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BETA zeolite made from mesoporous material and its hydrocracking performance

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Abstract

This paper presents a kind of BETA zeolite that was made out of mesoporous material. With MCM-41 mesoporous material being used as silicon source, this BETA zeolite shows improved physical and chemical properties. It not only keeps acidity advantage of microporous zeolite but also inherits some pore structure quality of mesoporous zeolite. Moreover, it also displays very small crystal granule close to the range of nanometer. Owing to these new characteristics, such BETA zeolite provides hydrocracking catalyst with enhanced activity and improved middle distillate selectivity when it is applied in hydrocracking catalyst for treating large molecule heavy hydrocarbon feed oil to produce middle distillates (jet fuel + diesel oil).

Keywords: Mesoporous material; Zeolite BETA; Nanometer; Hydrocracking; Catalyst

1. Introduction

Microporous zeolites have been widely used in modern chemistry industry because of its high acidity and unique pore structure. But such heterogeneous catalytic materials have their own limitations on large molecule reaction because of their small size of orifice and poor diffusion effect for reactants and resultants. Though emergence of mesoporous materials [1] suggests a new opportunity, their poor structure stability and weak acidity cannot take the place of microporous zeolites in many cracking reaction processes, such as fluid catalytic cracking (FCC) or hydrocracking process of petroleum chemical field.

At present, a popular resolvent is to prepare a composite zeolite material comprising of both the microporous zeolite matrix and mesoporous material by multi-step crystallization [2–4]. However, all of these methods mainly aim at modifying mesoporous material on its structure stability and acidity, whose level of standard are still far away from microporous zeolite. Particularly, Xiao improved acidity of mesoporous material by incorporating micro crystal of zeolite BETA precursor, a micro crystal of microporous zeolite matrix, into mesoporous material in the course of synthesis of mesoporous material [5]. This paper further presents a good acid catalytic performance of this composite mesoporous zeolite with enhanced acidity.

BETA zeolite is a kind of high silicon zeolite with 12-ring orifice and 3D pore structure [6,7]. Due to its good selectivity on chain hydrocarbon cracking, BETA zeolite is becoming more and more widely used in fields of fine organic catalysis [8–10] and petrochemical cracking [11,12]. Davis and co-workers prepared an organic-functionalized molecular sieves with a BETA-type structure by the route of MCM-41 containing intracrystalline phenethyl (PE) groups [13]. But this BETA zeolite is not suitable for catalyst but for adsorption because of its surface acidity and large size of granule and is not suitable for practical use because of its long time of synthesis (4 weeks).

In this paper, a kind of BETA zeolite was prepared by making use of a mesoporous material as silicon source. The used mesoporous material is a MCM-41 type mesoporous matrix which is prepared by using cheap inorganic silicon source, water glass. Therefore, many modified physical and chemical properties are showed on such specially synthesized BETA zeolite and it shows a beneficial performance on

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catalysis such as hydrocracking process for treating heavy oil feeds.

2. Experimental

Firstly, a mesoporous material was obtained by mixing cetyl-trimenthylammonium bromide surfactant (CTABr) and sodium silicate under agitating for 2 h with molar composition of the synthesis mixture being $1SiO_2$:0.25CTABr:$40H_2O$ and then undergoing hydrothermal crystallization in autoclave at fixed temperature for 20 h. After that, the mesoporous material product (sample MZ) was filtrated, dried and calcined to eliminate organic surfactant at 550 °C.

Crystallization of BETA zeolite under different condition has been described previously [14–18]. In this paper, the foregoing mesoporous material MSZ was mixed with tetraethyl ammonium hydroxide, sodium hydroxide and sodium aluminate on some fixed ratio to synthesize BETA zeolite at 140 °C for 3 days in hydrothermal process. This specially synthesized BETA zeolite with Si/Al mole ratio 60 was numbered as sample BA. Meanwhile, a BETA zeolite with same Si/Al mole ratio was also synthesized as a blank sample, which was numbered as sample BB.

XRD measurements were made on a D/max2500 powder diffractometer equipped with Cu Kα radiation (40 kV, 80 mA) at the rate of 5°/min over the range of 5–40° (2θ). N_2 adsorption/desorption tests were made on an automatic ASAP 2400 apparatus. FTIR spectra analysis was made on a Nicolet 560 spectrography infra-red optical bench from 400 to 4000 cm^{-1} wave band. The crystal size and morphology of the samples were determined from SEM micrographs on JSM-6301F instrument. Catalyst estimation is performed on pilot test installation with 200 ml fixed-bed. DTA analysis was run on Perkin-Elmer instrument and the samples was analysed at a heating rate of 30 °C min^{-1} with an air purge.

