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Improved catalytic performance and decreased coke formation in post-treated ZSM-5 zeolites for methanol aromatization

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ABSTRACT

The effects of the zeolite structure and acidity on the catalyst life and coke formation in the methanol-to-aromatics (MTA) reaction were investigated using several MFI zeolites with different degrees of mesoporosity and acidity. These zeolites were prepared by post-synthesis desilication, dealumination, and combined desilication and dealumination processes. The influence of the post-synthesis on the pore characteristics, crystallinity, morphology and acidity of the ZSM-5 zeolites were studied by XRD, N_2-adsorption, n-octane temperature-programmed desorption experiments, ^{27}Al and ^{29}Si MAS NMR, SEM, TEM and NH_3-TPD. Dealumination and/or desilication leads to an increase in the mesoporosity by widening the micropores and a decrease in the acid density. The MTA catalyst lifetime is increased by several times due to the enhanced mesoporosity and decreased acid density. The deactivated catalysts were characterized by thermogravimetry and N_2 adsorption/desorption experiments. More coke forms inside the micropores than on the external surfaces of the catalysts. Generalized and quantitative correlations between the mesoporosity and coke content and between the number of acid sites and coke content are given.

1. Introduction

Methanol-to-aromatics (MTA) conversion over microporous solid acid catalysts has drawn much industrial and academic interest in recent years because the MTA process enables coal and natural gas to be converted into chemicals [1–3] that would otherwise be derived from petroleum feedstocks. Over the past few decades, the potential of various molecular sieves for use as methanol-to-hydrocarbon (MTH) catalysts has been investigated [4,5]. HZSM-5, which has strong Brønsted acid sites and intermediate channel dimensions, has attracted significant attention due to its good resistance to deactivation by coke and its model behaviour for studying the MTA mechanism [6,7]. Nonetheless, the generation and deposition of carbonaceous residues often leads to severe diffusion restrictions and fast deactivation rates [8]. Hence, coke formation on the catalyst is an important cost-bearing factor not only in the MTH process but also in many other petrochemical processes that utilize zeolite catalysts, including hydrocarbon refining and fine chemical syntheses [9,10]. It is therefore very important to investigate the zeolite characteristics that affect coke deposition and catalyst deactivation.

Research on coke formation has mainly focused on the influence of the zeolite structure, acid site strength and concentration [11]. For example, Bleken and Park [12,13] correlated the deactivation rate with polycyclic aromatics formation. Based on the observed relation, it was suggested that coke formation occurs preferentially on the outer surfaces of zeolite crystals [14,15]. However, it was also hypothesized that external coke formation occurs only after the catalyst is deactivated by intraporous coke formation [16,17]. In contrast, Bjøgen et al. [18] did not find a correlation between the organic molecule concentration in the pores and zeolite deactivation at 643 K. They concluded that external coke deposition caused activity loss with time on stream. Recently, Müller et al. [19] reported that the outer surface of HZSM-5 is virtually carbon-free under the reaction conditions studied and that the catalyst deactivated rapidly at first and then at a much slower rate. During the initial phase, the deactivation rate was directly proportional to the methanol partial pressure, and the deactivation was caused by oxygen-containing surface species. These species were transformed

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into aromatic compounds with time on stream, and the deactivation then proceeded via aromatic compound methylation to form coke species typically produced during methanol-to-olefins processes.

The acid site concentration is also an important factor affecting the catalyst reactivity and product distribution [20,21]. Choudhary et al. [22] proposed that the strong acid sites in the HZSM-5 zeolite were the active sites for aromatics production. However, an increase in the strong acid site concentration also promoted coke formation, leading to rapid catalyst deactivation. Aguayo et al. [23] reported that the high acidic strength of a zeolite catalyst decreased the reaction energy barrier, thus leading to an increase in the reaction rate and accelerated deactivation. McLellan et al. [24] showed that an initial significant decrease in the acid site concentration was followed by a second slower deactivation phase. The initial deactivation regime was thought to be caused by acid site blocking at the channel intersections. The second deactivation stage was ascribed to external coking and/or topological blocking of the zeolite channels.

Obviously, the zeolite structure and acidity are the two most important factors affecting the catalyst activity, product distribution and coke formation. Much effort has focused on synthesizing zeolites with controlled structures and acidities; for example, nanosized [25,26] and hierarchical [27,28] zeolites have been prepared, and alkali/acid post-treatments have been applied [7,29] in an attempt to achieve the desired characteristics. To a certain extent, all of these methods improved the diffusion in the zeolites and enhanced their lifetimes in some catalytic reactions. Of these methods, mesopore generation by post-synthesis treatment with an alkaline and/or acid solution is particularly appealing, primarily due to its simplicity and reasonably broad applicability, as recently reviewed by Verboekend and Silaghi [30,31]. This method can be used to investigate the interplay between the acidity, pore structure, catalytic activity and selectivity. However, the combined effects of the zeolite structure and acidity on the catalytic performance and coke formation have not been studied in depth, which is obviously important for the industrial development of MTA technology.

