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Stable and efficient aromatic yield from methanol over alkali treated hierarchical Zn-containing HZSM-5 zeolites

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ABSTRACT

Fast deactivation of catalyst is the main problem in methanol-to-aromatics (MTA) process. Herein, Zn-containing HZSM-5 zeolites with hierarchical pores (H-Zn/HZSM-5) were prepared by treating directly synthesized Zn/HZSM-5 with NaOH solution. The changes in crystallinity, acidity and textural properties of Zn/HZSM-5 before and after alkali treatment were characterized by X-ray diffraction, NH_3-TPD, ^{27}Al MAS-NMR, N_2 physisorption, X-ray fluorescence and TEM techniques. MTA reaction under the operating conditions of $T = 400$ °C and WHSV $= 2.5\ h^{-1}$ showed that the aromatic yield was improved from 41.4% for HZSM-5 to 55.3%. Furthermore, H-Zn/HZSM-5 exhibited a high initial space time yield of 0.62 g $gcat^{-1}\ h^{-1}$ and a long lifetime up to 120 h. These results could be ascribed to the hierarchical pores and the providential acidity, which enhanced the adsorption and diffusion of intermediates/products during the reaction.

1. Introduction

Aromatic hydrocarbons, such as benzene, toluene and xylene (BTX), are fundamental raw materials in industry. The demand of BTX is increased sharply around the world in recent years. Nowadays, aromatic hydrocarbons are mainly produced by catalytic reforming or cracking gasoline hydrogenation, which strongly depend on the petroleum resource. It is desirable to find an alternative route to replace petroleum with non-petroleum resources. Methanol-to-gasoline (MTG) process is considered as a promising method for the production of value-added aromatics in large-scale from biomass, natural gas and coal through the syngas [1–5].

ZSM-5 based zeolites are the representative catalysts for MTA process due to its medium pore sizes. However, the one-pass selectivity to aromatics is usually low. For example, Chang et al. reported that the fraction of aromatics in the hydrocarbons was 41.1% [6]. Many efforts have been made to improve the performance of MTA catalysts. It was found that ionic metals like zinc, gallium and silver modification is effective to convert the intermediate alkenes to aromatics by dehydrogenation rather than hydrogen transfer reaction, thereby suppressing the formation of alkanes [7–11]. It was reported that gallium ions can promote the selectivity of aromatics and suppress the generation of C_2–C_4 alkenes [12,13]. Ag/ZSM-5 zeolites can provide an aromatic yield higher than 70%, but suffer from heavy aromatics and fast deactivation due to the coke formation [14,15]. Ni et al. [16] obtained the BTX yield of 64% over La/Zn/ZSM-5 zeolites under 437 °C, 0.1 MPa and 0.8 h^{-1}. However, the space time yield was very low and the lifetime of catalyst was unexceptional, which is very important for the industrial process. The catalytic lifetime is normally determined by its acidity and pore structure. During the coke formation process, the coking rate and coke capacity of the catalyst is of great matter. The coking rate (dc/dt) equation can be expressed as Eq (1):

$$\ln(dc/dt) = \ln A + \ln P - Ea/RT \qquad (1)$$

where A is pre-exponential factor, P is the pressure of methanol, Ea is coking activation energy, T is the reaction temperature [17]. Obviously, the higher temperature favored the coke formation [18]. In addition, coke formed much faster at higher methanol pressures

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and higher gas hourly space velocities (WHSVs) due to higher amount of hydrocarbon formed [11]. Therefore, the coking rate is very high at the industrial conditions with high methanol pressures and high WHSVs, which poses a huge challenge to the catalytic lifetime and aromatic yield [19]. Micropores of ZSM-5 favor the selectivity to aromatics, but the coke in micropores usually leads to short lifetime. In order to decrease the coke formation rate, nano-sized HZSM-5 was synthesized to shorten the diffusion distance of reagents/products. Although several improved results were obtained, the lifetime was still short [20]. Recently, ZSM-5 with hierarchical structure, which contains mesopores and micropores, was developed to prolong the lifetime of zeolite catalysts in some extent due to the enlarged coke capacity [21–23]. Furthermore, the existence of mesopores could adjust the acidic property of ZSM-5, thereby preventing the intermediates to form cokes and subsequently blocking the pores during MTA process [24,25]. For the aromatization of glycerol, for example, Xiao et al. [26] found that the BTX yield and catalyst lifetime over hierarchical HZSM-5 were two-fold and three-fold higher than those of the traditional microporous HZSM-5. However, excessive mesopores in ZSM-5 crystals will decrease the density and strength of acidic sites and even destroy the zeolite framework, which may also lead to rapid deactivation in MTA process. Up to now, it is still difficult to control the mesopore content in the hierarchical HZSM-5.

Alkali-treatment is an efficient way to generate intracrystalline secondary-pores in ZSM-5 crystals by selective removal of Si atoms in the framework [27–31]. After the alkali-treatment, HZSM-5 shows significantly improved lifetime in MTG process. Ni et al. revealed that the mesopores of alkali-treated HZSM-5 enhanced the synergetic effect of Zn species, acidic sites and the capability of coke tolerance in MTG [32,33]. Ryoo reported that the coke formation was much slower on hierarchical zeolite during MTG process, and the coke formed predominantly on the surface of mesoporous wall rather than on the inside of the micropores [34]. Chen found that the coke formation process mainly depended on the intermediate species adsorbed on the catalyst surface [35].

