

Catalytic Cracking of Butene to Propylene over Modified HZSM-5 Zeolites

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

Abstract—Catalytic cracking of butene to propylene was carried out in a continuous-flow fixed-bed reactor over HZSM-5 catalysts modified by nickel and phosphorus. The structure and acidity of catalysts were measured by N₂ adsorption, NH₃-TPD and XPS. The results revealed that surface area and strong acid sites both decreased with increasing phosphorus loadings. The increment of phosphorus loadings reduced the butene conversion but enhanced the propylene selectivity and catalyst stability.

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

I. INTRODUCTION

PROPYLENE is one of the most important raw materials in the modern chemical industry. Due to ever-increasing need of its derivatives, such as polypropylene, acrylonitrile, and isopropyl alcohol, the demand of propylene has continuously grown [1]. However, the traditional manufacturing processes, steam cracking and fluid catalytic cracking, cannot meet the required demand of propylene [2]. Recently, some new routes for producing propylene emerged. Among them, catalytic cracking of butene has attracted much attention, which can be integrated into a refinery or petrochemical plant [3].

Zeolites have been widely applied in industrial processes, due to their outstanding properties. Various zeolites have been tested as catalysts in catalytic cracking of butane [4], [5]. Compared with other zeolites, HZSM-5 has been considered as an effective catalyst to produce light olefins in catalytic cracking of hydrocarbons. Nevertheless, HZSM-5 still needs to be modified in order to improve its catalytic performance. Addition of phosphorus has been used to improve the stability of HZSM-5. Blasco et al adopted phosphorus modification for the cracking of n-decane over HZSM-5 and proposed that the framework aluminum pairs could be stabilized by extra-framework cationic species of orthophosphoric [6]. However, the activity of catalysts commonly decreases after

phosphorus modification.

Except phosphorus modification, transition metals, such as nickel, have also been used to modify HZSM-5 zeolites. Nickel has been introduced into HZSM-5 to improve the activity of catalysts. Meanwhile, nickel modification can also repress the side reactions. Maia et al discussed the effect of nickel on HZSM-5 for the isobutane cracking reaction and found that nickel modification improved the catalytic activity and ethylene selectivity [7].

Nevertheless, co-modification of phosphorus and nickel on HZSM-5 has not yet been discussed. Hence, the present work reports the catalytic performance of HZSM-5 modified by phosphorus and nickel for the cracking of 1-butene to propylene. The structure and acidity of catalysts were tested by N₂ adsorption, NH₃-TPD and XPS.

II. EXPERIMENTAL

A. Catalyst Preparation

HZSM-5 zeolite (Si/Al=25) was impregnated with (NH₄)₂HPO₄ solution, and the slurry was 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%. Nickel was introduced into HZSM-5 zeolite and phosphorus modified zeolites with Ni(NO₃)₂ solution. The mixture was dried overnight at 120°C and calcined at 550°C in air for 4 h. The loading of nickel in all zeolites was 2 wt%. The nickel modified HZSM-5 without phosphorus was designated as Ni-0P-Z, and the nickel and phosphorus catalysts were designated as Ni-1P-Z, Ni-2P-Z, Ni-3P-Z, Ni-4P-Z, and Ni-5P-Z, respectively.

B. Catalyst Characterization

N₂ adsorption was performed on a Micrometrics ASAP 2020 instrument at -196°C. Prior to N₂ adsorption, the catalysts were outgassed under vacuum at 350°C for 4 h.

NH₃-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, NH₃-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).

The XPS measurement was carried out on a Thermo Fisher ESCALAB 250Xi electron spectrometer using focused monochromatic Al K α radiation at 10 mA and 12 kV. Binding energies were corrected by charge referencing to the C 1s line at 284.9 eV. The intensity ratios of components were quantified with the area of the corresponding peaks after background

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subtraction. The overlapped peaks were deconvoluted using a Gaussian (80%)-Lorentzian (20%) curve fitting program.

C. Catalytic Test

The catalytic performance of catalysts was measured in a fixed-bed flow reactor with 10 mm inner diameter for 1-butene (>99.5% purity) cracking. Prior to the cracking reaction, the catalyst powder was pressed, crushed and sieved to 20-40 mesh particles. The catalyst was heated to 550°C and kept for 2 h under N₂ gas flow. Then N₂ 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. The operating conditions for the cracking of 1-butene are presented as follow: reaction temperature of 550°C, weight hourly space velocity of 5 h⁻¹, steam to 1-butene ratio of 0.5 g/g, and atmospheric pressure. The products were analyzed via a GC6890C gas chromatograph equipped with a 50 m HP-PLOT Al₂O₃ capillary column and a flame ionization detector (FID).

