

Effects of metal modifications of Y zeolites on sulfur reduction performance in fluid catalytic cracking process

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Abstract

The acidity of catalytically active component, e.g., ultra stable Y zeolite (USY), plays an important role in determining their cracking activity and selectivity. To develop advanced sulfur reduction catalytic cracking catalysts, different type of elements were used to modify USY and the resulting catalysts were evaluated in a confined fluidized bed reactor and a micro-activity testing unit. The relation between the acidity of the zeolite and the conversion of sulfur compounds as well as the distributions of fluid catalytic cracking (FCC) products were discussed. The results showed that the rare earth (RE) metal can stabilize the catalyst and increase the conversion, but cannot increase the selectivity to thiophene compounds; V can reduce the sulfur content by 36.3 m%, but decreases the overall conversion compared with the base catalyst. An optimum catalyst was obtained by the combined RE and V modification, over which the sulfur content in FCC gasoline can be decreased and the selectivity for the target products can be improved, with the sulfur content reduced by 30 m% and the selectivity to coke even decreased by 0.20 m% at a comparable conversion level of the base catalyst.

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1. Introduction

With increasingly stringent regulations to gasoline, refiners are currently developing strategies for meeting ultralow sulfur gasoline regulations [1–3]. The main problem of gasoline desulfurization is to remove sulfur from fluid catalytic cracking (FCC) naphtha that contributes about 35% to the gasoline pools in USA and Europe and roughly 80–90% to the total gasoline pool in China. There are several solutions [4–11], such as the pre-treatment of FCC feedstock, and sulfur removal by hydrotreatment or adsorption. To meet the current gasoline sulfur specifications and much lower sulfur specifications in the future, using high performance FCC catalysts or additives [11–23] can provide an easier and more desirable alternative, which allow refineries to produce lower sulfur gasoline more cost-effectively and more operation-flexibly.

It is known that the in situ sulfur reduction of FCC gasoline requires catalyst with higher hydride transfer ability and higher catalytic cracking activity. According to the conversion

mechanism of thiophene derivatives, the synergistic effects of Brönsted acid and Lewis acid in catalyst are also an important factor for sulfur reduction. Therefore, one of the key objectives in FCC catalyst development is to modify zeolite to achieve a suitable acidity to effectively remove sulfur, which has been scarcely discussed in open literatures. In this paper, the modification effects of different chemical elements on USY (ultra stable Y zeolite) zeolite were studied, and the resulting catalysts were evaluated in a micro-activity test unit (MAT) and a confined fluidized bed (CFB) reactor. The relation between the acidity of the zeolite and the conversion of sulfur compounds as well as FCC product distribution were studied.

2. Experimental

The USY used in this work was manufactured by Catalyst Plant of Lanzhou Petrochemical Company, PetroChina Company, Ltd. The RE or other metal elements were loaded on the USY zeolite by an ion-exchange method, then the samples loaded with the different metals were dried at 120 °C for 10 h, calcined at 600 °C for 2 h in air to obtain the metal-modified USY zeolites. In a typical catalyst preparation

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Table 1
Nomenclature of the catalysts

Catalysts No.	Zeolite	Modification element	Description of the catalysts
1	Z0	None	USY
2	Z1	Zn	Zn-USY
3	Z2	V	V-USY
4	Z3	Cu	Cu-USY
5	Z4	RE	RE-USY
6		None	USY, steamed 4 h
7		RE	RE-USY (2.06% RE), steamed 4 h
8-1		RE	RE-USY (4.28% RE), steamed 4 h
8-2		RE	RE-USY (4.28% RE), steamed 10 h
9	Z0	None	USY
10	Z1	Zn	Zn-USY
11	Z3	Cu	Cu-USY
12		None	USY
13		V	V-USY
14		RE	RE-USY
15		RE + V	V-RE-USY

process, one metal-modified USY, a kaolin matrix (Suzhou Kaolin Company, China), and a binder alumina (Catalyst Plant of Lanzhou Pertochemical Company, PetroChina Company, Ltd.) were mixed together and shaped by spray-drying to obtain a microspheroidal catalyst. A base catalyst was prepared by using USY without element modification. Table 1 lists the nomenclature of the catalysts.

