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Direct synthesis of hierarchical ZnZSM-5 with addition of CTAB in a seeding method and improved catalytic performance in methanol to aromatics reaction

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ABSTRACT

A series of ZnZSM-5 zeolites with hierarchical pores were prepared by a seed-induced method with the addition of cetyltrimethylammonium bromide (CTAB). The influence of the amounts of CTAB on the physicochemical properties of the zeolites was investigated by XRD, FTIR, SEM, TEM, N_2 adsorption and desorption, ICP-OES, XPS, NH_3-TPD and TG analysis. The results showed that Zn was partially incorporated in the zeolite framework; the addition of CTAB in the synthesis reduced the primary crystal size of the zeolite, but increased the specific surface area and mesopore volume. The catalytic performance of the prepared zeolites was evaluated for methanol to aromatics reaction in a fixed bed reactor. The lifetime of the catalysts was greatly enhanced by the addition of CTAB in the synthesis. The incorporation of Zn increased the selectivity of aromatics.

1. Introduction

Aromatics, especially benzene, toluene, and xylene, known as BTX, are important raw materials in the organic chemicals and the polymer industry. The demands for these aromatic hydrocarbons are increasing sharply around the world in recent years. At present, almost all aromatics are derived from crude oil using industrial processes such as reforming, cracking, and alkylation [1]. However, with the depletion of oil resources, it is desirable to find alternative sources to replace the conventional petrochemical processes. So far, the methanol-to-aromatics (MTA) process is considered to be a promising method and has attracted both industrial and academic interests, as methanol can be abundantly available via syngas from various sources, such as biomass, natural gas and coal [2].

Over the past few decades, ZSM-5 zeolite, with its strong Bronsted acid sites and unique shape selective properties, has been proved to be an efficient catalyst for the reaction of MTA [3]. However, the selectivity to aromatics over ZSM-5 alone is relatively low. So, some metal species like Zn, Ga, Ag, Cu, La/Zn, Zn-Sn, *etc*. were introduced to ZSM-5 to cover this shortage [4–11]. Up to now, Zn species has been proved to be the most attractive promoter owing to its low-cost, low-toxicity and high-effectiveness in promoting the aromatization of methanol. In addition, direct incorporation of metal ions into ZSM-5 zeolite in the synthesis, which can greatly affect the catalytic performance according to the reference [12], is another superior way to make the zeolites have a higher diffusion ability and better stability compared with the conventional incipient wetness impregnation and ion-exchanged methods. Recently, Ni et al. [13] synthesized nano-sized H[Zn, Al]ZSM-5 and applied them in the aromatization of methanol. Li et al. [14] prepared Fe-modified nanocrystalline ZSM-5 zeolites by a hydrothermal method and the catalytic performance was evaluated for methanol to gasoline (MTG) reaction. The above two researches indicated that the modified-ZSM-5 prepared by direct synthesis route exhibited a longer catalytic lifetime. However, these attempts were usually carried out by using tetrapropylammonium ions (TPA^+) as template, suffering negative impacts such as high cost and poor environment friendliness.

The main drawback of zeolites as catalysts for MTA reaction is that the stability is not satisfactory because of the formation of high poly aromatics and coke. Continuing efforts have been devoted to solving the problem and the synthesis of hierarchical zeolites with a wide pore size distribution is considered to be a favorable choice [15–17]. So far, several methods have been reported in literature, including post treatment [18–22] and templating methods [23–28].

The seeding method can overcome the drawbacks of high consumption of templates and long crystallization time. Considering recent successful examples for TPA^+-free synthesis of zeolites [29–33], the seeding method is an alternative approach for preparing nanozeolites or hierarchical zeolites. In our previous work, a series of ZSM-5 aggregates were prepared using the seed-induced method which exhibited excellent catalytic performances in both MTG and cyclohexene hydration

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reaction [34,35].

Cetyltrimethylammonium bromide (CTAB) is an effective template for the synthesis of mesoporous molecular sieve MCM-41. It has been used as a co-template for the synthesis of zeolites [36–42]. It was either added before the other template to imaginatively form mesopores first, then crystallize into zeolite [36–38], or after the other templates to imaginatively form zeolite nanoparticles, then form mesopores with the zeolite nanoparticles [39–42]. In our previous work, we prepared nanosized ZSM-5 zeolite by using silicalite-1 (S-1) as seeds with simultaneous addition CTAB. The zeolite showed a high stability and high propylene selectivity in methanol to propylene reaction [43,44]. We also synthesized hierarchical ZSM-11/5 composite zeolite through the addition of CTAB and seed, but in the absence of template. The composite zeolite exhibited excellent catalytic performance in the reaction of methanol to hydrocarbons [45].

In this work, we reported that ZnZSM-5 with hierarchical pores can be directly synthesized in a seed-induced method with addition of CTAB. At the same time, Zn was directly incorporated into the zeolite framework. The synthesized ZnZSM-5 zeolite exhibited excellent catalytic performance in MTA reaction.

2. Experiment

2.1. Materials

Sodium aluminum ($NaAlO_2$, AR), CTAB (AR), sodium hydroxide (NaOH, AR), ethanol (EtOH, AR), Zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$, AR), TPAOH (24.8 wt% in water) and methanol (AR) were obtained from Tianjin Guangfu Fine Chemical Research Institute Co., Ltd. Tetraethyl orthosilicate (TEOS, 98 wt%) was obtained from Tianjin Kemiou Chemical Reagent Co., Ltd. Silica sol (40 wt% suspension in water) was purchased from Qingdao Haiyang Chemical Co., Ltd. Ammonium nitrate (NH_4NO_3, AR) was purchased from Guangdong Xilong Chemical Co., Ltd.