3. Result and discussion

Fig. 1 gives the X-ray diffraction (XRD) pattern of MSA sample, which displays a typical mesoporous material XRD profile. Exactly, it can be identified as MCM-41 mesoporous zeolite as its XRD profile shows significantly the 1 0 0 and 1 1 0 X-ray diffraction peaks. Fig. 2 shows the XRD pattern of sample BA made out of MCM-41 mesoporous material and XRD pattern of sample BB. Based on JCPDS cards, samples BA and BB are all identified as BETA zeolites.

The XRD result of sample BA illustrates a crystal transition from mesoporous material to BETA zeolite in hydrothermal process. Compared with sample BB prepared by common way, it is also found that the crystallinity of sample BA is a little lower. This difference on their crystallinity is probably attributed to its heredity from long-range out-of-order structure of MCM-41 matrix. Moreover, the XRD profile of sample BB did not inherit characteristic peaks of mesoporous material at low 2θ angle just as MSZ displayed in Fig. 1, which suggests that the silica structure units probably come out of decomposition of original mesoporous material.

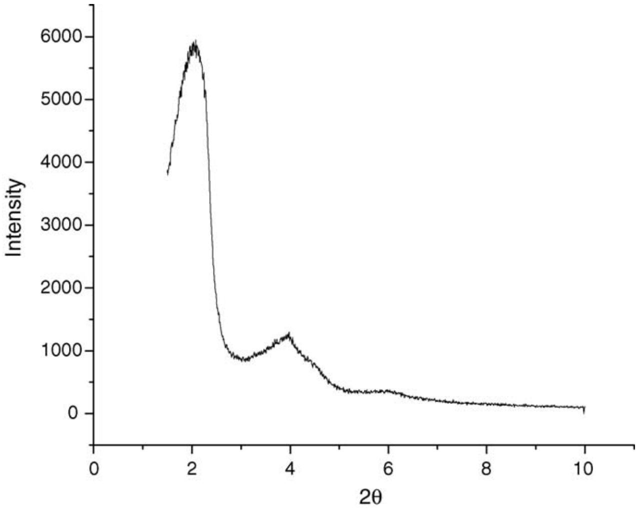

Fig. 1. XRD profiles of mesoporous material sample MSZ.

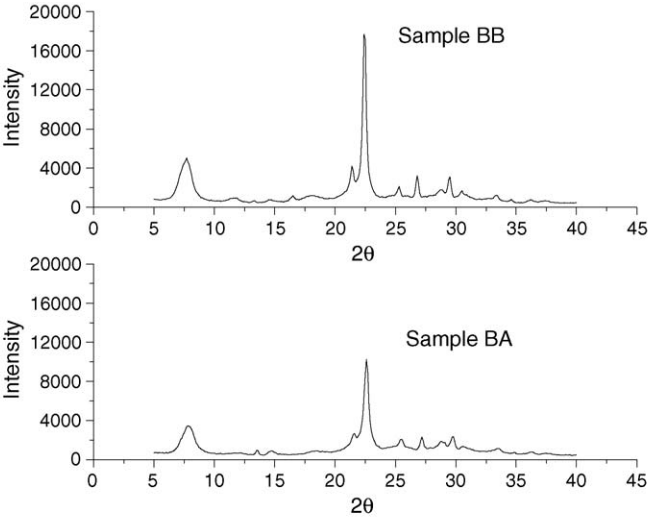

Fig. 2. XRD profiles of as-synthesized sample BA and sample BB.

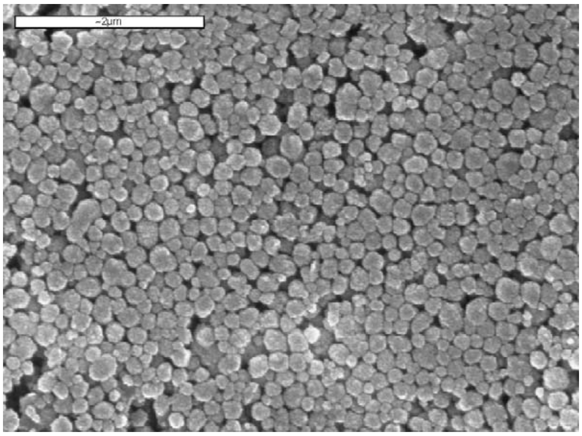

Fig. 3. SEM image of sample BA.

