

# Preparation and modification of NaY/Beta micro-microporous composite molecular sieve and desulfurization performance

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**Abstract**—NaY/Beta was firstly modified using two ion-exchanged and two calcinations method to prepare CeY/Beta and CaY/Beta composite molecular sieve, which were characterized by means of XRD and ICP-MS. The results showed that cerium ions and calcium ions had entered into the zeolite pores in stead of the sodium ions, and highly dispersed on the zeolite. Static adsorption experiments were carried out to study the adsorption of organic thiophene. The desulfurization adsorption effect of the modified molecular sieve was enhanced greatly, and CeY/Beta molecular sieve exhibited better performance in the desulfurization rate.

**Index Terms**—Adsorption, Desulfurization, Modifiability, Y/Beta composite molecular sieve

## 1 INTRODUCTION

Sulfur compounds in the fuel oil will bring greatly harm to the processing cause and the product application. In addition, they could cause pollution to our environment and poison human health. Recently, with the tighten of the environmental protection laws and regulations, it is obviously urgent to pay attention on deep desulfurization of fuel oil.

The common desulfurization methods mainly include Catalytic Cracking Desulfurization, Hydrodesulfurization<sup>[1]</sup>, Ultrasonic Desulfurization, Adsorption Desulfurization, Organic Solvent Extraction Desulfurization<sup>[2]</sup>, Biodesulfurization<sup>[3]</sup>, Ionic Liquid Desulfurization<sup>[4,5]</sup> and Photochemical Oxidation Desulfurization<sup>[6]</sup>. Compared with these desulfurization methods, Adsorption Desulfurization can selectively remove the sulfide in the fuel oil under room temperature without hydrogen, which is considered as a very promising technique. The basic principle of Adsorption Desulfurization is to use solid adsorbent to selectively adsorb sulfur compounds in the fuel oil so as to remove them. Therefore, the key is to develop the adsorbent with great desulfurization performance.

Bimicroporous composite zeolite Y/Beta has been receiving much more attention especially in the field of petroleum processing and deep processing of petrochemical products, such as in hydrogenation cracking<sup>[7,8,9]</sup>, catalytic cracking<sup>[10]</sup>, owing to its bimicroporous structures and adjustable composite acidities. Du<sup>[11]</sup> reported that Y/Beta composite molecular sieve had higher acid strength than Y, Beta and Y Beta physical mixture, and exhibited high activity and selectivity.

In this paper, NaY/Beta was firstly modified using two ion-exchanged and two calcinations method to prepare composite molecular sieve, and characterized by means of XRD and ICP-

MS. Static adsorption experiments were carried out to study the adsorption of organic sulfur compounds. The results showed the adsorption desulfurization performance of the modified molecular sieve was enhanced greatly.

## 2 EXPERIMENTAL

### 2.1 Preparation of NaY/Beta composite molecular sieve

A certain amount of sodium aluminate, sodium hydroxide and seed crystal glue were added in a beaker, agitating until they were completely dissolved in the distilled water (The mole ratio of the whole system were  $\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : \text{SiO}_2 : \text{H}_2\text{O} = 16:1:15:320$ . It is sealed at room temperature for 24 h in beaker). The mixture was crystallized at 423 K for 4 d. Then NaOH and tetraethyl ammonium hydroxide were added. This sample was mixed with a certain amount of silica sol, then placed in a high pressure stainless steel reaction kettle at 373 K for 4 h. After the crystallization, it was cooled to room temperature and dried in the oven for 4 h. Finally the reactant was roasted in muffle furnace at 823 K (heating rate:  $5^\circ\text{C min}^{-1}$ ) for 4 h to get NaY/Beta composite molecular sieves.

### 2.2 Modification of NaY/Beta composite molecular sieve

Two ion-exchanged and two calcinations method was adopted to modify NaY/Beta composite molecular sieve. Adequate amount of NaY/Beta molecular sieve,  $\text{Ce}(\text{NO}_3)_3$  (0.1 mol/L) or  $\text{Ca}(\text{NO}_3)_2$  (0.1 mol/L) were mixed in the flask (250ml) with three necks, then joined with nitrate standard solution. The flask with three necks was heated on heating jacket with back-flowing at 373 K for 6 h. After filtering out solid molecular sieve, it was dried and roasted for 3 h, and the molecular sieve was dried and roasted again to gain the modified zeolite.

