Synthesis of Hierarchical-Structured Zn/Mo-HZSM-5 and Its Application in Dimethy Ether Aromatization

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Abstract-The hierarchical-structured Zn/Mo-HZSM-5 catalyst was synthesized by two-step crystallization and impregnation method, and characterized by XRD, HRTEM and N_2 adsorption-desorption. The results indicates that the obtained catalyst has a large specific surface area and pore volume. The catalyst exhibits good activity and stability in DME aromatization. The selectivity of aromatics reaches 84.5% at 420°C. When the reaction time reaches 160h, the total aromatics selectivity remain at 71.2%.

Keywords-hierarchical-structured; Zn/Mo-HZSM-5; DME; aromatization.

I. INTRODUCTION

Benzene, toluene and xylene are called BTX, an important chemical raw material, and mainly derived from oil, widely used in synthetic fiber, resin, rubber, detergent and dye, medicine and other fields. At present, the BTX is derived from catalytic reforming process, pyrolysis gasoline and coal tar separation. However, shortage of raw materials, complex process, the selectivity is difficult to improve, so researching new process of producing BTX and other light aromatics, has very important theoretical and practical significance.

Today, with the rapid development of domestic coal chemical industry, the coal-to-DME production scale expanding unceasingly, it is important significance to the development of downstream products[1]. DME transformation mainly include hydroxylation, selective oxidation, oxidation coupling and reforming hydrogen and dehydration to olefin etc.[2]. DME has been converted to aromatic hydrocarbons, but the related research is less at home and abroad. Kecskemti first reported the study of DME aromatic hydrocarbons, the aromatics selectivity over Mo_2C/ ZSM-5 (5% Mo_2C) catalyst at 500°C was 60.8%[3]. ZSM-5 as catalyst with strong acid, high aromatic hydrocarbon selectivity, but the low stability of catalyst hindered its industrialization[4,5]. The study of catalyst for DME aromatization is focused on how to control the catalyst particle size, pore structure and acid amount, as well as the development of new catalyst materials[6].

In this paper, hierarchical-structured Zn/Mo-HZSM-5 zeolite has been synthesized by using mesoporous and microporous template agent. The structure and morphology of sample were characterized, and the catalytic performance was investigated in the DME aromatization.

II. EXPERIMENTAL

A. Preparation of Materials and Catalysts

The hierarchical-structured catalyst Zn/HMoZSM-5 (Si/Al=80) was synthesized by two-step crystallization. In synthesis procedure, the precursor ZSM-5 was prepared by mixing H_2O (deionized water), 13ml tetrapropylammonium hydroxide (TPAOH), 23ml tetraethyl orthosilicate (TEOS) and 0.26g aluminium isopropoxide while being continuously stirred for 24h. The mixture was then transferred to an autoclave and heated to 100°C for 4h. After cooling to room temperature, the resulting suspension was added with H_2O and 4.37g cetyltrimethyl ammoniumbromide (CTAB) solution containing 2g NaOH and Mo to obtain a final gel. The gel was continuously stirred for 2h at room temperature, then transferred to an autoclave and heated 170°C for 8h. The reaction product was filtered, washed, dried at 110°C for 12h and calcined at 550°C for 6h to obtain hierarchical-structured Mo-ZSM-5. Hierarchical-structured Mo-ZSM-5 was Carried on 3 times ion-exchange with a 0.1mol/L NH_4NO_3 solution at 75°C for 2h, followed by calcination. Then Zn was loaded on the hierarchical-structured Mo-HZSM-5 zeolite by impregnation to form hierarchical-structured Zn/Mo-HZSM-5 catalyst.

B. Characterization methods

X-ray diffraction (XRD) patterns were recorded using Bruke/D8 Powder X-ray diffractometer with Cu-Kα radiation. High resolution transmission electron microscopy (HRTEM) images were recorded using a JEM 2100 microscope with an accelerating voltage of 200 kV. N_2 adsorption–desorption isotherms were measured using an ASAP 2020 system after the sample was degassed under vacuum at 300°C for 3h. Pore size distribution was determined using the conventional Barrett–Joyner–Halenda (BJH) model.

C. DME aromatization reaction test

The DME aromatization reaction, under anaerobic conditions, was conducted in a fixed bed reactor operating at 0.1MPa. The cylindrical fixed bed reactor was made of

stainless steel, packed with 0.3g(size of 40-60 mesh) catalyst. Under N_2 atmosphere, heated to reaction temperature at a rate of 20 K/min, and keeping 0.5h to activate catalyst at reaction temperature. The DME (3ml/min) and the dilution gas N_2 (15ml/min) were passed into the reactor, the product was analyzed on-line using a GC9790 type gas chromatograph. Separation analysis conditions: Porapak-p packed column(3m), column temperature 200°C, gasification temperature 220°C, flame ionization detector (FID), the carrier gas (He), detector temperature 250°C, the 150mA current condition.

