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Influence of particle size of ZSM-5 on the yield of propylene in fluid catalytic cracking reaction

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ABSTRACT

In this paper, the influence of particle size of ZSM-5 zeolites on the yield of propylene and physicochemical properties of catalysts in fluid catalytic cracking reaction was investigated. Two kinds of ZSM-5 zeolites with different sizes, small particle and routine, were utilized to prepare the catalysts. The particle size of small particle and routine ZSM-5 zeolites was 1.99 μm and 5.48 μm, respectively. The attrite index of catalyst including small particle ZSM-5 zeolites was far lower than that of routine zeolites. More propylene and more clean gasoline can be obtained when the small particle ZSM-5 was used as a component of catalyst. The suitable content of small particle ZSM-5 zeolites remained the cracking activity of heavy oil, and at the same time, was helpful for the enhancement of propylene yield.

1. Introduction

As we all known, light olefins are the base feedstock for petrochemical industry [1–3]. Among the various downstream operations applied to adapt product yields to market demand, fluid catalytic cracking (FCC) is still one of the most important [4,5]. At present, there is an increasing interest in maximizing propylene yield of FCC units [6]. In 2000, about 34% of the worldwide propylene production came from FCC units [7]. In the next decade, it is expected that worldwide propylene supply from FCC units will continuously increase. Therefore, new catalysts need to be developed to improve the propylene yield of FCC process.

FCC units typically produce around 3–5 wt.% propylene, depending on the feed properties, operating conditions and the nature of these catalysts. Besides the main Y zeolite in FCC catalysts, several additives may be applied in the FCC process in order to maximize the propylene yield. ZSM-5 zeolites with three-dimensional sinusoidal and straight channels of molecular dimension were first exploited by Mobil in 1972. It selectively promotes cracking of C7–C13 straight and short branched hydrocarbons of gasoline to C3–C5 olefins. ZSM-5 is the preferred catalyst or additive in petrochemical processing to increase the yield of light olefins [8]. Therefore, ZSM-5 zeolite is often employed as a FCC catalyst additive of great industrial importance to improve propylene yield and also to improve gasoline octane owing to its special pore structure and acidic properties for a long time [9–11]. Generally, to maximize propylene yield, the content of ZSM-5 in FCC catalysts should be increased.

The particle size of zeolite is very important in catalytic reaction. According to the above analysis, in the processing of catalytic cracking reaction, the content of ZSM-5 must be enhanced in order to improve the yield of propylene. However, the high content of routine ZSM-5 influences the attrite index of catalyst and decreases the utilization efficiency of FCC catalyst. In fact, the high content of routine ZSM-5 in the component of catalyst is not eligible. In this paper, we offer a small particle ZSM-5 zeolite and apply for the preparation of catalyst. In most of catalytic applications, the decrease in the zeolite crystal size possesses a positive effect as it favors the intracrystalline diffusion steps. Therefore, the use of small zeolite crystals can be favorable if shape selectivity effects are to be exploited.

2. Experimental

2.1. Preparation of catalyst

The routine and small particle ZSM-5 zeolites were purchased from the Catalyst Plant of Nankai University, China. The industry

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Table 1
Main properties of Xinjiang feedstock.

Items	Xinjiang VTB	Xinjiang VGO	Mixture (VTB/VGO = 3/7)
Density, ρ 20 (kg cm^{-3})	944.2	883.8	901.8
Residual coke (wt.%)	9.87	0.07	3.10
Average molecule (wt.%)	828	319	390
Simulated distillation (°C)			
Initial boiling point	420	286	306
10%	435	347	339
30%	465	392	372
50%	–	453	416
70%	–	500	460
90%	–	–	502

catalyst was prepared as followed. In a typical catalyst preparation process, one USY, a Kaolin matrix (Suzhou Kaolin Company, China), and a binder alumina (Catalyst Plant of Lanzhou Petrochemical Company, PetroChina Company Ltd., China), one ZSM-5 zeolite, were mixed together and shaped by spray-drying to obtain a microspheroidal catalyst. The catalysts including routine and small particle ZSM-5 zeolites were denoted as CAT-R and CAT-SP, respectively.

