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A novel method for enhancing on-stream stability of fluid catalytic cracking (FCC) gasoline hydro-upgrading catalyst: Post-treatment of HZSM-5 zeolite by combined steaming and citric acid leaching

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Abstract

This article describes a novel modification method consisting of steaming and subsequent citric acid leaching to finely tune acidity and pore structure of HZSM-5 zeolite and thereby to enhance the on-stream stability of the zeolite derived fluid catalytic cracking (FCC) gasoline hydro-upgrading catalyst. A series of dealuminated HZSM-5 zeolites and their derived catalysts were prepared and characterized by X-ray diffraction (XRD), X-ray fluorescence spectroscopy (XRF), ^{27}Al MAS NMR, nitrogen adsorption, temperature programmed desorption of ammonium (NH_3-TPD) and infrared (IR) spectroscopy of chemisorbed pyridine. The results showed that the citric acid leaching could preferentially remove the extra-framework Al (EFAl) species formed by steaming treatment and thus reopen the EFAl-blocked pore channels of the steamed zeolite. The steaming treatment at a suitable temperature and subsequent citric acid leaching not only decreased the strength of acid sites to a desirable degree but also increased the ratio of medium and strong Lewis acidity to medium and strong Brönsted acidity, both of which conferred the resulting catalyst with superior selectivity to aromatics, good hydroisomerization activity and gasoline research octane number (RON) preservability, as well as enhanced on-stream stability. The results fully demonstrated that the treatments by steaming and followed citric acid leaching can serve as an important method for adjusting the physicochemical properties of HZSM-5 zeolite.

Keywords: Fluid catalytic cracking (FCC) gasoline hydro-upgrading catalyst; On-stream stability; HZSM-5 zeolite; Steaming; Citric acid leaching

1. Introduction

In Asia countries, especially in China, one of the most urgent challenges encountered in producing clean vehicle fuels is the high olefin content in fluid catalytic cracking (FCC) gasoline that takes a share of 40–60% in commercial gasoline pool. To reduce the olefin content in FCC gasoline, many methods (such as optimization of the FCC process, use of novel olefin reduction FCC catalysts, and application of selective hydrogenation) have been attempted, but the resulting poorer process performance either in gasoline research octane number (RON) or in gasoline yield is still challenging refineries in Asia countries [1].

In the previous study [2], we developed a novel FCC gasoline hydro-upgrading catalyst system that used HZSM-5 zeolite and γ-Al_2O_3 as support and Ni and Mo as active metals. While having superior olefin reduction ability and excellent RON preservability, this catalyst system suffered from a quick loss in activity due to the coke buildup in long-term operation. It has been widely accepted that the coke deposit in hydrocarbon conversion catalysts can be related to the shape-selective reactions catalyzed by acid sites on the zeolites involved [3] and thus finely tuning zeolite acidity and pore structure is considered to be an effective way to lessen catalyst deactivation by coking and thereby to extend catalyst operational life. For this reason, steaming treatment techniques of zeolites have been developed and are now widely used to remove part of aluminum species in zeolite frameworks with the aim of decreasing the acidity of the resulting

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catalysts [4–6]. However, the extra-framework Al (EFAl) species formed during steaming usually have undesirable effects on the catalytic activity and diffusibility of zeolites [7–9], so subsequent acid leaching is usually employed. Inorganic acids (e.g., HCl) are commonly used as Al leaching reagents, but they unavoidably induce further dealumination of zeolites [6,10]. Therefore, a moderate dealumination method that does not seriously affect framework Al species while preferentially removing EFAl species should be pursued.

Recently, it has been reported that citric acid treatment can be used to optimize the acidity of ultra-stable Y (USY) [11] and β [12] zeolites, but to the best of our knowledge this method has not been applied to the modification of zeolite ZSM-5. Herein, we report a novel modification method consisting of steaming and subsequent citric acid leaching for finely tuning acidity and pore structure of HZSM-5 zeolite and its application in suppressing the deactivation of NiMo/HZSM-5-γ-Al_2O_3 FCC gasoline hydro-upgrading catalysts. In view of the fact that many industrially important processes, such as Cyclar [13], Z-former [14] and Alpha [5], use HZSM-5 zeolite as catalysts, the method introduced here may be also of significance for optimizing the performance of the catalysts involved.

