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Effect of phosphorus on HZSM-5 catalyst for C_4-olefin cracking reactions to produce propylene

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Abstract

A series of HZSM-5 catalysts with various phosphorus (P) loadings (0–2.1 wt%) were prepared by impregnation of phosphoric acid. The effect of phosphorus on the structure and acidity of HZSM-5 catalyst and its catalytic performance for C_4-olefin cracking reactions were studied by XRD, N_2 adsorption, NMR, NH_3-TPD, FTIR spectra of adsorbed pyridine, TGA, and catalytic tests. The results revealed that the structure of HZSM-5 samples was scarcely damaged with increasing P loadings, whereas strong acidity of them was weakened mainly due to the dealumination of tetrahedral framework aluminum (TFAL) after P modification. The results of C_4-olefin cracking reactions showed a great increment of the propylene selectivity for the P-modified HZSM-5 with the optimal propylene yield at a P-loading of 1.5 wt%. It was found that both coke deposition and dealumination were the crucial factors in the deactivation of HZSM-5. Due to the dealumination and thus elimination of part of the strong acid sites, P-modified HZSM-5 showed excellent anticoking ability. TFAL of P-modified HZSM-5 changed mainly to distorted tetrahedral aluminum (DTAL) or pentacoordinated aluminum (PAL) species in the process of C_4-olefin cracking reaction, which can still act as stable active centers for C_4-olefin cracking to produce propylene. Thus, P-modified HZSM-5 shows excellent stability. A possible reaction pathway for C_4-olefin cracking reactions has been proposed based on the reaction results.

Keywords: Cracking; Phosphorus; HZSM-5; C_4-olefin; Propylene

1. Introduction

Propylene is one of the most important basic chemical intermediates. It is produced primarily as a byproduct of petroleum refining and of ethylene production by steam cracking of hydrocarbon feedstock. The petrochemical industry is presently facing a major squeeze in propylene availability as a result of the increasing demand for propylene derivatives (e.g., polypropylene). The traditional methods for propylene production are not satisfactory to meet this increased demand. For example [1], the naphtha steam-cracking process, which produces about twice as much ethylene as propylene, is expensive due to the high capital investment and high cost of feedstock. Propylene also can be generated in FCC units, but its yield in this process is relatively low. On the other hand, the route for producing propylene from metathesis of ethylene and butylenes is an unengaging way, because it will consume the same highly valuable ethylene as the main feedstock. Consequently, there is a need for a high-yield propylene production method that can readily be integrated into a refinery or petrochemical plant, taking advantage of feedstock that is less valuable for the market place.

Zeolites, because of their outstanding thermal and hydrothermal stability, acidity, and shape selectivity, have been widely used in industrial processes [2–6]. Recently, there has been an increasing interest in catalytic cracking of mixed C_4- or C_5-olefin to produce propylene and ethylene over various zeolite catalysts, such as ZSM-5 [7–12], ZSM-48 [13], ZSM-23 [14], and MCM-22 [15]. These zeolites were found to have high se-

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lectivity and yield of propylene in C_4-olefin cracking reactions. However, because of the strong tendency of the polymerization of olefin-containing reactants and/or products on the acidic catalysis, one of the most crucial problems for such reaction is catalyst deactivation. Unfortunately, to date, few papers [11] have been published on effective methods for prolonging the stability of zeolites in C_4-olefin cracking, especially when the water vapor exists in feed gas. On the other hand, the effects of P on the catalytic properties of zeolite have attracted much research [16–20], and it has been proved that P modification would be an effective method to elevate the hydrothermal stability of ZSM-5. To the best of our knowledge, the role of P in the catalytic cracking of C_4-olefin to produce propylene over ZSM-5 catalysts is still seldom reported so far.

In this study, a series of P-modified HZSM-5 samples were prepared and well characterized by various methods, and these samples were used in C_4-olefin cracking reactions. The main physical–chemical properties of these fresh catalysts and used catalysts (downloaded from the reactor after 53 h of TOS) were compared, with the aim of analyzing the role of P in C_4-olefin cracking reactions to produce propylene over ZSM-5. The results showed that P-modified HZSM-5 was an excellent catalyst due to its fine stability and high selectivity in the production of propylene. The correlation between their physicochemistry and catalytic properties was discussed, and the possible reaction pathway for C_4-olefin cracking reactions on such catalyst was proposed based on the reaction results.

2. Experimental

2.1. Catalyst preparation

ZSM-5 zeolite with SiO_2/Al_2O_3 molar ratio of 40 was synthesized hydrothermally in a stainless steel autoclave with the capacity of 100 ml. Tetrapropylammonium bromide (TPABr) was used as the template. In one typical run for the synthesis of ZSM-5, the aluminum source $Al_2(SO_4)_3\cdot 18H_2O$ was added into the mixture containing quantitative distilled water, NaOH, and TPABr under stirring. Then quantitative colloidal silica (40% SiO_2) was added. After being aged at room temperature for 2 h, the mixture was transferred into an autoclave and crystallized at 100–150 °C for 1–3 days. The products were filtered, washed, and dried at 120 °C in air for 10 h and then calcined at 600 °C for 3 h. Activation of zeolite sample was performed by repeated ion exchange with 5 wt% NH_4NO_3 solutions to obtain its ammonium form (i.e., NH_4ZSM-5). The mixture of 50 wt% NH_4ZSM-5 was extruded with 50 wt% SiO_2 and then calcined at 600 °C for 3 h, thereby obtaining the HZSM-5 catalyst. The P-modified HZSM-5 samples with various P contents were prepared by impregnating 20 g of HZSM-5 into 20 ml of aqueous solution containing desired amount of phosphoric acid, followed by drying at 50 °C for 24 h under vacuum and 120 °C for 4 h, and finally calcination at 600 °C for 3 h. The parent HZSM-5 was denoted as HZ, and P-modified HZSM-5 samples that contained x wt% ($x = 0-2.1$) of phosphorus were denoted as xPZ.

