Catalysis Communications 112 (2018) 10–14

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short communication

Synthesis of hierarchical ZSM-5 zeolites with CTAB-containing seed silicalite-1 and its catalytic performance in methanol to propylene

Hengbao Chen, Yaquan Wang*, Chao Sun, Xiao Wang, Cui Wang

Key Laboratory for Green Chemical Technology of the Ministry of Education, School of Chemical Engineering & Technology, Tianjin University, Tianjin 300072, PR China

ARTICLE INFO

Keywords:
Hierarchical ZSM-5
CTAB
Seed
Methanol to propylene reaction

ABSTRACT

Hierarchical ZSM-5 zeolites were synthesized with cetyltrimethylammonium bromide (CTAB) containing silicalite-1 (S-1) as seed. The characterization results revealed that the CTAB/SiO_2 ratio of 0.005–0.1 in S-1 created abundant intercrystal mesopores in ZSM-5 zeolites and resulted in less strong and weaker acid sites. The hierarchical ZSM-5 had a comparable catalytic performance in methanol to propylene (MTP) reaction with the zeolite synthesized by adding S-1 and CTAB directly in the precursor form as reported in the literature. However, in the present proposed method, the use of CTAB was greatly reduced. The very low-cost and facile method developed in this work is expected to be feasible for the synthesis of other zeolites.

1. Introduction

ZSM-5, a medium pore size zeolite with 3-dimensional channel-like pore structure [1], is commonly used for the conversion of methanol to hydrocarbons [2]. Because of the relatively medium pore size, ZSM-5 zeolite shows unique shape selectivity, accessibility of the acid sites and appropriate strength of Brönsted acid sites [3]. However, the small pore size of ZSM-5 zeolite, with respect to ca. mesoporous materials or other larger pore size zeolites, becomes a drawback only when bulky reactant feed molecules need to be processed [4,5].

To overcome this problem, great efforts have been made for the synthesis of nano-sized zeolites [6–8], MFI nanosheets [9–11] and mesoporous zeolite crystals [12–15]. However, for the industrial application, the large use of expensive OSDAs gives rise to significant high cost of the given synthesis and environment problems. The seed-induced method, as one of the common OSDAs-free methods, can overcome the above mentioned drawbacks, and it becomes an alternative approach for the synthesis of nano-sized and/or hierarchical zeolites [16]. In 2006, Serrano et al. [17] synthesized hierarchical ZSM-5 and beta zeolites from silanized seeds. This method shows the advantage of a decreased hydrothermal synthesis time [18], high degree of crystallinity and high yield [19]. The silicalite-1 (S-1) gel solution without purification was preferred as seeds feedstock in most of the seed-induced syntheses [20–22], and usually it was synthesized with TPA^+/SiO_2 ratios in the range of 0.16–0.3. For the seed-induced synthesis, the weight of seeds is less than 10 wt% with respect to the total SiO_2. According to these data, the TPA^+/SiO_2 ratio in the seed-induced synthesis is below 0.03, which is very small relative to that used in the template methods (ca. 0.2) [23,24]. Nano-sized ZSM-5 zeolites can be obtained easily through the seed-induced method. However, some additional secondary templates are needed in the synthesis precursor for the synthesis of hierarchical ZSM-5. For instance, Fang et al. [25] provided a combination of amphiphilic organosilane and seed-assisted synthesis pathway to fabricate hierarchical ZSM-5 aggregate with loosely packed nanoparticles. However, though the OSDAs are circumvented by these methods, a large amount of additional mesopores templates is still added.

Our previous work showed that nano-sized ZSM-5 aggregates (NS-Z5) with mesopores were facilely synthesized by a seed-induced method with the assistance of cetyltrimethylammonium bromide (CTAB), and exhibited excellent catalytic performance in the conversion of methanol to propylene [26–28]. However, though the CTAB/SiO_2 ratio was reduced down to 0.02, it is still too high for industrial applications.

Herein, we developed a different approach that a CTAB-containing S-1 was used as seed to greatly reduce the use of CTAB for the synthesis of hierarchical ZSM-5. The effects of the CTAB amount on the morphologies, texture properties and catalytic performance of the obtained ZSM-5 catalysts were investigated. Hierarchical ZSM-5 zeolites were successfully synthesized in very low CTAB/SiO_2 ratios (CTAB/SiO_2 = 0.008). Thus, this facile synthesis method shows potential industrial applications.

