Butene Catalytic Cracking to Propylene over Iron and Phosphorus Modified HZSM-5

Jianwen Li, Hongfang Ma, Haitao Zhang, Qiwen Sun, Weiyong Ying

Abstract—HZSM-5 zeolites modified by iron and phosphorus were applied in catalytic cracking of butene. N_2 adsorption and NH_3-TPD were employed to measure the structure and acidity of catalysts. The results indicate that increasing phosphorus loading decreased surface area, pore volume and strong acidity of catalysts. The addition of phosphorus significantly decreased butene conversion and promoted propylene selectivity. The catalytic performance of catalyst was strongly dependent on the reaction conditions. Appropriate reaction conditions could suppress side reactions and enhance propylene selectivity.

Keywords—Butene catalytic cracking, HZSM-5, modification, reaction conditions.

I. INTRODUCTION

PROPYLENE, as one of important raw materials for the production of a series of petrochemicals, such as polypropylene, acrylonitrile, and isopropyl alcohol, is mainly produced as the byproduct of petroleum refining and steam cracking [1], [2]. Its demand has been continuously increasing, but the traditional methods for propylene production cannot meet the increased demand. Therefore, the on-purpose propylene production technologies have been becoming significant [3], [4]. Amid them, the catalytic cracking of butene has been considered as one of the most effective approaches to producing propylene. Moreover, the butene cracking can also be integrated into a refinery or petrochemical plant and MTO (methanol to olefins) to improve the yield of propylene in these processes [5].

Recently, due to the outstanding properties, HZSM-5 zeolite has been broadly used as the catalyst in the catalytic cracking of butene to produce propylene [3], [6]. However, one of crucial problems for the cracking on HZSM-5 catalyst is deactivation. Hence, HZSM-5 needs to be modified to improve its stability, especially with the existence of water vapor. Phosphorus modification has shown significant improvement on hydrothermal stability. Blasco et al. [7] impregnated HZSM-5 with phosphorus in form of H_3PO_4 and $NH_4H_2PO_4$ and pointed out that extra-framework cationic species formed by

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protonation of orthophosphoric acid stabilized the framework aluminum pairs. Xue et al. [8] suggested that the non-framework aluminum species stabilized phosphorus species which significantly improved the stability and catalytic performance of catalysts in the cracking of butene.

Iron has also been used to improve catalytic performance of HZMS-5 in the cracking of hydrocarbons. Lu et al. [9] reported that both catalytic activity and the selectivity of light olefins on FeHZSM-5 samples with a small amount of iron were greatly enhanced compared with unmodified HZSM-5 in the catalytic cracking of isobutane. In the present work, the catalytic performance of HZMS-5 co-modified by phosphorus and iron was investigated. The structure and acidity of catalysts were measured by N_2 adsorption and NH_3-TPD. The influence of reaction conditions on the catalytic performance of the catalyst was reported.

II. EXPERIMENT

A. Catalyst Preparation

HZSM-5 zeolite ($SiO_2/Al_2O_3=50$) was impregnated with $(NH_4)_2HPO_4$ solution, dried overnight at 120°C and calcined at 550°C in air for 4 h. The phosphorus contents were 1, 2, 3, 4 and 5 wt%. Iron was added into phosphorus modified HZSM-5 zeolites with $Fe(NO_3)_3$ by incipient-wetness impregnation method. The mixture was dried overnight at 120 °C and calcined at 550°C in air for 4 h. The loading of iron in all zeolites was 2 wt%. The iron and phosphorus modified HZSM-5 catalysts were designated as Fe-xP-Z (x = 1, 2, 3, 4, 5).

B. Catalyst Characterization

N_2 adsorption was performed on a Micrometrics ASAP 2020 instrument at -196°C. Prior to N_2 adsorption, the catalysts were outgassed under vacuum at 350°C for 4 h.

NH_3-TPD spectra were measured on a Micrometrics AutoChem II 2920 instrument. Samples were first flushed with He gas flow at 600°C for 1 h in an U shaped quartz tube, and then cooled to 100°C. Ammonia was adsorbed at 100°C for 0.5 h. After flushing with He gas flow to remove physically absorbed ammonia, NH_3-TPD was started from 100 to 600°C at a heating rate of 10°C/min. The desorbed ammonia was detected on the thermal conductivity detector (TCD).

C. Catalytic Test

The catalytic cracking of butene was carried out in a fixed-bed flow reactor under atmospheric pressure. Prior to the cracking reaction, the catalyst was heated to 550°C for 2 h under N_2 flow. Then, N_2 was switched to 1-butene. Meanwhile,

water was injected by a pump to a preheating section in which water was gasified to pass through the reactor. Before the cracking, catalysts were pressed, crushed and sieved to 20-40 mesh particles. The cracking was carried out at 470-630°C with WHSV (weight hourly space velocity) of 3-15 h^{-1} and steam ratio (the weight ratio of steam to olefins in feed) of 0.2-1 g/g. The products were analyzed via an Agilent GC6890N gas chromatograph.

