

# The development of FCC catalysts for producing FCC gasoline with high octane numbers

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**Abstract** The effects of acidity and pore properties of rare earth modified USY on heavy oil conversion were investigated. USY with varied rare earth contents were prepared with impregnation method. FCC catalysts were also prepared with modified USY and tested by micro activity tests (MAT) and advanced catalytic evaluation (ACE). The results showed that USY3 had a good performance in cracking polycyclic hydrocarbons in heavy oil and diesel to aromatics and iso-olefins that exist in gasoline; the surface area and pore volume of USY3 increased by 54 m<sup>2</sup>/g and 0.032 ml/g, respectively, after porosity cleaning; the new optimized FCC catalysts improved the cracking of polycyclic aromatic hydrocarbons (PAHs) to form gasoline with high octane numbers. When tested on a pilot riser unit at 500 °C and 1.89 s with a catalyst-to-oil ratio of 5.6, the new catalyst Cat-3 had a 0.24 % higher propylene yield and a 1.52 % higher liquid yield compared with the reference catalyst Cat-1. However, it had a 7.89 % lower olefin content in FCC gasoline with the same octane numbers.

**Keywords** USY · Pseudo-boehmite · Aluminum debris · Octane number · Olefin

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## Introduction

Gasoline in refineries comes mainly from the units such as steaming of crude oil, catalytic cracking, catalytic reforming, hydrocracking and alkylation. The fluid catalytic cracking (FCC) process is one of the most important means in deep process of crude oil due to its applicability, flexibility and good economical feasibility. In China, more than 75 % of motor gasoline is provided by fluid catalytic cracking (FCC) units. However, the octane numbers of FCC gasoline is too low to meet the requirements of motor fuels. On the other hand, the increasing severe crude oil supplies worldwide and more attention on environmental regulations are promoting the tendency of converting heavy oil into high qualified gasoline with high octane numbers by FCC process [1, 2]. Besides, with the rapid development of China's automobile industry, car ownership especially imported high-end cars and domestic joint ventures has been increasing substantially. To work with high compression as well as to meet the requirements of increasingly stringent environmental regulations on automobile engines, gasoline upgrading and the demand of high-octane gasoline are increasing prominently and had been rapidly increasing in recent decades.

Besides, FCC gasoline generally has high content of olefins which has high octane numbers. However, extravagant olefins make the gasoline stability worse and increase the emission of CO and NO when combusted in engines. The olefin content in end gasoline products is also strictly restricted. Therefore, controlling the olefin content simultaneously to improve the octane numbers of FCC gasoline is the key to improving current and future end gasoline product's qualities. Among numerous methods, the use of catalysts or additives to improve the FCC gasoline octane is the most cost-effective, direct and effective way to upgrade petrol problem.

In this work, USY has been modified with rare earth to adjust their acidity and pore structures. Thereafter, the corresponding FCC catalysts have been prepared, characterized and tested using MAT, ACE evaluation and riser to investigate their performance in hydrocarbon cracking and producing high-octane FCC gasoline.

## Experimental section

### Modification of USY

The modified USY was obtained by ion exchange method and impregnation method, using commercial zeolite NaY as raw material. The ion exchange of NaY was carried out in the solution of lanthanum chloride and ammonium salt at 80–100 °C for 1 h. USY was obtained in sequence of filtration, washing, drying of the above suspension and finally heating in the presence of water steam at 500–600 °C for 2 h. USY1, USY2 and USY3 with different rare earth contents were finally prepared after impregnation and calcination.

### Catalyst preparation

The matrix was firstly prepared by mixing chemical water, binder and functional component. The catalysts were obtained by adding modified USY into the above matrix under stirring and then treated in sequence of spray drying, washing and drying. The catalysts were, respectively, marked as Cat-1, Cat-2 and Cat-3 containing corresponding USY1, USY2 and USY3.

