

# Study on the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> Ratio of Starting NaY Zeolites on USY Zeolites Properties and Hydroaromatization Catalyst Performance

Fucun Wang<sup>1,\*</sup>, Zhongyang Zhang<sup>2</sup>, Baodong Jin<sup>2</sup>, Baojing Cui<sup>2</sup>, Baojun Jia<sup>2</sup>,  
Famin Sun<sup>1</sup>, Tiezhen Zhang<sup>1</sup>, Jinling Zhu<sup>1</sup>

<sup>1</sup>Daqing Petrochemical Research Center of PetroChina, Daqing, Heilongjiang, 163714, China

<sup>2</sup>PetroChina Fushun Petrochemical Company, Fushun Liaoning 113001, China

\*Corresponding author: [fucunwang@yeah.net](mailto:fucunwang@yeah.net)

Received March 04, 2022; Revised April 06, 2022; Accepted April 12, 2022

**Abstract** The modifications of NaY zeolites with different SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio were carried out, the results revealed that modified USY zeolites showed some mesopores, as the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of USY increased, the weak acidity strength of USY had little change, medium and strong acidity strength of USY decreased, the weak acidity and medium-strong concentration decreased. The selective ring opening evaluation of tetralin revealed that hydro-upgrading catalyst with different USY zeolites had different tetralin conversion, different yield and selectivity of ROP. The catalyst prepared with USY zeolite modified from NaY with the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of 5.7 showed best hydro-upgrading performance, which had higher tetralin conversion, higher yield and selectivity of ROP. Acidity and Si/Al ratio of USY zeolites both were important factors affecting catalyst performance.

**Keywords:** NaY type zeolite, SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio, USY zeolite, catalyst, performance

**Cite This Article:** Fucun Wang, Zhongyang Zhang, Baodong Jin, Baojing Cui, Baojun Jia, Famin Sun, Tiezhen Zhang, and Jinling Zhu, "Study on the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> Ratio of Starting NaY Zeolites on USY Zeolites Properties and Hydroaromatization Catalyst Performance." *Journal of Materials Physics and Chemistry*, vol. 10, no. 1 (2022): 17-22. doi: 10.12691/jmpc-10-1-3.

## 1. Introduction

Diesel is extensively used as a fuel since the diesel engine is 25-40% more fuel-efficient than the gasoline engine [1]. Therefore, LCO (light cycle oil) from FCC units will need to be processed in the refineries to supply the high quality diesel. However, high aromatics content of FCC LCO lowers diesel fuel quality and brings about the formation of undesirable emissions in exhaust gases from diesel engines. Since the gradual change to more stringent environmental regulations, much attention has been paid to the deep reduction of aromatics in diesel. In such a case, there is considerable interest in the new catalyst development for FCC LCO hydro-upgrading [2-8].

It has been proved that the addition of acidic components into the traditional alumina-supported hydrotreating catalysts can greatly enhance their hydro-upgrading performance. As an important catalytic material, Y zeolite has tunable acidity, well-organized pore structure, larger specific surface area, hydrothermal stability and excellent catalytic performance, it has been widely used in petrochemical industry in recent years [9-11]. But the synthesized NaY zeolite is not acidic, the pore diameter is also smaller, only modified USY zeolites can be used in the catalytic field, Y zeolite modified from

different Si/Al ratio starting NaY are not as well-documented.

In this study, we examined the effect of Si/Al ratio of the starting NaY on the USY zeolites, and used different Y type zeolites as cracking component for hydro-upgrading catalysts. Y type zeolites were characterized by various methods, and the selective ring opening evaluation of tetralin on different hydro-upgrading catalysts was examined in detail. The different Si/Al ratio of Y type zeolites may play an important role in dispersion of active phases and catalytic activity of hydro-upgrading catalyst. In this study, we examined the effect of the Si/Al ratio of starting NaY zeolites on USY zeolites properties and hydroaromatization catalyst performance. We found that suitable Si/Al ratio of USY zeolites was very important on the performance of hydro-upgrading catalyst, and laid a solid foundation for the commercial application of Y type zeolites in hydro-upgrading catalysts.

