Available online at www.sciencedirect.com

ScienceDirect

Catalysis Today 125 (2007) 173–177

CATALYSIS TODAY

www.elsevier.com/locate/cattod

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

Xinmei Pang [*], Li Zhang, Shuhong Sun, Tao Liu, Xionghou Gao

Petrochemical Research Institute, Lanzhou Petrochemical Company, PetroChina Company, Ltd., Lanzhou 730060, China

Available online 26 April 2007

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.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Sulfur reduction; Metal element modification; Acidity; USY zeolite; FCC catalyst; Gasoline; Coke yield

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 Pertochemical 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 obtained the metal-modified USY zeolites. In a typical catalyst preparation

---

[*] Corresponding author. Tel.: +86 931 7935564; fax: +86 931 7935564.
E-mail address: pangxinmei@petrochina.com.cn (X. Pang).

0920-5861/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2007.03.019

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

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

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:

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

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

The in situ pyridine-adsorption analyses for measuring Brönsted and Lewis acid sites in the zeolite samples were 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_{Strong}/L_{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 (%).

Table 4
Conversion of thiophene/diesel over the catalysts prepared with different USY zeolites

	Catalyst				
	1	2	3	4	5
	Z0[a]	Z1[a]	Z2[a]	Z3[a]	Z4[a]
MAT conversion (%)	89	91	89	87	89
Sulfur in liquid product (μg/mL)	622	412	365	510	615
Sulfur reduction rate of liquid product (%)	Base	33.8	41.3	18.0	1.1
Sulfur conversion (%)	77	87	87	79.2	75.5

[a] Zeolite.

with RE led to a remarkable increase in the density of Brönsted acid sites, while the USY modifications with Zn, V and Cu resulted in an increase in Lewis acidity both in quantity and in strength. The USY modifications with Zn and V mainly increased the weak Lewis acid (75–80% of total Lewis acid), while the USY modification with Cu increased strong Lewis acid (51% of total Lewis acid), owing to their different electronegativities.

3.2. *Effects of acidity on thiophene conversion*

The catalysts prepared with the different zeolites and deactivated in 100% steam at 800 °C for 4 h were evaluated in the MAT unit and the results are listed in Table 4. The catalysts prepared with Zn, V and Cu modified USY zeolites, such as the V-USY based catalyst, increased the conversion of thiophene; on the contrary, the catalyst prepared with the RE-modified USY decreased the conversion of thiophene. The reason was that the RE ion-exchanged into the zeolite functions to zeolite acidity differently from Zn, V and Cu. The acidity analysis results listed in Table 3 show that Zn, V and Cu increase the Lewis acidity of the zeolites, while RE increases the Brönsted acidity that benefits the cracking activity. Since Lewis acidity could facilitate the adsorption of thiophene molecules [23], Lewis alkaline in nature can increase their conversion. Brönsted acid does not affect the adsorption of sulfur-containing compounds, so the RE-USY catalyst does not cause any change in the sulfur content of the liquid product.

Table 5 gives the MAT results of the catalysts prepared with the USYs of different RE contents (all catalysts except for catalyst 8-2 were deactivated in 100% steam at 800 °C for 4 h. The steaming time for catalyst 8-2 was adjusted to have a MAT conversion approach to 75% with the aim of providing a comparable severity of operation). The results show that the unit cell size (a_0) of the USY zeolites increases with the increasing RE content, indicating the stabilizing effect of the RE modification on USY zeolite. Table 5 also shows that both the MAT conversion and the sulfur conversion increase with the increasing RE content, similar to those reported in literature [20]. The larger the unit cell size, the lower the sulfur concentration in FCC gasoline. When the MAT conversion of catalyst 8-2 was adjusted to 76% (while that of catalyst 7 that has a lower RE content was 75% for comparison), however, the sulfur conversion was not increased with the increasing RE content. This phenomenon further confirms that the USY modification by RE does not affect the selectivity of thiophene conversion.