2.2. Catalysts characterization

The crystallinity of the samples was determined on a Rigaku D/max 400 X-ray diffractometer with Ni-filtered CuK_α radiation. The surface areas of the samples were analyzed by a multipoint N_2 adsorption–desorption method at liquid-N_2 temperature (77 K) with a Micromeritics TriStar 3000 surface area analyzer. The acidic properties (Brönsted and Lewis acid sites) of the samples were investigated by FTIR of adsorbed pyridine in an in situ cell with CaF_2 windows. Self-supported sample discs with weight of ca. 12 mg and radius 2.0 cm were activated at 300 °C for 4 h under 10^{-2} Pa. Pyridine vapors were admitted to the cell after the self-supported wafers were cooled to room temperature. Then excess pyridine was desorbed by evacuation of the samples at the desired temperature for 30 min, and the spectra were recorded on a Bruker IFS 88 spectrometer with a resolution of 4.0 cm^{-1}. NH_3-TPD was carried out on a conventional setup equipped with a thermal conductivity detector. A 50-mg sample of 20–40 mesh particle size was first flushed with He gas flow (25 ml min^{-1}) at 600 °C for 1 h, then cooled to room temperature. Ammonia was adsorbed at 30 °C in a He gas stream containing 9 vol% of NH_3. After flushing with He at 100 °C to remove the weakly absorbed ammonia at this temperature, NH_3-TPD was promptly started at a heating rate of 10 °C min^{-1} from 100 to 600 °C. The desorbed ammonia was detected on the TCD and then trapped in a 0.01 N H_2SO_4 aqueous standard solution. The amount of trapped ammonia was determined by titrating the excess of H_2SO_4 in the NH_3-trapped solution with a 0.01 N standard NaOH solution to estimate the total acid quantity quantitatively. ^{29}Si MAS NMR was recorded with tetramethylsilane as the reference at 79.49 MHz with pulse length of 2 μs (45°) and pulse interval of 80 s. ^{31}P MAS NMR was recorded with 85% phosphoric acid as the reference at 161.98 MHz with pulse length of 3 μs (60°) and pulse interval of 60 s. ^{27}Al NMR was carried out with $Al(H_2O)_6^{3+}$ as the reference at 104.26 MHz, with the pulse of 0.5 μs ($<\pi/12$), and pulse interval of 60 s. All of the data were acquired at a spinning speed of 4 kHz. The coke content of the used catalysts was determined by combustion in a thermogravimetric analyzer. The temperature was raised from 80 to 700 °C with the ramp rate of 10 °C min^{-1}. The weight loss between 350 and 700 °C was recorded as coke content.

2.3. Catalytic testing

C_4-olefin, obtained from Shanghai Petrochemical Company, was used as reactants without further purification. The feedstock consists of 0.1 wt% of propylene, 3.7 wt% of isobutane, 12.6 wt% of n-butane, 19.5 wt% of *trans*-2-butylene, 50.9 wt% of 1-butene, 13.0 wt% of *cis*-2-butene, and 0.2 wt% of 2-methyl-2-propene. The cracking of C_4-olefin test was carried out in a continuous-flow fixed-bed system with a stainless steel tubular reactor (∅10 mm × 530 mm) equipped with a laboratory-scale piston pump for C_4-olefin input. To ensure that the feedstock existed in liquid state in piston pump, the exit pressure of the piston pump was set at about 808 kPa by adjusting the needle-like valve. After flowing through the valve, the feedstock changed to a gaseous state before entering the reactor by decreasing the pressure to atmospheric pressure. The amount of catalyst was 2.0 g. The reaction was conducted at preset temperatures under atmospheric pressure. Before the experiments, the catalyst was heated in situ at a ramp rate of 5 °C min^{-1} to reaction temperature in a N_2 flow (100 ml min^{-1}) and maintained at this temperature for 2 h. Then the N_2 was switched to C_4-olefin feed mixtures at weight hourly space velocity (WHSV) of 3.2 h^{-1}. The output products were analyzed online via an HP 4890 gas chromatograph equipped with a flame ionization detector (FID). The conversion of C_4-olefin and the selectivity and yield of the products were calculated by the following equations:

$$\text{conversion} = \frac{(W_{C_4^=})_0 - (W_{C_4^=})_t}{(W_{C_4^=})_0} \times 100\%, \tag{1}$$

$$\text{selectivity} = \frac{(W_{C_n})_t}{(W_{C_4^=})_0 - (W_{C_4^=})_t} \times 100\%, \tag{2}$$

$$\text{yield} = \text{conversion} \times \text{selectivity}. \tag{3}$$

Here $(W_{C_4^=})_0$, $(W_{C_4^=})_t$, and $(W_{C_n})_t$ represent the weight percentages of C_4-olefin in the reactants, of C_4-olefin in the products, and of C_n olefins or alkanes in the products, respectively.

3. Results and discussion

3.1. *Effect of P on the structure of the catalyst*

The XRD patterns (not shown here) indicated that parent HZSM-5 sample was a typical material corresponding to the MFI structure [21]. For HZ- and P-modified samples, a very broad peak in the range of 18–28° can be seen due to the addition of amorphous SiO_2 binder when catalysts were extruded. The framework structure of HZSM-5 was well maintained, and no peak of impurities could be detected after P modification, even at P loadings of 2.1 wt%. Also, the patterns of P-modified samples were of relatively lower intensity due to the decreased crystallinity of P-modified HZSM-5. The crystallinity loss of P-modified samples was calculated with parent HZSM-5 as the reference and were approximately 4.9% for 0.6PZ, 8.2% for 1.5PZ, and 16.1% for 2.1PZ. The decreased XRD crystallinity of the P-modified samples is most likely due to the framework defects caused by dealumination, as demonstrated in ^{29}Si MAS NMR and ^{27}Al MAS NMR spectra (Figs. 1 and 2), during the process of P modification.

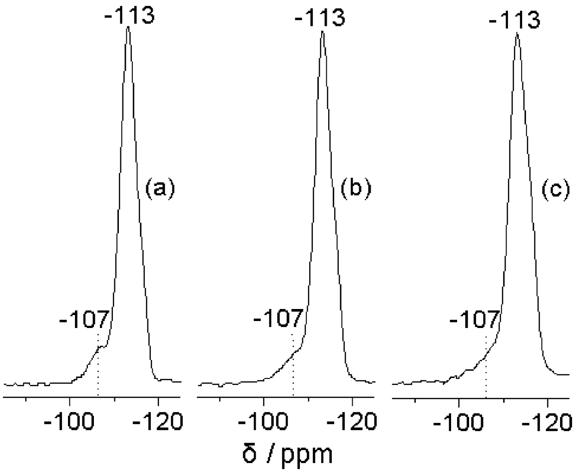


Fig. 1. ^{29}Si MAS NMR of parent and P-modified HZSM-5: (a) HZ, (b) 1.5PZ, and (c) 2.1PZ.