2.2. Catalytic cracking tests

The model catalyst was examined by micro-activity (MAT) experiment in accordance with ASTM test procedure D-3907. The catalyst was initially deactivated for 17 h at 800 °C in the presence of 100% steam before the testing. The quantity of catalyst was 5 g, and the catalyst/oil ratio was 3.2. Dagang light diesel was used as the feed for the MAT evaluation.

The catalytic cracking performances of the catalysts were tested on an advanced catalyst evaluation (ACE, Kayser Corp.) bench unit. The tests were carried out under the typical conditions for FCC units: cracking temperature 535 °C, catalyst to oil mass ratio 5.0, contact time 90 s. The chemical composition of the product FCC gasoline was determined by an on-line GC–MS. The feedstock was a mixture of 70% Xinjiang vacuum gas oil (VGO) and 30% Xinjiang vacuum tower bottom (VTB) and their properties were listed in Table 1.

2.3. Physicochemical characterization

The X-ray fluorescence spectrum (XRF) of the phosphorus content was analyzed on a Rigaku ZSX primus operated at 50 kV and 40 mA.

The X-ray diffraction (XRD) patterns of the as-synthesized catalyst were obtained on a Rigaku D/Max-3C diffractometer using Cu Kα radiation with a Ni filter.

Particle size and morphology of sample were investigated using scanning electron microscope (SEM).

Attrite index was measured in a home-made attrite machine.

FT-IR of pyridine adsorption was conducted by the FT-IR spectrometer (BIO-RAD, FTS3000) equipped with an in situ cell containing CaF_2 windows. The Brönsted and Lewis acid sites could be distinguished by the bands of chemisorbed pyridinium ion at different wave numbers.

Table 2
The physicochemical characterization of ZSM-5 zeolites.

Sample	Cauterant decrease, m%	Na_2O, m%	Relative crystallinity, %	Average size, µm
Routine ZSM-5	9.9	0.06	91	5.48
Small particle ZSM-5	9.9	0.08	94	1.99

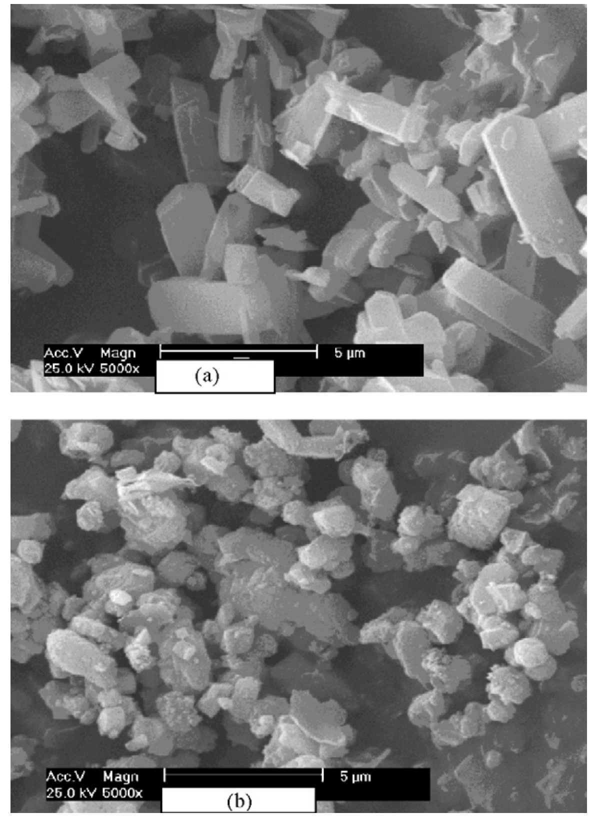

Fig. 1. SEM images of the routine ZSM-5 (a) and small particle ZSM-5 (b).

Textural properties were determined by N_2 adsorption at 77 K on an ASAP-2010 instrument (Micromeritics, USA). Prior to measurement, the sample was outgassed at 573 K for 12 h. Micropore volumes and external surface areas were calculated from the *t*-plot method.

3. Results and discussion

3.1. Physicochemical characterization of ZSM-5 zeolites

Fig. 1 showed the TEM images of routine and small particle ZSM-5 zeolites. As can be seen from Fig. 1, the particle size of small particle ZSM-5 was about 1.99 µm, which was smaller than that of routine ZSM-5. The average particle size was obtained by laser scattering.

