CHARACTERIZATION AND CRACKING PERFORMANCE OF THE MODIFIED USY ZEOLITES WITH MIXED ORGANIC ACID

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Introduction

Fluid catalytic cracking (FCC) is one of the most important refining processes, and plays a key role in whole petroleum refining industry. 70-80% gasoline, 30-40% diesel oil and 50% propylene is come from catalytic cracking units, especially in China. Industrially, cracking reaction of hydrocarbons is catalyzed by the acid-form zeolite, especially by Ultrastable Y zeolites, which were prepared by steam dealumination of Y zeolite at high temperatures.[1] The distribution of the cracking products depends on the performance of zeolites and the reaction conditions. Hence the nature of acid sites of zeolites may strongly influence the performance of the catalytic cracking of hydrocarbon. Therefore many researchers have attempted to modify or post-synthesize zeolites to obtain optimum number and strength of acid sites and suitable pore structure with high activity and given selectivity. In addition, with the feedstocks of FCC being heavier and poorer and the tendency of increasing lighter olefins and diesel, the features of the mesopores and acid sites of USY zeolites will not meet the variation of materials in the future. Thus the modification of USY zeolite have been further paid much attention.[2]

There are different ways to modify the Y zeolite, such as hydrothermal treatment, vapor phase substitute dealumination of the high temperature, post-synthesis using $(NH_4)_2SiF_6$ and extraction by acid complexation.[3] Here the USY zeolites were treated with tartaric acid and citric acid in unbuffered system. In this process, the skeletal aluminum atom might be coordinately extruded by complex form from the skeleton of zeolite. Furthermore, the crystal structure, physical adsorption property, stability, catalytic cracking property of the modified zeolites were investigated by XRD, N_2 adsorption, FT-IR and micro-activity test(MAT). The nanopore volume, distribution and cracking Performance of the modified USY zeolites were extensively investigated in this paper.

Experimental

Preparation of modified USY zeolites. The USY parent zeolite supplied by Lanzhou Work of catalyst, whereas USY is already in its hydronium form, in which Si/Al ratio is 11.8 and the unit cell constant is 2.4432 nm. The process as follows: 6 gram of USY zeolite was placed into a three-necked flask with a certain amount dilute nitric acid as the solvent and this mixture was stirred and heated to 90℃. Then the mixed tartaric acid and citric acid solution was added. The solution was stirred for 4 h at 90℃. After reaction, the gel was filtered, washed, and dried overnight at 120℃.

Characterization Methods. The crystal structure parameter of samples was measured by X-ray diffraction (XRD) technique with a Rigaku D/max-IIIA X-ray diffractometer using Cu Kα radiation. N_2 adsorptions for the samples were carried out on a Micromeritics ASAP-2010 instrument using nitrogen as adsorbate at 77K. Before adsorption measurements the samples were degassed for 4 h at 673K. The mesopore size data were analyzed by the BJH method. The micropore size distribution was obtained by H-K method.

Micro-activity test (MAT). The modified sample was powdered, and mixed with kaolin clay matrix in the proportion of 30:70 wt% to prepare modified zeolite catalyst, while the diameter of catalyst particle is about 100-150 mesh. The catalyst was treated at 800°C with 100% steam for 4 hours prior to catalytic reaction. The catalytic cracking activity of the catalyst was assessed with an MRCS-8006 type microreactor, which is designed according to ASTM D-3907-80. The feedstock is Shenghua VGO, supplied by Shenghua Oil Refinery Factory, University of Petroleum. The density of feedstock is 0.8857 g/cm^3(20°C). Reaction temperature was 550°C and the ratio of catalyst to oil was 3. The liquid products were analyzed by HP5880A chromatography of simulating distillation. The vapor products were analyzed by HP5890Ⅱ GC equipped with a FID and a 50m fused silicon capillary column. The reacted catalyst were analyzed by self-made carbon mensuration, and worked out coke content of catalyst. The amount of gasoline and of diesel was calculated by simulating distillation. The distillates <204°C was distributed to gasoline part, and between 205 and 350°C was assigned as diesel part, and >350°C referred to heavy oil part, which might be assigned as the not converted feed part.

Results and Discussion

USY zeolite is typical active component for hydrocarbon cracking catalysts, which has special nanopore and acid sites. The special nanopores insure the product selectivity and acid sites hold out the high conversion of heavy hydrocarbons. It means that optimization of nanopore and acid sites of zeolites might be the key to design the effective catalyst of hydrocarbons cracking. The current USY zeolites that has been employed industrially is obtained by hydrothermal dealumination under high temperature. Its dealumination degree is rather limited, and that the non-framework aluminum formed during the steam treatment may affect the catalytic performance of zeolites catalysts. Here USY zeolites were modified with tartaric and citric acid in unbuffered system. The modification results indicate that modified zeolite samples with higher Si/Al ratio can be prepared by this method, which shows higher yields of lighter olefin and diesel oil in traditional FCC process. The investigation indicates that the PH value and the amount of the tartaric and citric acid have greatly influence, and that the treatment time and the drop velocity of the acids has little influence on the modification.

