

High performance phosphorus-modified ZSM-5 zeolite for butene catalytic cracking

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Abstract—Phosphorus-modified ZSM-5 zeolites were prepared with a novel method, hydrothermal dispersion. XRD showed that the catalysts prepared by the hydrothermal dispersion had better hydrothermal stability than that by impregnation. At the same time, more pronounced cracking activity and higher yield of ethylene plus propylene were obtained on the phosphorus-modified ZSM-5 catalysts prepared by hydrothermal dispersion. Highest yield of ethylene plus propylene was obtained when the loading of phosphorus was 0.68%. The higher amount of phosphorus fixed on the pores of zeolite, higher hydrothermal stability and appropriate acid amount were the possible reasons for obtaining higher yield of ethylene plus propylene.

Key words: Butene Catalytic Cracking, Propylene, ZSM-5 Modification, Phosphorus, Hydrothermal Dispersion

INTRODUCTION

The light olefins (ethylene and propylene) are the important feedstock in the petrochemical industry [1,2]. At present, ethylene is primarily produced by steam cracking, and propylene is the main byproduct in this process. Another major source of propylene comes from the fluid catalytic cracking (FCC) reaction [3]. Recently, the demand for propylene has been increasingly growing, driven primarily by the high growth rate of the polypropylene industry [4]. The method of steam cracking or FCC reaction for producing ethylene and propylene cannot satisfy the fast growing demand. Therefore, new routes need to be developed to improve the output of ethylene and propylene.

In recent years, there has been an increasing interest in catalytic cracking of butene to produce ethylene and propylene over various zeolite catalysts, such as ZSM-5, ZSM-23, ZSM-48, MCM-22 and SAPO-34 [5-8]. These zeolites were found to have high selectivity and yield of propylene in butene catalytic cracking reactions. Among these zeolites, ZSM-5 zeolite exhibited the most outstanding properties for catalytic cracking because of the unique structure, thermal stability, acidity and shape selectivity [9]. Many elements, such as Fe, Cr, P and rare earth, have been utilized to modify ZSM-5 zeolite for the further enhanced activity [1,10-12]. It has been found that introducing phosphorus increased the attrition resistance of the catalyst particles and also increased the hydrothermal stability of the ZSM-5 zeolite. Therefore, many publications reported the modification of ZSM-5 zeolite with phosphorus for butene catalytic cracking [13,14]. In the case of ZSM-5 zeolite, phosphorus compounds interact with bridged OH groups, decreasing zeolite acidity and, consequently, catalytic activity and shape selectivity enhance.

As we all know, the existing key issue of industrialization of butene catalytic cracking is the low activity of catalysts. The phosphorus-modified ZSM-5 zeolite is often prepared by ion exchange or impregnation. However, the corresponding conversion and the yield of ethylene plus propylene are so limited that it is not realistic to promote the industrialization of butene catalytic cracking reaction. Therefore, the exploration of new method to enhance the activity of catalysts is very important. In this paper, a novel method, hydrothermal dispersion, was first developed and the catalysts prepared utilizing the new method were also tested for butene catalytic cracking. Compared with impregnation, the phosphorus-modified ZSM-5 zeolite prepared by hydrothermal dispersion showed far higher yield of ethylene plus propylene for butene catalytic cracking. The high activities of new prepared catalysts are hoped to promote the industrialization of butene catalytic cracking.

EXPERIMENTAL

1. Preparation of Modified ZSM-5

The ZSM-5 zeolites used in this work were obtained from the Catalyst Plant of Nankai University, China. The phosphorus element was loaded on the ZSM-5 zeolite by a hydrothermal dispersion method [15]. In a typical process, ZSM-5 was stirred with $(\text{NH}_4)_2\text{HPO}_4$ solution and reacted at 140 °C and 0.3 MPa for 2 h. Then, the mixture was filtered and dried at 100 °C for 8 h, calcined at 600 °C for 2 h in air to obtain the phosphorus-modified ZSM-5 zeolite, which was denoted as ZPS. The phosphorus-modified ZSM-5 zeolite obtained by impregnation at the same conditions was named as ZPI. The loadings of phosphorus and corresponding serial number are shown in Table 1. The prepared ZSM-5 zeolites were directly used as the catalyst of butene catalytic cracking.