### Characterization

The element content was determined by X-ray fluorescence (XRF) using a Rigaku ZSX Primus spectrometer. The degree of crystallinity and unit cell size (UCS) were obtained on a Rigaku D/MAX-3CX diffractometer. The pore properties of catalysts were carried out in a Coulter Omnisorp 360 analyzer. The samples were first outgassed at 300 °C for 4 h with a vacuum degree of  $1.33 \times 10^{-7}$  Pa. The thermal stability of catalysts was tested on a PCT-II TG–DTA analyzer. NH<sub>3</sub>-TPD was measured on a Micromeritics 2910 analyzer. The samples were firstly treated at 550 °C for 2 h and then absorbed in an NH<sub>3</sub> gas stream (25 ml/min) at 100 °C for 0.5 h. The signal was collected at a heating rate of 10 °C/min to 900 °C in a N<sub>2</sub> gas stream of 50 ml/min.

### Catalytic evaluation

The micro activity tests (MAT) of catalysts were performed in a bench-scale unit WF-2006. The catalytic

reactions occurred at 460 °C for 70 s with a catalyst-to-oil (CTO) ratio of 3, using 5.0 g catalyst and Dagang light diesel as feed. The catalysts were hydrothermally treated in 100 % water steam at 800 °C for 4 h before catalytic tests.

The evaluation of cracking activity was performed in a Kayser ACE catalytic cracking unit and LPEC/SINOPEC XTL-5 riser unit [3, 4]. The properties of feedstock are displayed in Table 1. The catalysts were hydrothermally treated in 100 % water steam at 800 °C for 17 h before ACE tests and 10 h before riser tests, respectively. The ACE tests were performed at 530 °C with a CTO ratio of 5 and the riser tests were performed at 500 °C with a CTO ratio of 6.

The resulting cracking gases were collected and analyzed by an Agilent CP3000 gas chromatograph (GC). The compositions of gasoline, diesel and heavy oil were analyzed by simulated distillation on a HP 6890 GC. The gasoline fraction was in the boiling points below 205 °C and diesel fraction was in the boiling point in the range of 205–350 °C.

## Results and discussion

### Rare earth modified USY

It is wide acknowledged that the majority of active sites of FCC catalysts which are responsible for the cracking of heavy oil into light hydrocarbons exist on zeolite. Therefore, the activity stability, acidity distribution and unit cell size (UCS) of zeolites determine the ability of FCC catalysts to crack heavy oil, selectivity of products and octane numbers of FCC gasoline. NaY modification with rare earth ions is mostly used to prepare REUSY with adjustable rare earth contents and thermal and/or hydrothermal stabilities. In this process, one or more of the metal or nonmetal ions are usually used to change the acidity and stability of zeolites. In this work, three USY with varied rare earth contents were prepared and their properties are shown in Table 2. It was shown that USY1 with the lowest rare earth content possessed the smallest UCS but the highest collapse temperature and retention of crystallinity after modification. Additionally, the cell parameters were increased by rare earth doping.

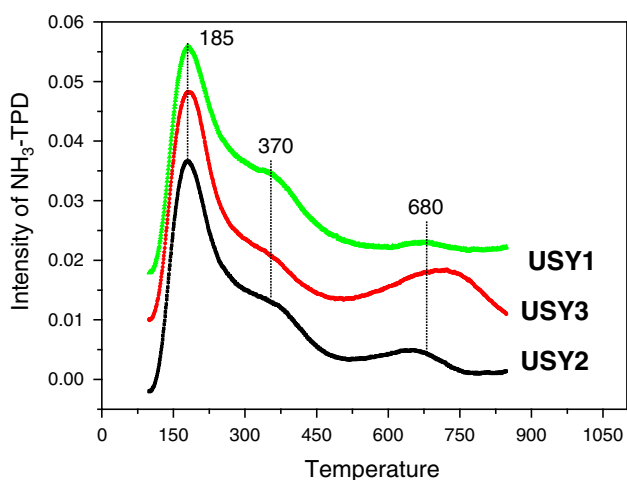
The acidity properties of rare earth modified USY were measured using NH<sub>3</sub> as probe molecules (Fig. 1). Three desorption peaks were observed at 185, 370 and 680 °C, which belonged to weak, medium and strong acidic sites, respectively. Obviously, the amount of the total acidic sites and the strong ones of USY3 were the highest and the corresponding desorption peak of strong acidity shifted to higher temperature. In contrast, the amounts of medium strong acidic sites of USY1 and USY2 were much higher

