COMPARISON STUDY ON THE CATALYSIS PERFORMANCE OF MCM-49 AND BETA ZEOLITE ON THE TRANSALKYLATION OF PIPB

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ABSTRACT

Zeolite MCM-49 and Beta were synthesized by dynamic hydrothermal method, which were characterized by different techniques, such as XRD, SEM, N₂ adsorption-desorption and NH₃-TPD. The catalyst performance of MCM-49 and Beta on the transalkylation of polyisopropyl-benzene (PIPB) had been studied, comparatively. The influence factors of catalytic performance were investigated, such as reaction temperature, raw materials ratio and space velocity. Results indicate that MCM-49 shows better catalytic activity for TIPB under a relatively low reaction temperature, which should be mainly due to a large amount of structurally accessible acid sites caused by its high external surface area.

KEYWORDS

MCM-49, Beta, Transalkylation, PIPB.

1. INTRODUCTION

MCM-49 is a kind of layered microporous materials with MWW topology structure, being widely used in some important industry process, such as alkylation, catalytic cracking, isomerization and disproportionation [1-10]. Previous studies have shown that the external acid sites play an important role on the catalysis performance of MCM-49 [11-14]. It prohibits a great potential in the catalytic transformation of macromolecules.

Isopropyl-benzene (IPB) is an important organic chemicals, mainly used in the synthesis of phenol and acetone, which is produced by liquid phase alkylation of benzene with propylene. Inevitably, by-products of polyisopropyl-benzene (PIPB) will be obtained including disopropylbenzene (o-DIPB, m-DIPB and p-DIPB) and trisopropyl-benzene (TIPB). Traditionally, PIPB could be converted to IPB through transalkylation process.

The catalytic performance of zeolites on the transalkylation of benzene with DIPB had been reported [15]. However, the study on the transalkylation of benzene with PIPB (including both DIPB and TIPB) is rarely. Because of the larger molecules size of TIPB and the diffusion inhibition of zeolite channel, a higher reaction temperature is necessary to obtain a high conversion of TIPB. Unfortunately, according to literature earlier, reaction temperature above 493K will bring to obviously increase of n-propylbenzene (NPB), which will decrease the quality of phenol dramatically. So, there is a challenge to explore a kind of catalyst with suitable porous structure, channel size and acid properties, which can conversion both TIPB and DIPB, effectively.

In this work, layered MCM-49 zeolites were prepared by dynamic hydrothermal method. All samples were characterized by means of XRD, SEM, N₂-adsorption/desorption and NH₃-TPD. The catalytic performance of MCM-49 on the transalkylation of PIPB was investigated compared to Beta.

2. EXPERIMENTAL

2.1 Materials Preparation

HBeta zeolite (SiO₂/Al₂O₃=20) was synthesized by dynamic hydrothermal method according to reported previously [16]. NaMCM-49 zeolite was synthesized from a gel having the following composition: Si/Al = 10.2, Na/SiO₂ = 0.15, HMI/SiO₂ = 0.30, H₂O/SiO₂ = 20 as reported previously [13]. This gel was crystallized in a Teflon-lined autoclave at 170 °C for 72 h with rotating rate of 45 rpm. The precursor of MCM-49 was recovered by filtration, washed with distilled water, dried at ambient temperature and calcined in air at 540 °C for 6 h to give the NaMCM-49 zeolite. The protonic forms of MCM-49 zeolite was obtained by three times exchanges with 1.5 M ammonium acetate solution for 10 h at 90 °C, followed by calcination in air at 540 °C for 6 h to give HMCM-49.

2.2 Catalytic Characterization

The textural properties of samples were obtained in a Micromeritics ASAP2020 apparatus. X-ray diffraction (XRD) patterns were collected by a Shimadzu XRD-6000 diffractometer using Cu K α radiation (λ =0.1542 nm). Temperature-programmed desorption of ammonia (NH₃-TPD) was carried out on a Finesorb 3010D chemisorption apparatus [9]. A Zeiss JSM-6490LV instrument operating at a 20 kV was used to perform the scanning electron microscopy (SEM) and the energy dispersive analysis of X-rays (EDAX).

2.3 Reaction Conditions

Transalkylation of polyisopropyl-benzene was performed in a fix-bed stainless microreactor. The diameter of the reaction tube is 10 centimeter. The reactor was charged with 1 g of catalysts crushed and sieved to 40-60 mesh particles. The reaction mixture ($\omega_B:\omega_{DIPB}:\omega_{TIPB}=50\sim100:25:7$) was fed to the reactor by a pump. Catalytic tests were carried out under the following conditions: reaction pressure=3MPa; temperature=170-230°C; WHSV=0.5~2.5 h⁻¹.

3. RESULT AND DISCUSSION

3.1 Characterization of Catalysts

Figure 1 shows the X-ray patterns of as-made MCM-49, calcined MCM-49 and calcined Beta zeolite. All these patterns are in good agreement with those previously reported [1, 16]. For as-made MCM-49, the diffraction peaks seems sharp, and exits three diffraction peaks at $2\theta=26^\circ\sim 29^\circ$ ($d=0.343\sim 0.308\text{nm}$). For calcined MCM-49, it shows an obviously increase in the intensity of diffraction peaks at 15° . It shows that synthesized MCM-49 sample is pure and well crystallized.

Figure 1: XRD pattern of (a) as-made MCM-49; (b) calcined MCM-49; (c) Beta.