## 2. Experimental

### 2.1. Different Si/Al Ratio NaY Modification

Five USY samples, USY1, USY2, USY3, USY4 and USY5 were obtained with starting NaY1, NaY2, NaY3, NaY4 and NaY5 zeolites of different SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio by

the same modified method. The modified procedures are as follows: USY1, USY2 and USY3 were prepared by  $\text{NH}_4^+$  exchange of five NaY zeolites using a 2.0N aqueous solution of  $\text{NH}_4\text{Cl}$  at  $80^\circ\text{C}$  for 2 h under agitation, followed by washing until absence of  $\text{Cl}^-$  and drying at  $100^\circ\text{C}$  overnight. Then samples were submitted to a steaming treatment at  $600^\circ\text{C}$  for 6 h. Finally, the samples were calcined in the dry air at  $550^\circ\text{C}$  for 3 h.

## 2.2. Preparation and Performance of Five Ni-W/USY Catalysts

Five hydro-upgrading catalysts using USY zeolites as acidic component, Ni-W as hydrogen component were prepared by pore volume co-impregnation method, respectively. The tetralin selective ring opening evaluation of five hydro-upgrading catalysts were carried out.

## 2.3. X-Ray Diffractometer (XRD)

The relative crystallinity and unit cell parameters of zeolites were calculated from XRD patterns recorded with a SIMADU XRD6000 diffractometer and CuK $\alpha$  radiation (0.1542 nm, 40 kV and 40 mA). The zeolite powder was packed in the cavity of a XRD sample holder made of glass. Then the holder was kept in a closed vessel containing a saturated  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  solution for 16 h to make the moisture in the sample at constant. The relative crystallinity was estimated by comparing the peak intensities of the modified sample with standard NaY sample. The total intensities of the eight peaks, assigned to (311), (511, 333), (440), (533), (642), (822, 660), (555, 751) and (664) reflections, were used for the comparison according to the following equation:

$$X_i = X_R \left( \frac{\sum A_i}{\sum A_R} \right)$$

$X_R$ : the crystallinity of the standard NaY provided by Lanzhou catalyst company of Petrochina.

$\sum A_i$ : the sum of eight peaks area of Y zeolites to be determined.

$\sum A_R$ : the sum of eight peaks area of standard NaY sample.

The unit cell parameters were determined from the reflection peak of the silicon powder ( $2\theta=28.443^\circ$ ) as an internal standard and calculated from the (555) reflection peak position. The framework Si/Al ratio was obtained from the calculated unit cell parameters by using Breck-Flanigen equation [12].

## 2.4. Low-temperature $\text{N}_2$ Adsorption-desorption

Nitrogen adsorption/desorption measurements were performed on an ASAP2405M type surface area and pore structures instrument of American Mike Instrument Company. Before adsorption, the samples were calcined at 823 K for 4 h. Powder samples of 30-40 mg were degassed in a sample preparation station under 473 K and a vacuum of  $1.33 \times 10^{-3}$  Pa for 15 h, then switched to the analysis station for adsorption and desorption at 77 K in liquid nitrogen. Surface area was calculated with the multipoint BET equation with linear region in the  $P/P_0$  range of 0.05-0.35. Pore volume was calculated from

the maximum adsorption amount of nitrogen at  $P/P_0 = 0.99$ .

## 2.5. IR Spectra

IR spectra were recorded on an American PerkinElmer Company GS-2000 type FT-IR Instrument. The samples and potassium bromide were mixed evenly at the ratio of 1:150, then fully ground and pressed samples into slices, and the spectrum of potassium bromide was used as reference, scan range was  $400\text{--}4000\text{cm}^{-1}$ , the infrared spectra of the samples were recorded.

## 2.6. XRF (X-ray Fluorescence Spectroscopy)

$\text{Na}_2\text{O}$  contents were determined using a RIX3000-type X-ray fluorescence spectrocomparator of Rigaku Corporation.