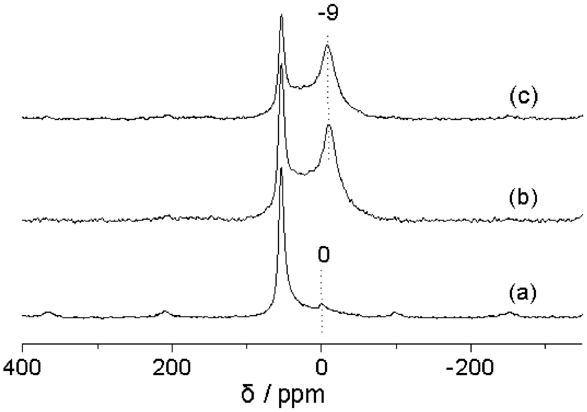


Fig. 2. ^{27}Al MAS NMR spectra of parent and P-modified HZSM-5: (a) HZ, (b) 1.5PZ, and (c) 2.1PZ.

Fig. 1 shows the ^{29}Si MAS NMR spectra of parent and P-modified samples. HZ shows two overlapping signals at the chemical shifts of −107 and −113 ppm. The band at −113 ppm was assigned to Q^4 [$Si(OSi)_4$] species, and the band at −107 ppm was assigned to silicon-oxygen tetrahedron (SiO_4) surrounded by three SiO_4 and one aluminum–oxygen tetrahedron (AlO_4^-), normally denoted as Si (3Si, 1Al) [22]. The intensity of the signal at −107 ppm decreased with increasing P loading. The decreased intensity of the signal at −107 ppm of the P-modified samples can be attributed to dealumination and/or to the insertion of the phosphorus group into the framework, thus resulting in the lack of the SiO_4 with adjacent AlO_4^-.

^{27}Al MAS NMR has been extensively used as an effective technique to identify states of the aluminum atoms in zeolites, such as framework aluminum atoms in tetrahedral coordination (TFAL) and extra-framework aluminum atoms in octahedral or pentacoordination (EFAL) [23–26]. ^{27}Al MAS NMR spectra of parent and P-modified HZSM-5 samples after calcination at 600 °C are shown in Fig. 2. For the HZ sample, a strong signal assigned to TFAL can be seen clearly at 53 ppm. A weak resonance at 0 ppm also can be observed, indicating the existence of a small quantity of EFAL atoms in HZ catalysts. When HZSM-5 zeolite was modified with certain amounts of P, a new broad peak at −9 ppm appeared. It is well known that classical hydrated octahedral Al in extra-framework appears at 0 ppm, so the peak at −9 ppm can be attributed to octahedral Al attached to phosphorus atom. With increasing P loadings, the peak at −9 ppm became stronger while that at 53 ppm became weaker, indicating that the introduction of P resulted in the dealumination of TFAL in the HZSM-5 framework.

Fig. 3 shows the ^{31}P MAS NMR spectra of P-modified HZSM-5 samples. As shown in Fig. 3, the ^{31}P MAS NMR spec-

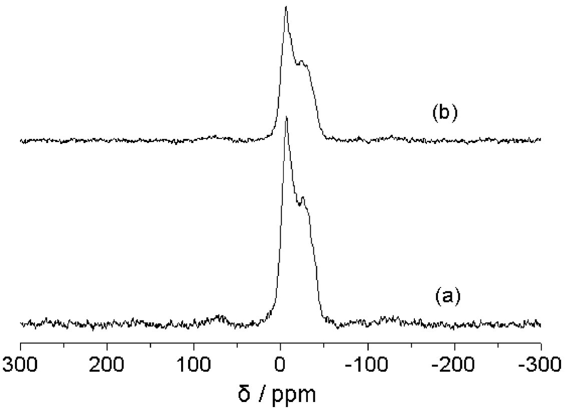


Fig. 3. ^{31}P MAS NMR spectra of P-modified HZSM-5: (a) 1.5PZ and (b) 2.1PZ.

tra obtained from P-modified HZSM-5 samples (1.5 and 2.1PZ) exhibited two major resonance peaks with chemical shifts of about -6 and -30 ppm, which have been attributed to $H_4P_2O_7$ or pyrophosphate and $AlPO_4$ or $(SiO)_xAl(OP)_{4-x}$ species, respectively [19,27]. For both 1.5PZ and 2.1PZ, the intensity of the signals at -6 ppm was stronger than that of the signals at -30 ppm, indicating that P existed mainly as $H_4P_2O_7$ or pyrophosphate species in P-modified HZSM-5.

The textural properties of parent and P-modified HZSM-5 samples are listed in Table 1. The results indicate that the specific surface area (BET and Langmuir surface area), microporous surface area (A_M) and microporous volume (V_M) of P-modified HZSM-5 all decreased with increasing P loadings, which could be attributed to the overlay or destruction of some micropores in HZSM-5 during the process of P modification. The average pore size increased with increasing P loading, probably implying the generation of the mesopores due to the dealumination and/or to the washing out of the amorphous species in the HZSM-5 crystals during P modification. Obviously, the production of the larger pores would be more helpful for the diffusion of feed gas and product molecules.

Table 1
Textural properties of parent and P-modified HZSM-5[a]

Catalysts	A_{BET} ($m^2\,g^{-1}$)	A_L ($m^2\,g^{-1}$)	A_M ($m^2\,g^{-1}$)	V_M ($m^2\,g^{-1}$)	PD_{AA} (nm)
HZ	215	305	122	0.060	5.4
0.6PZ	193	273	114	0.056	6.5
0.9PZ	177	248	110	0.054	6.4
1.5PZ	172	242	109	0.053	6.7
2.1PZ	162	228	105	0.052	6.8

[a] A_{BET}: BET surface area; A_L: Langmuir surface area; A_M: micropore area; V_M: micropore volume; PD_{AA}: adsorption average pore diameter (4V/A by BET).