TABLE I
SUMMARY OF SURFACE AREAS AND TOTAL PORE VOLUMES OF CATALYSTS

Catalyst	$S_{BET}(m^2/g)$	$V_P(cm^3/g)$
Fe-1P-Z	246.99	0.15
Fe-2P-Z	203.39	0.13
Fe-3P-Z	179.25	0.12
Fe-4P-Z	144.04	0.09
Fe-5P-Z	115.05	0.07

S_{BET}: BET surface area, V_P: total pore volume

III. RESULTS AND DISCUSSION

A. Textural Properties

The textural properties of catalysts are listed in Table I. The specific surface area was calculated using BET method, and the total pore volume was taken as the total uptake at p/p_0=0.99. The results indicate that BET surface area and pore volume both decreased with increasing phosphorus loadings, which could be attributed to the formation of polymeric phosphates species that blocked micropore of catalysts or the destruction of some micropore caused by phosphorus modification [10].

B. Temperature Programmed Desorption of Ammonia

NH_3-TPD was used to measure the amount and strength of acid sites on modified HZSM-5. Fig. 1 shows the NH_3-TPD profiles of catalysts in the temperature range of 100 to 600°C. Fe-1P-Z exhibited two major desorption peak at about 200 and 432°C, corresponding to weak and strong acid sites, respectively. With the increment of phosphorus loading, the high temperature peak which is attributed to strong acid sites shifted to lower temperature, and its intensity decreased. When

phosphorus loading increased to 4 wt%, the high temperature peak almost disappeared. The results imply that phosphorus modification drastically reduced the concentration and strength of strong acid sites [11]. The addition of phosphorus could lead to dealumination and the formation of aluminum phosphate, and then decreased the amount and strength of strong acid sites [12], [13]. On the other hand, with the increment of phosphorus loading, the area of low temperature peak gradually increased. This means that the introduction of phosphorus resulted in the formation of some new weak acid sites [8]. However, as phosphorus loading increased, the peak of weak acid sites slightly shifted to lower temperature, indicating that the new formed weak acid sites had lower strength.
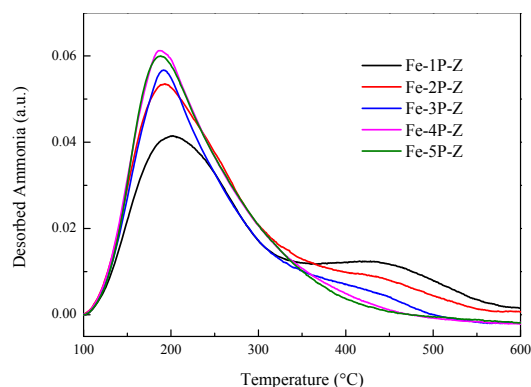

Fig. 1 NH_3-TPD profiles of catalysts

C. Catalytic Cracking of Butene on Modified HZSM-5

The conversion of butene and selectivities of major products are listed in Table II. The results indicate that butene conversion decreased with increasing phosphorus content. Strong acid sites play a key role in the catalytic cracking of butene [5]. As shown in the spectra of NH_3-TPD, the addition of phosphorus could significantly reduce the concentration and strength of strong acid sites. Therefore, the increment of phosphorus reduced butene conversion.

TABLE II
CATALYTIC PERFORMANCE OF CATALYSTS FOR BUTENE CRACKING

Catalyst	Conversion (%)	Selectivity (%)					
		$CH_4+C_2H_6$	C_2H_4	C_3H_8	C_3H_6	C_4H_{10}	C_5H_{10}
Fe-1P-Z	85.01	3.55	20.64	14.21	34.87	10.39	4.01
Fe-2P-Z	79.02	2.72	18.29	12.71	37.10	8.22	8.95
Fe-3P-Z	70.21	0.79	16.97	4.47	54.02	6.71	11.48
Fe-4P-Z	53.84	0.30	9.66	1.56	60.01	4.77	16.07
Fe-5P-Z	40.79	0.29	6.78	0.70	54.70	4.52	25.80

All the data were obtained at 2 h of time on stream

The catalytic cracking of butene is a complex process and involves the main cracking reaction, isomerization, oligomerization, and hydrogen transfer reaction. The main products in the cracking include methane, ethane, ethylene, propane, propylene, butane and pentene. Methane and ethane are mainly produced from protolytic cracking and aromatics dealkylation, and the two reactions occur on the strong acid sites [14]. Hence, selectivities of methane and ethane are

related to the acid strength of catalysts. According to NH_3-TPD results, the increment of phosphorus loading decreased acid strength. As a result, their selectivities decreased with the increase of phosphorus amount. Propane and butane are mainly produced from hydrogen transfer reaction. The reaction has low reactivity on weak acid sties [14]. Consequently, selectivities of propane and butane also reduced as phosphorus loading increased.