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

Catalyst	S _{BET} (m ² /g)	V _P (cm ³ /g)
Ni-0P-Z	260.77	0.18
Ni-1P-Z	244.33	0.16
Ni-2P-Z	218.41	0.15
Ni-3P-Z	176.93	0.13
Ni-4P-Z	148.29	0.11
Ni-5P-Z	118.80	0.08

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/p₀=0.99. From the results, it can be seen that the BET surface area and pore volume all decreased with the increase of phosphorus loadings. It might be explained by the formation of polymeric phosphates species that located inside and blocked the channel of catalysts [8].

B. Temperature Programmed Desorption of Ammonia

NH₃-TPD was used to measure the amount and strength of acid sites on HZSM-5. Fig. 1 shows the NH₃-TPD profiles of catalysts in the temperature range of 100 to 600°C. Ni-0P-Z showed a typical NH₃-TPD spectrum with two desorption peaks at about 217°C and 462°C, clearly suggesting the existence of corresponding weak and strong acid sites, respectively. As the addition of phosphorus increased to 1 %, the high temperature peak which is assigned to strong acid sites shifted to lower temperature at 435°C, which means the strength of strong acid sites reduced after introducing phosphorus [9]. Meanwhile, the intensity of the peak drastically decreased. This could be explained by the dealumination resulting from the introduction of phosphorus [10]. Dealumination mainly happened on the framework aluminum atoms in tetrahedral coordination which majorly became extra-framework aluminum coordinated to phosphate groups.

When the loading of phosphorus rose to 2%, the amount and intensity of strong acid sites all decreased.

On other catalysts with more phosphorus loading, the high temperature peak almost disappeared, meaning the intense diminution of strong acid sites. On the other hand, the area of the low temperature peak on Ni-1P-Z decreased compared with Ni-0P-Z. However, with the further increment of phosphorus loading, the area of the low temperature peak increased gradually, indicating that new weak acid sites emerged with the addition of nickel. Nevertheless, the low temperature peaks of catalysts with phosphorus shifted to lower temperatures contrasted with Ni-0P-Z, implying that newly formed weak acid sites had lower strength [11].

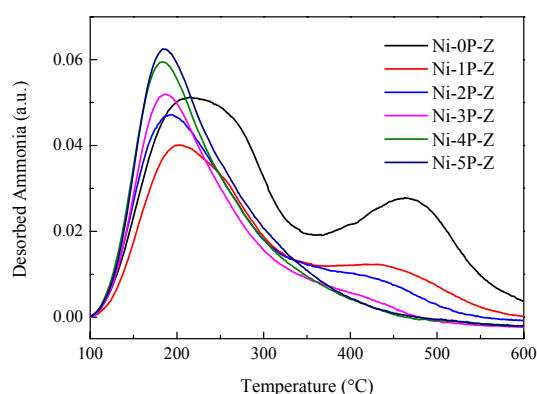


Fig. 1 NH₃-TPD profiles of catalysts

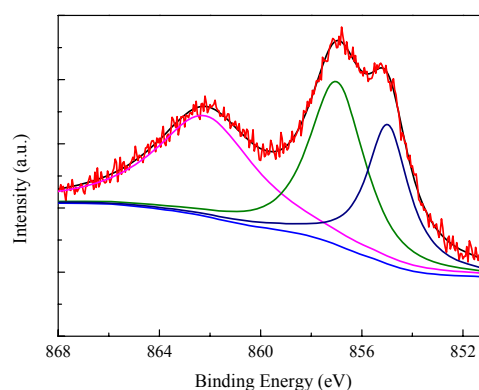


Fig. 2 XPS spectrum of Ni-0P-Z for the Ni 2p_{3/2} level after deconvolution

C. X-ray Photoelectron Spectroscopy

XPS has been a widely-used analytical technique for investigating the chemical composition of catalyst surfaces [12]-[14]. Fig. 2 shows the XPS spectrum of Ni 2p_{3/2} core levels for Ni-0P-Z. The XPS spectrum with its satellite at 862.3 eV revealed two peaks at ca. 855 eV and 857 eV, corresponding to stoichiometric nickel oxide and nickel aluminate [14]-[16], respectively. The binding energy data with the contribution percentage of different nickel containing species for all catalysts in relation to the Ni 2p_{3/2} peaks after deconvolution are summarized in Table II. For Ni-1P-Z, Ni-2P-Z, Ni-3P-Z,

Ni-4P-Z and Ni-5P-Z, binding energies of NiO at 855.2-855.7 eV are higher in comparison with Ni-0P-Z which was not modified by phosphorus, suggesting a weak interaction with the support [17]. Meanwhile, with the increment of phosphorus loadings from 0% to 5%, the relative amount of nickel aluminate increased, whereas that of nickel oxide decreased. This might demonstrate that phosphorus promoted the interaction between nickel and aluminum species.