2. Experimental

2.1. HZSM-5 zeolite modification

The parent HZSM-5 zeolite (Sample PHZ, SiO_2/Al_2O_3 molar ratio = 51.2, Shanghai Huaheng Chemical Plant, PR China) was steamed in 100% water vapor flowing at weight hourly space velocity (WHSV) 1 h^{-1} at different temperatures for 4 h to obtain a series of Samples SHZ-T (the letter "T" denotes steaming temperature) and was leached with a 1.2 M citric acid solution (10 mL/g zeolite) at 65 °C for 6 h to obtain Sample AHZ, respectively; then, Samples SHZ-T were further treated with a 1.2 M citric acid solution (10 mL/g zeolite) at 65 °C for 6 h to obtain Samples SAHZ-T. All of them were used as catalyst support.

2.2. Catalyst preparation

Firstly, different preformed extruded sticks (Ø1.5 mm × 2–3 mm) were obtained by extruding the HZSM-5 zeolites obtained above using 30 wt.% pseudoboehmite (usually referred as SB powder, Condea, Germany) as binder; then, the sticks were dried at 110 °C overnight and calcined at 520 °C for 5 h; finally, they were impregnated with aqueous solutions of ammonium molybdate and nickel nitrate successively. After each impregnation step, the solids were dried at 120 °C for 5 h and calcined at 480 °C for 4 h to obtain a series of NiMo/HZSM-5-γ-Al_2O_3 catalysts, which hereafter will be referred as C-x, where "x" indicates the corresponding zeolite used.

2.3. Catalytic performance test

Using FCC gasoline from a refinery in China as feedstock, the catalytic performance of the catalysts was assessed in a 10 mL continuously flowing fixed bed microreactor under the following conditions: 390 °C, 1.8 MPa, H_2/gasoline volumetric ratio 200, gasoline WHSV 2 h^{-1}. The catalysts were presulfurized for 1 h at 150, 230 and 260 °C and for 4 h at 290, 320 and 340 °C, respectively, with a CS_2 (3 wt.%)/*n*-octane mixture as vulcanizer and hydrogen as carrier gas. The feedstock and the products were analyzed by an Angilent gas chromatograph installed with a 50 m long PONA capillary column.

2.4. Characterizations

X-ray diffraction (XRD) analysis was carried out on a Shimadzu Lab XRD-6000 diffractometer that uses Cu Kα radiation and works at 40 kV, 30 mA, and a scan rate of 4°/min. The compositions of the different samples were obtained by X-ray fluorescence (XRF) analyses conducted on a ZSX-100e 4580 instrument. The ^{27}Al MAS NMR spectra were recorded on a Varian $^{\mathrm{Unity}}$Inova 300 spectrometer. Nitrogen adsorption was used to measure the surface areas and pore volumes of the samples. Acid type distributions were determined by infrared (IR) spectroscopy of chemisorbed pyridine.

Temperature programmed desorption of ammonia (NH_3-TPD) was carried out as follows. The sample (0.10 g) to be tested was first pretreated in flowing He (30 mL/min) at 500 °C for 30 min, then cooled down to 100 °C and saturated with NH_3 to equilibrium state. The He flow was then flushed until the baseline of the integrator was stable. NH_3-TPD was then started from 100 to 600 °C at a heating rate of 15 °C/min. The concentration of ammonia in the exit gas was monitored continuously by a gas chromatogram installed with a thermal conductivity detector.

3. Results and discussion

3.1. Structure characterization

The XRD patterns of the different samples are shown in Fig. 1. The diffraction patterns of the four HZSM-5 samples show almost the same peaks, indicating that the steaming or/and the followed citric acid leaching did not significantly change the structure of the HZSM-5 zeolite. As shown in Table 1, however, the crystallinity of Sample SHZ-480 decreased to 94% because of the formation of the amorphous phase during the steaming process [10]. It is also interesting to note that the citric acid leaching of the parent zeolite PHZ and steamed Sample SHZ-480 yielded two samples AHZ and SAHZ-480 with increased crystallinity because of the removal of the amorphous phase, which is formed either during the calcination of the as-synthesized zeolite for removing the organic template and the subsequent treatment with dilute HCl solution for producing the H-form zeolite PHZ or during the steaming treatment of Sample PHZ. Moreover, no signals ascribed to NiO and MoO_3 phases are observed in the XRD patterns of all the catalysts prepared, indicating that the metals are well dispersed. The slight decrease in the intensities of the main diffraction peaks in