### 2.3 Characterization of molecular sieve

XRD results were analysed at  $2\theta = 5 \sim 40^\circ$  on a D/max2500 diffractometer instrument operating at 40 kV and 80 mA with Cu target and  $\text{K}\alpha$ -ray irradiation.

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## 2.4 Preparation of model oil

N-hexane as the solvent and thiophene as the solute were mixed to get the model oil with sulfur content 200 PPM. Thiophene of 0.2625 g and N-hexane were added into a small beaker, mixing with glass rod, and diverted the solution into a volumetric flask (500mL). This solution was washed by the N-hexane for 5-6 times, taken into volumetric flask, conformed the constant volume, mixed up, and sealed without air and light.

Sulfur content was determined by means of WK-2D Microcoulometry Analyzer.

## 3 RESULTS AND DISCUSSION

### 3.1 XRD Characterization of NaY/Beta composite molecular sieves

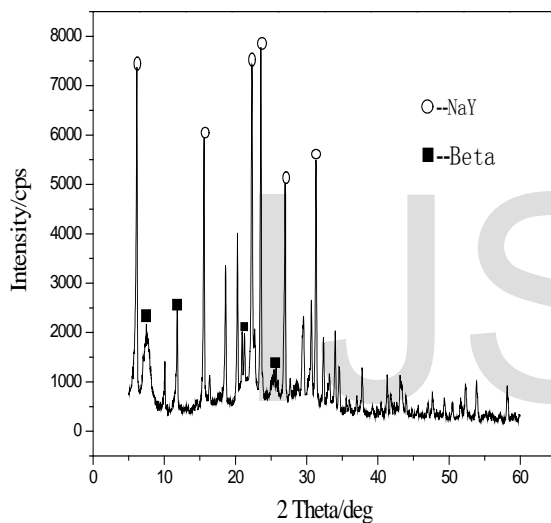


Fig.1 XRD patterns for zeolite NaY/Beta (large angle diffraction)

Figure 1 showed the XRD patterns for zeolite NaY/Beta (large angle diffraction). On one side, in Figure 1, six strong peaks appeared at 6°, 16°, 23°, 24°, 27° and 32°, which were typical characteristic peaks for zeolite Y. On the other side, four weak peaks appeared at 8°, 22°, and 25°, which were typical characteristic peaks for zeolite Beta. Therefore, this sample not only included both Y and Beta molecular sieve structure but also had the double microporous structure.