XRD was carried out to investigate the possible structural difference in ZSM-5 zeolite. Small particle ZSM-5 exhibited a diffraction pattern very similar to that of the routine sample (Fig. 2). The relative crystallinity was calculated according to the aggregate intensities of the three peaks at 2θ of 23.07°, 23.28° and 23.90° [12]. The relative crystallinity of small particle and routine ZSM-5 was maintained at 94% and 91%, respectively (Table 2). The relative crystallinity of calcined sample remained identical with the parent one, which indicated the stability of ZSM-5 was very good.

As for small particle and routine ZSM-5 zeolites, the two samples showed the similar cauterant decrease and Na_2O content. The data in Table 2 showed that the two samples had comparable physicochemical properties except the particle size.

3.2. Physical chemical properties of catalyst

The physical chemical properties of the prepared catalyst are shown in Table 3. According to the analysis of XRF, the CAT-

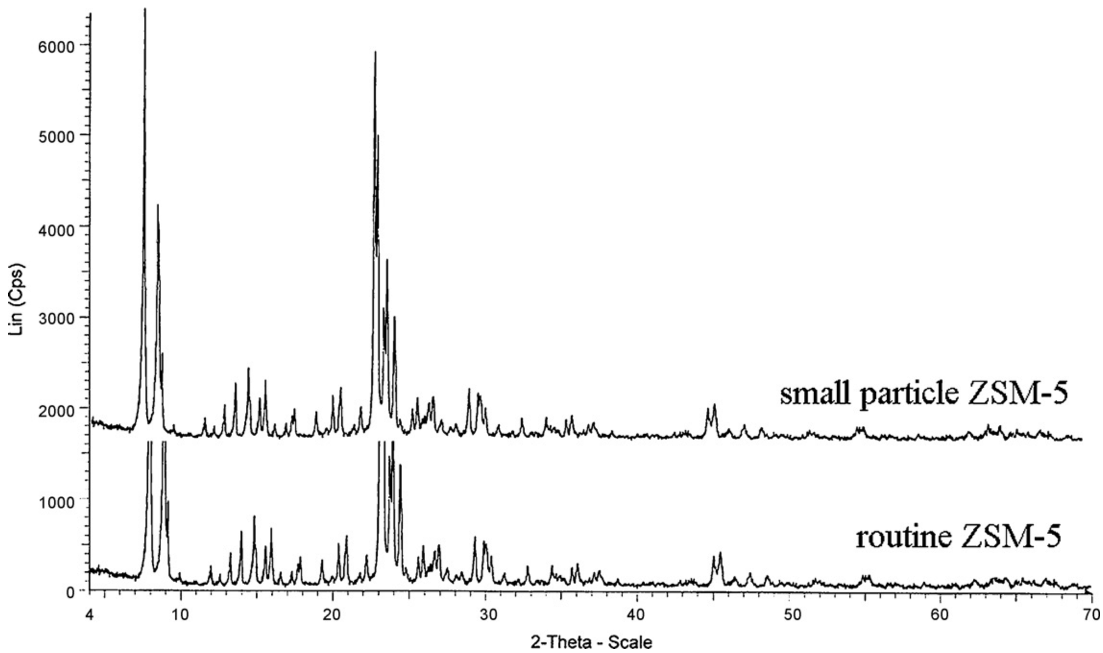

Fig. 2. XRD patterns of small particle and routine ZSM-5.

SP and CAT-R catalysts showed the similar content of Na_2O and RE_2O_3. At the same time, the two catalysts held the similar pore volume and surface area based on the measurement of N_2 adsorption/desorption method. However, attrite index showed obvious difference. The corresponding attrite index was 1.3 and 2.4 for the CAT-SP and CAT-R catalyst, respectively. The difference was mainly due to the particle size of ZSM-5 zeolite. Small particles were helpful for the decrease of attrition.

The catalysts containing different zeolites were deactivated in 100% steam at 800 °C for 17 h and evaluated in the MAT unit, and the detailed results were listed in Table 3. The two catalysts showed the close conversion, which indicated that the activity of catalyst was decided by the physicochemical properties of ZSM-5 zeolite.