* Corresponding author.
E-mail address: yqwang@tju.edu.cn (Y. Wang).

https://doi.org/10.1016/j.catcom.2018.04.017
Received 4 January 2018; Received in revised form 17 April 2018; Accepted 18 April 2018
Available online 21 April 2018

2. Experimental

2.1. Preparation of hierarchical ZSM-5

CTAB-containing S-1 seed gel was prepared based on our previous work [26,27]. The main difference with previous work is the addition of CTAB in the synthesis precursor, following a molar composition of SiO_2: 0.176 TPAOH: 0.4 EtOH: 21 H_2O: x CTAB (x = 0.005, 0.05, 0.1, 0.15, 0.2). The obtained CTAB-containing S-1 gel was directly used as seeds to synthesize ZSM-5 zeolites without any treatment.

To synthesize the hierarchical ZSM-5, NaOH and $NaAlO_2$ were dissolved in a certain amount of distilled water. Subsequently, S-1 seed and silica sol were added dropwise into the clear solution in sequence, where SiO_2 in the seed gel took up to 8 wt% in the total SiO_2. The mixture with a molar composition of 0.1 Na_2O: SiO_2: 0.006 Al_2O_3: 25 H_2O: 0.014 TPAOH: 0.08× CTAB, where TPAOH and CTAB resulted from the addition of S-1 gel, was stirred at ambient temperature for 1 h. Then the gel was transferred into a Teflon-lined autoclave, and crystallization process was carried out at 120 °C for 24 h and further at 170 °C for 12 h. After crystallization, the products were separated and washed until the pH reached about 8. The solids were dried at 100 °C overnight and calcined at 550 °C for 6 h. All the samples were ion-exchanged three times with 1 M NH_4NO_3 at 80 °C and calcined at 550 °C to obtain the H-type. The obtained samples are denoted as Z5-xC, where xC represents the CTAB/SiO_2 ratio in the S-1 seed gel (x = 0.005, 0.05, 0.1, 0.15, 0.2).

For comparison, conventional ZSM-5 (Con-Z5) was also synthesized by the above-mentioned approach without the addition of the CTAB-containing S-1 gel.

2.2. Catalysts characterization

Scanning electron microscopy (SEM) images were obtained on an S-4800 field emission scanning electron microscope. X-ray diffraction (XRD) patterns were recorded on a Rigaku D/max2500 diffractometer. Fourier transform infrared (FT-IR) spectra were recorded on a Bruker Vertex 7.0 spectrometer. Nitrogen adsorption and desorption isotherms of the samples were measured at 77 K using a Micromeritics TriStar 3000 automated physisorption instrument. Temperature-programmed desorption of ammonia (NH_3-TPD) measurements were recorded using a TP-5076 (Xianquan Industrial and Trading Co., Ltd) chemical adsorption instrument. The SiO_2/Al_2O_3 ratios were measured on an inductively coupled plasma (ICP) optical emission spectroscope using a Varian Vista-MPX emission spectrometer. The amount of carbon deposition was determined from 35 to 900 °C at a heating rate of 10 °C min^{-1} by thermogravimetric (TG) analysis on a Shimadzu TGA-50 apparatus.

2.3. Catalytic tests

The methanol to propylene (MTP) reaction was performed at 470 °C under atmospheric pressure in a fixed bed microreactor. 0.5 g of catalyst (mesh size: 20–40) was loaded. The weight hourly space velocity (WHSV) was set at 8 h^{-1}. The products were analyzed by an on-line gas chromatograph (GC-SP-3420) equipped with a 50 m capillary column (HP-PLOT-Q) and a flame ionization detector (FID). The methanol conversion and product selectivity were subsequently calculated based on the following Eqs. (1, 2):

$$Methanol\ conversion\ (\%) = \frac{N^i_{MeOH} - (N^o_{MeOH} + 2N^o_{DME})}{N^i_{MeOH}} \times 100 \quad (1)$$

$$Selectivity\ (\%) = \frac{x \times N^o_{C_xH_y}}{N^i_{MeOH} - (N^o_{MeOH} + 2N^o_{DME})} \times 100 \quad (2)$$

where, N is the number of moles. Superscript i and o are to the components at the inlet and outlet of reactor, respectively. x is the number of carbon atoms. Dimethyl ether (DME) is considered as reactant.