## 2.7. $\text{NH}_3$ Temperature Programmed Desorption ( $\text{NH}_3$ -TPD)

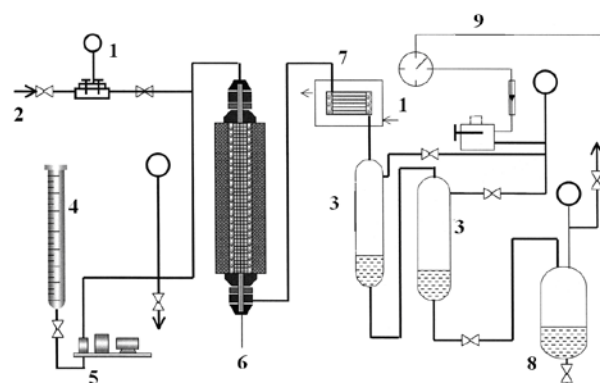
$\text{NH}_3$ -TPD spectra were recorded by Autosorb-1-C of Quantachrome Instruments Company. A sample of 0.2 g zeolite was heated at  $510^\circ\text{C}$  for 0.5 h under helium flow (30 mL/min). After the temperature was decreased to  $100^\circ\text{C}$ ,  $\text{NH}_3$  was introduced into the sample until saturation. After purging for 0.5 h with helium, the  $\text{NH}_3$  was desorbed by increasing the temperature to  $650^\circ\text{C}$  at a rate of  $20^\circ\text{C}/\text{min}$ . The desorbed  $\text{NH}_3$  was detected by TCD detector.

## 2.8. Non-framework Aluminum

The content of Y zeolite non-framework was determined using the equation  $N_{\text{EFAl}} = 1 - [(\text{Si}/\text{Al})_{\text{XRF}} / (\text{Si}/\text{Al})_{\text{XRD}}]$ .

## 2.9. Catalytic Performance Evaluation

Single-stage, once-through process was adopted in hydro-upgrading catalyst performance evaluation. It was conducted on a 200ml continuous flow fixed-bed hydrogenation test unit. The catalyst were sulfided in situ before evaluation, sulfidation oil was a kind of straight kerosene containing 2 wt%  $\text{CS}_2$ . Figure 1 showed the schematic diagram of 200ml hydrogenation test unit.



**Figure 1.** The schematic diagram of 200ml hydrogenation test unit (1-Pressure regulator; 2-High pressure  $\text{H}_2$ ; 3- High pressure separator; 4-Oil measurer; 5- Measurer pump; 6-Fixed bed reactor; 7-Water cooler; 8-Oil head; 9-Off gas)

### 3. Results and Discussion

#### 3.1. XRD and XRF

A combination of ion exchange-calcination-hydrothermal treatment methods was used for five different  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio NaY modification research. XRD patterns of five NaY zeolites are shown in Figure 2. The  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio, crystallinity and  $\text{Na}_2\text{O}$  content are listed in Table 1.

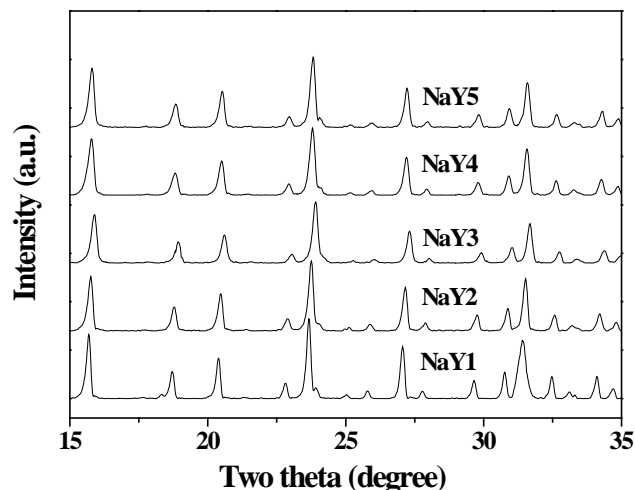


Figure 2. XRD patterns of NaY1, NaY2, NaY3, NaY4 and NaY5 zeolites

According to XRD patterns of NaY zeolites, there were no impurity crystals, and the crystalline form was complete.