3.3. Catalytic cracking tests

The catalytic cracking results were shown in Table 4. In these tests, the cut point of gasoline is 211 °C and that of diesel is 343 °C. From Table 4, it can be seen that compared with the FCC catalysts containing routine ZSM-5 zeolite, the catalysts containing small particle ZSM-5 zeolite can increase LPG and propylene yield by 0.41% and 0.08%, respectively. This indicated that the utilization of small particle ZSM-5 zeolite strengthened the cracking ability of catalyst. As we all known, small zeolite had the properties of short pore and more and well accessible acid sites. More accessible acidity facilitated the cracking of interim product. Therefore, more LPG can be produced in CAT-SP catalyst. At the same time, compared with the CAT-R catalyst, the CAT-SP catalyst can increase aromatics by 3.89% and decrease olefins by 1.71% in the gasoline component, respectively. The suitable increase of aromatics and decrease of olefins showed that the produced gasoline was cleaner.

Table 3
The physicochemical properties of catalysts.

Catalyst	CAT-SP	CAT-R
Na_2O (wt.%)	0.09	0.10
RE_2O_3 (wt.%)	2.33	2.40
Pore volume ($cm^3\ g^{-1}$)	0.32	0.31
S_{BET} ($m^2\ g^{-1}$)	313	307
Attrite index (%)	1.3	2.4
MAT conversion (%)	54	56

Table 4
Production distribution of the prepared FCC catalysts.

Catalyst	CAT-SP	CAT-R
Produce distribution (wt.%)		
Dry gas	2.51	2.41
LPG	23.62	23.21
Propylene	8.22	8.14
C_5^+ gasoline	42.04	42.78
Diesel	16.56	16.43
Heavy oil	7.02	7.04
Coke	7.56	7.45
Conversion	75.73	75.84
Liquid yield	82.22	82.42
Light oil yield	58.60	59.21
Gasoline component (v%)		
Normal paraffin (N-P)	3.99	4.05
Iso-paraffin (I-P)	33.39	36.22
Olefin (O)	25.72	27.43
Naphthenes (N)	9.26	8.74
Aromatics (A)	27.45	23.56
Research octane number (RON)	94.9	95.5

3.4. Influence of ZSM-5 content on the propylene yield

In this part, small particle ZSM-5 zeolites were used in all catalysts. The relationship of ZSM-5 content and propylene yield is shown in Fig. 3. As can be seen from Fig. 3, the propylene yield increased with the increasing of ZSM-5 content. But when the content of ZSM-5 zeolite is too high, two aspects will be influenced. On one hand, the ability of heavy oil conversion decreased and the activity of catalyst reduced. On the other hand, the price of ZSM-5 zeolite is costly and influences the total price of catalyst. Therefore, the selectivity of suitable ZSM-5 content is very important. As shown in Fig. 3, the propylene yield is about 11% at suitable ZSM-5 content.

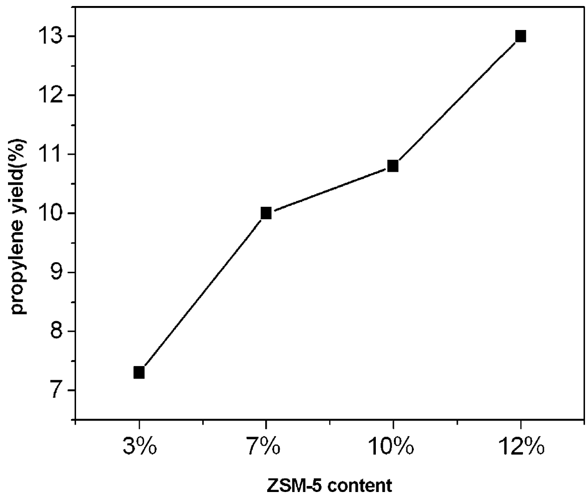

Fig. 3. The relationship of ZSM-5 content and propylene yield.

4. Conclusions

Two kinds of ZSM-5 zeolites, small particle and routine, were characterized and applied for fluid catalytic cracking of heavy oil. The two zeolites had similar physicochemical properties except the different particle size. Particle size of ZSM-5 zeolite was smaller and attrite index of corresponding catalyst was lower. More propylene and more clean gasoline can be obtained when the small particle ZSM-5 was used as a component of catalyst. The content of ZSM-5 zeolites influenced the ability of heavy oil conversion and propylene yield. The suitable content of ZSM-5 zeolites was helpful for the enhancement of propylene yield.

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