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Short communication

Aggregates of nano-sized ZSM-5 crystals synthesized with template-free and alkali-treated seeds for improving the catalytic performance in MTP reaction

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A B S T R A C T

A seed-induced method was developed to synthesize aggregates of nano-sized ZSM-5 crystals by template-free MFI seeds and cetyltrimethyl ammonium bromide (CTAB). Various MFI zeolites after calcination, including: nano-sized silicate-1, nano-sized ZSM-5 aggregates and commercial bulk ZSM-5 crystals were used as seeds. A trace of CTAB could accelerate the crystallization and pure MFI structure was obtained in the presence of CTAB. More importantly, the aggregates of nano-sized ZSM-5 crystals were dramatically synthesized by transforming the bulk seeds into smaller sizes with NaOH treatment before crystallization. The resulting solid exhibited an excellent catalytic performance in the methanol to propylene reaction.

1. Introduction

ZSM-5 zeolites are widely utilized as adsorbents and catalysts for petrochemical and fine chemical industries [1–3]. Methanol to propylene (MTP) process, is an important application of ZSM-5 zeolites and has attracted great attention and interest by both scientists and chemical industry [4,5]. However, the further improvement of catalytic lifetime and propylene selectivity over microporous H-ZSM-5 catalysts still is a challenge due to their poor capability for coke tolerance. To develop a rational design strategy for improving the mass transport properties of zeolite catalysts, a reduction of the internal pore diffusion path and an increase of the exterior surface area are well known key parameters to markedly improve activity and stability. During the recent years, a number of synthesis methods for ZSM-5 nanocrystals [6–8], MFI zeolite nanosheets [4,9–11] and hierarchical ZSM-5 zeolites [12,13] have been developed to effectively overcome the diffusion problem in micropores [14,15].

In these zeolites, nano-sized ZSM-5 crystals have displayed significantly improved characteristics, such as a decreased diffusion path and an increased external surface area, providing easier access to active sites on the external surface, and enhancing the resistance to coke formation [16,17]. Previous observations also indicate that decreasing the crystal size favors light olefins selectivity as well as propylene to ethylene (P/E) ratios in MTP reaction [18–20]. Furthermore, nano-sized ZSM-5 crystals can be synthesized by a seed-induced method, which circumvents the large usage of organic structure direct agents (OSDAs), especially tetrapropylammonium hydroxide (TPAOH), and shortens the crystallization time.

There have been numerous investigations related to the synthesis of nano-sized ZSM-5 crystals with the seed-induced method [21–24]. But most of them use the silicalite-1 (S-1) nanocrystals suspension, which still contains more or less TPAOH as seeds. S-1 powder after calcination has been rarely used as seeds for the synthesis of nano-sized ZSM-5. Of course, the lack of OSDAs may cause difficulties in obtaining the ZSM-5 phase and the controllable crystal size [25,26]. Recently, Li et al. [27] synthesized mesoporous aggregates with ZSM-5 nanoparticles by a seed-assisted synthesis method with a commercial ZSM-5 zeolite as the seed. However, an expensive amphiphilic organosilane was used as mesopore-directing agent and a considerable amount of tetrapropylammonium bromide was also used.

In this work, we report a facile OSDA-free process to prepare aggregates of nano-sized ZSM-5 crystals by a seed-induced method with adding cetyltrimethyl ammonium bromide (CTAB). The seed was prepared by treating commercial ZSM-5 with NaOH, which was required for the synthesis. Expensive TPAOH was avoided. Even though pure MFI zeolites can be synthesized using CTAB as structural directing agent [28,29], the product was bulk ZSM-5 crystals with the size of a few microns. However, we obtained the hierarchical aggregates of nano-sized ZSM-5 crystals, which showed an improved catalytic performance towards the MTP reaction.