The cracking of butene mainly followed the bimolecular mechanism: butene first dimerized to octene isomers and then converted to small molecules by β-scission [5], [15]. The selectivities of propylene and pentene increased with the increment of phosphorus loading, whereas the selectivity of ethylene decreased. This indicates that with more phosphorus loading the octene isomers were more inclined to crack to propylene and pentene rather than ethylene [16]. When phosphorus increased from 4 to 5 wt%, the selectivity of propylene decreased whereas that of pentene increased. The weak acidity on Fe-5P-Z depressed the further cracking of pentene and then decreased propylene selectivity.
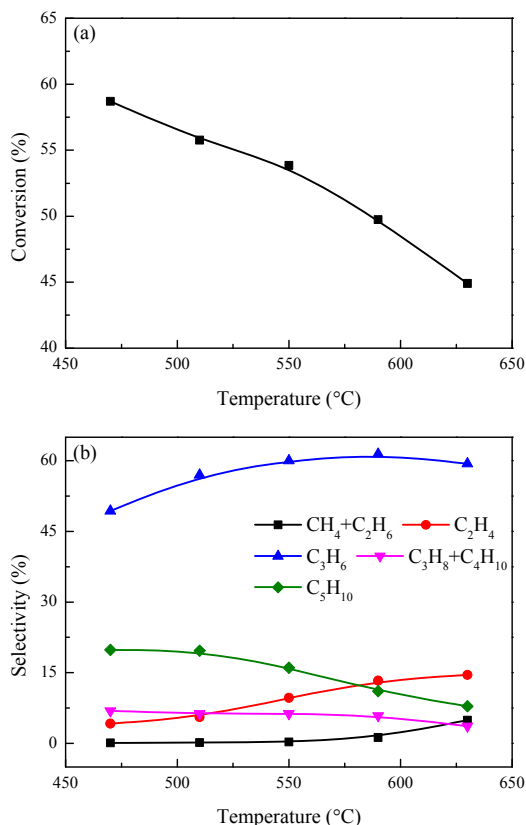
thermodynamically unfavorable and would be suppressed by temperature increase. Moreover, increasing reaction temperature could promote the cracking of pentene, and hence result in the decrease of its selectivity. As reaction temperature increased, propylene selectivity reached a maximum at 590°C and then decreased. Ethylene selectivity continuously increased with reaction temperature. The pentene cracking and suppression of hydrogen transfer reaction led to the increment of selectivities of ethylene and propylene, but high reaction temperature promoted the secondary transformation of propylene and then caused the decrement of its selectivity at 630°C [18].
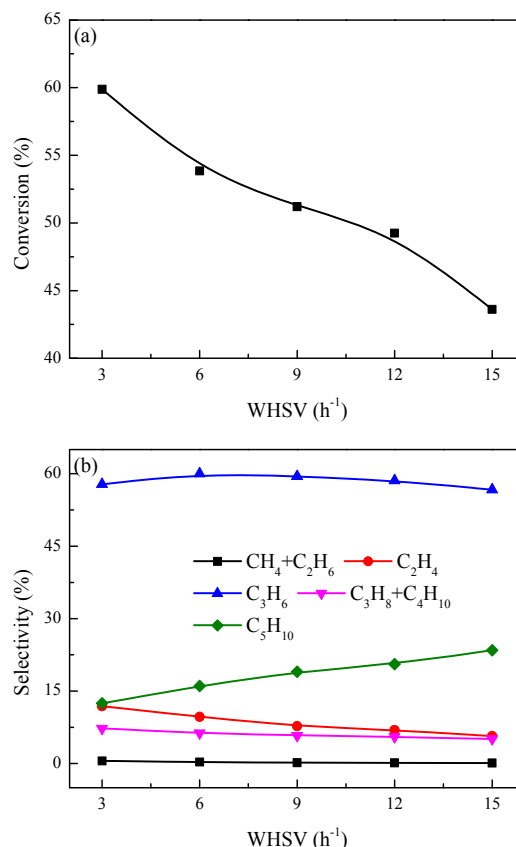

Fig. 2 Effect of reaction temperature on the reactivity of Fe-4P-Z in the cracking of butene. Reaction condition: WHSV = 6 h^{-1}, Steam ratio = 0.4 g/g.