3.2. *Effect of P on the acidity of the catalyst*

Fig. 4 illustrates the temperature-programmed desorption of ammonia (NH_3-TPD) of parent HZSM-5 and P-modified HZSM-5 samples. The parent HZSM-5 shows a typical NH_3-TPD spectrum with two maximum peaks at 220 and 400 °C, corresponding to NH_3 eluted from the weak and strong acid sites, respectively. After the introduction of P, the intensity of

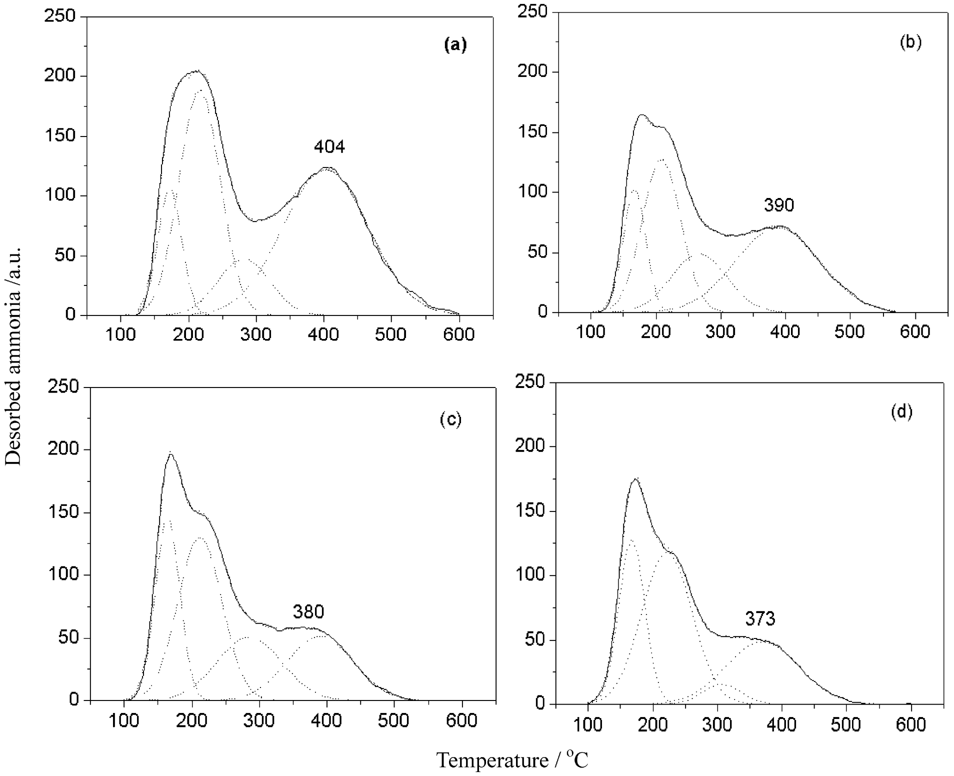


Fig. 4. NH_3-TPD profiles of parent and P-modified HZSM-5: (a) HZ, (b) 0.6PZ, (c) 1.5PZ, and (d) 2.1PZ ((—) for experimental spectra and (···) for deconvoluted results).

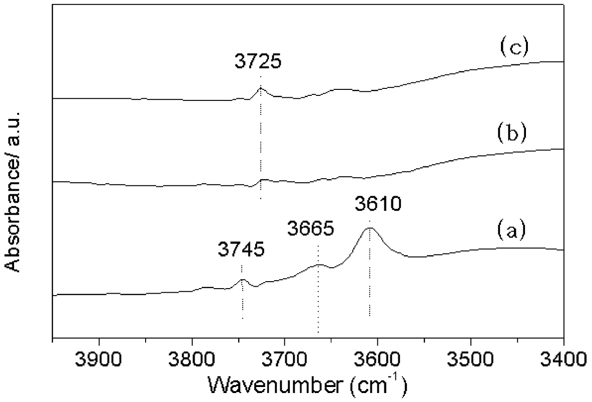


Fig. 5. FTIR spectra of parent and P-modified HZSM-5 samples in the region of hydroxyl group: (a) HZ, (b) 1.5PZ, and (c) 2.1PZ.

the high-temperature peak decreased and shifted toward low temperature (Fig. 4b). The more P introduced, the greater the reduction of the temperature and the intensity of the peak at high temperature, indicating decreased concentration and strength of strong acid sites caused by the introduction of P.

Table 2
Acidity properties of ZSM-5 and P-modified ZSM-5 samples

Desorption temperature (°C)	Brönsted acid sites ($\sim$1540 cm^{-1}) (a.u.)			Lewis acid sites ($\sim$1450 cm^{-1}) (a.u.)		
	HZ	1.5PZ	2.1PZ	HZ	1.5PZ	2.1PZ
100	1.10	0.71	0.41	0.69	0.24	0.23
150	1.06	0.30	0.22	0.39	0.09	0.07
200	1.01	0.19	0.14	0.32	0.04	0.04
250	0.96	0.14	0.04	0.28	–	–
300	0.82	0.10	–	0.24	–	–

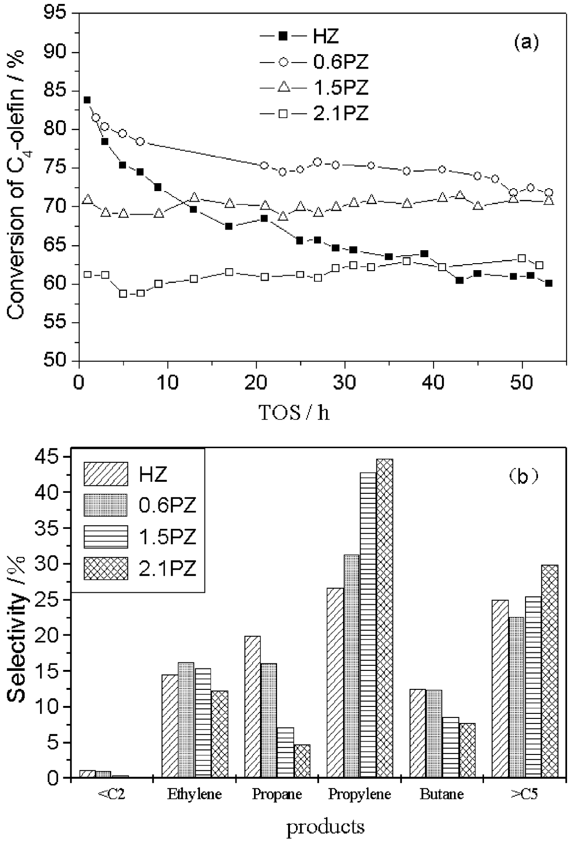


Fig. 6. Conversion of C_4-olefin (a) and initial selectivity of products (b) over parent and P-modified HZSM-5.

