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Synthesis and application of HZSM-5@silicalite-1 core–shell composites for the generation of light olefins from CH_3Br

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ABSTRACT

To improve activity and hinder deactivation, nonacidic polycrystalline silicalite-1 was contiguously coated on HZSM-5 to yield HZSM-5@silicalite-1 composites using a hydrothermal synthesis method. The obtained samples were examined as catalysts for the generation of light olefins (ethylene and propylene) from CH_3Br, and found to show high catalytic activity, stability and high selectivity to the desired products. The excellent performance is attributed to the silicalite-1 shell which causes passivation of acid sites on the external surface of HZSM-5. It was observed that the HZSM-5@silicalite-1 composite with thicker coating (ZS-2) shows much higher stability and selectivity to light olefins (up to 80%) than that with thinner coating (ZS-1), indicating that the surface of HZSM-5 crystals of the latter was less covered. Based on the characterization results, it is deduced that the catalytic stability of ZS-2 is due to the silicalite-1 shell that hinders HZSM-5 from deactivation as a result of surface coking.

1. Introduction

The methanol to hydrocarbon process over acid zeolites has received much attention in the academic as well as industrial sectors since its discovery in the late 1970s [1,2]. However, the production of synthesis gas (syngas) and the synthesis of methanol from syngas in the methanol to olefins (MTO) process are both costly and energy consuming. It has been recognized that methyl halides may work as platform molecules for the transformation of CH_4 to higher hydrocarbons [3,4]. Progresses were made on the direct transformation of chloromethane to light olefins [5,6]. However, the transformation of CH_3Br to light olefins [7,8] as another potential and efficient way for natural gas utilization is less studied.

The catalyst chosen by Mobil for the MTO process was HZSM-5 zeolite. The reasons for such a choice were the quality of the products and prior experience acquired in the methanol to gasoline (MTG) process. Subsequently, it was demonstrated that the selectivity to olefins can be improved with zeolite modifications [9,10]. ZSM-5 is a frequently used zeolite of MFI-type structure. The inner channel architecture (5.6 × 5.3 Å straight channels intersected with 5.3 × 5.1 Å sinusoidal pores) determines the catalytic activity and selectivity [11–13]. Nonetheless, the influence of external surface properties such as the acidic pore-mouth environment and external acid sites should not be neglected [14–17]. These surface characteristics can promote side reactions (e.g., oligomerization and H-transfer reactions). Therefore, recent endeavors were focused on the modification of external surface of zeolites to enhance reactivity and selectivity. Techniques such as acid leaching, steaming and element modification were applied to adjust the distribution of pores and acid sites [18–20]. However, partial destruction of pores and deposition of species may lead to blocking of pore opening, and consequently decline of catalytic activity.

Another effective strategy to manipulate catalytic properties in a desired manner is to grow a continuous shell to enclose the zeolite crystals. The thickness of such an over layer can be varied by tuning the composition of the solution for shell formation [21]. Mores et al. investigated the influence of an external silicalite-1 shell on the

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Abbreviations: HZ, HZSM-5@silicalite-1; MTO, methanol to olefins; MTG, methanol to gasoline; TPAOH, Tetrapropylammonium hydroxide; TEOS, Tetraethyl silicate; FE-SEM, Field emission scanning electron microscopy; TEM, Transmission electron microscopy; XRD, Powder X-ray diffraction; NH_3-TPD, Temperature-programmed desorption of ammonia; TCD, thermal conductivity detector; BET, Brunauer-Emmett-Teller; S_{BET}, specific surface area; WHSV, Weight Hourly Space Velocity; ZS-1(p), non-calcined HZSM-5@silicalite-1 (TEOS: 1.07 g); ZS-2(p), non-calcined HZSM-5@ silicalite-1 (TEOS: 2.14 g); ZS-0, HZSM-5@silicalite-1 (TEOS: 0 g).

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acidity and coking of HZSM-5 zeolite in MTO reaction [22]. They found that the shell prevents the growth of coke species at the external surface of zeolite. Recently, there were reports on the use of HZSM-5@silicalite-1 composite as catalyst for the formation of *p*-xylene, and *para*-selectivity superior to that of HZSM-5 was observed [23,24].

In this article, we report the generation of silicalite-1 shells of different thicknesses on HZSM-5 particles by a facile base-catalyzed sol–gel coating strategy using TPAOH as template and TEOS as silica source. We employed SEM, TEM, XRD, NH_3-TPD, and N_2 adsorption techniques for characterization. The influence of the silicalite-1 shells on catalytic activity and deactivation behavior for the generation of light olefins from CH_3Br was investigated.

2. Experiment

2.1. Sample preparation

HZSM-5 crystals with Si/Al = 75 were prepared by hydrothermal method using TPAOH as template, TEOS as silicon source, and aluminum sulfate as aluminum source. The resultant gel was kept in an autoclave at 180 °C for 24 h. The obtained product was washed with distilled water and dried at 80 °C for 12 h in air. The as-prepared Na-ZSM-5 zeolite was calcined at 550 °C for 4 h to remove the template, followed by ion exchange by using 1 M NH_4NO_3 at 80 °C for 8 h. The cation-exchanged zeolite was washed with distilled water and dried at 80 °C in air. Then the obtained HZSM-5 crystals were coated with silicalite-1 following the 1.22 g TPAOH-directed sol–gel coating route [23]. The shell thickness was tailored by adjusting the amount of TEOS. Briefly, TEOS (0, 1.07 and 2.14 g) was added to an aqueous solution that contained 3 g of HZSM-5 zeolite particles, and the mixture was heated in an autoclave at 180 °C for 48 h. After filtration, the samples were washed with distilled water, and dried overnight at 100 °C. The as-synthesized samples are named herein as ZS-0, ZS-1(p), and ZS-2(p), respectively. Finally, the organic template was removed through calcination at 550 °C for 5 h. The as-obtained samples are denoted herein as ZS-0, ZS-1, and ZS-2, respectively.