Table 1. Results of NaY Zeolites Determined by XRF and XRD Analysis

Sample	$n(\text{Si}_F)/n(\text{Al}_F)$	Relative crystallinity, %	$\text{Na}_2\text{O}$ , wt %
NaY1	4.2	98	10.8
NaY2	4.6	96	10.6
NaY3	5.1	99	10.2
NaY4	5.7	97	10.4
NaY5	6.2	98	10.1

Table 1 showed that Si/Al ratio of five NaY zeolites gradually increased, relative crystallinity and  $\text{Na}_2\text{O}$  content changed very little.

XRD pattern of five USY zeolites are presented in Figure 3.

Figure 3 revealed that (555) crystal face diffraction peak position of five USY zeolites gradually moved in a higher angle direction. According to calculation method of the unit cell parameter, with the increase of diffraction peak position, or  $2\theta$  angles of (555) crystal face, zeolite unit cell parameter reduced. Since the framework Al–O bonds of Y type zeolite were replaced by Si–O bonds during the modification process, but the bond length (0.163 nm) of Si–O bond is less than the bond length (0.171 nm) of Al–O bond [13], therefore led to zeolite unit cell contraction, unit cell parameter reduction.

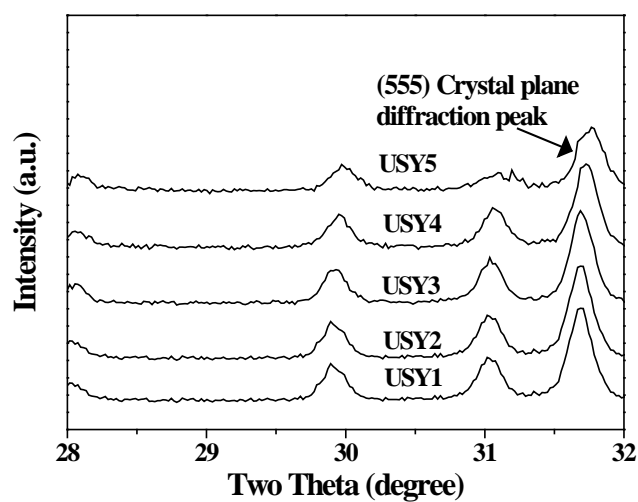


Figure 3. XRD patterns of USY1, USY2, USY3, USY4 and USY5 zeolites

$\text{Na}_2\text{O}$  content, framework Si/Al ratio, unit cell parameter, relative crystallinity and Al content of five zeolites are listed in Table 2.

Table 2 summarizes the results that under the same modification conditions, as the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of NaY increased, the framework Si/Al ratio and relative crystallinity of USY zeolites were increased accordingly, Si/Al ratio of starting NaY had an important influence on the performance of modified zeolite Y. Zeolite Y modified from higher Si/Al ratio of starting NaY also had higher framework Si/Al ratio and relative crystallinity, lower crystal lattice constant and better hydrothermal stability [14,15].

Table 2. XRD and XRF Results of Five USY Zeolites

Item		USY1	USY2	USY3	USY4	USY5
XRF analysis	$\text{Na}_2\text{O}$ , wt %	0.132	0.125	0.117	0.124	0.102
	$n(\text{Si}_F)/n(\text{Al}_F)$	2.25	2.51	2.82	3.14	3.37
XRD analysis	$a_0$ , Å	2.452	2.448	2.445	2.441	2.436
	Crystallinity, %	64	69	74	79	84
	$n(\text{Si}_F)/n(\text{Al}_F)$	8.1	9.5	10.9	13.2	17.7
Aluminum number per unit cell	$\text{Al}_T$	59.1	54.7	50.3	46.4	44.0
	$\text{Al}_F$	21.1	18.3	16.1	13.5	10.3
	$\text{Al}_{EF}$	38.0	36.4	29.9	32.9	33.7

$a_0$ –Unit Cell Parameter; Subscript: T–Total, F–Framework, EF–Extra-framework.