2. Catalytic Cracking Tests

The experiments were carried out over the prepared ZSM-5 cata-

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lys in a fixed-bed micro-reactor at atmospheric pressure. Mixed C4 alkenes (n-butane: 6.68%, propylene: 1.69%, cis-2-butene: 50.54%, trans-2-butene: 40.38%) were used as feedstock. The amount of the catalyst used for the small-scale reaction was 0.6 g for each run. The catalyst was pressed into pellets and then broken into pieces and sieved to retain particles between 20–40 meshes. The catalysts were pre-treated with 100% steam at 873 K for 4 h and mixed C4 alkenes with nitrogen as a carrier gas were injected into the reactor. The products were analyzed on-line using a gas chromatograph (Varian 3700) equipped with a capillary column (50 m × 0.32 mm, aluminum column) and an FID detector. The flow rate of C4 alkene and nitrogen was 7.5 ml min⁻¹ and 5 ml min⁻¹, respectively. The reaction temperature was 600 °C.

3. Physicochemical Characterization

The X-ray fluorescence spectrum (XFS) 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 K α radiation with a Ni filter.

Textural properties were determined by N₂ 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.

FT-IR of pyridine adsorption was conducted by the FT-IR spectrometer (BIO-RAD, FTS3000) equipped with an in situ cell containing CaF₂ windows. The Brønsted and Lewis acid sites could be distinguished by the bands of chemisorbed pyridinium ion at different wavenumbers.

RESULTS AND DISCUSSION

1. XRD Analysis

XRD was carried out to investigate the possible structural changes in ZSM-5 zeolite. Phosphorus-modified ZSM-5 (ZPS) exhibited a diffraction pattern very similar to that of the unmodified sample (Fig. 1). The relative crystallinity was calculated according to the aggregate intensities of the three peaks at 2 θ of 23.07°, 23.28° and 23.90° [16]. The framework, the long range ordering and the microporous structure of ZSM-5 zeolites were preserved in the process of modification. The relative crystallinity of sample ZPS-1 was maintained at 98% (Table 1). As for the samples with higher loadings of phosphorus, the typical diffraction peaks for ZSM-5 zeolite could also be observed, despite that its relative crystallinity decreased. The pore of ZSM-5 zeolite was partly blocked in the presence of phosphorus, which resulted in the scatter of X-ray light and the decrease of relative crystallinity.

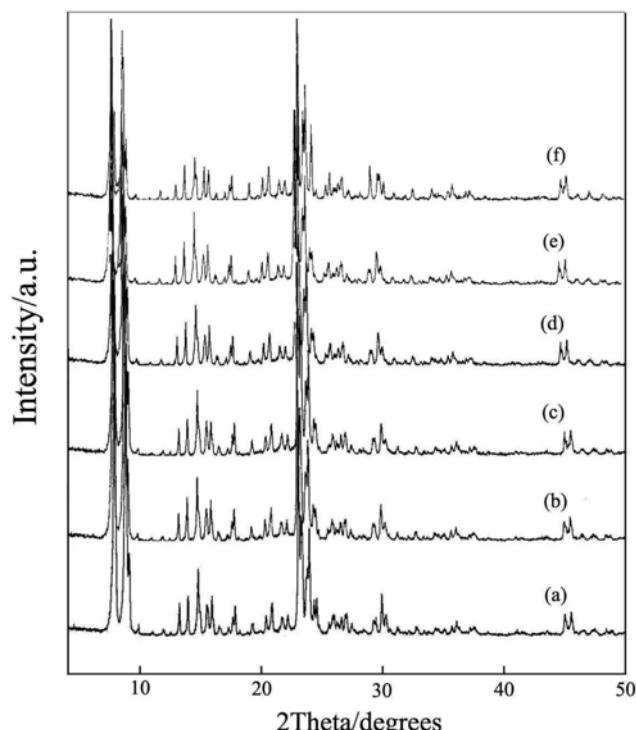


Fig. 1. XRD patterns of the prepared zeolites. Catalysts: (a) HZSM-5, (b) ZPS-0, (c) ZPS-1, (d) ZPS-2, (e) ZPS-3, (f) ZPI.