**Table 1** Properties of feed in ACE and riser unit evaluation

Density (20 °C)/(g cm <sup>-3</sup> )	w (SARA)/%				w (Metal)/(μg g <sup>-1</sup> )				
	Saturates	Aromatics	Resins	Asphaltenes	Ni	V	Fe	Na	Cu
0.901	63.5	25.8	10.7	0	7.46	4.40	3.98	5.00	0.66
Conradson carbon/%	w (Element)/%								
	C	H	N	S					
4.30	85.72	12.33	0.45	1.4					

**Table 2** The properties of rare earth modified USY

Item	Re <sub>2</sub> O <sub>3</sub> , m%	C/C <sub>0</sub> , m%	UCS, Å	Collapse temperature, °C	Crystallinity retention, %
USY1	1.8	64	24.52	1,030	74
USY2	8.1	52	24.63	1,004	61
USY3	12.8	53	24.67	1,014	65

**Fig. 1** The NH<sub>3</sub>-TPD curves of rare earth modified USY

than USY3. The gradient acidity distribution of modified USY was of great importance in catalytic cracking process.

The effects of modified USY on reactions

To investigate the effects of acidity and UCS of zeolite on catalytic reactions, three catalysts were prepared with modified USY and tested by ACE evaluation. The results (Table 3) showed that Cat-1 had the lowest conversion for heavy oil, while USY3 had the highest conversion which might be ascribed to its high content of strong acidic sites. However, the low acidity density of Cat-1 was responsible for the high olefin content and octane numbers. It could be ascribed to the decreased hydrogen transfer reactions which decreased the saturation of olefins. For Cat-3, the yields of iso-paraffins and aromatics were obviously higher which enhanced the octane numbers of FCC gasoline,

**Table 3** ACE evaluation results of modified USY containing FCC catalysts

Item	Cat-1	Cat-2	Cat-3
Zeolite	USY1	USY2	USY3
Yield, m%			
Dry gas	2.67	2.55	2.80
LPG	16.84	20.61	22.54
Gasoline	46.54	53.85	54.12
Diesel	15.58	12.45	10.58
Heavy oil	13.03	4.94	3.75
Coke	5.33	5.60	6.20
Conversion, m%	71.39	82.61	85.67
Total yields, m%	78.96	86.91	87.24
Light oil yields, m%	62.12	66.30	64.70
Properties of gasoline			
N-paraffins, v%	6.37	5.31	4.98
Iso-paraffins, v%	14.19	24.19	26.59
Olefins, v%	42.14	26.29	19.90
Naphthenes, v%	4.72	5.04	5.39
Aromatics, v%	32.58	39.16	43.15
MON	80.1	80.8	81.5
RON	90.9	89.7	90.8

especially for the motor octane number (MON). It was attributed to the higher cracking ability of Cat-3 on converting more PAHs in the heavy oil and diesel to aromatics and iso-paraffins, which compensated the loss of octane numbers due to the decrease of olefins.

The effects of pore structure of USY3 on reactions

The pore structures of catalysts are important for reactions. For FCC catalysts, three types of pores are involved according to the classification criterion by IUPAC. The micropores that are less than 2 nm are provided by the zeolites and acting as the main repository for cracking hydrocarbons. However, the heavy oil molecules are too big to enter into the micropores for its sizes are in the range of 3–10 nm. It was found out that the diffusion of molecules in pores of catalysts was not limited when the optimized pores were 2–6 times bigger than the sizes of