Table 3. Stretching Vibration Frequency of USY Zeolites

Item	USY1	USY2	USY3	USY4	USY5
Asymmetric stretching vibration, $\text{cm}^{-1}$	812	815	817	819	828
Symmetric stretching vibration, $\text{cm}^{-1}$	1039	1042	1047	1053	1062
Double ring vibration, $\text{cm}^{-1}$	452	453	454	455	457
T-O bending vibration, $\text{cm}^{-1}$	587	589	590	592	598
Pore opening vibration, $\text{cm}^{-1}$	393	394	395	396	396

### 3.2. IR Spectra

IR spectra data of five USY zeolites are given Table 3.

The results of Table 3 showed that as the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of USY increased, the frequencies of asymmetric stretching vibration, symmetric stretching vibration, double ring vibration, T-O bending vibration and pore opening vibration moved in the high wave direction, which revealed that as framework Si/Al ratio of USY zeolites increased, some Al atoms of USY zeolites were replaced by Si atoms, since Al-O bond length was longer than Si-O bond length, so framework vibration peak appeared blue shift.

### 3.3. BET

$\text{N}_2$  adsorption-desorption isotherms, pore size distribution curves and surface area and pore structure data of five USY zeolites are presented in Figure 4, Figure 5 and Table 4, respectively.

Figure 4 indicated that five USY zeolites all belonged to type IV isotherm and H4 hysteresis ring, which was due to the hydroxyl group generation after the removal of some framework Al in the water vapour environment, made zeolites pore channel connection and formed lots of mesopores [16]. Figure 5 revealed that five USY zeolites all generated some mesopores, the most probable pore diameter was 4 nm.

Pore structure data of five USY zeolites indicated that as the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of USY increased, specific surface area of USY zeolites showed the trend that increased first and then decreased, micropore volume changed a little, mesopore specific surface area showed the trend that increased first and then decreased, micropore volume decreased first and then increased, mesopore volume increased first and then decreased. It can be seen that specific surface area increasement was mainly due to the mesopore increasement. Specific surface area and mesopore volume of USY4 zeolite were both larger, which made macromolecules, such as aromatics in the diesel were more easier to contact the acid center in catalyst, and it

spreaded rapidly after the chemical reaction, avoided the occurrence of secondary cracking reactions.

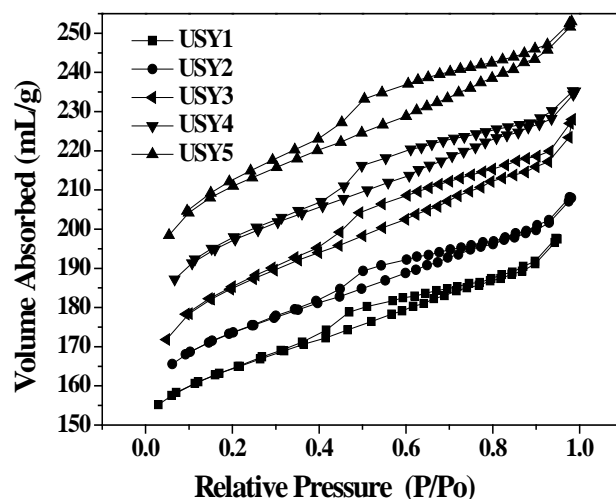


Figure 4. Nitrogen adsorption-desorption isotherms of five USY zeolites.