The changes in zeolite acidity resulting from P modification can also be reflected in the bridging hydroxyl groups of the zeolite. Fig. 5 shows the FTIR spectra of parent and P-modified HZSM-5 samples in the region of hydroxyl groups (OH) vibration. As shown, the spectrum of parent HZSM-5 had three bands at 3745, 3665, and 3610 cm^{-1}, corresponding to nonacidic external silanol groups, hydroxyl groups bonded to extra-framework alumina, and acidic bridging hydroxyls, respectively [28,29]. The modifications of phosphoric acid resulted in an obvious variation in the OH region of IR spectra. The intensity of these bands significantly decreased or disappeared after P modification, indicating that phosphoric acid interacts with both the acidic and nonacidic hydroxyl groups. It is generally accepted that strong acid sites are relate to TFAL in zeolite. In essence, strong acid sites come from the bridging hydroxyl group between a silicon atom and an aluminum atom, which can be observed by IR spectroscopy in the range of hydroxyl groups vibration (e.g., at $\sim$3610 cm^{-1} generally). From Fig. 5, it can be seen that the band at $\sim$3610 cm^{-1} decreased greatly with increasing P loadings, indicating a trend toward decreased strong acid sites after P modification. Notably, a new band at $\sim$3725 cm^{-1} appeared with the introduction of P and became the strongest peak at a P loading of 2.1 wt%. This band can be assigned to the interaction of the oxygen in silanol group with a lateral electron pair acceptor site [30]. The acidity of parent and P-modified HZSM-5 samples were measured using FTIR spectroscopy and pyridine as a probe molecule. All samples exhibited the characteristic bands at about 1540 and 1450 cm^{-1}, which are attributed to pyridinium ions (pyridine chemisorbed on Brönsted acid sites) and coordinatively bound pyridine (pyridine interacting with Lewis acid sites), respectively [31,32]. The intensities of the bands at $\sim$1540 and $\sim$1450 cm^{-1} were used to calculate the relative changes in the concentrations of acid sites, which are summarized in Table 2. The data show that modification with 1.5 wt% P led to a significant decrease in the concentration of both Brönsted and Lewis acid sites at the same desorption temperature, whereas further increasing P loadings to 2.1 wt% resulted in a further decrease in the concentration of the Brönsted acid sites but a slight decrease in the concentration of the Lewis acid sites. From Table 2, it also can be seen that in all samples, Brönsted and Lewis acid sites decreased with increasing desorption temperature (from 100 to 300 °C); however, the acid sites in the P-modified HZSM-5 samples decreased more quickly than those in the parent HZSM-5. The results reveal that P modification has weakened the acid strength of HZSM-5, which agree well with the results of NH_3-TPD characterization.

3.3. *Effect of P on the catalytic performance of the catalyst*

C_4-olefin cracking activities over parent and P-modified HZSM-5 samples as a function of time on stream (TOS) are shown in Fig. 6a. In the case of HZ, the activity of C_4-olefin cracking reaction decreased obviously with the TOS. The conversion of C_4-olefin over HZ decreased from an initial ∼84 to ∼60% after 53 h of TOS. Compared with HZ, although P-modified HZSM-5 catalysts showed lower initial activity of C_4-olefin cracking with increasing the P content, their stability was improved significantly, and 1.5PZ and 2.1PZ had even higher activity than their parent HZSM-5 after about 10 and 40 h, respectively. Fig. 6b shows the product distributions over the parent and P-modified HZSM-5 samples; it can be seen that the primary products of all catalysts are ethylene and propylene, and the byproducts include methane and ethane (denoted as <C2), propane, butane, aromatics and C_{5+} paraffin and olefins (denoted as >C5). These results indicate that the reaction of C_4-olefin over HZSM-5 samples is a very complicated process. Besides the main cracking reaction, oligomerization, isomerization, aromatization, and hydrogen transfer reactions also have occurred over these samples. Fig. 6b also shows that the product selectivity over these samples differed greatly. The initial selectivity of propylene increased obviously over P-modified catalysts; meanwhile, the selectivity of propane decreased with increasing P loading. Our previous research [13] showed that the strong acid sites play a key role in the reaction of C_4-olefin cracking. Thus, parent HZSM-5 had the highest initial conversion of C_4-olefin for its largest number of strong acid sites. The addition of P into HZSM-5 zeolite modified its acidic property and hence exerted a significant effect on catalytic performance. P modification on HZSM-5 not only decreased its concentration of strong acid sites, but also weakened its acid intensity (cf. Fig. 4). As a result, the decreased concentration of strong acid sites resulted in a decrease in C_4-olefin conversion, whereas the weakening of the intensity of strong acid sites resulted in the increment of propylene selectivity because of the low reactivity of relatively weak acid sites on hydrogen transfer reactions (e.g., propylene hydrogen transfer to propane).

Considering that C_4-olefin cracking reactions were usually carried out under the coexistence of the feed gas and water vapor, the hydrothermal stability of catalyst samples would be very important. To investigate the hydrothermal stability of parent and P-modified HZSM-5, both HZ and 1.5PZ samples were treated with 100% steam in situ at 600 °C for 4 h before C_4-olefin cracking reactions were conducted. The conversion of C_4-olefin as function of TOS over HZ, steam-treated HZ (St-HZ), 1.5PZ, and steam-treated 1.5PZ (St-1.5PZ) are compared in Fig. 7. It can be seen that St-HZ showed a lower initial conversion of C_4-olefin (∼65%) than HZ (∼84%), but St-1.5PZ and 1.5PZ had almost the same conversion (∼71%) in C_4-olefin cracking reactions. The results indicate that P modification could enhance the hydrothermal stability of HZSM-5 significantly. The reason could be that existence of the P species stabilizes the MFI zeolite structure by preventing the segregation of the FAL atoms during the steaming treatment, which has been proved previously [19,20]. It is well known that strong acid sites were related to TFAL in zeolite. To investigate the hydrothermal stability of HZM-5 and P-modified HZSM-5, acidity data for the same samples were obtained by NH_3-TPD and the acid–base titrating method after hydrothermal treatment. It was found that St-HZ retained only about 28% of the strong acid sites but St-1.5PZ retained about 64% of the strong acid sites after hydrothermal treatment. These results prove that P modification enhanced the hydrothermal stability of the HZSM-5 sample.

