

# MOLECULAR DESIGN OF USY ZEOLITES USED FOR THE FCC PROCESS\*

Xin-Mei Lui, Zi-Feng Yan\*\*, Ling Qian, and Chun-Min Song

*State Key Laboratory for Heavy Oil processing, University of Petroleum,  
Dongying 257062, CHINA*

**ABSTRACT** USY zeolites, ultrastabilized in hydrothermal treatment, were further modified by orthogonal design method with tartaric acid in an unbuffered system. The crystal structure, surface area and pore distribution, B acid sites and L acid sites, stability, and the activity for catalytic cracking of the modified samples were characterized by XRD, N<sub>2</sub> adsorption, FT-IR, DTA, and MAT. The research shows that the Si/Al ratio and the relative crystallinity of modified samples are both reasonably increased. Moreover, the pore system is developed further and the secondary mesopores are significantly greater than in the parent zeolites. The study has also shown that modified zeolites are preferable to deep cracking catalyst for producing lighter olefins and diesel oil with good yield and selectivity.

**Keywords:** USY; modification; tartaric acid; Si/Al ratio; pore distribution; activity; selectivity; lighter olefins

## INTRODUCTION

Catalytic cracking process has been one of major techniques for lightening heavy oil. It not only plays an important role in petroleum refining, but also it is one focus that people pay close attention to. The success of the catalytic cracking is mostly attributed to the development or modification of the catalyst. With the cracking gasoline octane number boost, environmental concerns and deeper conversion of residual and heavy oils, especially the employment of reformulated gasoline, and the requirement for lower carbon olefins is dramatically increased. It is an effective way to produce much lighter olefins by further modification of zeolites existing in mordent FCC industry. Simultaneously, it is useful to the research of the design or modification of the catalyst structure.

Our efforts have been devoted to strengthening of the acidity and expanding of the mesopore of the USY zeolite by extraction of aluminum with tartaric acid whose negative ions has great complexing ability for Al<sup>+</sup>. The negative ions and proton ions act in concert to Al-O band, which can achieve the de-alumination from the framework of the zeolites. The samples were prepared by orthogonal design (OD). The crystal structure parameter, physical adsorption property, stability, catalytic property of the modification zeolites was researched systematically by XRD, N<sub>2</sub> adsorption, FT-IR, DTA and MAT. The weight factors of effecting on the modification USY zeolites and optimum amount of each factor were explored.

## EXPERIMENTAL

### Materials and instruments

The parent USY zeolites were provided by Zhoucun Catalyst Company with the Si/Al ratio of 8.3, the unit cell constant of 24.528 Å and the relative crystallinity of 68.2%. Its crystal lattice was basically complete in the unbuffered acid system with the pH value above 2.0. Type 79-1 magnetic heating agitator was purchased from Zhongda Instrument Plant in Jiangsu.

\* This program is financially supported by Natural Science Foundation of Shandong Province.

\*\* To whom correspondence should be addressed

## Sample Preparation

A series of modified USY samples were synthesized by sol-gel method according to a  $L_4^5$  orthogonal design table, in which the strong interactions among the parameters, such as addition volume of tartaric acid, solvent pH value, solvent volume and temperature were practically considered. The modified zeolite was washed by the distilled water to pH = 7, then filtered and dried for 14 hours at the temperature of 200°C.

## Characterization of the Samples

The Si/Al ratio, unit cell constant, and relative crystallinity of the modified zeolite were determined by XRD with a Ricoh D/Max-III A X-Ray diffractometer using Cu  $K\alpha$  radiation. The pure NaY zeolite was used as calibration material. The Si /Al ratio was estimated from angles of 31~32 (2 $\theta$ ) XRD peaks.

The temperature of zeolite structure collapse was determined by DTA, with a CDR-1 DTA instrument of Shanghai Balance Instrument Plant.

The surface area and pore size distribution of modified samples were monitored by  $N_2$  adsorption with a Macromeritics ASAP 2010 unit.