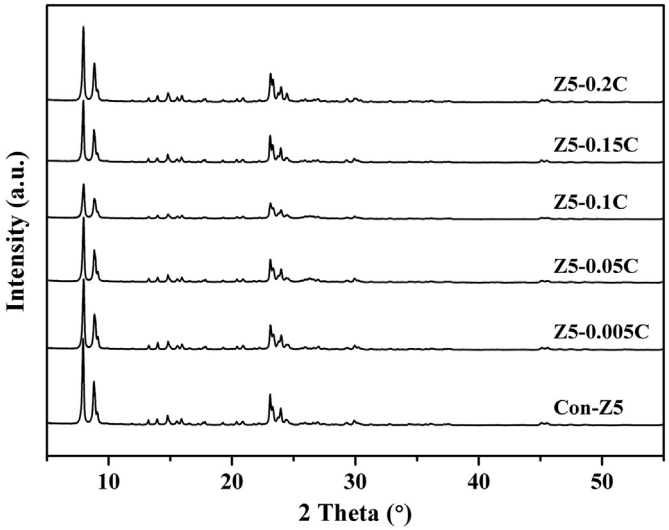

Fig. 1. Powder XRD patterns of all ZSM-5 samples prepared with different amounts of CTAB-containing S-1 as seeds.

3. Results and discussion

3.1. Structural and morphological properties of ZSM-5 zeolites

The SEM images of CTAB-containing S-1 seeds are shown in Fig. S1 (Supporting Information). The S-1 seeds show typical nanocrystals with sizes in the 200–300 nm range when the CTAB is not added or the CTAB/SiO_2 ratio is below 0.1. It is seen that the morphologies and sizes do not have appreciable differences. On the other hand, when CTAB/SiO_2 ratio is above 0.15, the sizes increase sharply and the zeolite morphologies are not the same. Because of the addition and the increasing amount of CTAB, the hydrolysis rate of TEOS and the formation rate of SiO_2 are accelerated and larger SiO_2 particles are formed, which are unfavorable for the synthesis of nano-sized S-1 crystals.

Fig. 1 shows the powder XRD patterns of all the prepared ZSM-5 samples with the CTAB-containing S-1 seeds. All the samples show the characteristic diffraction peaks at 2θ of 7.9°, 8.7°, 23.1°, 23.9° and 24.4°, corresponding to the MFI structure, and no evidence of other crystalline phases exist [29]. FT-IR analysis also demonstrates well ZSM-5 phase in all samples (Fig. S2).

The SEM images of the obtained ZSM-5 zeolites are shown in Fig. 2 and Fig. S3. The sample Con-Z5 presents a spherical morphology with a fuse of bulk crystals, as well as a particle size of 400 nm (Fig. S3a). After the addition of CTAB in the synthesis of S-1, the prepared sample Z5-0.005C (Fig. S3b) exhibits similar particle size, but a more loose morphology, due to the aggregation of many nanocrystals in the range of 50–180 nm. By continuing to increase the CTAB/SiO_2 ratio in the synthesis of S-1, the obtained samples Z5-0.05C and Z5-0.1C also show the aggregation of nanocrystals (Fig. 2a and b, respectively), which is also confirmed by TEM analyses (Fig. S4). However, the average crystal size of those decrease from 100 nm to 50 nm as a result of the inhibitory effect of CTAB on grain growth. In addition, intercrystal mesopores could be observed clearly. A further increase of the CTAB/SiO_2 ratio in the synthesis of S-1 results in a densely stacking of nanocrystals of the samples Z5-0.15C (Fig. S3c) and Z5-0.2C (Fig. S3d). Furthermore, a great increase in the mean secondary particle size from 3.5 μm of Z5-0.15C to 7.0 μm of Z5-0.2C is also observed.

A possible formation mechanism of hierarchical ZSM-5 is proposed as follows: when S-1 seeds were synthesized with the addition of CTAB,