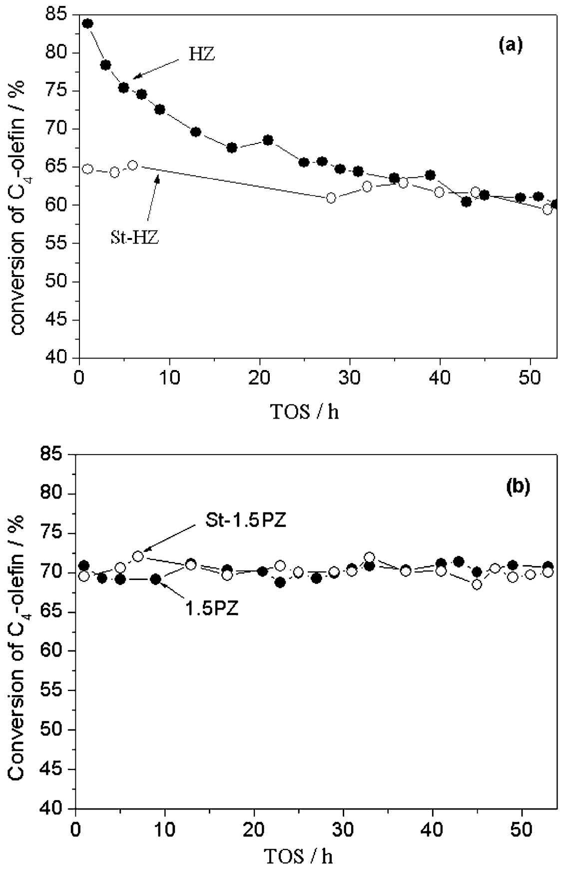


Fig. 7. Conversion of C_4-olefin as function of TOS over HZ and steamed HZ (a) and 1.5PZ and steamed 1.5PZ (b).

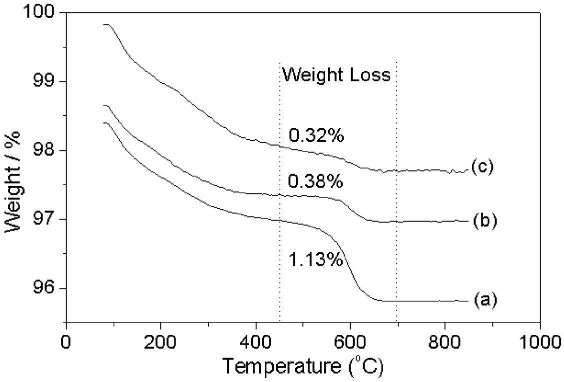


Fig. 8. TGA curves of used catalysts (after 53 h of TOS): (a) HZ, (b) 0.6PZ, and (c) 1.5PZ.

To further investigate why P-modified HZSM-5 has excellent stability for C_4-olefin cracking to produce propylene, all of the used catalysts were collected and characterized after 53 h of TOS. Thermogravimetric analysis (TGA) of these collected catalysts was conducted under the same conditions; the TGA curves are depicted in Fig. 8. The weight loss of used HZ at 450–700 °C, due to the burning-off the coke, was about 1.13 wt%. Whereas for 0.6PZ and 1.5PZ samples, the weight

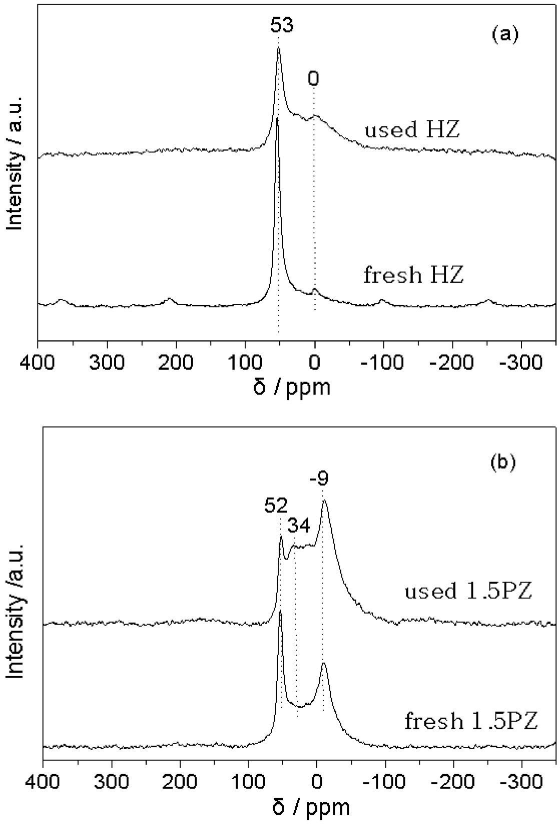


Fig. 9. Comparison of ^{27}Al MAS NMR of fresh and used HZ (a) and 1.5PZ (b) after 53 h of TOS.