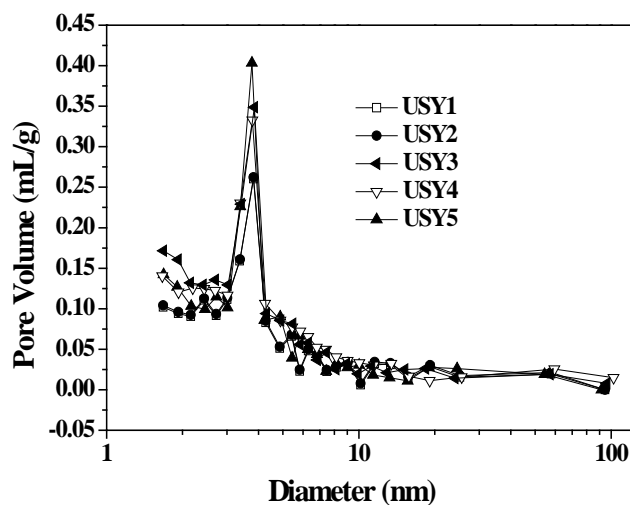


Figure 5. Pore size distribution curves of five USY zeolites

Table 4. Surface Area and Pore Structure Data of USY Zeolites

Sample	$S_{\text{BET}}$ , $\text{m}^2\cdot\text{g}^{-1}$	$S_{\text{mi}}$ , $\text{m}^2\cdot\text{g}^{-1}$	$S_{\text{me}}$ , $\text{m}^2\cdot\text{g}^{-1}$	$V_{\text{mi}}$ , $\text{mL}\cdot\text{g}^{-1}$	$V_{\text{BH}}$ , $\text{mL}\cdot\text{g}^{-1}$
USY1	613	513	100	0.25	0.13
USY2	630	517	113	0.23	0.16
USY3	646	513	133	0.21	0.18
USY4	642	515	127	0.19	0.22
USY5	619	509	110	0.22	0.19

$S_{\text{BET}}$ —Total specific surface area;  $S_{\text{mi}}$ —Micropore specific surface area;  
 $S_{\text{me}}$ —Mesopore specific surface area;  $V_{\text{mi}}$ —Micropore volume;  $V_{\text{BH}}$ —Mesopore volume

### 3.4. NH<sub>3</sub>-TPD

The acidity is one of the most important factors of the catalyst, it directly influences the cracking ability as well as ring opening, and thus hydrodearomatization performance and cetane number. The acidity of the catalyst is mainly originated from the zeolite, the study on the acidity of the zeolite is very important for the development of the catalyst, the NH<sub>3</sub>-TPD profiles of five USY zeolites are presented in Figure 6.

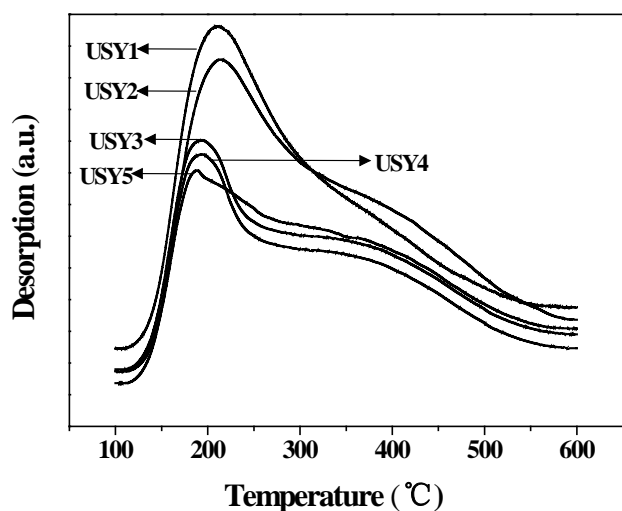


Figure 6. NH<sub>3</sub>-TPD profiles of five USY zeolites

According to NH<sub>3</sub>-TPD profiles of five USY zeolites, as the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of USY increased, the weak acidity strength of USY had little change, medium and strong acidity strength of USY decreased, the weak acidity concentration, medium-strong concentration decreased.

### 3.5. Performance of Five Ni-W/USY Catalysts

Performance results of five Ni-W/USY catalysts are listed in Table 5.

The selective ring opening evaluation of tetralin revealed that hydro-upgrading catalyst with different USY

zeolites had different tetralin conversion, different yield and selectivity of ROP. The catalyst prepared with USY4 zeolite showed best hydro-upgrading performance, which had higher tetralin conversion, higher yield and selectivity of ROP. Acidity and Si/Al ratio of USY zeolites both were important factors affecting catalyst performance.

