

Comparative study on the preparation of Co/HZSM-5 molecular sieves by ion exchange method and impregnation method

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One of the key technologies to improve the catalytic cracking of alkanes is the development of high-efficiency catalyst. This research prepared Co/HZSM-5 zeolites with the same metal oxide loading by ion exchange method and impregnation method respectively, and evaluated the reaction of catalysts with the fixed bed micro-reactor. The experimental results show that the n-heptane conversion ability of the catalyst prepared by ion exchange method is better than the catalyst prepared by impregnation method, the former has higher conversion level and gas product yield. However, the catalyst prepared by impregnation method has high selectivity for propylene and butane. The impregnation sequence has a great impact on the distribution of products, and the composite modification has a higher conversion capacity than the single metal modification.

Keywords: Catalytic cracking; Ion exchange method; Impregnation method; Fixed bed micro-reactor; Conversion capacity

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1. Introduction

Low carbon olefins are important organic chemical materials, such as ethylene, propylene and butane [1, 2]. And they are the main raw materials for rubber and plastic production. Now, the main production processes of low-carbon olefins include steam cracking process, catalytic cracking process, methanol to olefin technology, alkane dehydrogenation process and olefin translocation, among which steam cracking process is widely used. In 2019, the global demand for propylene and ethylene was 180 million tons and 230 million tons respectively, and the propylene/ethylene ratio was 0.78. However, the production ratio of propylene and ethylene was only 0.42, so the contradiction between supply and demand was quite serious [3]. Compared with steam cracking, naphtha catalytic cracking is characterized by mild operating conditions, high value-added product selectivity, and adjustable propylene/ethylene ratio [4]. It is considered as a potential alternative process for steam cracking. One of the key technologies to improve the catalytic cracking of alkanes is the development of high-efficiency catalyst [5–7]. This catalyst requires certain conditions, which can not only activate alkanes well, but also ensure high selectivity of low-carbon

alkenes [8–10].

Alkanes are difficult to crack, and alkenes are easy to crack. Alkanes have low selectivity for cracking propylene, but alkenes have high selectivity for cracking propylene. If in-situ conversion of alkanes into alkenes can be achieved in the cracking process, the conversion and selectivity of alkanes will be improved [11]. According to the research of our group, it is found that the dehydrogenation of alkanes is an efficient way to produce low-carbon alkenes [12]. To some extent, the cracking activity of n-heptane can be improved and the selectivity of low-carbon alkenes can be increased by adding appropriate metal dehydrogenation promoters in the cracking reaction catalyst [13]. Based on the previous exploration, we found that it is difficult to obtain a high conversion level and a high selectivity for low-carbon olefins by simply adding dehydrogenation assistant directly, but we also found that the close contact of dehydrogenation and cracking active sites is more favorable for the reaction and the reaction effect is better [14]. In addition, it has been reported that the proximity of the metal active center and the acid center of ZSM-5 can improve the catalytic activity and olefin selectivity [15]. In this research, the distance between them is minimized, and the

dehydrogenation active sites are introduced into the molecular sieves by the way of metal modification of molecular sieves. Firstly, the C-H bond of alkane molecules breaks at the dehydrogenation active site to form alkenes or alkene intermediates, and then breaks at the acid site nearby to provide the initial positive carbon ions for the activation of alkanes, and it can promote the conversion of alkanes. Fe-CuO_x/ZSM-5 catalyst was prepared for low-temperature selective catalytic reduction (SCR) of NO_x with ammonia by ultrasonic impregnation method [16]. Cu-ZSM-5 zeolite membrane catalysts coating on paper-like sintered stainless fibers were prepared by ion-exchanged method for the catalytic wet peroxide oxidation of phenol in a structured fixed bed reactor [17]. Cu-ZSM-5 zeolite membrane catalysts prepared by ion exchange method were synthesized on paper-like sintered stainless fibers with three-dimensional net structure for the catalytic wet peroxide oxidation of phenol in structured fixed bed reactor [18].

This research uses Co/HZSM-5 as an example, and Co/HZSM-5 zeolites with the same metal oxide loading were prepared by ion exchange method and impregnation method respectively. The reaction of catalysts was evaluated on the fixed bed micro-reactor.

2. Experimental method

2.1. Fixed-bed micro-reverse experiment device

The fixed-bed micro-reactor device used in this research can realize the response in two ways by controlling the direction of the six-way valve (Fig. 1). A route represents the intermittent pulse response and B route represent the continuous response. This research adopted a route. Before the reaction, the catalyst bed was first purged with nitrogen to remove the water absorbed by the catalyst, and the dosing tube was filled with raw materials by a flat-flow pump. During the reaction, the direction of the six-way valve could be switched. The nitrogen pushed the raw materials in the quantitative tube into the reactor, and the reaction completed under the action of the catalyst. After the reaction completed, the nitrogen was purged for 10 minutes. The gas and liquid products were obtained after the condensation of the oil and gas. The gas product was collected by the drainage gas collection method, and the volume of the reaction gas was measured according to the volume of the drainage. The liquid product was collected by a liquid collection bottle, and the quality of the liquid product was obtained by the subtractive method [19, 20].