2. Experimental

2.1. Preparation of template-free MFI seeds

Silicate-1 (S-1) gel and nano-sized ZSM-5 aggregates (NA) were

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synthesized following our previous work [30]. The obtained samples were calcined at 550 °C for 6 h to remove the TPAOH. In addition, bulk HZSM-5 zeolite (SiO_2/Al_2O_3 = 200) purchased from Catalyst Plant of Nankai University was calcined at 550 °C for 6 h and is denoted as NK. The obtained template-free MFI zeolites, S-1, NA and NK were used as seeds for the following synthesis.

2.2. Synthesis of ZSM-5 with various MFI seeds

Synthesis of ZSM-5 was carried out from a mixture with the molar composition of 10 Na_2O: 100 SiO_2: 0.4 Al_2O_3: 2500 H_2O: 2 CTAB. In a typical synthesis, 0.0536 g $NaAlO_2$ and 0.6275 g NaOH were dissolved in 15 g H_2O in a 50 ml round-bottom flask. After stirring for 5 min, 0.3922 g S-1 powder with respect to 8% of total SiO_2 and 0.6015 g CTAB were added into the clear solution and 11.2745 g silica sol was dropwise added. Then, the mixture was stirred at ambient temperature for 1 h, transferred into Teflon-lined steel autoclave and heated at 120 °C for 24 h and further at 170 °C for 12 h. After crystallization, the products were separated by centrifugation, washed with distilled water until the pH reached the value of ~8, dried at 120 °C for 12 h and calcined at 550 °C for 6 h. To obtain the H-type ZSM-5, the samples were ion exchanged three times in 1 M NH_4NO_3 solution at 80 °C for 2 h, and then calcined at 550 °C again. NA and NK seeds were also used for the synthesis with the same procedure. The obtained samples are denoted as S-1-Z5-CTAB, NA-Z5-CTAB and NK-Z5-CTAB, respectively.

For comparison, synthesis by the three seeds was also carried out in the absence of CTAB and the obtained samples are denoted as S-1-Z5, NA-Z5 and NK-Z5, respectively.

2.3. Synthesis of aggregates of nano-sized ZSM-5 crystals with the alkali-treated seeds

Synthesis was carried out according to the following procedure: $NaAlO_2$ and NaOH were dissolved in 15 g H_2O in a 50 ml round-bottom flask. After stirring for 5 min, NA or NK seed powder was added into the clear solution. Subsequently, the mixture was heated to 70 °C under stirring and reflux, and kept at this temperature for different time (10 h or 24 h). After cooling to room temperature, CTAB was added, and the following procedure was the same as that for the synthesis of NA-Z5-CTAB or NK-Z5-CTAB. The obtained samples are denoted as NA-Z5-CTAB-10h, NA-Z5-CTAB-24h, NK-Z5-CTAB-10h and NK-Z5-CTAB-24h, respectively.

2.4. Catalyst characterization

The morphologies of zeolite samples were examined by Field Emission Scanning Electron Microscopy (FE-SEM, S-4800 instrument). X-ray diffraction (XRD) patterns were obtained on a Rigaku D/max2500 diffractometer. Nitrogen adsorption and desorption isotherms of the samples were measured at liquid N_2 temperature (77 K) using a Micromeritics TriStar 3000 automated physisorption instrument. The SiO_2/Al_2O_3 molar ratios were measured with Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) using a Varian Vista-MPX emission spectrometer. The spent catalysts were analyzed by thermogravimetric (TG) analysis (NETZSCH TG 209 F3 Tarsus) using 12 mg sample and a linear temperature ramp (10 °C/min) from 35 to 900 °C.

2.5. Catalytic tests

The MTP reaction was performed in a fixed bed microreactor at 470 °C under atmospheric pressure. The catalyst load was 0.5 g and the weight hourly space velocity (WHSV) was kept constant at 8 h^{-1}. The products were analyzed using an on-line gas chromatograph (GC-SP-3420) equipped with a flame ionization detector and a 50 m capillary column (HP-PLOT-Q). The reaction performance in terms of methanol conversion and product selectivity was subsequently evaluated.