Performance results of five Ni-W/USY catalysts on was FCC diesel hydrogenation listed in Figure 7 The operating condition of performance evaluation: temperature of 360°C, LHSV of 1.0 h<sup>-1</sup>, pressure of 8.0 MPa, the ratio of hydrogen to oil of 800:1.

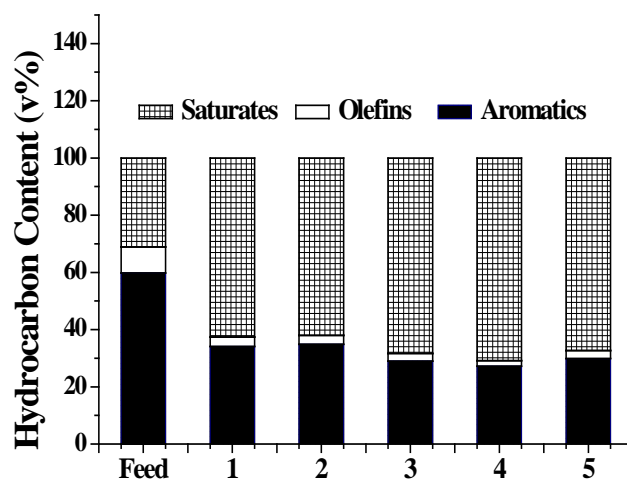


Figure 7. Saturates, olefins and aromatics contents of FCC diesel and diesel product (1: NiW-USY1; 2: NiW-USY2; 3: NiW-USY3; 4: NiW-USY4; 5: NiW-USY5)

Figure 7 showed saturates, olefins and aromatics contents of FCC diesel and diesel product. NiW-USY4 catalyst has the best hydrogenation performance than other catalysts, the result is consistent with the performance on tetralin hydrogenation. NiW-USY4 hydro-upgrading catalyst can greatly decrease aromatics content of inferior diesel, such as FCC diesel, straight run diesel and coker diesel, thus effectively improving the cetane number of inferior diesel, and the catalyst has a broad commercial application prospect.

Table 5. Tetralin Conversion and Product Yield of Ni-W/USY Catalysts

Item	NiW-USY1	NiW-USY2	NiW-USY3	NiW-USY4	NiW-USY5
Conversion of Tetralin, %	93.3	95.1	95.7	96.8	97.1
Rate Constant, mL·(g·s) <sup>-1</sup>	0.284	0.318	0.332	0.363	0.374
Relative Rate Constant, %	100	112	117	128	132
Product Yield, wt %					
Light paraffin	0.3	0.2	0.3	0.2	0.3
Light naphthene	1.3	1.0	0.8	0.7	0.8
Decalin	59.9	59.8	60.1	60.7	60.1
IsoDecalin	12.4	12.7	12.5	12.3	12.4
ROP	19.5	21.5	21.9	23.1	23.0
Tetralin	6.6	4.8	4.4	3.0	3.4
Total C <sub>10</sub>	98.4	98.8	98.9	99.1	98.9
Selectivity of ROP	12.19	17.92	19.90	25.67	20.91

Reaction conditions: pressure of 4.0 MPa, temperature of 320°C, LHSV of 2.0 h<sup>-1</sup>, H<sub>2</sub>/Oil of 500:1. Selectivity of ROP (Ring Opening of Product): ROP/Light Paraffin (C<sub>9</sub>)+Light Naphthene (C<sub>9</sub>).

## 4. Conclusions

It was found that Si/Al ratio of starting NaY had an important influence on the performance of modified zeolite Y. Zeolite Y modified from higher Si/Al ratio of starting NaY also had higher framework Si/Al ratio, less non-framework aluminum, better hydrothermal stability. The pore distribution of USY zeolites was very centralized, the most probable pore diameter was 4 nm, and USY zeolites had more mesopores and higher relative crystallinity. As the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of NaY zeolites increased, the weak acidity strength of USY had little change, the weak acidity and medium-strong acidity concentration, medium and strong acidity strength of USY decreased. The selective ring opening evaluation of tetralin and FCC diesel hydrodearomatization revealed that hydro-upgrading catalyst with different USY zeolites had different tetralin conversion, different yield and selectivity of ROP, and different dehydroaromatization. Acidity and Si/Al ratio of USY zeolites both were important factors affecting catalyst performance.