In this study, dealumination, desilication and a combination of dealumination and desilication post-treatments were used to prepare catalyst samples with different mesoporosities and acidities. The synthesized catalysts were employed in the MTA reaction. The effects of the mesoporosity and acidity on the catalytic performance and catalyst lifetime are discussed in detail. Coke formation was monitored, and its dependence on the catalyst mesoporosity and acidity was determined.

2. Experimental

2.1. Catalyst preparation

2.1.1. HZSM-5

The parent NaZSM-5 zeolite with a Si/Al molar ratio of 50 (Fushun Catalyst Plant, China) was calcined in air at 550 °C (heating rate of 10 °C/min) for 5 h to remove the hexanediamine template molecules. The protonated zeolite was obtained by the following procedure. Two consecutive ion exchange reactions were performed at 70 °C for 4 h using a 1.0 M NH_4NO_3 solution. The ratio of the NaZSM-5 mass (g) to the NH_4NO_3 solution volume (mL) was 1:10. After the first ion exchange reaction, the zeolite was filtered, washed with deionized water and then dried in an oven at 100 °C. After the second ion exchange reaction, the zeolite was dried in an oven at 100 °C overnight. Finally, the NH_3ZSM-5 product was calcined in static air at 500 °C for 3 h to obtain HZSM-5. The HZSM-5 zeolite is referred to as NZ5.

2.1.2. Acid or alkali treatment

The dealumination experiments were performed as follows. First, 10 mL of a 1.0 M HCl aqueous solution were heated to 100 °C. Then, 3.0 g of the parent HZSM-5 zeolite was added to the heated solution. The suspension was kept at 100 °C under stirring and reflux for either 8 or 12 h. The slurry was subsequently filtered and washed thoroughly with deionized water until a pH of 7.0 was achieved. The solid product was collected and dried at 120 °C in an oven overnight. The samples treated with HCl for 8 h and 12 h are referred to as DeAl8h and DeAl12h, respectively.

The desilication experiments were performed as follows. After treatment with a 1.0 M NaOH aqueous solution (the desilication reagent), the desilicated samples were ion-exchanged with a 1.0 M NH_4NO_3 solution at 80 °C for 3 h and then washed with deionized water repeatedly. After drying, the NH_4-form samples were calcined at 500 °C to produce the H-form. The samples treated with NaOH for 8 h and 12 h are referred to as DeSi8h and DeSi12h, respectively.

2.1.3. Acid/alkali and alkali/acid treatments

The DeAl8h sample was chosen for further desilication studies. The DeAl8h sample (3 g) was added to 10 mL of a 1.0 M NaOH aqueous solution at 100 °C, and the mixture was maintained at that temperature for 8 h under stirring and reflux. Then, the slurry was filtered, washed and dried at 120 °C overnight. The sample was subsequently ion-exchanged and calcined at 500 °C for 3 h. The recovered sample is denoted DeAl8h/DeSi8h.

The DeSi8h sample was further treated with a 1.0 M HCl solution. The powder recovered from the alkali treatment was added to 10 mL of the HCl solution and then heated to 100 °C under stirring for 8 h. The slurry was filtered, washed and dried at 120 °C overnight. The resulting sample is denoted as DeSi8h/DeAl8h.

2.2. Characterization

The powder X-ray diffraction (XRD) patterns of the prepared zeolite samples were recorded on an ARL X'TRA powder diffractometer using Cu Kα radiation ($\lambda = 1.54$ Å). The chemical compositions of the samples were determined by X-ray fluorescence (XRF) spectroscopy using an SRS-3400 X-ray fluorometer. The ^{27}Al and ^{29}Si nuclear magnetic resonance (MAS NMR) spectra were recorded using a Bruker Avance III 500 spectrometer with the 4 mm ZrO_2 rotor. Before the ^{27}Al MAS NMR spectrum test, all of the samples need to dip in an airtight container with the NH_4NO_3 saturated aqueous solution in order to absorption to saturation. The frequencies of the ^{27}Al and ^{29}Si MAS NMR were 130.3 and 99.4 MHz, respectively. The ^{27}Al MAS NMR spectrum with the single pulse sampling, pulse width was 0.22 μs ($\pi/12$) and the revolution of MAS was 12 kHz. The ^{29}Si MAS NMR spectrum with the single pulse sampling, pulse width was 2.5 μs and the revolution of MAS was 5 kHz. The sample morphology was examined by scanning electron microscopy (SEM) on a Leo 1430 microscope. Transmission electron microscopy (TEM) images were recorded on a Tecnai G220 S-Twin transmission electron microscope operating at an accelerating voltage of 200 kV. N_2 physisorption experiments were performed at 77 K on a Quantachrome AUTOSORB-1-MP adsorption analyser. Before adsorption, the samples were outgassed at 300 °C for 3 h. NH_3 temperature-programmed desorption (NH_3-TPD) experiments were performed using a conventional setup equipped with a thermal conductivity detector. The TPD profiles were recorded from 120 to 600 °C at a constant heating rate of 10 °C/min under an He flow (40 mL/min). *n*-Octane temperature-programmed desorption (*n*-octane-TPD) experiments were performed using a conventional setup equipped with a thermal conductivity detector. Before the *n*-octane-TPD experiments, the sample (ca. 200 mg) was activated in