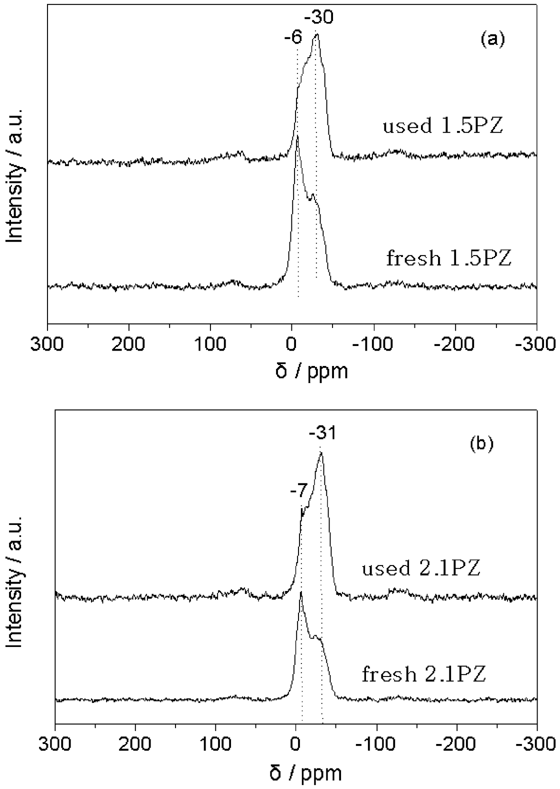


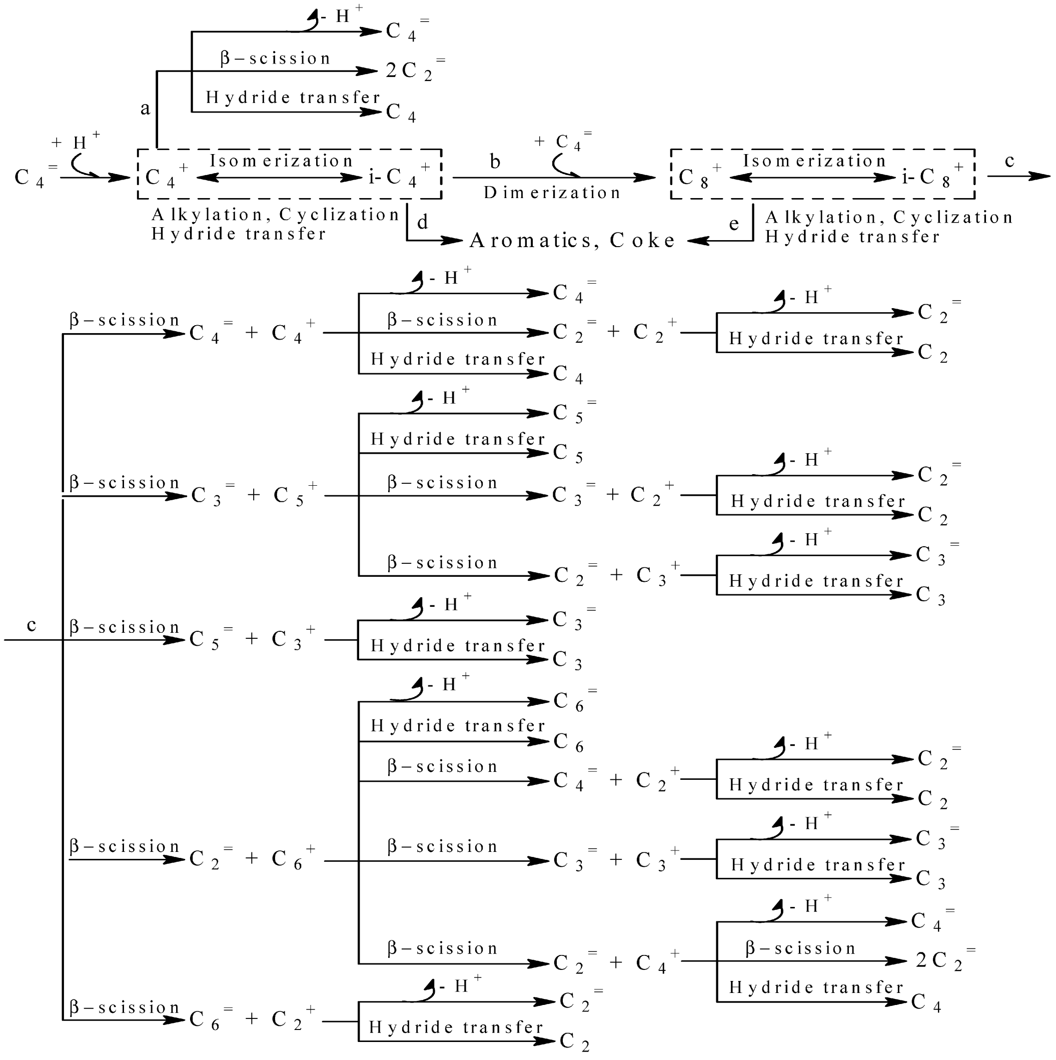
Fig. 10. Comparison of ^{31}P NMR of fresh and used P-modified HZSM-5 catalysts (after 53 h of TOS): (a) 1.5PZ, (b) 2.1PZ.

loss within the same temperature range decreased to 0.38 and 0.32 wt%, respectively. Considering that coke deposition is usually a main reason for the deactivation of acidic catalyst [13,33], the enhanced anticoking ability on P-modified HZSM-5 may be responsible for its high stability during the C_4-olefin cracking reaction. Combining this with the results of acidity and structure characterization could indicate that the enhanced anticoking ability on P-modified HZSM-5 can be attributed to dealumination and thus elimination of part of the strong acid sites in HZSM-5. P-modified HZSM-5 samples presenting a lower number of acid sites did not favor the bimolecular reactions involved in coke formation, and thus showed enhanced anticoking ability.

^{27}Al MAS NMR of these used catalysts was also conducted. To avoid the NMR-invisible aluminum, all samples were hydrated completely before NMR testing. This hydration can enhance the symmetry of the electric field at the aluminum nuclei, and thus reduce the quadrupole coupling constant and render all framework aluminum nuclei visible by NMR [34,35]. The results of ^{27}Al MAS NMR of the fresh and used catalysts are compared in Fig. 9. Compared with fresh HZ, the used HZ showed a relatively low TFAL peak at ∼53 ppm and a high octahedral EFAL peak at ∼0 ppm (Fig. 9a). Combining this result with that of C_4-olefin cracking reactions depicted in Fig. 8a clearly shows that along with coke deposition, dealumination is another major reason for the deactivation of HZSM-5 in the C_4-olefin cracking reaction. For the zeolite after P modification (e.g., 1.5PZ in Fig. 9b), although the used catalyst also showed weakened resonance at 52 ppm after 53 h of TOS, the 1.5PZ showed almost no deactivation during the course of the C_4-olefin cracking reaction (cf. Fig. 6a), implying that besides TFAL, probably there are other active aluminum species for C_4-olefin cracking reactions. In Fig. 9b, a broad signal at about 34 ppm appeared in the used 1.5PZ sample after 53 h of TOS, which may be assigned to distorted tetrahedral aluminum (DTAL) or pentacoordinated aluminum (PAL) species [20,36]. Because 1.5PZ showed no deactivation despite the decreased TFAL, it can be deduced that these new DTAL or PAL species also may be the active centers for the C_4-olefin cracking reaction. The ^{31}P MAS NMR results for fresh and used P-modified HZSM-5 (1.5 and 2.1PZ) are compared in Fig. 10. The figure clearly shows that after 53 h of TOS, the signals at −6 ppm attributed to P in pyrophosphoric acid or terminal groups of polyphosphates nonattached to Al decreased significantly, while the signals at about −30 ppm ($AlPO_4$ or $(SiO)_xAl(OP)_{4-x}$ species) obviously increased. These results further show that phosphorus interacts with aluminum during the course of C_4-olefin cracking reactions.

