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Research article

Effect of nickel on phosphorus modified HZSM-5 in catalytic cracking of butene and pentene

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A B S T R A C T

Nickel was introduced into phosphorus modified HZSM-5 (P/HZSM-5) with different loadings by an impregnating method. The effect of nickel loading on the structure and acidity of catalysts was investigated by XRD, N_2 adsorption, XPS, NMR, and FTIR of adsorbed pyridine. Nickel interacted with pre-introduced phosphorus, and the interaction promoted the migration of some phosphorus species from channels to external surface and broke part of the Al—O—P bonds. This increased the content of tetrahedral framework aluminum, and restored some Brønsted acid sites which were neutralized by phosphorus modification. In the cracking of butene and pentene, the performance of catalysts was strongly dependent on nickel content. For the cracking of butene, with increasing nickel content, butene conversion and ethylene selectivity increased, while propylene selectivity first increased, passed through a maximum and then decreased with further increment of nickel content; for the cracking of pentene, with increasing nickel content, pentene conversion, ethylene selectivity and propylene selectivity increased.

1. Introduction

Ethylene and propylene are important raw materials in the petrochemical industry. They are mainly produced through steam cracking and fluid catalytic cracking (FCC). In these traditional processes, the yield of propylene is relatively low. However, the demand of propylene has grown very fast in recent years. An imbalance between supply and demand of propylene has emerged. Therefore, on-purpose propylene production technologies, including olefin metathesis [1], propane dehydrogenation [2], and olefin cracking [3–5], are becoming increasingly important. Among them, catalytic cracking of C_{4+} olefins over zeolites, mostly converting large olefin molecules to propylene, has been considered as one promising method to fill the supply and demand gap of propylene. C_{4+} olefins, especially butene and pentene, are main byproducts of steam cracking, fluid catalytic cracking (FCC), and methanol to olefins (MTO) [5,6]. The cracking of these olefins can also boost propylene production and improve the efficiency of these technologies.

Zeolite-based acid catalysts have been widely used in the catalytic cracking of various hydrocarbons [7]. Due to its thermal stability, intrinsic acidity, and shape selectivity, HZSM-5 has been employed as an effective catalyst in the catalytic cracking for the production of light olefins [8]. However, coke formation over HZSM-5 catalysts, which may cover the acid sites, block the pores and decrease the activity of catalysts, is a serious problem in the cracking process [9]. Adding appropriate amount of steam in the feedstock can efficiently inhibit coke formation. At the same time, nevertheless, adding steam in the reaction is harmful to the tetrahedrally coordinated aluminum in HZSM-5, which can destroy the structure of HZSM-5 zeolite and decrease the stability of catalyst at high temperatures [10]. Researchers found phosphorus modification could effectively promote the hydrothermal stability of HZSM-5. Blasco et al. [11] studied the effect of phosphorus impregnation in the cracking of *n*-decane and proposed that the protonation of orthophosphoric acid formed extra-framework cationic species and stabilized the framework aluminum pairs. Xue et al. [12] suggested that the interaction between phosphorus species and silanol nests promoted the formation of hydrothermally stable acid sites during the steam treatment and the incorporated phosphorus species were stabilized by some extra-framework aluminum species. Moreover, it has been found that the addition of phosphorus could also increase the selectivity of light olefins in the cracking of hydrocarbons [4,13], but such modification led to obvious decrement of HZSM-5 catalyst activity owing to the reduction of acidity and pore volume.

Nickel modification has also been used to improve the catalytic performance of HZSM-5 zeolite in the catalytic cracking of hydrocarbons. Masalska [14] investigated catalytic properties of nickel HZSM-5 catalysts and found that the cracking activity of catalysts increased and the content of aromatic hydrocarbons in the products decreased as the

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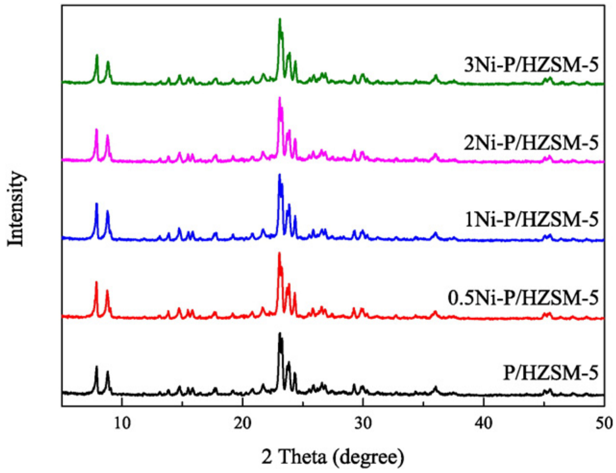

Fig. 1. XRD patterns of modified HZSM-5 catalysts.

amount of NiO rose to 4 wt%. Maia et al. [15] tested the activity of nickel modified HZSM-5 zeolites in the cracking of isobutane and *n*-butane and revealed that the introduction of Ni led to distinct enhancement in ethylene selectivity and cracking activity.

These above published literatures suggest that nickel modification can enhance the cracking activity of HZSM-5 catalysts, while phosphorus addition reduces the activity of HZSM-5 catalysts. Moreover, it has been reported that the interaction between nickel and phosphorus species existed in zeolite catalysts [16]. Hence, we anticipate that such interaction would further promote the catalytic performance of catalysts after adding nickel to phosphorus modified HZSM-5 in the cracking of hydrocarbons. The present work reports the effect of impregnating nickel into P/HZSM-5 in the cracking of butene and pentene. According to our previous work, P/HZSM-5 with phosphorus loading of 3% showed excellent stability, so in this study phosphorus loading was fixed at 3%. Several characterization methods, such as X-ray Diffraction (XRD), N_2 adsorption, X-ray Photoelectron Spectroscopy (XPS), Nuclear Magnetic Resonance (NMR) and Fourier Transform Infrared Spectroscopy (FTIR) of adsorbed pyridine, were used to investigate the structure and acidity of catalysts.