## References

- [1] A. Stanislaus, A. Marafi and M.S. Rana, Recent advances in the science and technology of ultra low sulfur diesel (ULSD) production, *Catal. Today*, 2010; 153(2); 1-68.
- [2] L. Huang, Q.L. Huang, H.N. Xiao and M. Eic, Al-MCM-48 as a potential hydrotreating catalyst support: I - Synthesis and adsorption study, *Microporous Mesoporous Mater.*, 2008; 111: 404-410.
- [3] T. Fujikawa, K. Idei, T. Ebihara, H. Mizuguchi and K. Usui, *Appl. Catal. A*, 2000; 192: 253-261.
- [4] C.S. Song, An overview of new approaches to deep desulfurization for ultra-clean gasoline, diesel fuel and jet fuel, *Catal. Today*, 2003; 86(1-4): 211-263.
- [5] D. Kubicka, N. Kumar, P. Maeki-Arvela, M. Tiitta, V. Niemi, H. Karhu, T. Salmi and D.Yu. Murzin, Ring opening of decalin over zeolites, *J. Catal.*, 2004; 227: 313-327.
- [6] L.H. Ding, Y. Zheng, Z.S. Zhang, Z. Ring and J. Chen, Hydrotreating of light cycle oil using WNi catalysts containing hydrothermally and chemically treated zeolite Y, *Catal. Today*, 2007; 125(3-4): 229-238.
- [7] F. Bataille, J.L. Lemberon, G. Pérot, P. Leyrit, T. Cseri, N. Marchal and S. Kasztelan, Sulfided Mo and CoMo and supported on zeolite as hydrodesulfurization catalysts: transformation of dibenzothiophene and 4,6-dimethyldibenzothiophene, *Appl. Catal. A*, 2001; 220: 191-205.
- [8] N. Kunisada, K.H. Choi, Y. Korai, I. Mochida and K. Nakano, Optimum coating of USY as a support component of NiMoS on alumina for deep HDS of gas oil, *Appl. Catal. A*, 2004; 276(1-2): 51-59.
- [9] D.P. Liu, PhD diss. Tianjin: Tianjin University, 2005; 60-61.
- [10] L. Ding, Y. Zheng, H. Yang and R. Parviz, LCO hydrotreating with Mo-Ni and W-Ni supported on nano- and micro-sized zeolite beta, *Appl. Catal. A: Gen.*, 2009; 353: 17-23.
- [11] T.L.M. Maesen, S. Calero, M. Schenk and B. Smit, Alkane hydrocracking: shape selectivity or kinetics, *J. Catal.*, 2004; 221: 241-251.
- [12] *Molecular Sieves*. Ed. by D. W. Breck and E.M. Flanigen, London, Society of Chemical Industry, 1968.
- [13] *Hydrocracking*. Ed. by X. C. Fang, Beijing, China Petrochemical Press, 2008.
- [14] B. Xu, S. Bordiga, R. and J.A. van Bokhoven, Effect of framework Si/Al ratio and extra-framework aluminum on the catalytic activity of Y zeolite, *Appl. Catal. A: Gen.* 2007; 333: 245-253.
- [15] A. Anuji, S.H. Lee, C.H. Shin Hong, S.B. Prins, R. van and J.A. Bokhoven, Influence of framework silicon to aluminium ratio on aluminium coordination and distribution in zeolite Beta investigated by <sup>27</sup>Al MAS and <sup>27</sup>Al MQ MAS NMR, *Phys. Chem. Chem. Phys.*, 2004; 6: 3031-3036.
- [16] F.N. Gu, F. Wei, J.Y. Yang, N. Lin, W.G. Lin, Y. Wang and J.H. Zhu, New Strategy to Synthesis of Hierarchical Mesoporous Zeolites, *Chemistry of Materials*, 2010; 22:2442-2450.