To investigate the possibility of long-run testing of the P-modified catalyst, the catalytic test was carried out for 860 h TOS. The results, shown in Fig. 11, indicate that the 1.5PZ catalyst demonstrated remarkable stability and high selectivity of propylene, indicating that P-modified HZSM-5 could be a promising catalyst for the industrial process of C_4-olefin cracking to produce propylene.

There are no major disputed issues regarding the mechanism of olefin cracking over solid acidic catalysts. It is gen-



Scheme 1. Reaction pathway of C_4-olefin cracking to produce propylene over HZSM-5.

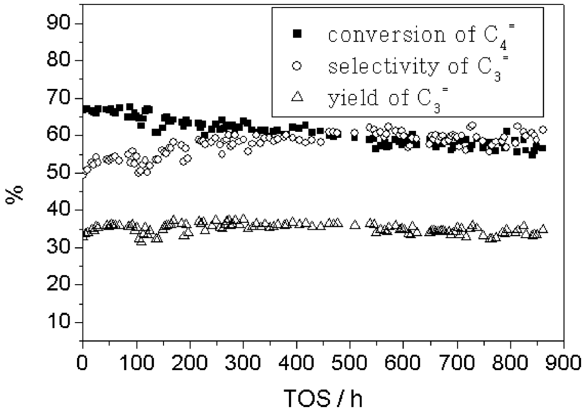


Fig. 11. Results of long-term test of 1.5PZ in C_4-olefin cracking reactions. Reaction conditions: $T = 500\,^\circ\text{C}$, WHSV $= 3.2\ \text{h}^{-1}$, $W_{H_2O}/W_{\text{feedstock}} = 2.0$.

erally agreed that the active centers in these reactions are Brönsted acidic centers on the catalyst surface and that the reactive species are carbenium [37]. Scheme 1 shows the possible reaction pathway of C_4-olefin cracking over HZSM-5. For a monomolecular mechanism, a C_4-olefin ($C_4^=$) molecule obtains a H^+ from HZSM-5 catalyst to produce a C_{4+} carbenium, which immediately isomerizes to a dynamic balance. Then, along path (a), C_{4+} converts to ethylene ($C_2^=$) and butane (C_4) by β-scission and a hydride transfer reaction. Generally, formation of ethylene from butylene is energetically less favorable, because it involves the formation of primary carbenium ion. But because of the small pores of ZSM-5, the electrical field in the pores is larger, and a relatively large interaction between the catalyst and the adsorbed carbenium ions exists [38,39]. However, the monomolecular mechanism cannot clearly explain the high amount of propylene ($C_3^=$) in the reaction products on both parent HZSM-5 and P-modified HZSM-5 catalysts. Thus, it can be deduced that a bimolecular mechanism (along way (b) to (c))—that is, a dimerization–β-scission mechanism—should be a dominant process under such reaction conditions. Two $C_4^=$ molecules first dimerize to an unstable C_8 unit, and then convert to $C_2^=$, $C_3^=$, $C_4^=$, $C_5^=$, and $C_6^=$ by β-scission (along way (c)). C_2, C_3, C_4, C_5, and C_6 formed through hydride transfer reactions from their corresponding carbenium ions. Moreover, aromatics and cokes form by alkylation, cyclization, and hydride transfer reactions along way e. According to this reaction scheme, dimerization–β-scission should produce equal amounts of $\sum C_3$ and $\sum C_5$ and also equal amounts of $\sum C_2$ and $\sum C_6$. However, it was observed that $\sum C_3 > \sum C_5$ and $\sum C_2 > \sum C_6$, indicating that secondary cracking reactions are more likely to occur with the larger C_5- and C_6-carbenium ions. Bimolecular mechanism can explain the high amount of $C_3^=$ in the reaction mixtures. To obtain $C_3^=$ with high selectivity in C_4-olefin cracking reactions, according to this reaction network, the hydride transfer reaction must be restrained. P modification can decrease the concentration and weaken the strength of the acid sites in HZSM-5, thus weakening its action in hydride transfer reactions. Thus, high selectivity of propylene in C_4-olefin cracking reactions was obtained over P-modified HZSM-5.

4. Conclusion

A series of catalysts for C_4-olefin cracking to produce propylene were prepared by impregnating the HZSM-5 in different amount of phosphoric acid, followed by calcination in air at high temperature. XRD patterns showed that the structure of zeolite framework was scarcely damaged after P modification. NH_3-TPD and IR spectra indicated decreased acidity in the P-modified HZSM-5. The modification also resulted in dealumination of the HZSM-5 framework. The introduction of a suitable amount of phosphorus into HZSM-5 zeolite can improve its catalytic performance in the cracking of C_4-olefins. Both coke deposition and dealumination were the crucial causes of HZSM-5 deactivation. It was found that P modification could enhance the catalyst's anticoking ability in C_4-olefin cracking reactions, which, due mainly to P modification, had caused dealumination and thus elimination of part of the strong acid sites in HZSM-5. The TFAL of P-modified HZSM-5 changed mainly to DTAL or PAL species in the process of the C_4-olefin cracking reaction, which still could act as stable active centers for C_4-olefin cracking to produce propylene; hence P-modified HZSM-5 showed excellent stability. The dimerization-β-scission mechanism was a dominant process for C_4-olefin cracking to produce propylene. HZSM-5 modified with appropriate amounts of P (1.5 wt%) was the optimal catalyst for C_4-olefin cracking to produce propylene (lifetime exceeding 800 h on a single process), and would be a promising catalyst for industrial process of C_4-olefin cracking to produce propylene.

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