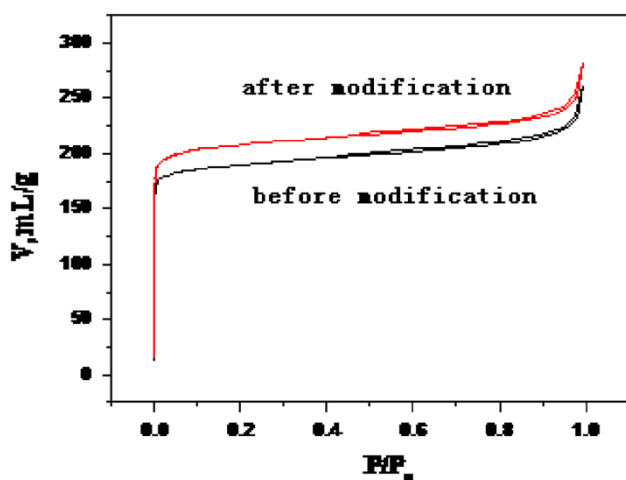


Fig. 2  $N_2$  sorption curves of USY3 before and after modification

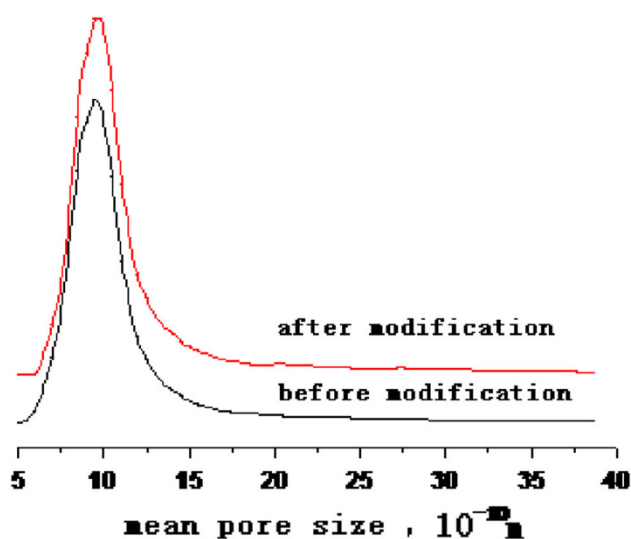


Fig. 3 Pore distributions of USY3 before and after modification

molecules. Therefore, the macropores ( $>50$  nm) mainly composed by the interpores between small particles were used for pre-cracking of heavy oil macromolecules. In contrast, the mesopores in between were the secondary pores of zeolites and are used for cracking cycloparaffins and side chains of aromatics into light cycle oil (LCO). The acidity in mesopores should be mild and its numbers were usually limited [5].

Generally, aluminum or silica fragments were formed and partially blocked the pores of zeolites in the process of catalyst preparation. At the same time, it caused a partial deactivation and over cracking of hydrocarbons. In this work, the USY3 was cleaned by modifier and the  $N_2$  sorption curves and pore distribution of USY3 before and after optimization were shown in Figs. 2 and 3, respectively. The data (Table 4) showed that the surface area and pore volume of catalyst increased after cleaning while the

**Table 4** The pore properties of USY3 before and after modification

Item	Surface area, $m^2/g$	Pore volume, ml/g
Before modification	578	0.41
After modification	629	0.44

**Table 5** ACE evaluation of FCC catalysts containing the USY3 before and after modification

Item	Before modification	After modification	Differences
<b>Yields, m%</b>			
Dry gas	2.74	2.70	-0.04
LPG	23.27	23.22	-0.05
Gasoline	52.33	52.85	+0.52
Diesel	10.77	10.63	-0.14
Heavy oil	4.10	3.93	-0.17
Coke	6.79	6.67	-0.12
<b>Selectivity, m%</b>			
Conversion, m%	85.12	85.44	+0.32
Total yields, m%	86.37	86.70	+0.33
Light oil yields, m%	63.11	63.49	+0.38
<b>Octane numbers of gasoline</b>			
MON	81.5	82.1	+0.6
RON	91.6	92.0	+0.4

**Table 6** Properties of Cat-3

$Na_2O$ , m%	$RE_2O_3$ , m%	Abrasive resistance, m%	Pore volume, ml/g	MAT (4 h), %
0.20	2.9	1.4	0.38	76

pore sizes remain the same. The results indicated that the fragments in the pores of zeolite were removed and the pores were much clearer.