Fig. 3 Effect of WHSV on the reactivity of Fe-4P-Z in the cracking of butene. Reaction condition: T = 550 °C, Steam ratio = 0.4 g/g.

Fig. 2 shows the effect of reaction temperature on the catalytic performance of Fe-4P-Z in the cracking of butene. In the cracking process, the dimerization of butene to produce octene isomers is the limiting step [17]. But butene dimerization is exothermic reaction and suppressed by increasing temperature. Therefore, with increasing reaction temperature, butene conversion decreased. Selectivities of methane and ethane increased with the reaction temperature, especially from 590 to 630°C, due to the enhanced protolytic cracking of hydrocarbons. Meanwhile, selectivities of propane and butane decreased with increasing reaction temperature, because hydrogen transfer reaction is exothermic and

Fig. 3 shows the effect of WHSV on the catalytic performance of Fe-4P-Z in the cracking of butene. With increasing WHSV, butene conversion decreased, because increased WHSV reduced the contact time between reactants and catalyst active sties. Selectivities of propane and butane decreased with the increment of WHSV, meaning the decreased contact time suppressed hydrogen transfer reaction. Meanwhile, pentene selectivity obviously increased with WHSV, due to the reason that the contact time was not long enough for its sufficient cracking. With increasing WHSV, ethylene selectivity decreased slowly, whereas propylene selectivity first increased, reached a maximum at 6 h^{-1} and then

slightly decreased. Compared with propylene, the formation of ethylene needed more contact time.

Fig. 4 presents the influence of steam ratio on the catalytic performance of Fe-4P-Z in the cracking of butene. The conversion of butene decreased with the increment of steam ratio. Increasing steam ratio could reduce the partial pressure of reactants and inhibit the dimerization of butene. Selectivities of propane and butane also decreased with the increment of steam ratio, which might be explained by the reason that hydrogen transfer reaction was the bimolecular or multiple-step reaction and more affected by lowering reactant concentration. The selectivity of pentene increased with steam ratio. With the increment of steam ratio, ethylene selectivity decreased, whereas propylene selectivity first increased and then remained constant at higher steam ratio.
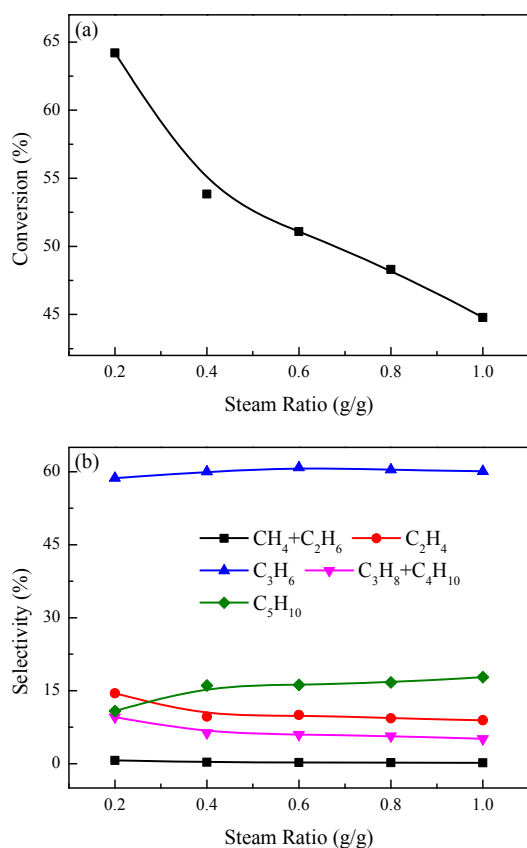

Fig. 4 Effect of steam ratio on the reactivity of Fe-4P-Z in the cracking of butene. Reaction condition: T = 550 °C, WHSV = 6 h^{-1}.

IV. Conclusion

HZSM-5 catalysts co-modified by phosphorus and iron were prepared for the cracking of butene. BET surface area and pore volume of catalysts both decreased with the increment of phosphorus loading. NH$_3$-TPD spectra indicate that the addition of phosphorus decreased the concentration and strength of strong acids sites of catalysts but led to the formation of some new weak acid sites with lower strength. The increment of phosphorus loading decreased catalyst activity but

increased propylene selectivity. Fe-4P-Z exhibited the highest propylene selectivity. Reaction conditions exerted significant impact on the catalytic performance of catalyst. Increasing reaction temperature inhibited butene dimerization and hydrogen transfer reaction, leading to the decrease of the conversion of butene and selectivities of propane and butane. With the increment of reaction temperature, ethylene selectivity increased and propylene selectivity reached a maximum at 590°C. Increasing WHSV and steam ratio both significantly decreased butene conversion.

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