Table 5
Conversion of thiophene/diesel over RE-USY catalysts

Catalyst	6	7	8-1	8-2
RE (m%)	0	2.06	4.28	4.28
Zeolite unit cell size (UCS, a_0) (nm)	2.427	2.433	2.444	2.438
MAT conversion (m%)	64	75	86	76
Sulfur in liquid product (μg/mL)	1049	967	788	970
Sulfur conversion (%)	37.3	42.7	58.2	42.2

3.3. *CFB assessment results*

The catalysts prepared with the Zn and Cu modified USYs were further evaluated in the CFB at 500 °C and the results are listed in Table 6. According to the carbonium mechanism for catalytic cracking reactions, Brönsted acid sites are the main active sites, and weak Lewis acid sites are also beneficial to convert larger molecules to smaller ones; strong Lewis acid sites incur the coke formation and accumulation in catalyst and thus decrease the reactivity and the conversion of the feedstock. This mechanism can be fairly applied to the present sulfur reduction results. The results in Table 6 show that the hydrogen and coke yields over the Cu-USY catalyst are much higher than those over the Zn-USY catalyst, because the Cu-USY has the increased strong Lewis acidity (51% of the total Lewis acid as shown in Table 3). Therefore, Cu is not suitable to modify FCC catalyst. The Zn-USY catalyst did not influence the distribution of the products, but reduced the sulfur content in gasoline by 24.8% compared with the base catalyst.

Table 6
CFB assessment data for the catalysts prepared from USY, Cu-USY and Zn-USY

	Catalyst[a]		
	9	10	11
	Z0[b]	Z1[b]	Z3[b]
C/O (m/m)	5.0	5	3.75
WHSV (h^{-1})	12	12	16
Products yield (m%)			
Dry gas	1.72	1.84	2.74
H_2	0.07	0.09	1.04
$C_3 + C_4$	15.30	18.45	18.06
C_5 + gasoline	51.60	51.94	41.05
LCO	18.83	15.96	19.03
HCO	7.09	5.58	8.00
Coke	5.10	5.62	11.00
Total	99.64	99.39	99.83
Conversion (m%)	73.72	77.85	72.85
Sulfur in gasoline (μg/mL)	617	464	/
Sulfur reduction (%)	Base	24.8	/

[a] The catalyst was aged at 800 °C in 100% steam for 10 h.
[b] Zeolite.

Table 7
CFB assessment data for the catalysts prepared from RE- and V-USY

	Catalyst[a]			
	12 Base[b]	13 V[b]	14 RE[b]	15 V + RE[b]
Products yield (m%)				
Dry gas	2.38	3.306	3.11	3.04
$C_3 + C_4$	13.67	11.57	18.34	14.92
C_5 + gasoline	46.29	39.19	52.00	49.55
LCO	20.52	22.58	15.21	19.14
HCO	12.363	17.74	5.48	8.23
Coke	4.42	5.59	5.41	4.64
Total	99.64	99.98	99.55	99.52
Coke selectivity (%)	6.63	9.41	6.86	6.43
Conversion (%)	66.67	59.41	78.86	72.15
Light liquid (m%)	66.81	61.77	67.21	68.69
Total liquid (m%)	80.48	73.34	85.55	83.61
Sulfur in gasoline (μg/mL)	694	442	631	486
Sulfur reduction rate (%)	Base	36.3	9.1	30.0

[a] The catalyst was aged at 800 °C in 100% steam for 10 h.
[b] Elements used.

3.4. Catalyst design, preparation and evaluation for sulfur reduction

According to the results shown in Table 4, V modification can significantly enhance the catalyst sulfur reduction ability, while RE modification can increase the catalyst heavy oil conversion ability (Table 5). Therefore, three sulfur reduction FCC catalysts were designed and prepared by using the zeolites modified with V, RE and their combination, respectively. The evaluation results in the CFB reactor are shown in Table 7. Compared with catalyst 12 (the base catalyst), catalyst 14 (with the RE-USY zeolite as the active component) increased the conversion roughly by 12% and decreased the sulfur content in gasoline by only 9.1 m%. This was in accordance with the results shown in Table 4. Catalyst 13 (with the V-USY zeolite as the active component), while decreasing the conversion roughly by 5%, surprisingly decreased the sulfur content in gasoline by 36.3 m%. For catalyst 15 (with the V-RE-USY as the active component), the conversion was increased by 5.5% compared with that obtained over the base catalyst, and the gasoline sulfur content was reduced from 7300 to 486 μg/mL, 208 μg/mL lower than that obtained over the base catalyst, i.e., the sulfur reduction was increased by 30.0 m%. To our surprise, the coke selectivity of catalyst 15 was also reduced by 0.20 m% at a comparable conversion level. These results are significantly different from those in literature [19], in which there was always an unwanted increase in coke yield along with the increasing sulfur reduction. According to the results in Table 3, we know that the USY modified with V mainly increases the weak Lewis acidity, which benefits the adsorption and conversion of thiophene molecules, and the USY modified with RE leads to an increase in the density of Brönsted acid sites, which benefits the activity of cracking and hydrogen transfer reactions. Hydrogen transfer reactions play an important role for reducing gasoline sulfur content. Thus, catalyst 15 prepared with the V-RE-USY could slightly reduce the cracking activity without increasing coke yield compared with catalyst 14 prepared with the RE-USY.