The laboratory evaluation of the FCC catalysts was performed in a fixed bed MAT unit (ASTM D-3907). MAT tests were performed at 460 °C for 70 s in steam. In each run, 5 g catalyst was loaded and the ratio of catalyst to oil was 3.2 (m/m).

To collect sufficient quantity of the products for property analyses, The CFB was also used. The experiment was performed under the conditions of 500 °C and 12 h⁻¹ (WHSV). In each run, 200 g catalyst was loaded with the ratio of catalyst to oil at 5.0 (m/m). Prior to a MAT or a CFB test, the catalyst was steam-deactivated at 800 °C for 4 or 10 h in a fluid bed in 100% steam.

A thiophene/diesel mixture with a sulfur content of 1341 µg/mL was used as the feed for the MAT evaluation. A high sulfur content paraffin feed (an atmospheric residue (AR) from Shenghua Refinery, China University of Petroleum) was used for all the CFB evaluation. The properties of the AR are listed in Table 2. The total sulfur contents in the feeding AR (S_{feed}), in the liquid products obtained by using the metal element modified USY catalysts (S_{liquid}) and by using the base catalyst (S_{base}) were measured by a WK-2C micro-coulometer. The sulfur reduction rate for the liquid products and sulfur conversion were calculated as follows:

$$\text{Sulfur reduction rate of liquid product (\%)} = (S_{\text{base}} - S_{\text{liquid}}) / S_{\text{base}} \times 100\%.$$

$$\text{Sulfur conversion} = (S_{\text{feed}} - S_{\text{liquid}} \times \text{liquid yield}) / S_{\text{feed}} \times 100\%.$$

The in situ pyridine-adsorption analyses for measuring Brönsted and Lewis acid sites in the zeolite samples were

Table 2
Properties of the feed used in the CFB assessment

Items		Shenghua Refinery AR
Density at 20 °C (g/cm ³)		0.9194
Viscosity (mm ² /s)	50 °C	599.53
	80 °C	67.88
Residual coke (%)		6.42
Group composition (wt%)	Saturated	43.60
	Aromatic	29.16
	Resin and asphaltene	27.24
Metal content (µg/g)	Ni	17.90
	V	1.00
	Fe	3.98
	Na	–
	Cu	–
Element analysis (wt%)	C	86.22
	H	12.33
	N	0.45
	S	0.73

carried out on a Nicolet 510P Fourier transformed infrared (FTIR) spectrometer in the wavenumber range of 1350–1800 cm⁻¹.

3. Results and discussion

3.1. Effects of metal element modification on acidity of USY

The USY zeolites were modified with zinc, copper, vanadium, and rare earth metal, respectively, and their acidities obtained by FTIR analysis are listed in Table 3. It can be seen that after modified with Zn, V, Cu and RE elements, the total acidities of the zeolites were increased. The USY modification

Table 3
Acidity of metal element modified USY zeolites

Zeolite	Element	Pyridine desorption temperature (°C)	B-acid A g ⁻¹	L-acid A g ⁻¹	$L_{\text{Strong}} / L_{\text{Total}}^a$ (%)
Z0	Base	200	6.2	6.1	16
		300	1.6	1.0	
		400	0.6	1.7	
Z1	Zn	200	7.7	37.5	25
		300	2.5	9.3	
		400	0.3	3.6	
Z2	V	200	7.1	39.8	20
		300	5.6	8.1	
		400	2.1	6.6	
Z3	Cu	200	12.5	32.3	51
		300	8.3	16.5	
		400	3.1	9.8	
Z4	RE	200	17.2	17.0	
		300	4.4	11.6	
		400	0	5.2	

^a The ratio of the mid-strong Lewis acidity to the total Lewis acidity (%).

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