 for alkane activation has been demonstrated by Stepanov et al. [30–35].

In order to investigate the effect of each Zn species to the aromatization activity, we varied the amount of Zn loadings and the loading techniques, which are IE and IWI methods. The comparable amount of Zn prepared by both methods was confirmed by atomic absorption spectroscopy (AAS). The species of Zn was studied by X-ray photoelectron spectroscopy (XPS) and extended X-ray absorption fine structure (EXAFS).

2. Experiment

2.1. Catalyst preparation

The NH_4ZSM-5 zeolites with SiO_2/Al_2O_3 ratios of 23, 30, 50, 80, and 280 were provided by Zeolyst International. The powdered catalysts were pelletized and sieved to 20–40 mesh to attain the suitable catalyst packing in the reactor. The catalysts were calcined in air at 550 °C with a heating rate of 10 °C/min for 5 h. The obtained catalysts are denoted as HZSM-5(x), where x is the SiO_2/Al_2O_3 ratios of HZSM-5. In order to study the effects of different Zn species, Zn-promoted HZSM-5 catalysts were prepared by IE and IWI methods. yZn/HZSM-5 (IWI) catalysts were prepared by incipient wetness impregnation of HZSM-5 (30), where y refers to the Zn loading (wt.%). The HZSM-5 (4 g) was impregnated with the aqueous solution containing desired amount of $Zn(NO_3)_2 \cdot H_2O$, followed by dried in an oven at 120 °C overnight and calcined at 550 °C (heating rate of 10 °C/min) in air for 5 h. yZn/HZSM-5 (IE) catalysts were prepared by aqueous phase ion-exchange method. The HZSM-5 (30) was stirred in an aqueous solution of 0.005–0.05 M $Zn(NO_3)_2 \cdot H_2O$ at 70 °C for 12 h. Subsequently, the obtained catalysts were washed with excess distilled water, followed by dried in

Table 1
Analysis of Zn loadings, textural properties, and acidity of HZSM-5 and Zn/HZSM-5 catalysts prepared by aqueous phase ion-exchange (IE) and incipient wetness impregnation (IWI) methods.

Catalysts	Zn loading (wt.%)	S_{BET} (m²/g$_{cat}$)	Acidity[a] (μmol/g$_{cat}$)
HZSM-5(23)	0	348.0	599
HZSM-5(30)	0	389.9	373
HZSM-5(50)	0	356.3	335
HZSM-5(80)	0	340.8	258
HZSM-5(280)	0	381.3	88
0.45Zn\HZSM-5(IE)	0.45	375.7	290
0.48Zn\HZSM-5(IE)	0.48	356.0	287
0.59Zn\HZSM-5(IE)	0.59	346.9	255
0.64Zn\HZSM-5(IE)	0.64	345.5	192
0.88Zn\HZSM-5(IWI)	0.88	338.8	237

[a] The acidity was determined from IPA–TPD. The mass monitored was propylene ($m/e = 41$).

an oven at 120 °C overnight and calcined at 550 °C (heating rate of 10 °C/min) in air for 5 h.

2.2. Characterization

The relative crystallinities of the HZSM-5 zeolites before and after loading Zn was analyzed by a Rigaku X-ray diffractometer (XRD) with Cu tube for generating CuKα radiation (λ = 1.5418 Å) at room temperature. The 2θ is in the range between 5 and 40 with a scanning rate of 5°/min. Zn loadings on the catalysts were determined by atomic absorption spectroscopy (AAS). The specific surface area and micropore volume of the samples were measured by the Brunauer–Emmet–Teller (BET) method. The temperature-programmed reduction (TPR) of Zn/HZSM-5 was performed under a reducing gas containing 10% H_2 in Ar with a thermal conductivity detector. The temperature was raised from 30 to 800 °C with a heating rate of 10 °C/min. The temperature programmed desorption of isopropylamine (IPA–TPD), water (H_2O–TPD), and ammonia (NH_3–TPD) were performed in a homemade flow apparatus using a quarter inch quartz tube reactor connected to an online MS detector (MKS Cirrus). The IPA–TPD and H_2O–TPD experiments were carried out in the range of 30–800 °C at a ramp rate of 20 °C/min, whereas NH_3–TPD experiment was monitored at the range of 100–700 °C at a heating rate of 10 °C/min. The X-ray photoelectron spectroscopy (XPS) of Zn/HZSM-5 samples was conducted using a Kratos Ultra X-ray photoelectron spectrometer. The monochromatic AlKα was used as an X-ray source (anode HT = 15 kV). The XPS peaks were referenced to the binding energy of C (1s) peak at 285 eV. The local properties of Zn atom was analyzed by an extended X-ray absorption fine structure (EXAFS) technique, performed at beamline BL8 station, Synchrotron Light Research Institute (SLRI), operated at 2.5 GeV with 10^6–10^8 mA of ring current. The data were recorded in fluorescence mode at room temperature using Ge(2 2 0) double crystal monochromator. The data analysis was performed using Arthena version 0.9.18.2.

2.3. Catalytic activity testing

The pure glycerol (>99.99%) was fed together with a N_2 carrier at a flowrate giving a molar ratio of N_2/glycerol of 10:1. The reaction was carried out at temperature of 400 °C, pressure of 300 psig, and W/F ranged from 0.07 to 1 h. The liquid products, including water, were collected in a cold trap and analyzed by an Agilent 5890 gas chromatograph equipped with a capillary HP-INNOWAX column. Non-condensed products were analyzed on-line by a Shimadzu GC-17A gas chromatograph equipped with a capillary HP-PLOT/Al_2O_3 "S" deactivated column. The glycerol conversion and products selectivity were calculated