III. RESULT AND DISCUSSION

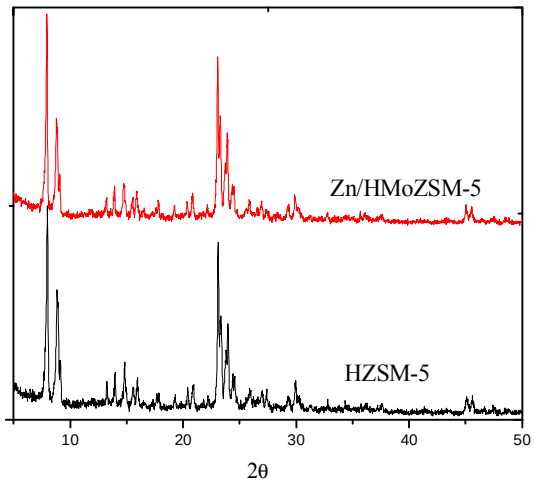

Fig.1: XRD patterns of Zn/Mo-HZSM-5 and HZSM-5

Fig.1 shows the XRD patterns of the Zn/Mo-HZSM-5 and standard HZSM-5. Zn/Mo-HZSM-5 has the sharp peaks in the ranges of 5°~40°, similar to the standard ZSM-5. The XRD peaks of Zn/Mo-HZSM-5 is still clearly observable. There is no any peaks of Mo and Zn in the ranges of 30°~80 °, it indicates that Mo and Zn dispersed evenly.

Fig.2 shows the HRTEM images of Zn/Mo-HZSM-5. Fig.2a shows that the Zn/Mo-HZSM-5 appears large cylindrical particles at 300-350nm in sizes, and particle size distribution is uniform. There are a small amount of mixed crystal around the zeolite, due to the parts of material are not crystallized completely in solution. Fig.2b shows the zeolite appears pore with different sizes.

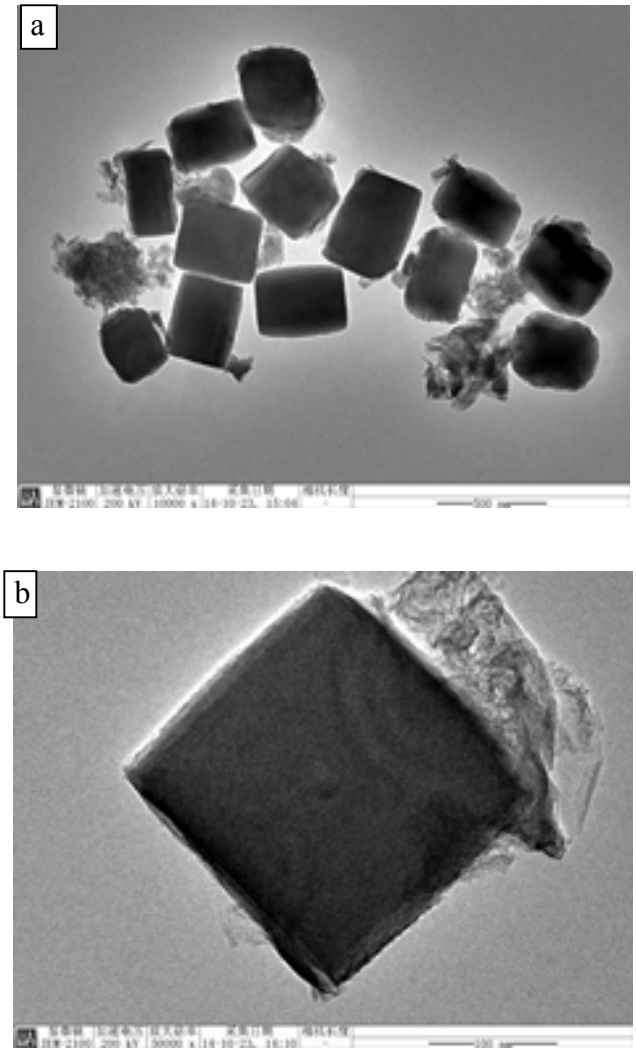

Fig.2: HRTEM images of Zn/Mo-HZSM-5

Fig.3 shows the N_2 sorption isotherm and pore diameter distributions of the Zn/Mo-HZSM-5. It can be seen that the zeolite exhibits a typical irreversible type IV adsorption and desorption isothermal, which is characteristic of mesoporous molecular sieves[7,8]. The pore size distribution reveals that there are two type pores in the zeolite centered at 3.8nm and 35.9nm by the BJH method.