2. Experimental

2.1. Catalyst preparation

Phosphorus modified HZSM-5 catalyst was prepared by an incipient-wetness impregnation method. HZSM-5 zeolite (Si/Al = 25) was impregnated with $(NH_4)_2HPO_4$ aqueous solution, dried overnight at 120 °C, and calcined at 550 °C for 4 h. The phosphorus loading was fixed at 3 wt%. The phosphorus modified HZSM-5 catalyst was denoted as P/HZSM-5.

Nickel was introduced into P/HZSM-5 catalyst by the incipient-wetness impregnation method using $Ni(NO_3)_2$ aqueous solution. The slurry was dried overnight at 120 °C, and then it was calcined at 550 °C for 4 h to get the nickel containing P/HZSM-5 catalysts. These catalysts that contained x wt% (x = 0.5, 1, 2, 3) of nickel were named as xNi-P/HZSM-5.

2.2. Catalyst characterization

XRD patterns were recorded on a Rigaku D/MAX 2550 VB/PC X-ray diffractometer with Cu Kα radiation at 40 kV and 100 mA. Specific surface areas and pore volumes of catalysts were obtained by N_2 adsorption at −196 °C using a Micrometrics ASAP 2020 instrument. Prior to N_2 adsorption, samples were outgassed at 350 °C under vacuum for 4 h. The surface area was calculated using the BET method, and the total pore volume was taken as the total uptake at $p/p_0 = 0.99$ [17].

The XPS measurement was carried out on a Thermo Fisher ESCALAB 250Xi electron spectrometer using focused monochromatic Al Kα radiation at 10 mA and 12 kV. Regions of Ni $2p_{3/2}$ and P 2p were recorded. Binding energies were calibrated using the C 1s contamination line at 284.8 eV as a reference. Intensity ratios of components were quantified with areas of the corresponding peaks after background subtraction. Overlapped peaks were deconvoluted using a Gaussian (80%)-Lorentzian (20%) curve fitting program.

^{31}P MAS NMR spectra were measured on a Bruker AVANCE III 400 spectrometer at a resonance frequency of 161.98 MHz. The spectra were obtained with a 10 kHz spinning rate, a 2.2 μs pulse width and a 5 s recycle delay. ^{31}P chemical shifts were reported relative to KH_2PO_4. ^{27}Al MAS NMR spectra were obtained at a resonance frequency of 104.27 MHz with a 10 kHz spinning rate, a 2 μs pulse width and a 1 s recycle delay. The chemical shifts were reported relative to $[Al^{3+}(H_2O)_6]$.

FTIR of adsorbed pyridine was carried out on a Nicolet Nexus 470 spectrometer. Self-supporting wafers with weight of ca. 10 mg were activated at 300 °C for 4 h under 10^{-2} Pa, and then cooled down to room temperature. Subsequently, pyridine vapors were admitted, and after equilibration samples were outgassed at desired temperatures (150 and 300 °C) for 0.5 h to evacuate the excess pyridine. Infrared spectra of catalysts were recorded with a resolution of 2.0 cm^{-1}.

2.3. Catalytic test

The catalytic cracking was performed in a fixed-bed flow reactor (length 650 mm, insider diameter 9 mm) under atmospheric pressure. The catalyst powders were pressed, crushed and sieved to 0.38–0.84 mm. Cracking reactions of 1-butene and pentene were separately investigated over modified HZSM-5 catalysts. Before the cracking reaction, each catalyst was pretreated at 550 °C for 2 h under N_2 flow. After that, for the cracking of 1-butene, N_2 was switched to 1-butene; for the cracking of pentene, pentene (90% of 2-methyl-2-butene, 10% of 2-methyl-1-butene) was sufficiently vaporized by passing through a preheating zone, N_2 was used as carrier gas, and the molar ratio of pentene to N_2 was 1: 4 (referring to the molar ratio of pentene to butene in MTO products [6]). Water was added in the feedstock and injected by a pump to the preheating zone. The cracking temperature was 550 °C, WHSV (weight hourly space velocity) was 5 h^{-1}, and the weight ratio of steam to olefin in feed was 0.5 g/g. WHSV was calculated considering the olefin flowrate alone. The amount of catalyst was 0.5 g. The interphase mass transfer limitations have been minimized in the experimental runs. The gaseous products were analyzed by GC 6890 equipped with a flame ionization detector (FID). For simplicity, hydrocarbon isomers were not specifically considered, all kinds of butene were grouped as one reactant, and all kinds of pentene were grouped as another reactant.

3. Results and discussion

3.1. Structural properties of catalysts

As shown in Fig. 1, all samples presented typical XRD patterns of MFI structure, suggesting that the framework structure of HZSM-5 was well

Table 1
Textural properties of modified HZSM-5 catalysts.

Catalyst	BET surface area (m^2/g)	Pore volume (cm^3/g)
P/HZSM-5	158.6	0.1028
0.5Ni-P/HZSM-5	167.3	0.1093
1Ni-P/HZSM-5	170.6	0.1220
2Ni-P/HZSM-5	174.3	0.1342
3Ni-P/HZSM-5	173.1	0.1293