### 3.2 IR spectra

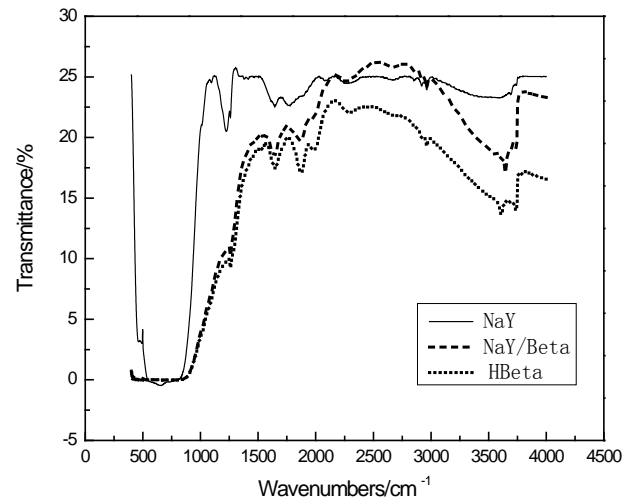


Fig.2 IR spectras of zeolite NaY, NaY/Beta, HBeta

The IR spectra of the zeolite NaY, Y/Beta, HBeta were shown in Figure 2. The IR spectra of the zeolite NaY/Beta corresponded both the zeolite Y's characteristic peak (Zeolite Y has the main characteristics of skeletal vibration peak: tetrahedron stretching vibration peak of 1145 cm<sup>-1</sup>, 1017 cm<sup>-1</sup>, 780 cm<sup>-1</sup>, 710 cm<sup>-1</sup>; Double 6-ring vibration peak of 570 cm<sup>-1</sup> and T-O bending vibration peak of 460 cm<sup>-1</sup>.) and zeolite H/Beta's characteristic peak (Zeolite Beta has the main characteristics of skeletal vibration peak: double 4-ring features vibration peak of 520 cm<sup>-1</sup>, double 5-ring vibration peak of 570 cm<sup>-1</sup>, double 6-ring features vibration peak of 610 cm<sup>-1</sup>, skeleton tetrahedron external connection antisymmetric stretching vibration peaks of 720 cm<sup>-1</sup>, 790 cm<sup>-1</sup>, 1187 cm<sup>-1</sup> and 1225 cm<sup>-1</sup>.), and showed that NaY/Beta composite molecular sieves sample includes both Y and Beta molecular sieve structure.

### 3.3 XRD Characterization of NaY/Beta, CaY/Beta and CeY/Beta

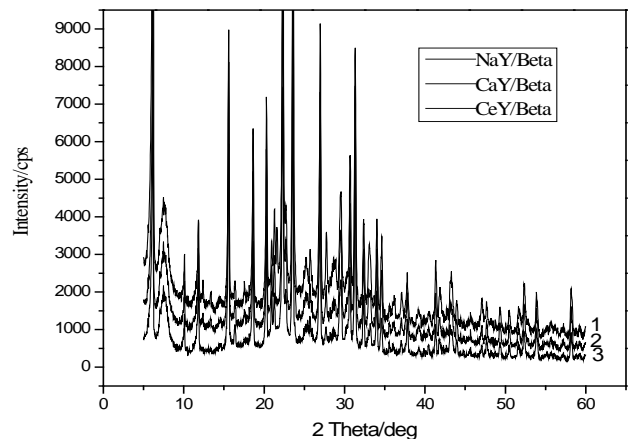


Fig.3 XRD patterns for NaY/Beta, CaY/Beta and CeY/Beta Zeolite (large angle diffraction)

Figure 3 showed the XRD patterns for NaY/Beta, CaY/Beta and CeY/Beta zeolite (large angle diffraction). As can be seen, molecular sieve characteristic peaks (dealt with the exchange of ion) were consistent with NaY/Beta molecular sieve characteristic peaks, which indicated that the main body crystal type of the molecular sieve kept unchanged and its strength increased slightly.

### 3.4 Analysis of ICP-MP

TABLE 1  
THE CHEMICAL COMPOSITION AND ION EXCHANGE DEGREE FOR NaY/BETA

zeolite	ion	Na <sup>+</sup> exchange degree	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> mole
NaY/ Beta	Na <sup>+</sup>	94%	5.1
CeY/ Beta	Ce <sup>3+</sup>	94%	5.1
CaY/ Beta	Ca <sup>2+</sup>	92%	5.1

Table 1 showed that the ion exchange degree of NaY/Beta was so high because that ion radius of Na<sup>+</sup> (0.101 nm), Ce<sup>3+</sup> (0.104 nm), Ca<sup>2+</sup> (0.100 nm) were less than or close to zeolite Y's β cage radius (0.12 nm), and this was why that Ce<sup>3+</sup>, Ca<sup>2+</sup> ion can enter into the β cage and exchange with Na<sup>+</sup> ion.

### 3.5 Adsorption desulfurization performance of molecular sieve

#### 3.5.1 Characterization of molecular sieve

The variables of molar ratio of adsorbent to oil, reaction temperature, and reaction time of the adsorption desulfurization were studied using NaY/Beta, CeY/Beta and CaY/Beta as the catalyst individually.