Activity for catalytic cracking of Shenghua heavy oil (343°C-515°C) was carried out at 823 K near atmospheric pressure in a fixed-bed stainless steel reactor. The catalyst, which consists of 30% modified zeolites and 70% pretreated kaolin, was heated at 1073 K in a flow of water vapor for 4 h prior to introducing into reactor. The gaseous products were analyzed by HP-5890II gas chromatography equipped with a FID and a 50 m fused silicon capillary column. The liquid part was identified from simulated distribution on a HP-5880A with a FID and a 508mm fused UCW-982 column.

The number of acid sites was determined by FT-IR.

## RESULTS AND DISCUSSION

### The relation of the weight factors

The  $L_4^5$  OD table is employed to find out the optimum synthesis conditions and investigate the interactions among factors. The  $SiO_2/Al_2O_3$  ratio, mesopore (20 ~ 80 Å) volume and micro-activity are used to evaluate the performance of the modified USY zeolites. It is found that the order of the weight factors for above parameters employed is tartaric acid volume > pH value > solvent volume > temperature > reaction time.

### The crystal parameters

The results of XRD show that the Si/Al ratio of the modified samples is obviously increased compared to the parent zeolites because the crystal unit cell content dramatically decreased, as observed in Table 1. This means that nearly only Al is extracted and therefore the skeletal Si/Al ratio is increased. The extracted Al dissolves in diluted de-alumination reagent solution and only partially remains in the zeolites. Owing to the stereo effect of the de-alumination acid, the frameworks Al is first depleted in the surface or subsurface and subsequently dissolves in solution. A similar transformation has been observed as a consequence of  $(NH_4)_2SiF_6$  used for the treatment of a NaY zeolite [1]. Here, the higher relative crystallinity value of the de-alumination samples when compared to the parent zeolite may suggest that part of the framework be rebuilt. It can also be attributed to some changes in the physico-chemical properties (Si/Al ratio and extraction of the non-framework aluminum), which may influence the relative intensities of the X-ray diffraction peaks in the characteristic region of 2 $\theta$  [2]. In addition, we also observed that when the relative crystallinity reaches the maximum, the content of crystal silicon of zeolite sample will amount to the maximum too, but the largest Si/Al ratio may not be obtained at this moment. This indicates that there is a portion of non-framework silicon existing in the zeolite. Furthermore, with the increase of silicon to aluminum ratio and decrease of crystal unit cell, the thermal stability of the modified zeolites is improved. This has been confirmed by the results of DTA. According to the OD results, it is postulated that the optimum modification conditions could be that the tartaric acid volume is 40 ml, pH value of solution is 1, the solvent volume is 40 ml, and the reaction time is 4 h.

## Pore distribution

We always hope that the active component of FCC catalyst should possess structure with developed secondary mesopore. On the one hand, the larger reactant molecules may enter the pore channels of zeolite. On the other hand, it can decrease the molecular diffusion resistance to the zeolite cages. Thus the speed of the molecular diffusion is faster than the chemical reaction speed in the pores, which makes the activity sites of the pore be effectively used and the activity of the catalyst increased. This results in the catalyst efficiency improved. Fig.1 shows that the pore distribution of modified samples displays remarkable variation as a result of the tartaric acid treatments. The amount of secondary mesopores is distinctly increased. This refers not only to the mesopore volume, but also to the content of mesopore (20 ~ 80 Å). It reveals that the de-alumination is accompanied by the formation of some skeletal vacancies or defects. This vacancy or defect can be replenished by non-framework Si to complete the substitution of Al with Si. It can also be used to enlarge the pore mouth to form secondary mesopore. The enlarging of the pore mouth is attributed to the connection among the framework vacancies or defects by the interruption points created by the extraction of aluminum. All this leads to an increase of the amount of the secondary mesopores. Here the secondary mesopore formation is superior to silicon substitution because of the less enough silicon sources. It is worth mentioning that the amount of micropores is also increased, moreover, the micropore volume is enlarged. This may be achieved not only from the rebuilding of the framework, which leads to the larger mesopore changing into several micropores, but also from the enlarging of existing micropore (such as hexagonal column cages) that can not be tested by nitrogen adsorption. The optimum pore diameter of USY zeolite for processing heavy or residual oil should be in 20 ~ 80 Å, because the average van der Waal radius of the molecule residual and heavy oil, is 25 Å. Thus, the pore of 20 ~ 80 Å might be employed to evaluate the OD performance. The superior OD conditions are deduced as follows: the tartaric acid volume is 20 ml, pH value of solution is 3, the solvent volume is 40 ml, the temperature is 363 K and the reaction time is 6 h.