4. Conclusions

The modification of USY zeolite with Zn, V, Cu and RE could increase the total acidity of the zeolite. Among the different modified zeolites, the USY modified with RE increased the Brönsted acid and thereby cracking activity, but had no effect on sulfur conversion; the USY zeolites modified with Zn, Cu and V increased the Lewis acid which benefits the adsorption and conversion of thiophene molecules. The assessment results indicated that the USY modified with Cu gave rise to serious coke deposition on the catalyst owing to its high dehydrogenation ability, while the USY zeolites modified with Zn and V only slightly increased coke yield, and the V-modified zeolite reduced the sulfur contents obviously. The USY modified with the combination of RE and V yielded the superior catalyst that showed both high sulfur reduction performance and desirable product selectivity.

Acknowledgments

The authors thank the Ministry of Science and Technology of China for providing financial support through the National Basic Research Program (Grant No. 2004CB217806).

References

[1] M. Lesemann, C. Schult, Hydrocarbon Process. 82 (2003) 66.
[2] C. Song, Catal. Today 86 (2003) 211.
[3] X.J. Zhao, Preprints 49 (2004) 318.
[4] G.D. Lamb, E. Davis, J. Johnson, NPRA Annual Meeting, AM-00-13, 2000.
[5] R.H. Thomas, B.B. Garland, P.G. John, et al. NPRA Annual Meeting, AM-00-11, 2000.
[6] G.J. Byron, D. Kidd, G. Greenwood, et al. NPRA Annual Meeting, AM-01-14, 2001.
[7] D. Kidd, NPRA Annual Meeting, AM-02-47, 2002.
[8] J.A. Valla, A.A. Lappas, I.A. Vasalos, C.W. Kuehler, N.J. Gudde, Appl. Catal. A: Gen. 276 (2004) 75.
[9] A.A. Lappas, J. Valla, I.A. Vasalos, C.W. Kuehler, J. Francis, P. Connor, N.J. Gudde, American Chemical Society, Division of fuel Chemistry Preprints of Symposia, vol. 47, 2002, p. 50.
[10] R.F. Wormsbecher, G. Kim, US Patent 5,525,210 (1996).
[11] K.P. Scott, NPRA Annual Meeting, AM-02-37, 2002.
[12] H.B. Francisco, C.M.M. Juan, Q.S. Roberto, S.V. Jaime, P.A. Francisco, F. Francois, Appl. Catal. B: Environ. 42 (2003) 145.
[13] H.B. Francisco, C.M.M. Juan, Q.S. Roberto, S.V. Jaime, P.A. Francisco, P.L. Miguel, Appl. Catal. B: Environ. 34 (2001) 137.
[14] X.M. Pang, S.H. Sun, C.Y. Li, H.H. Shan, C.H. Yang, S.B. Li, American Chemical Society, Division of fuel Chemistry Preprints of Symposia 2002, vol. 47, 2002, p. 312.
[15] M.Q. Daniel, A.D. Paul, Hydrocarbon Eng. 7 (2002) 45.
[16] A. Humphries, C.W. Kuehler, NPRA Annual Meeting, AM-03-57, 2003.
[17] P-O.F. Andersson, M. Pirjamali, S.G. Jaras, M. Boutonnet-Kizling, Catal. Today 53 (1999) 565.

[18] C.F. Dean, A.M. Aitani, M.R. Saeed, M.A. Siddiqui, Pet. Sci. Technol. 21 (2003) 1265.

[19] T. Myrstad, H. Engan, B. Seljestokken, E. Rytter, Appl. Catal. A: Gen. 187 (1999) 207.

[20] A.A. Lappas, J.A. Valla, I.A. Vasalos, C. Kuehler, J. Francis, P. Connor, N.J. Gudde, Appl. Catal. A: Gen. 262 (2004) 31.

[21] M.A.B. Siddiqui, S. Ahmed, A.M. Aitani, C.F. Dean, Appl. Catal. A: Gen. 303 (2006) 116.

[22] A.V.T. Ana, C.G. Rogelio, F.P.A. Luis, R.S. Jorge, J.G.L. Antonio, Catal. Today 107/108 (2005) 713.

[23] R.F. Wormsbecher, G. Kim, EP 0,609,971 (1993).