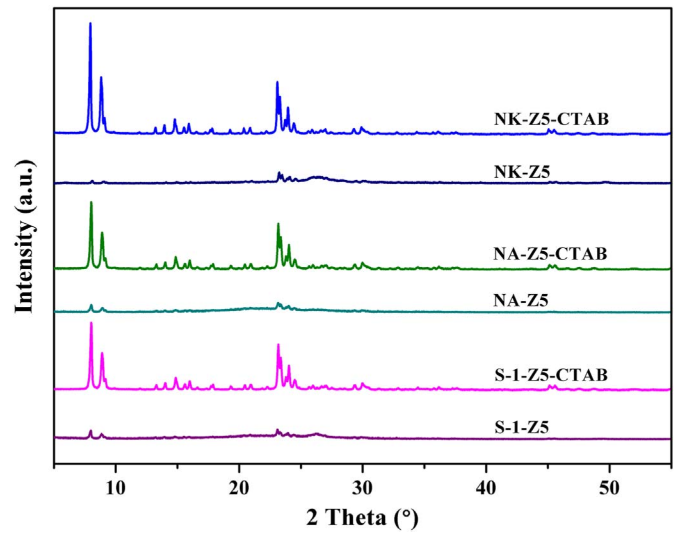

Fig. 1. XRD patterns of the samples synthesized by the seed-induced method with different MFI seeds after calcination without or in the presence of CTAB.

3. Results and discussion

3.1. Characterization of zeolites synthesized with different MFI seeds

The SEM images of the S-1, NA and NK seeds as shown in Fig. S1a, b and c, display spherical crystals with 120 nm sizes, spherical aggregates composed of 30 nm primary crystals and coffin-shaped bulk crystals with 1.5 μm sizes, respectively. After the three seeds are used for the seed-induced synthesis in the absence of CTAB, the SEM images of the obtained three samples, S-1-Z5 (Fig. S1a-1), NA-Z5 (Fig. S1b-1) and NK-Z5 (Fig. S1c-1), all demonstrate that a lot of amorphous material exists.

The XRD patterns of the three samples (Fig. 1) show no obvious diffraction peaks at 2θ of 7.9, 8.7, 14.8, 23.2, 24.0 and 24.5°, corresponding to the MFI structure [31]. The results of nitrogen adsorption and desorption for S-1-Z5, NA-Z5 and NK-Z5 samples (Table 1) indicate relatively low micropore surface areas and micropore volumes. The characterization results indicate that it is very difficult to synthesize pure phase ZSM-5 zeolites by the seed-induced method with template-free MFI seeds, in comparison to the unpurified seed suspension on the basis of our previous work [32]. Valtchev et al. [21] also employed the calcined seeds for the same synthesis, where a low crystallinity ZSM-5 material was obtained, which was attributed to the irreversible aggregation, the elimination of TPA cations and the passivation of the external surface of the crystals by calcination.

Interestingly, after the addition of a trace amount of CTAB, the samples with pure MFI structure are successfully obtained, as shown in Fig. 1. Thus, it is speculated that CTAB can accelerate the crystallization rate due to the amphipathy of CTAB. The SEM images of S-1-Z5-CTAB, NA-Z5-CTAB and NK-Z5-CTAB samples (Fig. S1) also demonstrate that no amorphous substance exists after the addition of CTAB. The samples display different particle sizes, the smallest for S-1-Z5-CTAB with 400 nm sizes (Fig. S1a-2 and a-3), while the largest for NK-Z5-CTAB with uneven sizes of 2–8 μm (Fig. S1c-2 and c-3). The specific surface areas of the three samples are all as high as 390 $m^2 g^{-1}$ (Table 1), but the external surface areas decrease in the order of: S-1-Z5-CTAB > NA-Z5-CTAB > NK-Z5-CTAB. The seed-induced approach is considered as that the seeds may be firstly dissolved into small species at a certain extent [23], and then induce the zeolite growth following the seed surface crystallization mechanism [22]. Thus, the differences observed in the samples are due to the different sizes and crystallinity of various MFI seeds.