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Effect of variations in acid properties of HZSM-5 on the coking behavior and reaction stability in butene aromatization

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Abstract

In order to investigate the effect of acid properties on the coke behavior and stability of butene aromatization, we prepared the AHZSM-5 samples with various acid properties by the methods of hydrothermal treatment and K addition. The reaction of butene aromatization was carried out at 350 °C and 0.5 MPa in a continuous flow fixed bed. The characterization of the fresh/coked catalysts with NH_3-TPD, N_2 adsorption–desorption measurement, and TG techniques has shown that a large amount of acid sites (high acid density) of the AHZMS-5 catalyst can cause a large quantity of coke deposit and serious channel blockage, and so result in a rapid loss of aromatization activity. On the contrary, after a great reduction in strong acid sites of AHZSM-5 catalyst resulting from some K-modification, the presence of only many weak acid sites also could not lessen the formation of coke nor improve the reaction stability of butene aromatization. Interestingly, the simultaneous reduction in the strong and weak acid sites to a desirable level by hydrothermal treating the AHZSM-5 catalyst at a proper temperature can effectively suppress the coke formation and channel blockage, and thus improve its olefin aromatization stability.

Keywords: Butene aromatization; ZSM-5 zeolite; Hydrothermal treatment; Reaction stability; Acid properties

1. Introduction

In recent years, much attention has been focused on ZSM-5 catalyzed-transformation of light hydrocarbons, especially light alkanes, into benzene, toluene, and xylene (BTX), which were used as important chemicals, as well as high-octane gasoline blending components [1–4]. Owing to the high inertness of light alkanes, the transformation of light alkanes into aromatics required a relatively high reaction temperature, which inevitably generates a considerable amount of fuel gas, such as methane and ethane. Alkenes are more active than alkanes with the same carbon number and can be transformed into aromatics at a relatively lower reaction temperature. From the viewpoint of reactivity, olefins or olefin-rich feeds are advantageous. However, the catalyst was easier to deactivate via coking, when using olefins as feed [5]. Few studies have concentrated on olefin aromatization over ZSM-5 [6–8].

Studies on the coking behavior of ZSM-5 are many and wide-ranging [9–14]. A universally accepted idea is that coking occurs preferentially on the strong acid sites. In any case, the carbonaceous deposit on ZSM-5 zeolite would decrease catalytic activity, and even cause a complete loss of catalytic activity by covering the acid sites or by blocking the access of reactant molecules to the acid sites. How to overcome the barrier of the catalyst deactivation by coking and how to prolong the life of the catalyst are very important and interesting topics. One commonly used method for improving its coking behavior is the removal of aluminum in zeolite framework by hydrothermal treatment at relatively high temperatures [7,15]. Since the framework Al is mainly responsible for the acidity of zeolite, the hydrothermal treatment would reduce many acid sites. Thus, the formation

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of coke would be inhibited. de Lucas et al. [14] investigated in detail the relationship between the variation of strong acid sites by hydrothermal treatment and the amount of coke formed. However, steam-treatment at high temperatures would also cause a reduction in weak acid sites as well as strong acid sites. Till now, there was almost no knowledge about the effect of the reduction in weak acid sites during the steaming-treatment on the deactivation behavior of catalyst.

Previously, we investigated the correlation between the aromatization activity and the acidity of the catalyst. Mono-olefin aromatization is catalyzed only by strong acid sites and dienes or cycloolefins can be transformed into aromatics over both strong and weak acid sites [16]. The objective of the present research is to investigate the effect of variations in acid properties caused by the hydrothermal treatment and by the K-modification of the catalyst, on the coking behavior and stability on-stream for butene aromatization.