2.2. Catalyst characterizations

The morphology of HZSM-5 and HZSM-5@silicalite-1 composites were examined using a field emission scanning electron microscope (FE-SEM) (Hitachi S-4800). Transmission electron microscopy (TEM) images were taken using a JEM-3010F transmission electron microscope at an accelerating voltage of 200 kV. Powder X-ray diffraction (XRD) investigation was conducted on a Rigaku Automatic Diffractometer (Rigaku D-MAX) with monochromatized Cu Kα radiation ($\lambda = 0.15406$ nm) at a setting of 40 kV and 80 mA. Temperature-programmed desorption of ammonia (NH_3-TPD) experiments were conducted on a Micromeritics 2920 apparatus equipped with a thermal conductivity detector (TCD). The surface area of catalyst was measured by the Brunauer–Emmett–Teller (BET) method on a Tristar 3000 instrument, and the BET specific surface area (S_{BET}) was calculated based on the adsorption data in the relative pressure range of 0.04–0.2.

2.3. Catalytic evaluation

The reaction was conducted over a continuous fixed-bed quartz reactor with experimental setting similar to that described elsewhere [23–28]. The CH_3Br was prepared from methanol and hydrobromic acid over commercial HZSM-5 (SiO_2/Al_2O_3 = 380) at 210 °C. We observed complete conversion of methanol and 100% selectivity to CH_3Br. Then CH_3Br was separated and carried by N_2 (with a N_2/CH_3Br molar ratio of 1) into the reactor that was loaded with 0.5 g of catalyst. The outlet gas was sampled (using a syringe) at every 20-min interval and quantitatively analyzed on a Shimadzu GC 2010 Plus equipped with TCD and a RT-Q-BOND (30 m × 0.53 mm × 20 μm) column.

3. Results and discussion

3.1. Catalysts characterization

In order to understand the structure-function relationship, we used the XRD, SEM, TEM, NH_3-TPD and N_2 adsorption-desorption techniques to characterize selected samples of the catalysts. The XRD patterns of ZS-0, ZS-1 and ZS-2 are showed in Fig. 1. For all the samples, we did not observed the amorphous feature in the $2\theta = 20°\sim30°$ region, and only those assignable to MFI structure ($2\theta = 7.9°, 8.8°, 23.1°, 23.9°, 24.4°$) are detected. Since there are no signals that suggest the presence of impurity phases, it is deduced that there is successful synthesis of HZSM-5 and HZSM-5@silicalite-1 zeolites [23].

The FE-SEM and TEM images of HZSM-5 and HZSM-5@silicalite-1 composites are displayed in Fig. 2. Fig. 2A shows that the HZSM-5 crystals have an average dimension of 780 × 730 × 400 nm, and show pillow morphology with smooth surfaces. With silicalite-1 coating, the HZSM-5@silicalite-1 composites retain the pillow morphology but with the surfaces roughened and the corners smoothened. And it is apparent that there is a contiguous silicalite-1 layer on the surface of the HZSM-5 crystals (Fig. 2C and E). Furthermore, the ZS-2 composite is better covered by silicalite-1 than ZS-1 (Fig. 2D and F).

The acid strength and amount of acid sites of HZSM-5 and HZSM-5@silicalite-1 composites were estimated by the NH_3-TPD technique (Fig. 3), and the acid amounts are listed in Table 1. There are two NH_3 desorption peaks detected for all the samples. For ZS-0, one at 144 °C and the other at 309 °C attributable to weak and strong acid sites, respectively. Over ZS-1 and ZS-2, there is decrease of peak intensity and slight peak shift to lower temperature, indicating the lowering of the number of acid sites as well as decline of acid strength. In our previous work [29], we proved that the silicalite-1 samples are extremely low in acidity. The weakening of acidity and the reduction in the number of acidic sites can be related to the surface of HZSM-5 being covered by silica. Meanwhile, with the increase of shell thickness, the amount of acid sites decreases (ZS-1>ZS-2). It is hence deduced that ZS-2 is better covered by silicalite-1 than ZS-1.

The BET surface areas and pore volumes are listed in Table 2 and Fig. 4. Based on the facts that the BET surface area and total pore volume of ZS-1 and ZS-2 are similar to those of HZSM-5, it is

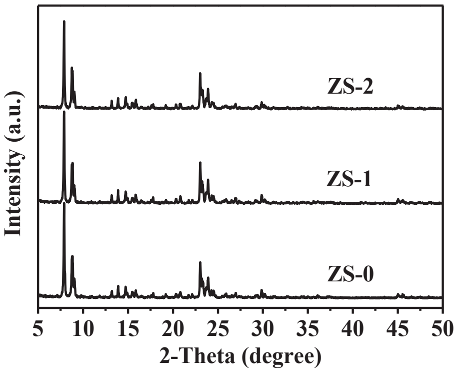

Fig. 1. XRD patterns of ZS-0, ZS-1 and ZS-2.