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Differences between Zn/HZSM-5 and Zn/HZSM-11 zeolite catalysts in alkylation of benzene with dimethyl ether

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Abstract

HZSM-11 zeolite supported Zn catalysts with different Zn contents (xZn/HZSM-11A) were prepared. In the alkylation of benzene with dimethyl ether (DME) in a fixed bed reactor, the catalyst with Zn content of 6 wt% (6Zn/HZSM-11A) showed appropriate performance. Focus was put on the comparison between 6Zn/HZSM-5 and 6Zn/HZSM-11 with the same crystal size of 600–800 nm, and also with the similar BET surface area, micropore volume, Si/Al2 molar ratio, and acidity. In the alkylation of benzene with DME, the 6Zn/HZSM-11 showed better activity and stability, and especially enhanced the conversion of benzene and selectivities to xylene and trimethylbenzene, compared with the 6Zn/HZSM-5. This was mainly related to the higher adsorption capacity and adsorption-desorption rates to the three adsorbates (benzene, m-xylene and 1,3,5-trimethylbenzene) over the 6Zn/HZSM-11 in comparison with the 6Zn/HZSM-5.

Key words

dimethyl ether; benzene; Zn/ZSM-11; Zn/ZSM-5; sorption

1. Introduction

Alkylation and hydroxylation of benzene and aromatization of hydrocarbons are both very important process for hydrocarbon industry [1−9]. As a reaction intermediate in methanol conversion to aromatics or gasoline, dimethyl ether (DME) is easily converted to aromatics [1]. Moreover, compared with methanol, the reaction conditions are more moderate with DME acting as feed, and DME is a more active methylation agent [2]. Although ethene [3], propene [4], methanol [5] and ethanol [6] are the mostly used alkylation reagents, DME [8] has also attracted considerable interest. The addition of benzene to DME can markedly promote the formation of C_7–C_9 aromatics over the ZSM-5 zeolite at and above 350 °C [8]. Moreover, adding ZnO to ZSM-5 greatly promotes the formation of various aromatics, such as toluene, xylene and C_9 aromatics in the aromatization of methanol [9] and DME [1].

ZSM-5 and ZSM-11 zeolites have been widely used in the alkylation of benzene and aromatization of hydrocarbons. Generally, they show comparable similar reaction performances due to their similarity of the framework density and the pore size. Despite of these similarities, the ZSM-5 topology consists of intersectional straight and sinusoidal channels, whereas the ZSM-11 topology has only intersectional straight channels. It is the channel difference that results in the higher aromatics selectivity for 1-hexene aromatization over the ZSM-11 in comparison with the ZSM-5 [10]. On the basis of the work, the effect of Zn loading on the catalytic performance in the alkylation of benzene with DME was investigated. Meantime, the performances of 6Zn/HZSM-5 and 6Zn/HZSM-11 catalysts were compared and associated with their aromatics adsorption-desorption behaviors measured by the intelligent gravimetric analyzer (IGA) instrument.

2. Experimental

Preparation of Zn/HZSM-11A (300−400 nm) zeolites (Information of parent ZSM-11A (300−400 nm) zeolite is available in Ref. [10]) containing 0−10 wt% Zn was carried out by the wet impregnation with aqueous solution of $Zn(NO_3)_2$, subsequent drying at 85 °C for 2 h and calcination at 550 °C for 3 h. The obtained catalysts were denoted as xZn/HZSM-11A, in which x signified the Zn content. The synthesized ZSM-5 and ZSM-11 (both 600−800 nm) zeolite

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samples with similar Si/Al_2 molar ratio, crystal size and acidity [10] were transformed into the H-form. Subsequently, a Zn content of 6 wt% was loaded onto HZSM-5 and HZSM-11 as shown above, and the obtained catalysts were denoted as 6Zn/HZSM-5 and 6Zn/HZSM-11, respectively. After the 50 h reaction, the spent 6Zn/HZSM-5 and 6Zn/HZSM-11 catalysts were designated as 6Zn/HZSM-5-U and 6Zn/HZSM-11-U, respectively. All the samples were pressed, crushed and sieved into 0.38–0.85 mm particles before they were loaded into the reactor.

XRD, XRF, TPO, NH_3-TPD, IGA, N_2 adsorption-desorption and diffuse reflectance infrared Fourier transform (DRIFT) experiments were similar to previous works [10−13].