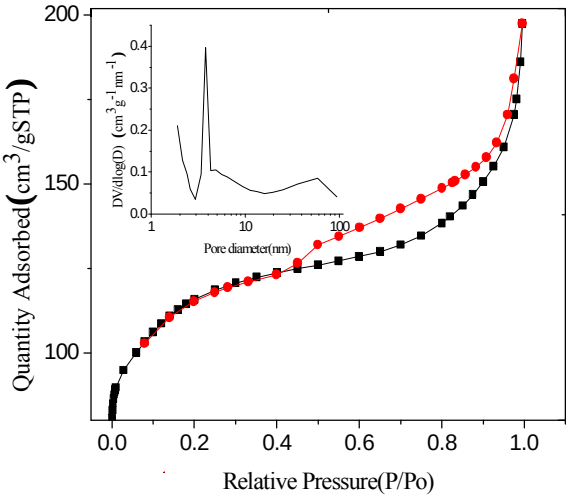

Fig.3: N_2 sorption isotherm and pore diameter distributions of the Zn/Mo-HZSM-5

Fig.4 describes the influence of reaction temperature on the aromatization of DME over hierarchical H-ZSM-5 and Zn/Mo-HZSM-5. As can be seen, DME aromatization already occurred at the condition of 180°C, which indicates that hierarchical H-ZSM-5 and Zn/Mo-HZSM-5 both have high activity for DME aromatization. Moreover, the aromatization activity of Zn/Mo-HZSM-5 is obviously higher than that of H-ZSM-5, it suggests that the metal centers of Zn/Mo-HZSM-5 play an important role in the reaction. As the reaction temperature increase, the selectivity of aromatics increase rapidly, and leveled off after 420°C. This suggests that higher reaction temperatures benefit to aromatization reaction[9].

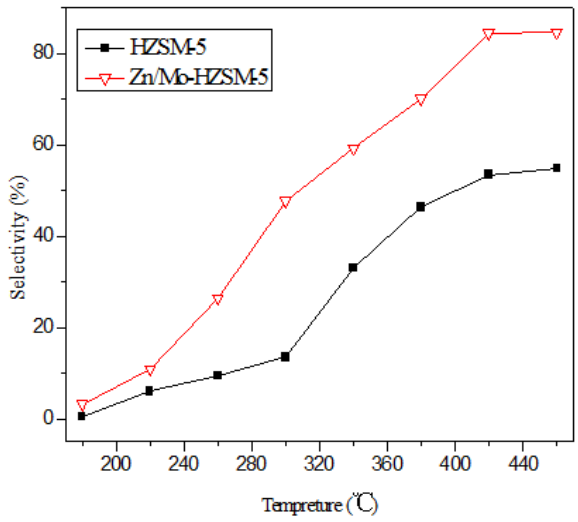

Fig.4: Effect of reaction temperature on performance in the aromatization of DME over hierarchical HZSM-5 and Zn/Mo-HZSM-5

The activity and stability of Zn/Mo-HZSM-5 zeolite were researched in DME aromatization at the optimal reaction condition (conversion rate 100%). Fig.5 shows the aromatics selectivity over all samples. The Zn/Mo-HZSM-5 catalyst exhibits good activity and stability in DME aromatization. The aromatics selectivity decrease with reaction time, but the total aromatics selectivity remain at 71.2% when the reaction time reaches 160h. Comparing with the traditional ZSM-5 zeolite, the existence of the hierarchical structural pore, make it easier for the product spreading out from the channel, carbon deposit produced difficultly, thus the stability of Zn/Mo-HZSM-5 increases significantly.

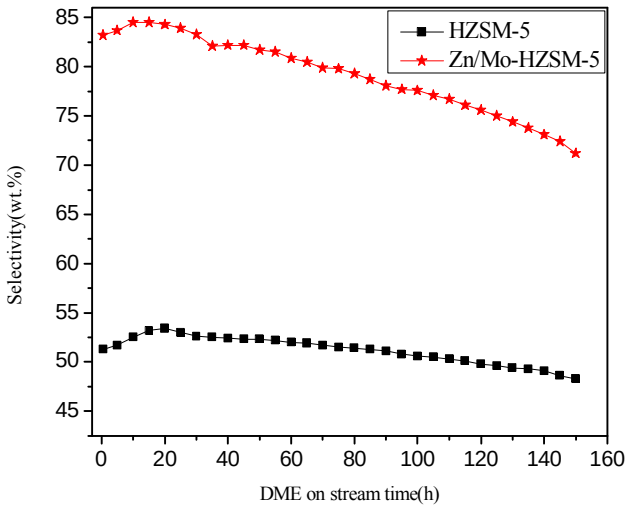

Fig.5: The activity and stability testing of zeolites

IV. CONCLUSION

Given the above observations, hierarchical-structured Zn/Mo-HZSM-5 zeolite was synthesized by two-step crystallization. The morphology of sample is almost unaffected after Mo and Zn modified; The aromatics selectivity for DME aromatization over Zn/Mo-HZSM-5 reaches 85% at 420°C. Compared with the traditional ZSM-5, the stability of Zn/HMoZSM-5 zeolite increases significantly, which is due to the existence of mesoporous structure.

ACKNOWLEDGMENTS

This work was financially supported by the Subject and specialty construction special fund of Guangdong Provincial Higher Education Institution (No. 2012CXZD0024, No. 2013KJCX0081).

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