Preparation of Small Crystalline ZSM-5 and Its Application in Conversion of Methanol to Aromatic

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Abstract. Small crystalline ZSM-5 was synthesized by a hydrothermal synthesis procedure and was characterized by XRD, SEM and N_2-absorption. The results show that small crystalline ZSM-5 particles grow into larger agglomerates with a diameter of 100-400 nm, resulting in mesopore and higher surface area. During conversion of methanol to aromatics, small crystalline ZSM-5 catalyst performances better than micron-size ZSM-5 catalyst in aromatic selectivity and lifetime. The aromatic selectivity could reach to 21.7%, and the small crystalline ZSM-5 catalyst shows no deactivation during first 24h.

Introduction

Aromatics, especially benzene, toluene, xylene (BTX), are important basic organic chemical raw materials and are in great demanding. Most of aromatic are derived from petrochemical processes such as reforming, cracking and alkylation using crude oil. However, oil shortage problem is becoming more and more serious. Methanol as a bulk products, has widespread sources. Thus conversion of methanol to aromatic (MTA) attracts more and more attention.

Currently, most researchers focus on development of metal exchanged ZSM-5 as MTA catalyst. However, metal exchanged ZSM-5 leads to higher selectivity to aromatics, yet it also favors carbon deposition on MTA catalysts, reducing activity of ZSM-5. Above 400 ^oC, sintering may take place, leading to catalytic deactivation. And catalytic dehydration of methanol produces large amounts of water vapor, which would do great harm to MTA catalyst [1]. ZSM-5 with small or nano-sized crystallite has larger external surface, high surface energy and shorter channel compared to large size ZSM-5, which could achieve excellent catalytic performance in certain reactions.

In this work, small crystallite ZSM-5 was prepared by hydrothermal synthesis and was successfully applied into methanol to aromatics in a fixed-bed reactor. The small crystallite ZSM-5 could lead to high selectivity to aromatics, especially to toluene and trimethylbenzene, and could keep stable in product selectivities and methanol conversion.

Experimental

Preparation of small crystalline HZSM-5 catalyst and micron-size catalyst. The synthesis of small crystalline ZSM-5 in this work utilized the advantages of several literature reports [2-5]. In a typical synthesis procedure, aluminium isopropoxide (AIP) was added to 25 wt.% aqueous solution of tetrapropylammonium hydroxide (TPAOH), followed by stirring the mixture at ice water bath to obtain a clear solution. Then tetraethyl orthosilicate (TEOS) was added to the mixture and the

mixture was stirred at room temperature for several hours followed by heating to obtain super saturated solution. Then the mixture was transferred to an autoclave and was heated to and maintained at 150 ℃ for 100 h. The resulting solid was separated by centrifugation, washed with distilled water, dried and calcined. After ion-exchange with NH_4NO_3, small crystalline HZSM-5 was crushed into 40 - 60 mesh with pseudoboehmite as a binder.

The detailded synthesis of micron-size ZSM-5 is as follow. 59.2 g H_2O, 11.3 g of 25 wt.% TPAOH, 21.2 g TEOS and 0.26 g AIP was mixed together and the mixture was continuously stirred for 4 h. Then the mixture was then transferred to an autoclave and heated to and maintained at 150 ºC for 24 h. The following processes including washing, ion-exchange, and catalyst preparation were in accordance with the preparation of small crystalline ZSM-5 catalyst.

Catalyst characterization. The synthesized small crystalline ZSM-5 sample and micron-size ZSM-5 sample were characterized by XRD, SEM, and the small crystalline ZSM-5 sample was also characterized by N_2-absorption.

Catalyst evaluation. The MTA catalyst was tested in a cylindrical fixed bed reactor (10mm in internal diameter, and 1fm in length) packed with 5.5 ml of MTA catalyst. A plunger pump was used to feed liquid methanol (AR) into an evaporator where it was mixed with N_2 as the carrier gas, heated and evaporated at 180 ºC. All lines to and from the reactor were heated to avoid the condensation of products. The preheated reactant gas then entered the reactor at WHSV = 1.0 h^{-1}. The exit stream of the reactor was separated into gas, liquid hydrocarbons and water fractions using an ice-cooled condenser, which are analysed by gas chromatograph. An atomic carbon balance between the input stream (carbon in methanol) and the exit stream (the sum of carbon in all identified species, including unreacted methanol) under a steady state run was typically within 5%.