Metal leaching from metal-containing HZSM-5 under high-temperature steam is regarded as another reason for catalyst deactivation. It is believed that directly hydrothermal synthesis process can promote metal species entering the ZSM-5 framework and thus reduce the metal loss. Niu et al. investigated the influence of preparation method on the performance of Zn/HZSM-5 catalysts in MTA reaction and found that Zn/ZSM-5 prepared by direct synthesis route exhibited the longest catalytic lifetime [36]. However, the serious coke formation is still inevitable on metal modified ZSM-5 prepared by direct synthesis route. Effective combination of Zn/HZSM-5 prepared by direct synthesis and improved diffusion property resulting from hierarchical ZSM-5 may be beneficial to prolong the lifetime and increase the aromatic yield during the MTA process under high WHSVs.

In this study, we developed an effective way to prolong the catalytic lifetime and increase the aromatic yield in MTA process by introducing mesoporosity into Zn/HZSM-5 with direct alkali treatment. The resistance to coke formation and catalyst deactivation were significantly enhanced through the hierarchical structure. Accordingly, several techniques were performed to investigate the structure-activity relationship and catalysis details.

2. Experimental section

2.1. Catalyst synthesis

ZSM-5 zeolites were prepared by hydrothermal route using n-butylamine and ethylamine as templates. As a typical synthesis of ZSM-5 and Zn/ZSM-5 zeolites, 100 g of water glass ($SiO_2 = 25.2\%$, Shanghai Chem.) was mixed with 2.2 g of n-butylamine under stirring to get a suspension A. 9.9 g of H_2SO_4 (98%) together with the calculated ethylamine solution was dispersed in 33.4 g of deionized water containing 2.2 g of $Al_2(SO_4)_3\ 18H_2O$ and desirable amount of zinc nitrate under stirring, giving a clear solution B. Finally, Solution B was added slowly into the suspension A to form a starting gel with the molar ratios of ZnO/SiO_2 of 0 and 1%, respectively. After being stirred for 2 h at room temperature, the mixture was transferred into an autoclave to crystallize at 175 °C for 2 days. The products were collected by filtration, washed with deionized H_2O and dried at 100 °C overnight, then calcined at 550 °C for 4 h to remove the template. Hierarchical Zn/ZSM-5 (designated as H-Zn/ZSM-5) was prepared by mixing 10 g of as-synthesized Zn/ZSM-5 and 100 g of 0.2 M NaOH solution at 70 °C for 2 h. After being stirred for 2 h, resultant solids were collected by filtration, washing and drying.

HZSM-5, Zn/HZSM-5 and H-Zn/HZSM-5 were obtained by the ion-exchange with 1 mol/L of ammonium nitrate solution at 90 °C for 1 h (10 g of zeolite mentioned above in 100 ml of solution), and the ion-exchange process was repeated three times followed by calcination at 550 °C for 4 h.

2.2. Characterizations

The X-ray diffraction (XRD) patterns were collected on a Bruker AXS D8 diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å) operated at 40 kV and 40 mA. The relative crystallinity is calculated by comparing the total XRD peak area in range of $2\theta = 22–25°$ of a zeolite sample with that of HZSM-5 with the largest area. The morphology of samples was observed with a field emission scanning electron microscopy (FE-SEM) on a JSM-6700F electron microscope (JEOL, Japan). TEM experiments were performed on a high resolution transmission electron microscope with an acceleration voltage of 120 kV (JEOL, JEM-2010). Diffuse reflectance ultraviolet–visible spectra (Uv–vis DRS) were measured on a SHIMADZU Uv-2700 spectrophotometer equipped with an integration sphere. ^{27}Al MAS NMR spectra were recorded on a Bruker AVANCE III 400 WB spectrometer. The specific surface area and pore volume of the catalysts were conducted on a volumetric adsorption apparatus (ASAP 2020M, Micromeritics) at −196 °C, Prior to the measurement, the zeolite sample was degassed under high vacuum at 300 °C for 8 h. The surface area was calculated from the adsorption branch in the range of relative pressure from 0.05 to 0.25 by Brunauer-Emmett-Teller (BET) method and the pore size distribution was derived from the adsorption branch by Barrett-Joyner-Halenda (BJH) method. Pore volume was estimated at a relative pressure of 0.99. X-ray fluorescence (XRF) analysis was carried out on an AXIOS with Rh radiation. The ammonia adsorption and temperature-programmed desorption (NH_3-TPD) was performed on a TP-5080. Typically, 0.2 g of the samples was pre-treated at 400 °C in Ar flow (30 ml/min) to remove the adsorbed water and then contacted with NH_3 at 100 °C at the rate of 10 ml/min for 30 min. After that, Ar flow was passed to remove the weakly adsorbed NH_3 molecules at 100 °C for 40 min. Finally, desorption was carried out at a ramping rate of 10 °C/min to 600 °C. The thermal gravimetric (TG) analyses were characterized by NETZSCH STA 449 F3 instrument in air at a heating rate of 10 °C/min from room temperature to 800 °C.

2.3. Methanol-to-aromatics reaction

MTA reaction was performed in a fixed bed equipped with continuous-flow stainless steel reactor (12 mm I.D., 550 mm length) under atmospheric pressure. In a typical run, 2.0 g of catalysts (20–40 mesh) were charged at the center of the reactor.