



Studies on the preliminary cracking: The reasons why matrix catalytic function is indispensable for the catalytic cracking of feed with large molecular size[☆]

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ABSTRACT

The matrix catalytic function when cracking the feed oil with large molecular size was systematically studied using three different catalyst configurations, including staged bed, partly mixed bed and completely mixed bed. Results showed that molecules in the feed oil with large molecular size indeed preferred to be first precracked on the matrix surface and then entered into the zeolite pores during the practical reaction process. Furthermore, the matrix catalytic function exhibited a great matrix-precracking ability to large feed molecules, which considerably increased the catalyst activity and the light oil selectivity. Besides the much better accessibility, the matrix-precracking ability was also from the similar capability to crack large feed hydrocarbons into the moderate fragments with that of the zeolite component. More interestingly, the interactions between the matrix catalytic function and the zeolite catalytic function made the catalyst not only exhibit much more catalytic advantages of the zeolite component, but also retain the matrix-precracking ability. As a result, the interactions enhanced the catalyst activity and improved the product distribution at the same time. The matrix catalytic function is indispensable for the catalytic cracking of feed with large molecular size, although the matrix component itself presented an inferior catalytic performance than the zeolite component did.

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1. Introduction

Due to the great ability to process very large amounts of heavy oil fractions [1–3], and enough flexibility to direct production preferentially to liquid petroleum gas (LPG) olefins, gasoline or diesel, with minor modifications of the unit or even the operation conditions [4,5], the fluid catalytic cracking (FCC) is still a main conversion unit in oil refinery processes [6–9]. A typical FCC catalyst is mainly composed of Y zeolite and matrix. The zeolite component provides essentially all the cracking activities while the matrix component with large amounts of mesopores mainly performs the physical function [10–13].

In recent years, the demand for FCC products, such as liquid products and small olefins, is growing every year; on the other hand, the FCC feed stocks are gradually replaced by heavier ones

[13]. For molecules in heavy feeds, the critical diameters are in the range of 1.2 to 15 nm [14], while the pore diameter of Y-zeolite, the main active component of FCC catalysts, is only 0.74 nm, which is considerably smaller than the critical diameter of the molecules in heavy feeds. Even when the deformable ability is considered, the size of molecules allowed to penetrate into Y-zeolite pores is less than 1.02 nm [15]. It is possible for hydrocarbons with less than 20 carbons to enter into the micropores of Y-zeolite, but this process can hardly occur for fractions with boiling point higher than 400 °C. Post synthesis treatment of Y-zeolite [16–18] and/or introducing mesoporous zeolites [19–22] can enlarge the pore size of the zeolite component, but the former cannot enhance the diffusion process in Y-zeolite pores for large hydrocarbons obviously, because the mesopores created by post synthesis treatment cannot connect with each other [23]; on the other hand, the hydrothermal stability of the mesoporous zeolites cannot meet the required for the FCC process [24]. The acid sites on the external surface of Y-zeolite have a good accessibility, but the external surface area is too small, which accounts for 2%–10% of the total of Y-zeolite [25,26]. Therefore, the catalytic function of the matrix component, the one possesses large amounts of mesopores but is usually used to provide physical function for FCC catalysts, is increasingly important for the FCC process due to its precracking function

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[10,13,27], i.e., precracking large feed molecules into moderate ones making them capable of diffusing into zeolites to be further selectively cracked.

In the research field of the matrix catalytic function, Ballmoos and coworkers [27] loaded a matrix and a zeolite layer in different orders, and found that the feed conversion was higher when the reactant molecules of VGO first contacted with the matrix layer. Consequently, they proposed that the matrix component possessed percracking function for FCC feed stocks. Realizing the significance of the matrix catalytic function, Otterstedt and coworkers [28] added alumina into matrices to increase the matrix activity, but found that the introduction of the alumina gave rise to an inferior performance than catalysts with an inactive matrix. This result was consistent with the research of Al-Khattaf [12]. After that, Feng and coworkers [29] and Xu and coworkers [30] prepared new materials with large amounts of Brönsted sites as matrices, and found that the catalysts with these matrices presented a significantly higher activity and greater selectivity than catalysts with a conventional matrix. Recently, we systematically investigated the effects of different matrix acidity on the FCC process [31], and found that weak Brönsted acidity was most desirable for matrix when cracking feed with large molecular size. Besides, many other researchers [11,32–35] also found that different matrix materials would always result in different product distribution and different product quality.

In conclusion, the importance of matrix properties, especially matrix acidity, to the FCC process has been acknowledged. However, for the matrix catalytic function itself, it still lacks for systematical and deep studies [14]. For example, the reasons why the matrix catalytic function possesses the precracking ability except for its better accessibility, whether large feed molecules are first precracked on the matrix surface or not, the effects of the interactions between the matrix catalytic function and the zeolite catalytic function on the FCC process, and the new catalytic characteristics of the catalyst after the interactions, are still ambiguous.