The zeolite was deactivated for 4 h at 800 °C in the presence of 100% steam. As shown in Table 1, the higher residual ratio of crystallinity was obtained on the ZPS zeolite than that on the ZPI and parent ZSM-5 zeolite, showing that the catalysts prepared by the hydrothermal dispersion method had better hydrothermal stability.

2. N₂ Adsorption/Desorption Characterization

Specific surface area and pore volume of P/HZSM-5 were investigated according to the nitrogen adsorption/desorption isotherms, and the corresponding data were summarized in Table 2. It could be seen from Table 2 that the BET surface area and pore volume decreased obviously with increasing the phosphorus loading. Similarly, suitable decrease of micropore surface area and micropore volume happened on the ZPS-0, ZPS-1 and ZPS-2 zeolites. 3% or even higher content of phosphorus will drastically reduce the micropore surface area and micropore volume of ZSM-5 zeolite, which may result from the blockage of channel by phosphorus covering on the surface of zeolite. These results showed a part of phosphorus entered the pore of ZSM-5 when the catalysts were prepared by hydrothermal method.

Compared with parent ZSM-5, the BET surface area decreased obviously on the ZPI. However, the micropore surface area was

Table 1. XRD and XRF results

| Sample | ZPS-0 | ZPS-1 | ZPS-2 | ZPS-3 | ZPI | ZSM-5 |
|--|-------|-------|-------|-------|------|-------|
| Loadings of phosphorus (wt%) (a) | 0.31 | 0.68 | 1.89 | 3.12 | 1.35 | - |
| Relative crystallinity (%) (b) | 86 | 84 | 76 | 64 | 78 | 86 |
| Relative crystallinity (%) (after 4h deactivation) (c) | 81 | 78 | 72 | 59 | 70 | 75 |
| Residual ratio of crystallinity (%) (d=c/b) | 94.2 | 92.8 | 94.7 | 92.2 | 89.7 | 87.2 |

Table 2. Textural properties of parent and phosphorus-treated ZSM-5 samples

| Samples | ZSM-5 | ZPS-0 | ZPS-1 | ZPS-2 | ZPS-3 | ZPI |
|--|-------|-------|-------|-------|-------|-------|
| S_{BET} (m^2g^{-1}) | 354.3 | 318.0 | 293.8 | 198.6 | 124.9 | 258.3 |
| S_{micro} (m^2g^{-1}) | 229.5 | 197.6 | 179.0 | 172.9 | 119.4 | 212.5 |
| V_{total} (cm^3g^{-1}) | 0.256 | 0.214 | 0.223 | 0.128 | 0.074 | 0.186 |
| V_{micro} (cm^3g^{-1}) | 0.116 | 0.099 | 0.091 | 0.100 | 0.069 | 0.104 |

almost no change. This indicated that most of phosphorus was dispersed on the surface of ZSM-5 when the catalysts were prepared by impregnation method.

3. FTIR Characterization

The Brønsted (B) and Lewis (L) acidities of the samples were determined by FT-IR spectroscopy after adsorption of pyridine. As shown in Fig. 2, all samples exhibited the characteristic bands at about 1,540 and 1,450 cm^{-1} when the desorption temperature was 200 $^{\circ}\text{C}$, which were attributed to pyridinium ions (pyridine chemi-