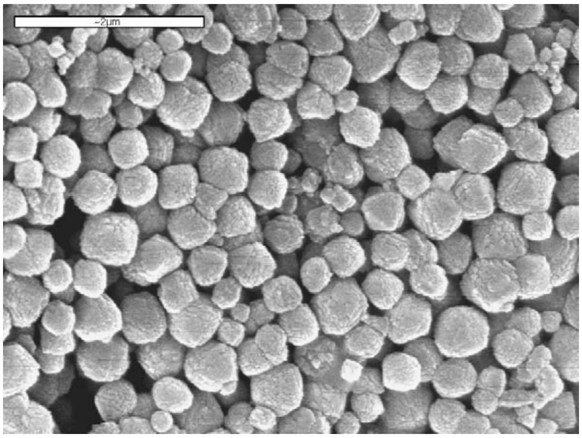

Fig. 4. SEM image of sample BB.

As XRD patterns of sample BA and sample BB suggest no significant essential difference on their fundamental micro structure, their SEM images are different. As shown in Fig. 3, the crystal size of sample BA is around 150 nm, which is approximately in the range of nanometer size. Contrastingly, the crystal size of sample BB is about 400 nm as showed by Fig. 4. The crystal size of sample BA is more than one time smaller than that of sample BB.

This phenomenon should be explained as following. On the one hand, MSZ mesoporous matrix which was used as silicon source was a very small granule with close size of nanometer as showed by Fig. 5. On the other hand, in the course of hydrothermal process, MSZ mesoporous matrix gradually decomposed and then recombined into BETA zeolite. So, not like ordinary amorphous silica source, mesoporous matrix directly provided sample BA with exited primary silica structure units to congregate and stack for the formation of BETA zeolite silicon structure. Meanwhile, BA, thus, also inherited the mesoporous matrix characteristic of MSZ, whose size of granule also affected the formation of particles BA sample.

Table 1
Pore properties results of samples

Sample	Specific surface area (m^2/g)	Pore volume (ml/g)	Average pore diameter (nm)
BA	628	0.41	2.0
BB	510	0.25	1.5

Table 2
DTA results of samples

Sample	Temperature of structure damage (°C)
A	1050
B	1080

Table 3
IR acidity of samples

Sample	Total acidity (mmol/g)	B acidity (mmol/g)	L acidity (mmol/g)
Na type BA	0.31	0.09	0.22
H type BA	1.10	0.71	0.39
Na type BB	0.89	0.03	0.86
H type BB	1.36	0.58	0.78

Apart from the effect on crystal size, structure of mesoporous matrix brings more second-pore structure for sample BA, which is reflected on its pore properties. According to N_2 adsorption/desorption analysis in Table 1, pore diameter of sample BA is over 30% larger than sample BB and pore volume is 60% more than sample BB. The results of Table 1 are also conformed with SEM images, since smaller crystal size to some extent means more surface area. Beyond all doubt, larger pore diameter and much more pore volume of catalytic material usually suggests potential benefit for large molecule reaction.

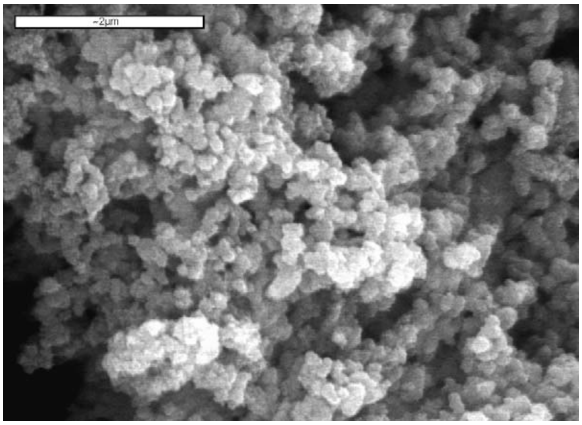

Fig. 5. SEM image of mesoporous matrix MSZ.

In spite of improved pore structure, the BETA zeolite made out of mesoporous material has high structure stability whose structure damage temperature is over 1000 °C as showed in Table 2. It is well known that good acidity, in particular B acidity, is an advantage for microporous zeolite, which play an important role in cracking reaction process. As shown in Table 3, sample BA, both sodium type and hydrogen type, have more B acidity than sample BB but less L acidity. Generally, L acidity comes from exposed aluminum ions and much L acidity means more surface defects. Such specially synthesized BETA zeolite made out of mesoporous matrix probably brings fewer defects than BETA zeolite made out of amorphous silica source.