2.2. Analysis of reaction products

The resulting gas products were analyzed by Brooke Dalton 450-GC chromatograph. The contents of hydrogen, nitro-

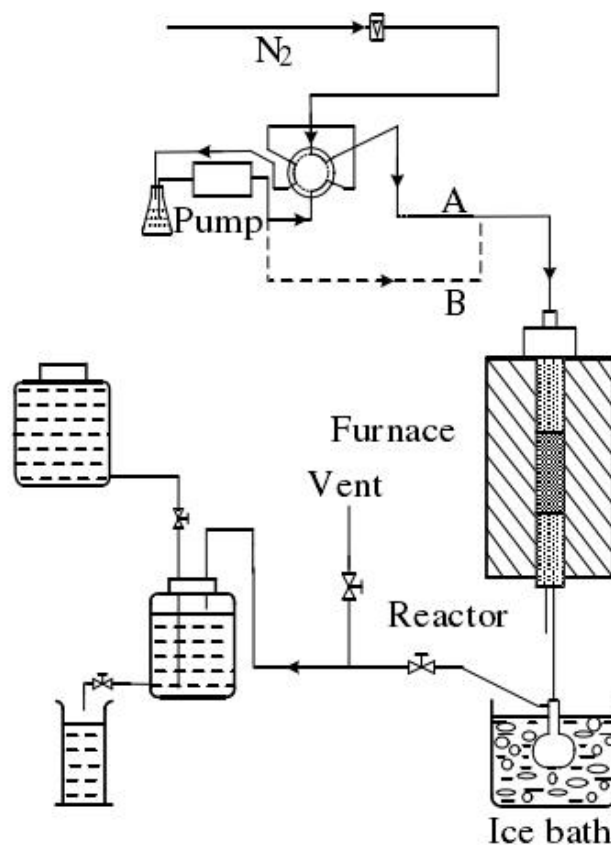


Fig. 1. Scheme of fixed bed reactor unit.

gen, oxygen, CO and CO₂ in the products were analyzed by TCD detector, and the compositions of C₁~C₅ hydrocarbons in the products were analyzed by FID flame ion detector. The composition of liquid products was analyzed by Agilent 890 gas chromatograph.

The composition of dry gas includes hydrogen, methane, ethane, and ethylene, and the composition of liquefied gas includes propane, propylene, butane and butylene. The calculation formulas of reaction conversion rate, yield and selectivity of each product are as follows.

$$\text{Conversion} = \frac{\text{mass of n-heptane converted}}{\text{mass of n-heptane}} \times 100\%$$

$$\text{Yield of product } i = \frac{\text{mass of product } i \text{ formed}}{\text{mass of n-heptane}} \times 100\%$$

$$\text{Selectivity of product } i = \frac{\text{yield of product } i}{\text{Conversion of n-heptane}} \times 100\%$$

3. Determination of modification scheme of HZSM-5 molecular sieve

3.1. Modification methods

As one of the group metal elements, cobalt shows a good oxidative dehydrogenation activity. At present, cobalt mod-

ified molecular sieve catalysts have been widely used in dehydrogenation, aromatization and other aspects. HZSM-5 zeolite modified by Co exhibited good activity of n-butane dehydrogenation and cracking, and the selectivity of butylene was significantly improved. This research prepared Co/HZSM-5 zeolites with the same metal oxide loading by ion exchange method and impregnation method respectively. The results of XRF analysis show that the impregnation amount is 1.52 % and 1.49 % respectively. The fixed bed micro-reactor was used to evaluate the reaction of catalysts, and the reaction results are shown as table 1. The reaction conditions are as follows: the temperature is 600°C, the catalyst loading is 5 grams, the pulse feeding is 0.85 grams, the carrier gas flow rate is 30 ml/min.

Table 1 show that the reaction effect of catalysts modified by the two methods is quite different. The n-heptane conversion ability of the catalyst prepared by ion exchange method is better than the catalyst prepared by impregnation method, the former has higher conversion level and gas product yield. However, the catalyst prepared by impregnation method has high selectivity for propylene and butane.

Table 1. Influence of modified methods on reaction results.

