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Catalytic cracking of *n*-hexane to light alkene over ZSM-5 zeolite: Influence of hierarchical porosity and acid property

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ABSTRACT

ZSM-5 is active in *n*-hexane cracking to light alkenes, but with the disadvantage of fast deactivation. A long lifetime ZSM-5 with high activity and anti-carbon deposition performance was of great concern for industrial application. The hierarchical ZSM-5 zeolites (xHF-ZSM5) were obtained by chemical etching with fluoride ions and characterized by XRD, FTIR, NH_3-TPD, SEM, TEM, N_2 adsorption-desorption. They showed higher BET surface area, larger mesoporous volume, less defect zones, commensurable microporous structure and acid property compared with that of the parent ZSM-5. The defects were dissolved resulting in higher crystallinity zeolite. They showed better catalytic performance with less carbon deposition in catalytic cracking of *n*-hexane due to superior channel structure, large mesoporous and macroporous structure. In order to reduce the amount of carbon deposition further, 0.5HF-ZSM5 was selected and made phosphorus modification. After phosphorus modification, the catalytic activity and stability was maintained at a high level, and the carbon deposition of *n*-hexane cracking was restrained due to the gradual decreasing of acid amount with the increase of phosphorus content. The amount of carbon deposition decreased and reached the minimum of 23 mg g^{-1} for 0.5HF-ZSM5-1P, which was four times less than that of the parent ZSM-5.

1. Introduction

Light alkenes, important raw materials for chemical engineering, are mainly produced from thermal cracking of hydrocarbons [1]. But thermal cracking to alkenes costs much energy [2], and the vast demands of light olefins pursues efficient and selective catalysts for catalytic cracking [3]. In catalytic cracking, more light olefins can be generated and carbon deposition can be restrained to some extent compared with thermal cracking [4]. Therefore, catalytic cracking of hydrocarbon to light alkenes has drawn much attention in recent years [5–8].

Among the catalytic cracking catalysts, ZSM-5 zeolite has been reported to be potential for hydrocarbon cracking to light olefins due to its thermal and hydrothermal stability [9–11]. ZSM-5 zeolite showed high activity, less susceptible to deactivation by carbon deposition and better product selectivity compared with H-MOR, H-BEA and USY in *n*-hexane cracking [12]. But the application of the conventional ZSM-5 zeolite is also restricted due to its simple microcellular structure, long diffusion pathways and redundant strong acid [13,14]. The diffusion of the molecules, especially for large molecule, is hindered by the simple microcellular structure and long diffusion pathway [15,16]. The carbon deposition easily generates and aggregates in the micro-channels, resulting in the deactivation of catalyst [17].

Therefore, many efforts were paid to improve the catalytic performance by enhancing the molecule diffusion efficiency and restraining the generation of carbon deposition [18–23]. Hierarchical ZSM-5 zeolite showed enhanced catalytic activity due to its higher molecule diffusion efficiency [15,16,24,25]. Coppens et al. [26,27] developed a facile synthesis route to prepare hierarchical ZSM-5 zeolite with TPAOH as the structure-directing agent. The size of the mesoporous can be adjusted by varying the Si/Al ratio and crystallization time. Mesoporous ZSM-5 zeolite can be obtained by the sodium hydroxide treatment following with hydrochloric washing, and it has been proven the newly formed mesoporous could facilitate the molecule diffusion and catalytic activity [28]. Besides, hierarchical zeolites can also be obtained by fluoride etching [29]. After HF treatment, the aluminum can be selectively removed, resulting in increase of the external surface areas and mesoporous volumes, and decrease of the strong acid sites. Thus the stability of ZSM-5 zeolite in methanol to gasoline reaction was enhanced significantly [30]. While after treatment with NH_4F-HF

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solution, the aluminum and silicon can be dissolved simultaneously, resulting in increase of pore volume and similar Si/Al ratio. The treated zeolite showed better activity due to the increased diffusion efficiency [31,32].