The ACE evaluation results of FCC catalysts containing the USY3 before and after modification are shown in Table 5. It showed that after modification, the yields of heavy oil and coke decreased by 0.17 and 0.12 %, respectively, while the total yields increased by 0.33 %. For FCC gasoline, the MON and RON increased by 0.6 and 0.4 unit, respectively. It indicated that the clean pores were in favor of fast diffusion of high octane components before over cracking.

Catalytic tests of new catalysts on a riser

The properties of newly prepared FCC catalysts are displayed in Table 6. It indicated that the FCC catalyst Cat-3 met the requirements of industrial catalysts.

**Table 7** The reaction results obtained on a riser

Item	Cat-1	Cat-3
Yields, m%		
Dry gas	1.72	1.63
LPG	24.81	24.68
Gasoline	41.32	42.64
Diesel	15.95	16.28
Heavy oil	9.17	6.79
Coke	6.79	7.66
Propylene	10.31	10.55
Conversion, m%	74.88	76.93
Total yields, m%	82.08	83.60
Composition of gasoline, v%		
N-paraffins	4.80	4.87
Iso-paraffins	23.70	27.73
Olefins	44.27	36.38
Naphthenes	8.33	8.93
Aromatics	18.90	22.09
MON	83.1	83.0
RON	93.6	93.7

The results of riser evaluation in Table 7 showed that the new catalyst Cat-3 had higher propylene yield by 0.24 % and decreased heavy oil yield by 2.38 % compared with reference catalyst Cat-1. At the same time, the total liquid yields of Cat-3 increased by 1.52 %. It was noted that the olefin yield of FCC gasoline decreased 7.89 % and the yields of iso-paraffins and aromatics increased significantly. As a result, both the RON and MON of FCC gasoline remained almost unchanged. Using USY with higher content of rare earth, it will convert heavy oil to FCC gasoline with lower olefin and high aromatics. Its total acidic sites and the strong ones and higher surface area could produce higher cracking ability. The outstanding performance was attributed to the higher cracking ability of Cat-3 on converting more PAHs in the heavy oil and diesel

to aromatics and iso-paraffins, which compensated the loss of octane numbers due to the decrease of olefins. The total acidic sites and the strong ones.

## Conclusions

When adopting the modified USY3 as the active component, FCC catalyst had better cracking activity when converting PAHs of heavy oil and diesel to aromatics and iso-paraffins into gasoline fraction. In addition, USY possessed higher surface area and pore volume by 51 m<sup>2</sup>/g and 0.03 ml/g after cleaning up zeolite skeleton fragments. Compared with Cat-1, the results of Cat-3 carried out on a riser showed that it had a good performance in cracking the heavy hydrocarbons and lowering the olefin yield of gasoline with unchanged gasoline octane numbers.

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## References

1. Long J, Yang G (2003) The development history and future direction of our gasoline standard for vehicle. *Pet Process Petrochem* 34:41–47
2. Wang Q (1988) Recent development and research trend of octane cracking catalysts abroad. *Pet Process Petrochem* 9:1–4
3. Sun Y, Zhang C, Cao L, Yanqing MA, Fan J, Liao Y (2013) Evaluation of reaction performance of catalytic cracking catalysts by ACE experimental device. *Petrochem Technol Appl* 31:477–481
4. Liu Z, Gao Y, Zhang Z, Wang Li (2009) Performance of LIP-200B catalyst for maximizing propylene yield and heavy oil conversion. *Pet Process Petrochem* 40:10–13
5. Chen Junwu (2005) Fluid catalytic cracking technology and engineering. China Petrochemical Press Co., Ltd, Beijing