2.2. Synthesis of S-1

The seeds suspension with a molar composition of $100SiO_2{:}24TPAOH{:}800EtOH{:}2400H_2O$ was prepared according to our previous work [46]. TEOS, used as silica source, was added droprise into the mixture of TPAOH, deionized water and EtOH. After homogenizing at room temperature for 2 h, the mixture was hydrothermally treated at 105 °C for 96 h. Then, the obtained S-1 was used as seeds for the synthesis of ZSM-5 without any further treatment.

2.3. Preparation of hierarchical ZnZSM-5

The hierarchical ZnZSM-5 zeolites were synthesized based on the method developed previously in our lab with modification [43]. The molar composition of the initial mixtures was $100SiO_2{:}2Al_2O_3{:}8Na_2O{:}2500H_2O{:}1ZnO{:}xCTAB$ (x = 0, 1, 2, 3 and 4), SiO_2 in the S-1 seeds took up 2% of the total SiO_2. $NaAlO_2$, distilled water and NaOH were mixed together with stirring. Then, $Zn(NO_3)_2{\cdot}6H_2O$ and different amounts of CTAB were gradually added. After vigorously stirring for 1 h, the S-1 seeds and silica sol were dropwisely added into the mixture in sequence under stirring and stirred for 2 h further at room temperature. This synthesis mixture then was transferred to a Teflon-lined stainless steel autoclave, aged at 120 °C for 24 h and subsequently crystallized at 170 °C for 12 h. After crystallization, the products were centrifuged and washed with distilled water until pH reached about 7, dried at 120 °C for 12 h, and calcined at 550 °C for 6 h. All 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 in air for 5 h to obtain H-type. The obtained samples were denoted as ZnZSM-5-xC.

For comparison, a conventional ZSM-5 was prepared and treated under the same procedure for ZnZSM-5-xC samples but without the addition of $Zn(NO_3)_2{\cdot}6H_2O$ and CTAB, and named as Con-ZSM-5.

2.4. Catalyst characterization

XRD patterns were determined at room temperature on a Rigaku D/max2500 diffractometer with Cu Kα radiation (λ = 0.1542 nm) and a scanning rate of 8 min^{-1} in the range of 2θ from 5° to 55°.

SEM and TEM were used to determine the size and morphology of the primary crystals and aggregates. SEM images were obtained on an S-4800 field emission scanning electron microscopy with an accelerating voltage of 3 kV. TEM was carried on a JEM-2100F instrument operating at 200 kV.

FT-IR spectra of the samples were recorded in a Bruker Vertex 7.0 spectrometer, using the KBr wafer technique. The infrared absorbance spectra were recorded from 1600 to 400 cm^{-1} with a resolution of 4 cm^{-1}.

The Zn content and SiO_2/Al_2O_3 ratios in zeolites were determined by an inductively coupled plasma optical emission spectroscopy (ICP-OES) on a Varian Vista-MPX emission spectrometer.

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. Prior to the measurements, all the samples were degassed at 300 °C for 4 h. The total specific surface area (S_{BET}) was derived from the Brunauer-Emmett-Teller (BET) equation. The external surface area (S_{ext}) was derived from the t-plot method, and the micropore surface area (S_{micro}) was calculated by subtracting S_{ext} from S_{BET}. The total pore volume (V_{total}) was obtained from the absorption amounts calculated at $p/p_0 = 0.99$. The micropore volume (V_{micro}) was also derived from the t-plot method, and the mesopore volume (V_{meso}) was calculated by subtracting V_{micro} from V_{total}.

Temperature-programmed desorption of ammonia (NH_3-TPD) measurements were recorded using a TP-5076 chemical adsorption instrument (Xianquan Industrial and Trading Co., Ltd). 100 mg zeolites were pretreated in a nitrogen flow at 400 °C for 1 h, cooled down to 100 °C, and then ammonia was introduced with nitrogen as the carrier gas. After 60 min, the flow was switched to nitrogen, and the sample was heated to 700 °C at a rate of 10 °C min^{-1}. The desorbed ammonia was monitored by a thermal conductivity detector.

X-ray photoelectron spectra were collected using was carried out on a Perkin-Elmer PHI 1600 ESCA XPS instrument with an Al Kα X-ray radiation source (1486.6 eV). The binding energies were calibrated referring to C 1s peak at 284.6 eV.

Carbon deposition after reaction was evaluated by thermogravimetric (TG) analysis (Shimadzu TGA-50) with 12 mg spent sample using a temperature ramp from 35 to 900 °C at a heating rate of 10 °C min^{-1} in oxygen atmosphere.

2.5. Catalytic tests

The MTA reaction was carried out in a continuous flow fixed bed reactor with an internal diameter of 10 mm at 400 °C under atmospheric pressure and a weight hourly space velocity (WHSV) of 16 h^{-1}. In a typical run, the catalyst particles with 20–40 mesh were obtained with a compression method. 0.5 g catalyst diluted with 2.0 g quartz particles of the same sizes was loaded in the central zone of the reactor. The temperature of the catalyst bed during the reaction was measured using a thermocouple that reached the middle of the reactor. The catalyst was activated in the flow of 50 ml/min N_2 at 400 °C for 2 h before reaction and then the feed of methanol was pumped into the reactor by a micropump. The entire products were separated into gas, liquid hydrocarbons and water fractions using an ice-cooled condenser. The gas fractions were analyzed using a gas chromatograph (GCSP-3420A) equipped with a flame ionization detector (FID) and a KB-PLOTQ (50 m × 0.32 mm × 10.00 μm) capillary column. The liquid hydrocarbons were analyzed using a gas chromatograph (GCSP-3420A)