Another effective strategy to enhance the catalytic activity of ZSM-5 zeolite is to prepare nano-sized zeolite, which has a shorter diffusion pathway and the diffusion efficiency can be improved efficiently [21,33–35]. ZSM-5 zeolite between 5.5 and 40 nm was synthesized by tuning the synthesis parameters, including hydrothermal treatment temperature, synthesis duration, and pH value [36]. By studying the influence of crystal size and acid sites of nano- and micro-sized ZSM-5 zeolites on the selectivity of light alkenes in *n*-hexane cracking, it was concluded that the uniform nano-sized ZSM-5 zeolite shows higher light olefins selectivity and higher anti-carbon deposition capacity compared with micro-sized ZSM-5 zeolite [37]. It was attributed to that the larger external surface area of the nano-sized ZSM-5 zeolite offered a higher number of pore entrances and therefore enhancing the diffusion efficiency inside the pore channels compared with that of micro-sized zeolites.

In 2009, a stable single-unit-cell nanosheets of MFI zeolite was prepared for the first time, and it showed high diffusion efficiency for large organic molecules and high catalytic activity [38]. The MFI nanosheet zeolites showed the feature of higher surface area, large mesoporous and ultrathin lamellar structure. It showed a better performance than the conventional ZSM-5 zeolite when it was used in the catalytic cracking of hydrocarbon. Recently, isomorphous MFI nanosheet zeolites with aluminum replaced with gallium or iron were prepared, and they showed different acid strength. It was concluded that the decrease of acidity strength to some extent showed a positive effect on the catalytic cracking of hydrocarbon [39].

Besides, it was reported that element or compound modification was also effective to increase the catalytic performance [40–46] or suppress the generation of carbon deposition [47–49]. An optimal lanthanum content could restrain hydrogen transfer activity, and thus reduce the carbon deposition and improve the productivity of light olefins on catalytic cracking of C5 raffinate [50]. The acid sites on the external surface, which could facilitate the carbon deposition, were selectively removed by HNO_3 treatment and therefore, the stability of the catalyst was extended remarkably [51]. Phosphorus modification can also increase the activity of zeolite [52–54]. After modification, the Al in the framework of zeolite can be stabilized and therefore enhances its hydrothermal stability [55]. The strong acid sites decreased with the increase of phosphorus content, which could restrain the over-reaction of primary products. As a result, the selectivity of light alkene increased and carbon deposition decreased [48]. Besides, after phosphorus and lanthanum co-modification, the acidity and basicity property can be adjusted. With moderate acidity and basicity content, the catalytic activity and stability of ZSM-5 zeolite can be improved by restraining the deposition of carbon and blockage of microporous [56]. After co-modification of iron and phosphorus, ZSM-5 zeolite showed higher selectivity to propylene in catalytic cracking of 1-butene [57].

In general, hierarchical or nanosized ZSM-5 zeolites show improved catalytic activity by enhancing the diffusion efficiency of reactants. Element or compound modifications could also enhance its activity and stability by suppressing the generation of carbon deposition. However, it is unclear whether combining these two strategies could result in synergistic effect by improving the catalytic performance further, and so far as we know, few studies on this point were reported. Therefore, we combined both strategies of hierarchical zeolites and element modification, and tried to develop a catalyst with high activity and high ability against carbon deposition. In this work, a number of hierarchical ZSM-5 zeolites prepared by fluoride media etching were used in the catalytic cracking of *n*-hexane. The catalytic activity and stability was determined and compared with that of the parent ZSM-5 zeolite. Then the catalyst with the highest activity was selected to modify with phosphorus to suppress the generation of carbon deposition further.

2. Experimental

2.1. Material

ZSM-5 zeolite (SiO_2/Al_2O_3 = 50, Nankai University Catalyst Plant (Tianjin, China)) was used as starting material. Hydrofluoric acid (HF), ammonium fluoride (NH_4F), diammonium hydrogen phosphate ($(NH_4)_2HPO_4$) and *n*-hexane (n-C_6H_{14}) were purchased from Sinopharm Chemical Reagent Co., and used without further purification.