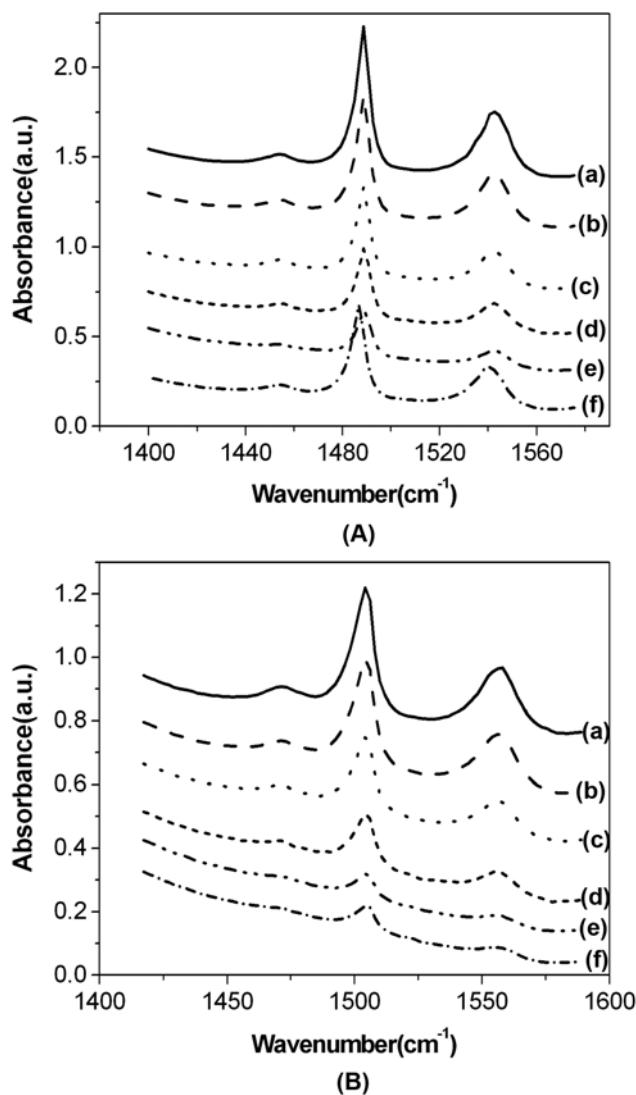


Fig. 2. FTIR spectra of the prepared zeolites at 200 $^{\circ}\text{C}$ (A) and 350 $^{\circ}\text{C}$ (B). Catalysts: (a) HZSM-5, (b) ZPS-0, (c) ZPS-1, (d) ZPS-2, (e) ZPS-3, (f) ZPI.

Table 3. Acidity properties of parent and phosphorus-treated ZSM-5 samples

| Sample | 200 $^{\circ}\text{C}$ | | 350 $^{\circ}\text{C}$ | |
|--------|--|--|--|--|
| | L acid sites (μmolg^{-1}) | B acid sites (μmolg^{-1}) | L acid sites (μmolg^{-1}) | B acid sites (μmolg^{-1}) |
| ZSM-5 | 69.9 | 790.8 | 51.6 | 435.8 |
| ZPS-0 | 71.4 | 707.2 | 43.9 | 405.5 |
| ZPS-1 | 71.4 | 474.4 | 42.1 | 251.5 |
| ZPS-2 | 46.2 | 245.1 | 29.9 | 155.9 |
| ZPS-3 | 21.7 | 198.2 | 13.3 | 54.5 |
| ZPI | 49.9 | 491.3 | 23.3 | 261.4 |

sorbed on Brønsted acid sites) and coordinatively bound pyridine (pyridine interacting with Lewis acid sites), respectively. However, the bands shifted to higher wavenumber when the desorption temperature was 350 $^{\circ}\text{C}$. The intensities of the bands at about 1,540 and 1,450 cm^{-1} were used to calculate the relative changes in the concentrations of acid sites, which are summarized in Table 3. The data showed that modification of ZSM-5 zeolites with phosphorus led to a significant decrease in the concentration of both Brønsted and Lewis acid sites at the same desorption. From Table 3, it also could be seen that in all samples, Brønsted (B) and Lewis (L) acid sites decreased with increasing desorption temperature (from 200 $^{\circ}\text{C}$ to 350 $^{\circ}\text{C}$). These results revealed that modification of ZSM-5 zeolites with phosphorus had weakened the acid strength, which agrees well with other literature [17].

4. Catalytic Cracking Performance Evaluation

The catalytic cracking performance of parent and phosphorus-modified ZSM-5 on C4 alkene conversion was investigated. Table 4 shows C4 alkene conversion and selectivity of ethylene and propylene, respectively. The results in Table 4 indicate that the catalytic cracking activity of the prepared ZPS was superior to the parent one and ZPI. The catalytic cracking activity of the catalysts changed with the loading content of phosphorus. The catalytic cracking activity first increased with the increase of the content of phosphorus and then decreased. The highest catalytic cracking activity was obtained over ZPS-1, and the corresponding conversion reached 96.17%. The selectivity of ethylene plus propylene over ZPS was also far higher than that over the parent one and ZPI. The highest catalytic cracking selectivity of ethylene plus propylene was obtained over ZPS-2 sample, and the value reach 90.41%.