Results and discussion

Catalyst characterization. The XRD patterns of the synthesized small crystalline ZSM-5 sample (nano ZSM-5)and micron-size ZSM-5 sample (micron ZSM-5) are shown in Fig. 1. The synthesized ZSM-5 zeolite shows similar patterns with micron-size ZSM-5 zeolite. The synthesized ZSM-5 zeolite has a high intensity diffraction peaks at 7.89 ºC and 23.0 ºC, which indicating that the synthesized ZSM-5 zeolite has a high crystallinity. Compared with micron-size ZSM-5 zeolite, the small crystalline ZSM-5 zeolite has a width characteristic diffraction peak and the intensity of diffraction peak at 23.0ºC weakens. This may be due to the extinction effect of small crystalline zeolite on X-ray.

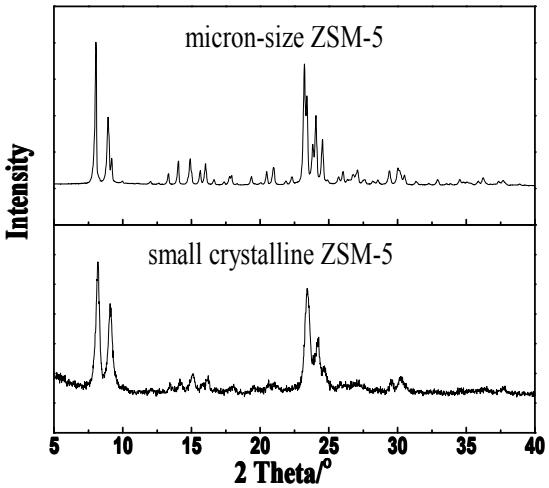

Fig.1 XRD patterns of the synthesized ZSM-5 and micron-size ZSM-5 sample

Representative SEM micrographs for tthe synthesized small crystalline ZSM-5 sample and micron-size ZSM-5 sample are shown in Fig. 2. In Fig. 2(b), there are many irregularly shaped aggregates with a cauliflowerlike morphology, which may be intergrowths formed from nano-sized primary ZSM-5 particles. The larger aggregates have a diameter between 100 - 400nm and it is difficult to determine

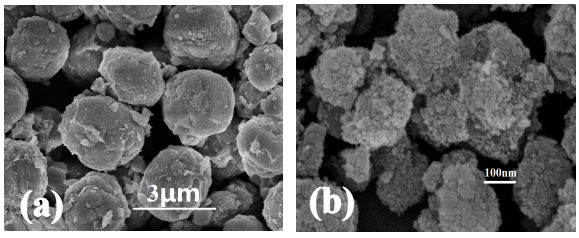

Fig.2 SEM of nano ZSM-5 and micron ZSM-5 sample. (a) micron ZSM-5; (b) nano ZSM-5

the primary ZSM-5 particle size from the SEM images alone. As shown in Fig.2 (a), it could notice that the micron-size ZSM-5 has a uniform particles diameter of 3μm and smooth surface.

Fig.3 (a) shows the adsorption-desorption isotherms of the synthesized small crystalline ZSM-5 sample. The patterns show that small crystalline ZSM-5 sample exhibits a typical irreversible type IV adsorption/desorption isotherm which usually is associated with the filling and emptying of mesopores by capillary condensation. And from the pore size distribution in Fig. 3 (b), two types of pores could be noticed in the composites centered at 4.0 and 5.0 nm, respectively, corresponding to the average pore diameter of 4.36 nm by BET method. The presence of mesopore in the synthesized ZSM-5 sample may be due to the inter-particle voids of the zeolite nano-particles [3], which could lead higher aromatics selectivity and reduced carbon deposition.

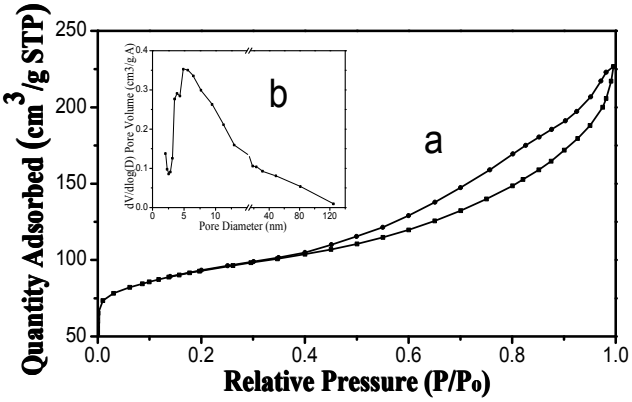

Fig.3 Adsorption desorption isotherms of nano ZSM-5.