2. Experimental

2.1. Catalyst preparation

ZSM-5 zeolite powder ($SiO_2/Al_2O_3 = 50$, obtained from Fushun catalyst plant) was extruded with alumina as binder (30 wt.%). After drying at 120 °C for 2 h, the extrudate was calcined in flowing air at 550 °C for 5 h to remove the hexanediamine template. Then, the calcined sample was converted into NH_4-form by exchanging with a 0.8 M ammonium nitrate solution for three times at 90 °C. Subsequently, the exchanged sample was washed thoroughly with deionized water and dried at 120 °C for 3 h. Finally, the ZSM-5 in NH_4-form was calcined at 530 °C for 3 h to convert into the H-form. The obtained sample was denoted as AHZSM-5. K/AHZSM-5 samples containing various K-loadings were prepared according to the procedure previously reported [16].

Hydrothermal treatment was conducted as follows. The AHZSM-5 sample prepared above was placed in a quartz reactor with a thermocouple situated in the middle of the catalyst bed. As the sample was heated up to the required temperature, 100% steam with a WHSV of $4\ h^{-1}$ was introduced into the reactor. Two hours later, the catalyst was cooled down to room temperature. The steamed AHZSM-5 sample was designated as AHZSM-*t*, and the letter "*t*" stands for the steaming temperature. All the catalysts were crushed and sieved to 20–40 mesh particles before they were loaded into the reactor.

2.2. Catalytic evaluation for butene aromatization

Butene aromatization reaction was carried out in a continuous flow fixed-bed reactor (i.d. 11 mm) provided with a thermocouple in the center of the catalyst bed, which presented the reaction temperature. The catalyst was pretreated in a flow of nitrogen at 500 °C for 1 h prior to the reaction. As the catalyst bed was cooled down to the required temperature, the liquid feed (as shown in Table 1) passed through the catalyst bed with a double plunger pump. The reaction conditions were as follows: $T = 350$ °C, $P = 0.5$ MPa. The products were cooled down to 0 °C and periodically discharged. Aqueous fraction (belonging to gasoline range, including C_4–C_{11} hydrocarbons) and gaseous fraction (C_2–C_4 hydrocarbons) were collected separately and analyzed by a GC (Varian-3800), with a PONA capillary column (100 m) connected to a FID.

2.3. Catalyst characterizations

2.3.1. NH_3-temperature programmed desorption (NH_3-TPD)

The acidity of the catalysts was determined by NH_3-TPD technique. The sample (0.14 g) was loaded into a stainless U-shaped microreactor (i.d. 5 mm) and pretreated at 600 °C in flowing He for 0.5 h. After the pretreatment, the sample was cooled down to 150 °C and saturated with NH_3 gas. Then, the NH_3-TPD began to carry out under a constant flow of He (20 ml/min). The temperature was raised from 150 to 650 °C at a heating rate of 18 °C/min. The concentration of ammonia in the exit gas was determined continuously by a gas chromatograph (SHIMADZU) equipped with a TCD.

2.3.2. N_2 adsorption isotherms

The nitrogen adsorption isotherms were measured at −196 °C using a NOVA 4000 gas adsorption analyzer (Quantachrome Corp.). Each sample was degassed at 350 °C for 5 h before the measurement. The total surface area was calculated according to the BET isothermal equation, and the micropore volume and external surface area were evaluated by the *t*-plot method.

2.3.3. Thermal gravimetric analysis (TG)

TG profiles were recorded on a Perkin-Elmer TG 1700 instrument. The coked catalyst particles (0.015 g) were heated from room temperature to 700 °C at a heating rate of 10 °C/min in an air stream. The flow rate of air was 30 ml/min. In the recorded profiles, the weight loss before 300 °C was attributed to desorption of water. The decrease of weight from 300 to 700 °C was caused by burning-off the coke.

Table 1
Composition of LPG feed

Component	wt.%
$C_3^=$	0.2
C_3^0	1.10
nC_4^0	10.7
iC_4^0	39.1
$1-C_4^=$	16.5
$t-C_4^=-2$	19.6
$c-C_4^=-2$	12.8