Modified method	Impregnation	Ion exchange
Conversion, wt%	18.20	21.06
Yield, wt%		
H ₂	0.09	0.15
CH ₄	0.50	0.67
C ₂ H ₆	1.57	1.92
C ₂ H ₄	2.30	2.70
C ₃ H ₈	1.95	2.25
C ₃ H ₆	5.72	6.23
C ₄ H ₁₀	1.06	1.35
C ₄ H ₈	2.69	2.90
Dry gas	4.41	5.44
LPG	11.42	12.73
Selectivity, wt%		
C ₂ H ₄	12.63	12.82
C ₃ H ₆	31.43	29.58
C ₄ H ₈	14.78	13.77

The impregnation method uses an aqueous solution of cobalt nitrate, and it is impregnated to the surface of the molecular sieve within three times. The cobalt ions exist in the form of hydrated ions. The inner and outer layers of cobalt ions are tightly wrapped by water molecules to form hydrated ions of Co(H₂O)₆²⁺. The diameter of these hydrated ions is larger than the pore diameter of HZSM-5

molecular sieve, so most of the modified elements can't enter the framework of the molecular sieve, but distributed on the surface of the molecular sieve. If the impregnation amount is large, they will aggregate on the surface of molecular sieve. When the molecular sieve is exchanged by ion-exchange method, the molecular sieve is added to the prepared cobalt nitrate solution and then stirred in a water bath at 80°C for 2 h. The hydrated ion structure of cobalt is partially destroyed during the stirring, and part of cobalt species can enter into the molecular sieve skeleton in the form of simple ions. This can reduce the accumulation of cobalt on the surface of molecular sieve. The content of transition metal particles on the surface of the molecular sieve is not the only factor that determines the acidity and catalytic properties of the molecular sieve. The distribution of metal particles on the molecular sieve has a great influence on the acid strength and catalytic properties of the molecular sieve.

In addition, the two methods have their own shortcomings. The utilization rate of raw materials of ion exchange method is low, especially for the expensive precious metals and rare metals. And the cost of this method is too high. In order to achieve higher exchange capability, ion exchange method usually takes a long time. Although the utilization rate of raw materials is very high, the uniformity of load components is poor. In order to achieve uniform dispersion, a few times of impregnation method is used and the operation is complicated. From the perspective of producing more low-carbon olefins and reducing costs, the impregnation method is more suitable for the modification of HZSM-5 molecular sieve. Therefore, the impregnation method is recommended for the modification of active components of the catalyst.

3.2. Modification sequence

The previous experimental results show that the catalytic effect of HZSM-5 zeolite modified by metal elements is very limited, whether by ion exchange or impregnation. The introduction of metal may damage the structure of molecular sieve and affect its catalytic performance. Now some scholars use the common modification method of metal and La or P to modify the molecular sieve, and this has achieved good results. It has been reported that the presence of P can inhibit the hydrogen transfer activity of the transition metal modified zeolite catalyst and improve the olefin selectivity. Previous studies have found that the interaction of metal elements and phosphorus on molecular sieve is much better than the single element. The modification of molecular sieves was carried out by common impregnation of metal elements and P in this research. For the two-component

Table 2. Effect of modification sequences on product distribution.

Catalyst	Conversion wt%	Yield, wt%										
		H ₂	C ₁	C ₂ ⁼	C ₂ ⁰	C ₃ ⁰	C ₃ ⁼	C ₄ ⁰	C ₄ ⁼	Dry gas	LPG	Olefins
CoPZ	32.18	0.15	0.88	2.77	4.16	3.45	9.83	1.87	4.70	7.85	19.85	18.69
PCoZ	27.06	0.15	0.73	2.20	3.46	2.50	7.65	1.34	3.46	6.55	14.95	14.57
LaPZ	38.79	0.25	0.79	2.73	4.37	5.37	10.81	2.92	5.39	8.15	24.49	20.56
PLaZ	32.02	0.15	0.61	2.21	3.50	3.34	9.32	2.17	5.02	6.47	19.84	17.83

CoPZ is the HZSM-5 catalyst modified by Co and then P, PCoZ is the HZSM-5 catalyst modified by P and then Co. LaPZ is the HZSM-5 catalyst modified by La and then P, PLaZ is the HZSM-5 catalyst modified by P and then La.

modified catalyst, the modification sequence is one of the important factors that affect the activity of the catalyst. The influence of modification sequence was investigated and the results are shown as Table 2. The reaction conditions are as follows: the temperature is 600°C, the catalyst loading is 5 grams, the pulse feeding is 0.85 grams, the carrier gas flow rate is 30 ml/min, the impregnation amount of cobalt and La is 1.5%, the impregnation amount of P is 4%.

Table 2 shows that the impregnation sequence has a great impact on the distribution of products, and the composite modification has a higher conversion capacity than the single metal modification. Whether P is modified by the rare metal La or the transition metal Co, the effect of impregnating metal elements followed by P is better than the effect of impregnating P followed by metal elements. For the method of impregnation of metal elements followed by P, the conversion rate and the yield of each product are significantly higher than that of the method of impregnation of P followed by metal elements.

4. Conclusions

This research prepared Co/HZSM-5 zeolites with the same metal oxide loading by ion exchange method and impregnation method respectively, and evaluated the reaction of catalysts with the fixed bed micro-reactor.

(1) The impregnation method is recommended for the modification of active components of the catalyst.

(2) The impregnation sequence has a great impact on the distribution of products, and the composite modification has a higher conversion capacity than the single metal modification.

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