This paper aims to systematically study the matrix catalytic function for the catalytic cracking of feed oil with large molecular size. In the first part of the work, the necessity and reasons of the matrix-precracking ability were studied. Then, we continued to investigate the practical reaction process of large feed molecules. After that, the effects of the interactions between the matrix and zeolite catalytic function on FCC process, and the new catalytic characteristics of catalyst after the interactions were further studied.

2. Experimental

2.1. Materials

A commercial fresh REUSY ($\text{Si}/\text{Al} = 2.77$, $\text{Na} = 1.08 \text{ wt\%}$, $\text{Ce} = 0.6 \text{ wt\%}$, $\text{La} = 0.3 \text{ wt\%}$, particle size = $3.55 \mu\text{m}$) was obtained from the Catalyst Factory of PetroChina. The hydrothermal ones (S-REUSY) were obtained from the commercial fresh REUSY with 100% steam at 765°C for 4 h.

A conventional active matrix was prepared using the following procedures: pseudoboehmite powder (Aluminum Corp. of China) was dispersed in distilled water under vigorous stirring. Then, a

12 M HCl solution was added dropwise at 30°C until the pH value of the pseudoboehmite sol was 3. After that, a certain of kaolin (Suzhou Kaolin, China) was dispersed in the pseudoboehmite sol under vigorous stirring. The pseudoboehmite sol, working as a binder in the matrix product, contained an amount of alumina corresponding to 30 wt% alumina in the matrix product. The mixture was stirred for 2 h, dried at 140°C for 12 h, and calcined at 700°C for 2 h in air. The as-prepared solid was pressed, crushed and sieved to obtain particles in the range of $80\text{--}180 \mu\text{m}$. Then these particles were dispersed in $0.5 \text{ M H}_3\text{PO}_4$ solution, and the suspension was stirred vigorously at 30°C for 20 min. After that, the suspension was filtered and the obtained particles were dried at 40°C for 24 h, and calcined at 600°C for 2 h in air. The resulting particles were treated with 100% steam at 780°C for 4 h before reaction. The properties of the matrix are summarized in Table 1. Of note was that, in order to avoid the property modifications of the matrix as well as S-REUSY during the catalyst preparation process [10,13,36], the FCC catalyst used in our experiments was the physical mixture of S-REUSY and the matrix.

2.2. Catalyst characterization

Nitrogen adsorption-desorption experiments were conducted on an autosorb instrument (Quantachrome). The total surface (S_{BET}) was calculated according to the Brunauer–Emmet–Teller (BET). To estimate the pore volume and pore size distribution of micropores, the SF method was used. To estimate the pore volume and pore size distribution of mesopores, the BJH method was used. The total acid sites number of catalysts were characterized by ammonia temperature-programmed desorption ($\text{NH}_3\text{-TPD}$). Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet 6700 spectrometer equipped with a MCT liquid nitrogen cooled detector. Particle size and crystal morphology of samples were examined with a scanning electron microscope (SEM).

2.3. Catalyst evaluation

Three different catalyst combinations of S-REUSY and the matrix were used in this study (Fig. 1). First, a matrix bed (85 wt%) and a S-REUSY bed (15 wt%) were loaded in different orders, named as staged bed (Fig. 1a). Second, a matrix bed, a S-REUSY bed and a bed of the physical mixture of the matrix and S-REUSY were loaded in different orders, with the mixture bed being always in the middle, named as partly mixed bed (Fig. 1b). In the partly mixed bed, the weight ratio of the zeolite content in both the mixture layer and all the catalyst bed was 15 wt%. The weight ratio of the mixture layer to the all catalyst bed was defined as the mixing degree. Third, S-REUSY (15 wt%) and the matrix powder were mixed completely and physically, named as completely mixed bed (Fig. 1c).

Catalytic experiments were carried out in a fixed-bed reactor of a microactivity test (MAT) unit. The reactions were carried out at 500°C and with a time on stream of 60 s. The catalyst to oil ratio (CTO) was varied in a range of 0.5–5 g/g keeping the amount of catalyst constant (3 g), and changing the amount of oil fed, in order to vary the conversion [11]. The conversion was defined here

Table 1. Characteristics of the samples tested.

Sample	Surface area (m^2/g)	Pore volume (cm^3/g)		Mean pore diameter (nm)	Acidity	
		Micropore	Mesopore		A_T (mmol/g) ^a	A_B/A_L ^b
S-REUSY	188.6	0.060	0.25	6.5	0.11	0.18
Matrix	76.1	0.0096	0.15	3.8	0.32	0.20

^a The total acid number characterized by $\text{NH}_3\text{-TPD}$.

^b The ratio of the Broñsted acid number (A_B) to Lewis acid number (A_L) characterized by Py-FTIR.

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