2.2. Catalyst preparation

The hierarchical structured ZSM-5 zeolite was obtained by chemical etching with fluoride ions according to the literature with slight modification [31]. Firstly, 15 g NH_4F was dissolved in 90 mL HF aqueous solution with HF concentration at 0.1, 0.2, 0.5, 1.0 $mol\,L^{-1}$, respectively. Then 3 g parent ZSM-5 zeolite was added into the above solution and reacted at 25 °C for 10 min with magnetic stirring at 200 rpm. Finally, all samples were washed to neutral with deionized water and calcined at 550 °C for 3 h to obtain hierarchical structured ZSM-5 zeolites. For convenience, the samples treated with 0, 0.1, 0.2, 0.5, 1.0 $mol\,L^{-1}$ HF aqueous solution were designated as ZSM5, 0.1HF-ZSM5, 0.2HF-ZSM5, 0.5HF-ZSM5, 1HF-ZSM5, respectively.

The phosphorus-modified zeolites were prepared by wet-impregnation method according to our previous report. Firstly, 15 mL $(NH_4)_2HPO_4$ aqueous solution with proper concentration was prepared, and then 1.5 g of 0.5HF-ZSM5 zeolite was added into the $(NH_4)_2HPO_4$ solution and reacted at 65 °C for 6 h under stirring. Finally, the residual water was evaporated and the solid powders were calcined at 550 °C for 3 h [48]. The phosphorus content was set as 0, 0.25, 0.5, 0.75, 1 wt%, respectively. Correspondingly, they were designated as 0.5HF-ZSM5, 0.5HF-ZSM5-0.25P, 0.5HF-ZSM5-0.5P, 0.5HF-ZSM5-0.75P, 0.5HF-ZSM5-1P, respectively.

2.3. Characterization of catalysts

The XRD patterns were acquired on an X'pert PRO MRD Diffractometer under 40 kV and 40 mA using Cu Kα radiation. An EDAX Apollo XL-SDD in Scanning Electron Microscope (SEM) was used to detect phosphorous via elements mapping. N_2 adsorption-desorption curves were obtained at 77 K on Builder SSA-4200 (Beijing Builder Co. Ltd, China) to determine the specific surface area (S_{BET}), pore volume (V) and average pore radius (R). FTIR spectra and pyridine-absorbed FTIR were characterized on Bruker TENSOR37 FTIR spectrometer. Pyridine-absorbed FTIR was determined after absorbing pyridine and desorbing pyridine at 150 °C. Temperature programmed desorption of NH_3 (NH_3-TPD) was conducted on Builder PCA-1200 (Beijing Builder Co. Ltd, China) to determine the acidity properties according to our previous research [39,48]. The SEM images were taken on FEI Quanta FEG 250. TEM images were obtained on JEOL JEM-2100 with accelerating voltage of 200 kV (Cs = 1 mm, point resolution 0.25 nm).

In the *n*-hexane adsorption experiments, *n*-hexane was injected by N_2. The N_2 flow rate was 30 $cm^3\,min^{-1}$. The catalyst weight was 0.2 g. The ratio of catalyst weight to feed flow rate (W/F) was about 0.067 h. The adsorption amount was measured by gravimetry.

2.4. Catalytic cracking tests

The tests on catalytic cracking of *n*-hexane were performed on a fixed bed reactor at 650 °C for 12 h. For each test, 0.15 g of catalyst (40–60 mesh) was put into the reactor. The catalyst was activated for 1 h at 650 °C under N_2 atmosphere before *n*-hexane was fed into the reactor carrying by N_2. The ratio of catalyst weight to feed flow rate (W/F) was about 0.05 h. Different ratios of catalyst weight to feed flow rate (W/F) was obtained by varying the mass of catalyst. The products were collected and analyzed by gas chromatography (Agilent 6890)