Table 4. The conversion, selectivity and yield of ethylene plus propylene over P-modified ZSM-5 and parent ZSM-5 for butene catalytic cracking

| Catalysts | Conversion (mol%) | Selectivity (mol%) | | Yield (mol%) |
|-----------|-------------------|--------------------|--------------------|--------------|
| | | Ethylene+Propylene | Ethylene+Propylene | |
| ZSM-5 | 75.44 | 52.19 | 52.19 | 39.37 |
| ZPS-0 | 88.97 | 66.26 | 66.26 | 58.95 |
| ZPS-1 | 96.17 | 89.59 | 89.59 | 86.16 |
| ZPS-2 | 90.59 | 90.41 | 90.41 | 81.90 |
| ZPS-3 | 82.94 | 89.52 | 89.52 | 74.25 |
| ZPI | 88.25 | 53.26 | 53.26 | 47.00 |

Table 5. The relationship of conversion and yield with reaction time over the ZPS-1 catalyst

| Time (h) | Conversion (mol%) | Yield (mol%) |
|----------|-------------------|--------------|
| 2 | 96.17 | 86.16 |
| 50 | 94.36 | 83.67 |
| 100 | 91.09 | 81.24 |
| 200 | 85.63 | 77.38 |

The yield of ethylene plus propylene in C4 alkene catalytic cracking reactions over the catalysts is shown in Table 4. It can be seen there that the yields of ethylene and propylene over ZPS were apparently higher than those of parent ZSM-5 and ZPI. Especially for the ZPS-1 sample, the yields of ethylene plus propylene reached 86.16%. However, the corresponding value was 39.37% and 47.00% for the parent ZSM-5 and ZPI, respectively.

It can be seen from Table 3 and Table 4 that the acid amount decreased with increasing the phosphorus loadings, while the conversion and yield of ethylene plus propylene was first increased and then decreased. The cracking activity of catalyst was very weak when the acid amount was too low. However, the hydrogen transfer was excessive when the acid amount was too much. Therefore, suitable acid amount was suitable.

The stability of ZPS-1 catalyst was investigated (Table 5). The conversion decreased from 96.17% to 85.63%, and the yield changed from 86.16 to 77.38%. The results in Table 5 indicate that the catalyst showed good stability after 200 h run.

The conversion and selectivity, together with yield of ethylene plus propylene, showed the catalytic cracking performance of ZPS was superior to the other modified samples and the parent sample. The possible reason for this behavior is due to three aspects. First, XRD results confirmed that the catalysts prepared by the hydrothermal dispersion method had better hydrothermal stability. As we all know, butene catalytic cracking is performed at high temperature under steam environment. The stable framework structure of ZSM-5 is very important and helpful for prolonging the life of catalysts. At the same time, the higher residual ratio of crystallinity on the ZPS zeolite is helpful for the higher yield of ethylene plus propylene. Second, it was proven that phosphorus had been fixed in the pore of ZSM-5 over the ZPS prepared by hydrothermal dispersion [3]. However, most of phosphorus was only adsorbed on the surface of ZSM-5 as for ZPI catalyst. Phosphorus in the pores of ZSM-5 contacted with the reactants more effectively than that on the external surface. In addition, the suitable acid amount promoted the cracking of C4 alkenes and suppressed the hydrogen transfer. Therefore, it is reasonable that the catalysts prepared by hydrothermal dispersion had higher activity than that by impregnation. These total results show that hydrothermal dispersion is an effective method to synthesize the element-modified zeolite for butene catalytic cracking reaction.

CONCLUSIONS

Phosphorus-modified ZSM-5 zeolites were prepared by hydro-

thermal dispersion. The phosphorus added by this method had been preferentially preserved in the pores of ZSM-5 zeolite versus that added by impregnation. The corresponding hydrothermally-prepared catalyst showed higher conversion and yield of ethylene plus propylene because of stronger shape-selection capacity. The best result was obtained when the content of phosphorus in the ZSM-5 zeolite was 0.68%, where the yield of ethylene plus propylene reached 86.16%. At the same time, this catalyst showed excellent stability. The higher amount of phosphorus fixed on the pores of zeolite, higher hydrothermal stability and appropriate acid amount were the possible reasons for obtaining higher yield of ethylene plus propylene.

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