## Acid property

The active sites of catalytic cracking reaction are acid components of the zeolites. Catalytic acidity of USY zeolites is attributed to acidic aluminum sites in both framework structure and non-framework debris<sup>[3]</sup>. Thus the extraction of the aluminum either from framework or non-framework of the zeolites should decrease the number of acid sites. The results of FT-IR really prove that the number of acid sites of the modified samples is decreased with the increase of Si/Al ratio. The Bronsted acid lies in the 1540  $\text{cm}^{-1}$  and Lewis acid is in 1450  $\text{cm}^{-1}$ , which is accordance with the literature<sup>[4,5]</sup>. The results are shown in Fig. 2.

## Activity and selectivity

The MAT data reveal considerable changes as a result of the tartaric acid treatments. The results are shown in Fig. 3 and Fig. 4. From the above results, it can be seen that the modified USY samples possess the more reasonable pore system structure, the greater  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio, and better distributed aluminum, which leads to the selectivity of all kinds of object product improved. The acidity of USY zeolites governs their activity. So with the de-aluminating, the active sites are decreased. But with the increase of the secondary mesopores and the enlarging of average total pore openings, the activity sites are effectively used. Though the acid sites are decreased, the catalyst total activity is not dropped clearly; conversely, some catalyst's activity is improved. This change is exhibited by the conversion change as the results of Fig.3. Moreover, the extraction of aluminum results in the increase of acid strength, which restrains the inter-molecular hydrogen migration of hydrocarbon intermediates. So the selectivity to the  $\text{C}_3$  ~  $\text{C}_6$  hydrocarbons in the gas is raised, however, due to the difference of the gas selectivity of each catalyst, the yield of the  $\text{C}_3$  ~  $\text{C}_6$  hydrocarbons is less even if selectivity of some catalysts is greater. The deep conversion is a tendency for FCC process. It is controlled by accumulation of coke on catalyst surface not by activity of catalyst. Thus, the selectivity of the coke is the principal focus to which attention is paid. In order to prolong the catalyst life span and reduce the load of its regeneration, we always hope that the coke yield is as low as possible in the case of satisfying our need for the object products. Fortunately, our goal is achieved. The decrease of the coke has two reasons. One is the increase of the acid strength; this leads to the reduction of the speed of condensation reaction. The other is the decrease of the external

surface area; this cuts down the chances of the inter-molecular hydrogen migration reaction that can produce coke. According to the results, it is postulated that the optimum modification conditions are the same as the pore distribution conditions. Using this modified zeolites, the products distribution are as follows: the light oil yield is 69.4%, the coke yield is decreased from 3.73% to 3%, the selectivity and the yield of  $C_3 - C_6$  are respectively 51.7% and 15.53%.

## CONCLUSIONS

The results indicate that it is a new effective method to modify USY zeolites with tartaric acid in the unbuffered system. In this way, the thermally more stable samples with higher  $SiO_2/Al_2O_3$  ratio, higher relative crystallinity, more well developed secondary mesopore system can be prepared. These samples may be benefit to heavy oil and residual oil deeper cracking. Furthermore, lighter olefins with good yield and selectivity may be obtained in the FCC procedure.