In the alkylation of benzene with DME, 2 g catalyst was loaded in the middle part of the stainless fixed bed reactor with 320 mm in length and 12 mm in diameter. Catalyst was activated at 500 °C for 1 h in a nitrogen flow before the reaction. DME and benzene were introduced after the temperature lowering to 350 °C. Both gas and liquid products were collected and analyzed in a GC (Agilent 7890A) equipped with a FID, and a PONA capillary column (50 m×0.2 mm×0.5 μm). Conversion and selectivity were calculated according to the Equations (1) and (2):

$$\text{Conversion}\ (\%) = \frac{\text{Amount of benzene (or DME)\% in the feed} - \text{amount of benzene (or DME)\% in the products}}{\text{Amount of benzene (or DME)\% in the feed}} \times 100\% \quad (1)$$

$$\text{Selectivity of } i\ (\%) = \frac{\text{Amount of } i\% \text{ in the products}}{\text{Amount of } i\% \text{ in the products}} \times 100\% \quad (2)$$

where, i denoted one of the gas or liquid products. All the values in the equations, tables and figures of this paper are in weight percent.

3. Results and discussion

3.1. Physicochemical properties of the samples

The XRD patterns shown in Figure 1 indicate that the xZn/HZSM-11A has a typical MEL-type structure and no additional phase is observed when Zn content is 1 wt%–10 wt%, indicating that ZnO can be highly dispersed on the ZSM-11A when Zn content is under 10 wt%. Besides, there is some decrease in the relative crystallinity with the addition of ZnO in comparison with HZSM-11A. Figure 2 shows that the 6Zn/HZSM-5 and 6Zn/HZSM-11 samples have high relative crystallinities. It also indicates that the crystal sizes of the two catalysts keep similar with corresponding H-form zeolites at the range of 600−800 nm [10], since their peak widths are essentially unchanged after ZnO loading. The N_2 adsorption-desorption isotherms of the 6Zn/HZSM-5 and 6Zn/HZSM-11 samples are type I (not shown), with the specific surface areas evaluated by BET method of 319 and 341 m^2/g (external surface areas of 99 and 104 m^2/g), micropore volumes of 0.102 and 0.110 cm^3/g, respectively.

Si/Al_2 molar ratios determined by XRF are 51.6 for 6Zn/HZSM-5 and 52.0 for 6Zn/HZSM-11. The NH_3-TPD has been performed to investigate the acid properties of both Zn type samples (Figure 3), and the corresponding acidity of HZSM-5 and HZSM-11 zeolites can be obtained from the Ref. [10]. One main peak centered at ca. 280 °C appears in the curves. The peak area ratio of 6Zn/HZSM-5 to 6Zn/HZSM-11 is 1.08, indicating a similar total acid amount of the two

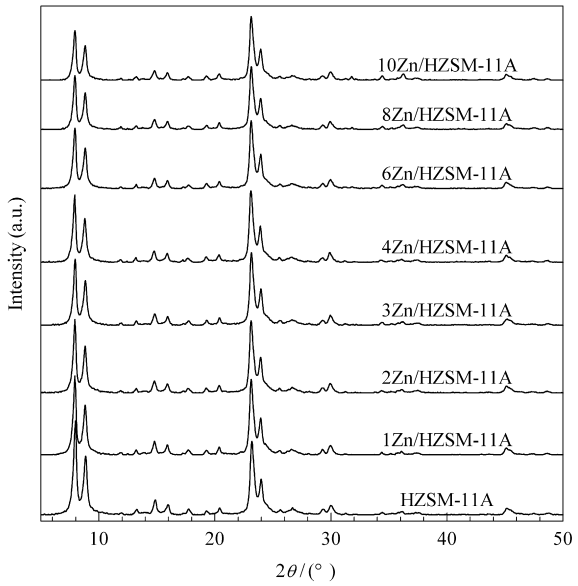

Figure 1. XRD patterns of xZn/HZSM-11A catalysts

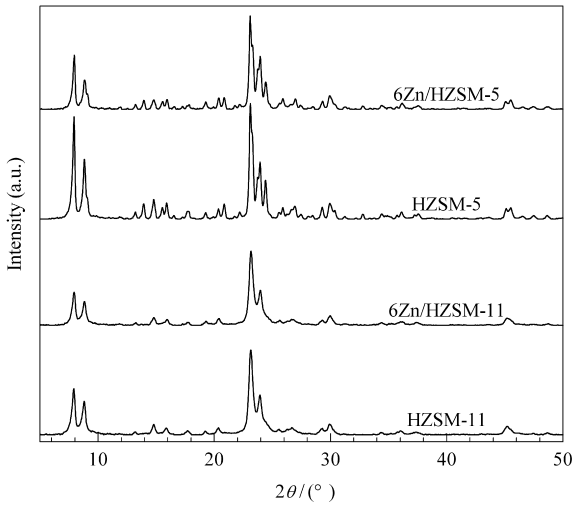

Figure 2. XRD patterns of 6Zn/HZSM-5 and 6Zn/HZSM-11 catalysts