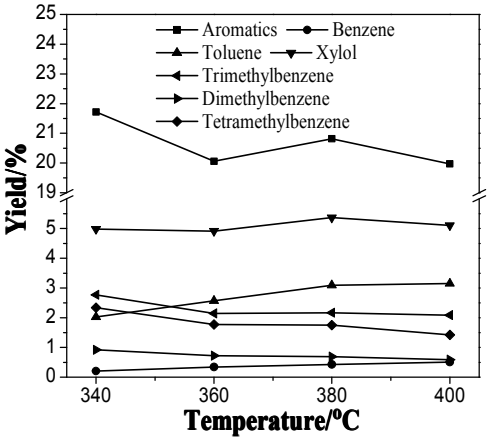

Fig.4 Main aromatic yield and total aromatic yield at different temperatures for MTA over nano ZSM-5 catalyst [W/F (g cat*h/g of methanol fed) = 1, P = 1 MPa]

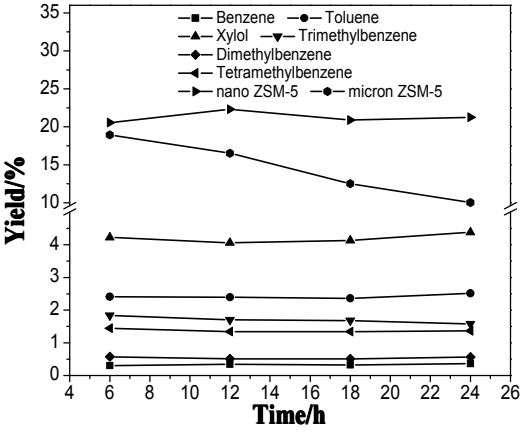

Fig.5 Main aromatics yield over nano ZSM-5 and total aromatics yield over nano ZSM-5 and micron ZSM-5 as a function of time for MTA [W/F = 1, P = 1 MPa, T=380°C]

Catalytic performances. The effect of temperature on main aromatic yield and total aromatic yield is shown in Fig.4. As the temperature increases from 340 °C to 400 °C, the total aromatics yield decreased slightly and reach to 21.7%. At lower temperature, hydrogen transfer reaction and aromatization of hydrocarbons would occur in competition [6]. Higher temperature favors aromatization of hydrocarbons, leading high selectivity of aromatics. At the same time, Aromatics are derived from small olefins. High temperature also favors hydrogen transfer and cracking of hydrocarbon and both reactions produce large amounts of alkanes and olefins, changing the original distribution pattern of olefins. Yet it is difficult for alkanes to activation, which further reduces the aromatic selectivity. Therefore, the aromatics yield changes slightly with the increase of temperature at the work of these two opposite reactions.

It is found that the content of benzene is lowest among main aromatics. Due to strong alkylation ability of methanol, methyl cat ion is easy to be attacked to phenyl ring and other electron-rich system to produce xylene or other benzene derivatives, depleting as-synthesized benzene [7]. A phenomenon is noticed that the yield of aromatic with more than three methyls decreases as

temperature increases, and aromatic with less than three methyls shows a opposite trend. As the temperature rises, the alkylation/dealkylation equilibrium of benzene and benzene derivatives with ethene and propene shift to the dealkylation side. Consequently, yields of trimethylbenzene, dimethylbenzene and tetramethylbenzene decrease at high temperature, while yields of benzene, toluene and xylol increase.

The total duration of run was kept for 24 h in order to study the small crystalline ZSM-5 catalyst and micron-size ZSM-5 catalyst activity with time on stream. From Fig.5, it is noticed that the synthesized small srystalline ZSM-5 catalyst has much higher aromatic yield and longer lifetime than the micron-size ZSM-5 catalyst. During the first 24h, main aromatics yields for MTA over nano ZSM-5 catalyst changes slightly, and conversion of methanol keeps above 99.5%. The nano-sized crystals in the catalyst are more resistant to coke [8]. This may be due to the excellent product diffusion, reducing the deep carbon deposition that deactivates catalyst.

Summary

Small crystalline zeolite has higher surface areas and reduced diffusion path lengths relative to conventional micron-size zeolites. Small crystalline ZSM-5 was prepared via hydrothermal synthesis and its physicochemical properties were characterized by XRD, SEM and N_2-absorption. The small crystalline ZSM-5 particles grow into aggregates, a possible source for the formation of intercrystalline voids in the range of mesopores. The catalytic performance of small crystalline ZSM-5 catalyst and micron-size ZSM-5 catalyst in the conversion of methanol to aromatic has been studied both with respect to catalyst durability and aromatic selectivity. Small crystalline ZSM-5 catalyst could get a aromatic yield of 21.7%, and shows no activity decline during the first 24 hours. Compared to micron-size ZSM-5 catalyst, the small crystalline ZSM-5 catalyst could lead to high aromatic selectivity and has longer lifetime.

Acknowledgment

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