## References

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Table 1. The crystal structure parameters of zeolites

Experiment order	Si/Al ratio	relative crystallinity $C_{RX}\%$	crystal unit cell param. $a_0/\text{Å}$	content of crystal silicon S
1	10.2	64	24.463	157.6
2	10.1	65	24.466	159.7
3	10.4	66	24.460	162.7
4	10.6	67	24.455	165.8
5	11.6	68	24.435	170.4
6	11.6	67	24.435	167.9
7	12.6	68	24.419	172.1
8	10.4	69	24.461	170.1
9	12.9	68	24.415	175.1
10	12.8	66	24.416	167.4
11	10.8	77	24.451	191.1
12	11.0	74	24.448	184.0
13	11.9	75	24.431	188.4
14	12.2	77	24.427	194.0
15	11.9	72	24.431	180.9
16	12.2	77	24.426	194.1
Parent sample	8.3	68	24.528	161.0

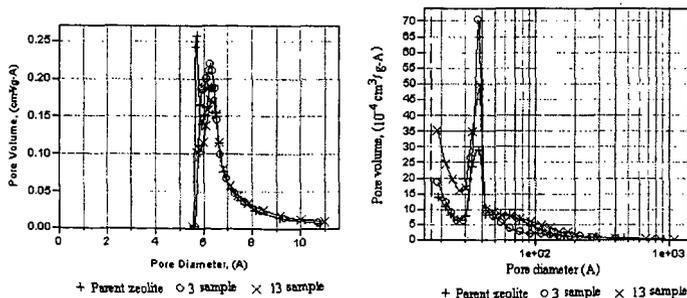


Fig.1 Profile of the pore size distribution of modification samples

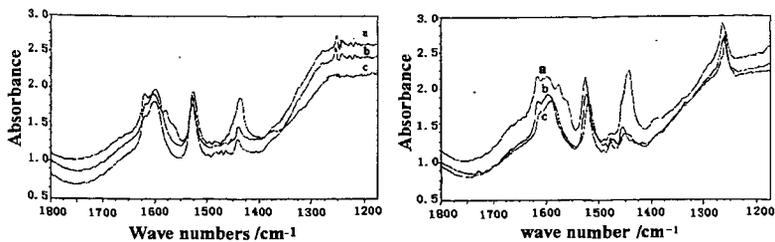


Fig.2. Profile of the acid site of modification samples. a---423K; b----523K; c-----623K

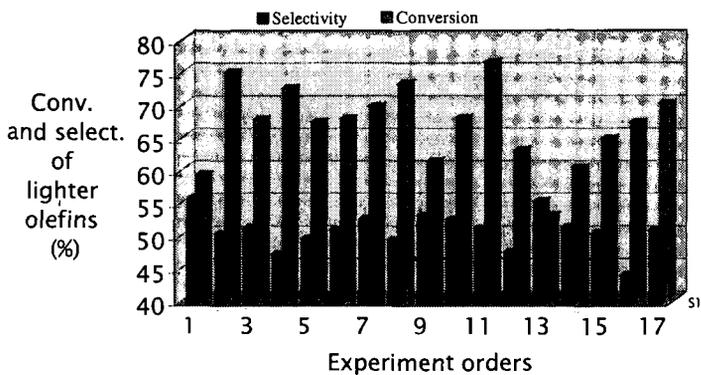


Fig.3 Profile of the conversion and selectivity of  $C_3-C_6$

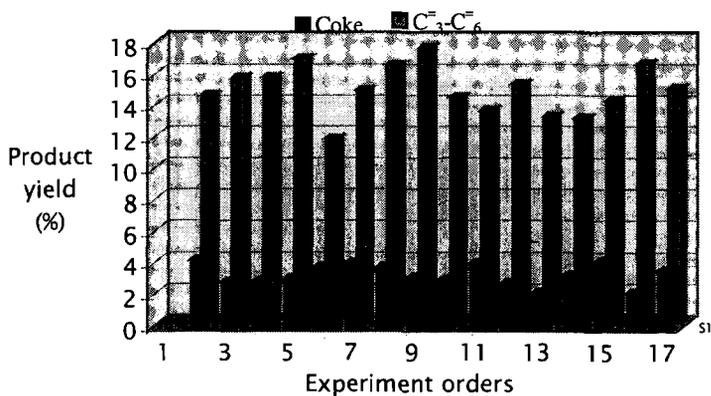


Fig.4 Profile of the product yield