Hydrocracking process is a refinery process for producing light fuels from heavy petroleum feeds by cracking large molecules of hydrocarbon in the presence of hydrogen. Catalyst is key in this process. The pore texture and acidity of catalytic materials it used play an important role in the performance of

Table 4
Properties of feed oil

Feed oil	Iran VGO
Density (g/cm^3)	0.918
Distillation range (°C)	340–520
RCC (m%)	0.04
S (m%)	2.07
N (μg/g)	1805
BMCI index	48.6

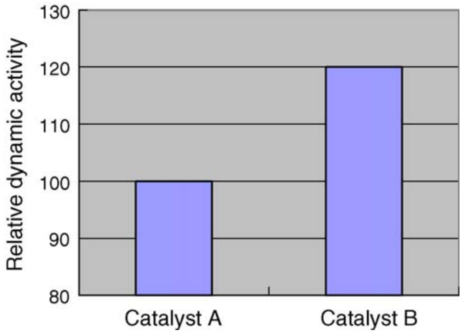

Fig. 6. Relative dynamic activity of hydrocracking catalyst.

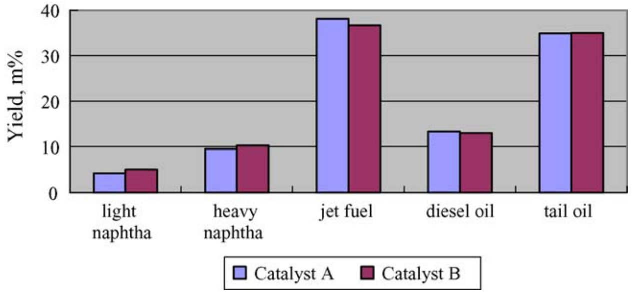

Fig. 7. Hydrocracking product distribution of catalyst.

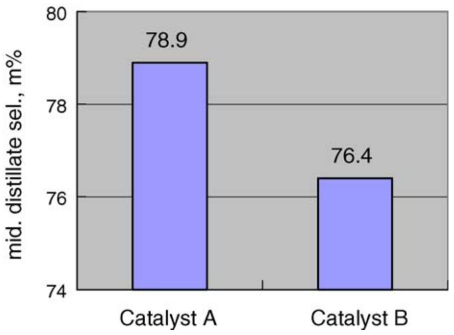

Fig. 8. Middle distillate selectivity of hydrocracking catalyst.

the catalyst. In this paper, the two BETA zeolites, sample BA and sample BB of hydrogen type, were used, respectively, to prepare catalyst CA and catalyst CB.

The two catalysts were evaluated in pilot test. When treated with heavy Iran vacuum gas oil, a inferior heavy hydrocarbon feed oil because of its distillation range, high sulfur content and high aromatic content as shown in Table 4, catalyst CA shows over 20% dynamic activity enhancement based on benchmark of catalyst CB as shown in Fig. 6. Moreover, Fig. 7 shows that catalyst CA produces more middle distillates such as jet fuel and less naphtha compared with catalyst CB. As to middle distillate selectivity showed by Fig. 8, catalyst CA is 2.5% higher than that of catalyst CB.

For a million ton scale industrial hydrocracking unit, only 1% increase of middle distillate selectivity means huge profits for refinery. Thanks to the BETA zeolite made out of MCM-41 mesoporous matrix, promotional pore structure decrease occurring of second cracking and, thus, restrains much more yields of small molecule product, which reflects great enhancement on middle distillate selectivity.

The reason that BETA zeolite sample BA made out of MCM-41 matrix shows better catalytic performance in hydrocracking process for treating large molecule heavy hydrocarbon probably lies in its smaller granular size effect and better pore diffusion effect. Firstly, its smaller crystal size which is close to nanometer is helpful to more exposition of activity centers. Secondly, its larger pore diameter and pore volume is helpful to diffusion of large molecule reactants and various resultants. Therefore, when being applied in hydrocracking catalyst for treating heavy hydrocarbon feed oil, its enhanced activity and improved selectivity can be observed.

4. Conclusion

Mesoporous zeolite can be used as silicon source to synthesize zeolite BETA. This specially synthesized BETA zeolite not only keep the advantage of microporous zeolite but also inherits some pore structure quality of mesoporous zeolite. Besides good acidity, bigger pore diameter and larger pore volume, this BETA zeolite made out of mesoporous matrix gives very small crystal granule close to nanometer size. When applied in hydrocracking catalyst, it makes catalyst to be suitable for cracking large molecule heavy feed oil and provides it with enhanced activity and improved middle distillate selectivity.

Acknowledgments

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