TABLE II
BINDING ENERGIES AND CONTRIBUTION OF Ni 2P_{3/2} AFTER DECONVOLUTION

Catalyst	Binding energies (contribution percentage)	
Ni-0P-Z	855.0 (42%) ^a	857.0 (58%) ^b
Ni-1P-Z	855.2 (33%) ^a	857.1 (67%) ^b
Ni-2P-Z	855.5 (25%) ^a	857.0 (75%) ^b
Ni-3P-Z	855.6 (18%) ^a	857.1 (82%) ^b
Ni-4P-Z	855.5 (8%) ^a	857.0 (92%) ^b
Ni-5P-Z	855.7 (6%) ^a	857.3 (94%) ^b

^a stoichiometric nickel oxide, ^b nickel aluminate

TABLE III
CATALYTIC PERFORMANCE OF CATALYSTS FOR BUTENE CRACKING

Catalyst	Conversion (%)	Selectivity (%)					
		CH ₄ +C ₂ H ₆	C ₂ H ₄	C ₃ H ₈	C ₃ H ₆	C ₄ H ₁₀	C ₅ H ₁₀
Ni-0P-Z	88.01	4.49	22.50	8.38	25.07	11.62	5.27
Ni-1P-Z	82.56	3.44	21.73	6.7	41.07	7.64	6.70
Ni-2P-Z	79.93	2.10	18.59	6.18	43.54	7.75	11.95
Ni-3P-Z	73.01	1.85	16.03	5.67	50.80	7.29	13.12
Ni-4P-Z	58.22	0.47	11.33	2.05	56.46	6.29	14.91
Ni-5P-Z	42.41	0.37	6.48	0.63	55.66	4.68	25.70

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

Even though phosphorus modification reduced the butene conversion at 2 h TOS, the stability of catalysts was enhanced by the introduction of phosphorus. Fig. 3 shows butene conversion over catalysts as a function of TOS. With the increase of phosphorus loading, the decrement of butene conversion diminished. When phosphorus amount reached to 4%, the modified catalyst presented excellent stability.

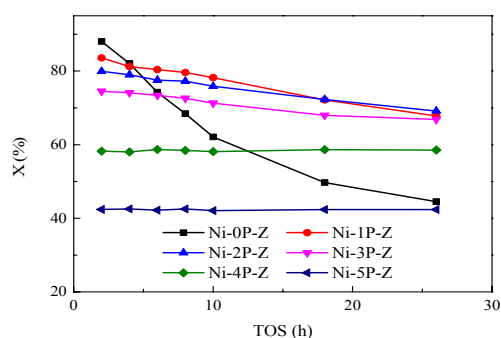


Fig. 3 Butene conversion with time on stream

Methane and ethane are mainly from protolytic cracking and aromatics dealylation that occur on the strong acid sites [2]. The existence of phosphorus decreased such acid sites. As a result, selectivities of methane and ethane decreased with increase of phosphorus amount. Hydrogen transfer reactions

D. Catalytic Cracking of 1-Butene on Nickel and Phosphorus Modified HZSM-5

Catalytic cracking of 1-butene is a complicated process, involving cracking reaction, isomerization, oligomerization, and other reactions [2]. Besides propylene and ethylene, it has other products, such as methane, ethane, propane, butane and pentene. The selectivities of these products and the conversion of butene are listed in Table III. The results indicate that the butene conversion declined with more loadings of phosphorus. In butene cracking, strong acid sites of catalysts exert important effect and affect the conversion of butane [3]. Phosphorus introduction could obviously decrease the amount and strength of strong acid sites as shown in the results of NH₃-TPD. Hence, phosphorus modification, significantly diminishing strong acid sites, led to the decrement of butene conversion.

also depend on strong acid sites [2]. Therefore, the selectivities of propane and butane which are mainly produced from such reactions, also reduced as phosphorus loadings rose. It also can be seen that with increment of phosphorus contents the selectivities of propylene and pentene increased while the selectivity of ethylene decreased. This might imply that butene oligomerized to octene isomers and these isomers were inclined to crack to propylene and pentene rather than ethylene with the existence of phosphorus [18]. Ni-5P-Z, with 5% of phosphorus, had lower propylene selectivity than Ni-4P-Z. This might be explained by the decreased pore volume which delayed diffusion of propylene.

IV. CONCLUSION

Nickel and phosphorus modified HZSM-5 catalysts were prepared for the cracking of 1-butene. BET results show such modification decreased the surface area and pore volume of catalysts. NH₃-TPD spectra indicate that the increase of phosphorus amount decreased strong acid sites of catalysts. The modification also resulted in dealumination of HZSM-5. The existence of phosphorus promotes the interaction between nickel and aluminum species. The introduction of phosphorus decreased the activity of catalysts, but enhanced stability of catalysts and increased the selectivity of propylene. Ni-4P-Z had the highest propylene selectivity.

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