Table 1: Textural property of MCM-49 and Beta zeolite

Sample	S_{BET} [m^2/g]	$S_{\text{t-plot micro.}}$ [m^2/g]	$S_{\text{t-plot external}}$ [m^2/g]	V_{total} [cm^3/g]	$V_{\text{t-plot micropore}}$ [cm^3/g]
MCM-49	476	378	83	0.58	0.17
Beta	580	395	47	0.59	0.26

Figure 3 shows the SEM photograph of MCM-49 and Beta. MCM-49 synthesized by dynamic hydrothermal method presents a well dispersed layered morphology. The size of the layered crystal is about 1-2 μm along a, b dimension, and 20-30 nm along c dimension. For Beta, it shows an irregular particle morphology, and the size of particle agglomerates is about 3-8 μm .

Figure 3: SEM photograph of (a) Beta and (b) MCM-49

The acid properties of HMCM-49 and HBeta were characterized by temperature-programmed desorption (TPD) of ammonia (see Figure 4). Both NH_3 -TPD profiles show two peaks at around 225 $^\circ\text{C}$ and 399 $^\circ\text{C}$, which can be attributed to the presence of weak acidic sites and relatively strong acid sites (mainly Brønsted acidity), respectively. Compared to HBeta, HMCM-49 shows a similar total acid amounts and a bit lower strong acid amounts, which is in accordance with the Si / Al mole ratio of two samples.

The nitrogen adsorption-desorption isotherms of samples are presented in Figure 2, which indicates that both HMCM-49 and HBeta are microporous materials. The inflection point appears at relative pressure 0.1. Table 1 gives the textural property of MCM-49 and Beta zeolite. The BET surface area and external surface area of MCM-49 is $476\text{ m}^2\cdot\text{g}^{-1}$ and $83\text{ m}^2\cdot\text{g}^{-1}$ respectively. The total pore volume and micropore pore volume is $0.58\text{ cm}^3/\text{g}$ and $0.17\text{ cm}^3/\text{g}$. Compared to MCM-49, the BET surface area and micropore surface area of Beta is higher, however the external surface area is obviously lower.

Figure 2: Nitrogen adsorption-desorption isotherm of (a) MCM-49 and (b) Beta.

Figure 4: Temperature-programmed desorption of NH_3 for (a) HMCM-49 and (b) HBeta

3.2 Catalytic Performance

The transalkylation of PIPB with benzene was catalyzed by HMCM-49 and HBeta, respectively. Figure 5 shows the comparison results in the conversion of benzene (CB), DIPB (CD), TIPB (CT), and the yield of IPB (YI) for MCM-49 and Beta. Results indicate that MCM-49 shows a better catalytic activity for the conversion of TIPB, as well as Beta is more suitable for the conversion of DIPB. For Beta zeolite, a higher yield of IPB was obtained.

The effects of reaction temperature on the catalytic performance of MCM-49 and Beta zeolite on the transalkylation were investigated in detail (Figure 6). Increase in the reaction temperature would improve the convention of TIPB and the yield of IPB. Results suggest that MCM-49 zeolite shows excellent catalytic activity for the conversion of TIPB under a relatively lower reaction temperature. When the reaction temperature is between 180 to 200 $^\circ\text{C}$, the conversion of TIPB for MCM-49 is obviously higher than Beta. When the reaction temperature is above 220 $^\circ\text{C}$, HMCM-49 exhibits 100% convention of TIPB and 72.25% yield of IPB.

Figure 7 shows that the mass hour space velocity (MHSV) has a considerable effect on the conversion of TIPB and the yield of IPB. It is observed that the largest yield was obtained when MHSV is 1h^{-1} . As it is further increased, the conversion and the yield will decrease. The yield of IPB is about 74%, which is similar for both MCM-49 and Beta.

So, MCM-49 shows a excellent catalytic activity for the conversion of TIPB at a relatively low reaction temperature, which could be attributed to its numerous acid sites on the external surface, which helps to promote the reaction of macromolecules and reduce the diffusion resistance.

Figure 6: Effect of the reaction temperature on the conversion of TIPB and the yield of IPB ($P=1.8\text{MPa}$, $\omega_B:\omega_{\text{PIPB}}=2.3$, $\text{WHSV}=1\text{h}^{-1}$ T.O.S.=10h)

Figure 7: Effect of the mass space velocity on the conversion of TIPB and the yield of IPB ($P=1.8\text{MPa}$, $T=220^\circ\text{C}$, $\omega_B:\omega_{\text{PIPB}}=2.3$, T.O.S.=10h)

4. CONCLUSIONS

Pure and well crystallized MCM-49 and Beta zeolite have been synthesized by dynamic hydrothermal method. XRD and SEM reveals that MCM-49 presents a well dispersed layered morphology. The characterization of textural and acid properties shows a exiting of higher external surface area for MCM-49 zeolite and a similar acid strength. MCM-49 shows a better catalytic activity for the conversion of TIPB at a relatively low reaction temperature, and Beta is more suitable for the conversion of DIPB. The catalytic performance of MCM-49 could be attributed to the exiting of numerous acid sites on the external surface, which promote the reaction of macromolecules and reduce the diffusion resistance.

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Figure 5: Comparison of the conversion of benzene (C_B), DIPB (C_D), TIPB (C_T), and the yield of IPB (Y_I)

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