The results showed that desulfurization effects of the modified zeolites were better than NaY/Beta, and the best conditions on the highest desulfurization rate of the CeY/Beta were found to be the adsorbent/oil mass ratio of 0.05, reaction temperature of 363K and adsorption time of 4 h. The thiophene compounds contained the special structure of lone pair electron in the sulfur atoms, and if loading some high charge radius ratio (with a strong positive electric field) of metal ion or transition metal ions onto the zeolite molecular sieve, the adsorbent's sulfide adsorption ability would be enhanced. Ce<sup>3+</sup> can coordinate with transition metal complex and, still can form intermolecular Van Der Waals' force. These two kinds of effects increased the CeY/Beta's function of thiophene sulfide absorption. Whereas, Na<sup>+</sup> and Ca<sup>2+</sup> reflected the less performance on desulfurization. Under the optimal conditions, the best desulfurization rate could reach 94.98% and the function of CeY/Beta was better than CaY/Beta and NaY/Beta. The best desulfurization reaction conditions of CaY/Beta were found to be a adsorbent/oil ratio of 1:20, temperature of 363 K and time of 3 h with a desulfurization rate of 42.16%. The best desulfurization reaction condition of Na

Y/Beta was found to be a ratio of adsorbent/oil of 1:20, temperature of 373 K and adsorption time of 4 h with a desulfurization rate of 26.82%

#### 3.5.2 Orthogonal experiment and analysis of variance

The results of orthogonal experiment and analysis of variance were listed in the following two tables for CeY/Beta.

TABLE 2  
THE RESULTS AND ANALYSIS OF ORTHOGONAL EXPERIMENT

Experiment number	error term	adsorbent/oil ratio	Temperature (°C)	Time(h)	Desulfurization rate (%)
1	1	1:40	60	3	68.34
2	1	1:20	90	4	94.98
3	1	1:10	100	6	65.27
4	2	1:40	90	6	70.82
5	2	1:20	100	3	76.52
6	2	1:10	60	4	67.32
7	3	1:40	100	4	72.18
8	3	1:20	60	6	82.17
9	3	1:10	90	3	68.18
K1	228.59	211.34	217.83	213.04	
K2	214.66	253.67	233.98	234.48	
K3	222.53	200.77	213.97	218.26	
Average 1		70.45	72.61	71.01	
Average 2		84.56	77.99	78.16	
Average 3		66.92	71.32	72.75	
Range		17.64	6.67	7.15	

TABLE 3  
ANALYSIS OF VARIANCE

Source of error	Deviate	Degree of freedom	Mean square error	Value F
Adsorbent/oil ratio	523	2	261.5	17.43
Temperature	75	2	37.5	2.5
Time	84	2	42	2.8
Error	30	2	15	

In the aim of ensuring the best desulfurization reaction conditions, three variable factors (the ratio of adsorbent to oil, reaction temperature and reaction time) and three levels orthogonal test were carried out by analyzing the single factors. As shown in Table 2 and 3, the influencing order of three factors on the desulfurization rate was determined to be Adsorbent/oil ratio > Time > Temperature. According to the analysis of variance, it was necessary to choose the best level based on the significant factors, otherwise, for other test results of the less affected factors, it was significant to select the appropriate level based on the actual demand. Take these factors into account, the best conditions were the adsorbent/oil ratio of 1:20, temperature of 363K and time 4 h.

#### 4 CONCLUSIONS

(1) The NaY/ Beta double microporous composite molecular sieve, prepared by two step hydrothermal crystallization, not only has both Y type molecular sieve structure and Beta type molecular sieve structure characteristics, but also exhibits the best effect.

(2) The desulfurization adsorption effect of the modified molecular sieve was enhanced greatly; and CeY/Beta molecular sieve exhibited the highest desulfurization rate. The optimal conditions of CeY/Beta were found to be a ratio of adsorbent to oil of 0.05, a reaction temperature of 90°C and a reaction time of 4h, under which the desulfurization rate can reach 94.98%.

(3) The results of orthogonal experiment and analysis of variance showed that the adsorbent/oil ratio was the main influence factors, the reaction temperature and adsorption time was the secondary influence factors.

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