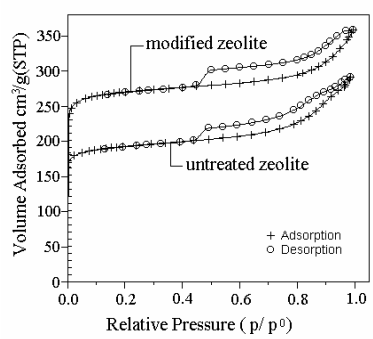

Figure 1. Nitrogen adsorption isotherms of untreated zeolite and modified zeolite.

The results of XRD patterns show that the Si/Al ratio of modified samples increases as compare to that the parent zeolite. This indicates that chemical dealumination of USY zeolite result in framework reconstruction of USY zeolite skeleton. Aluminum is subsequently removed from the zeolite crystal as a soluble tartaric and citric aluminum complex. Simultaneously, some extraframework silica fills the skeleton vacancies left by dealumination. Thus, the

structure differences exist between USY and midified samples due to framework dealumination and formation of mesopores.

The isotherms of nitrogen adsorption shown in **Figure 1** indicate that this is in good agreement with the reported in the literature[4], which attribute to type Ⅳ with a distinct hysterasis loop. Furthermore, the nitrogen adsorption amount of the modified samples is increased, but the shape of the isotherm is not change. The micropore distribution of modified samples shown in **Figure 2** indicates that the number of micropore is increased. It means that the pore volume of modified samples is rather more developed than that of the untreated zeolite and the pore distribution gradient is not obviously changed.The increase of micropore may be beneficial not only to the rebuilding of the framework, which leads to the transformation of larger mesopores into several micropores, but also to the enlarging tendency of the existing micropores. Micropore is the major nanopore in modified zeolite. However, it might be favor the deep cracking reactions to produce much more LPG or lighter olefins due to micropore volume increasing.

The mesopore distribution of modified zeolite and untreated zeolite is shown in **Figure 3**. It indicate that secondary mesopore volume is positively improved, and the secondary mesopore diameters of modified samples were concentrated at ca. 3.8 nm, which might be desirable for FCC processes of residual oil or heavy feedstocks. Furthermore, it is also advantage for production of diesel fraction in FCC process.

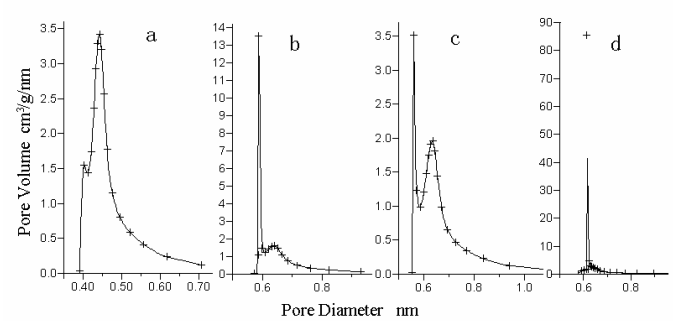

Figure 2. The micropore distribution of modified zeolites(where a is untreated zeolite; b, c and d are modified zeolites).

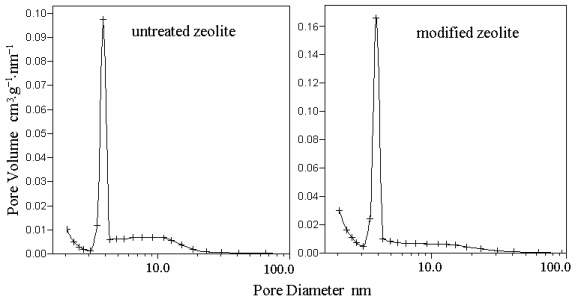

Figure 3. The mesopore distribution of modified zeolite and untreated zeolite

The IR spectra show that the hydroxyls with IR bands of 3610 and 3575 cm^{-1} in the micropors or small cages bears the stronger acidity and much more sites than those in mesopore or larger cavities. The special acid distribution is rather preferable to produce more diesel oil and lighter olefins in FCC process. The catalytic performance of the modified zeolite catalyst is shown in **Figure 4** and **Figure 5**. The result indicates that the diesel yields of the modified samples are effectively improved, and the activity of the modified catalyst have slightly decreased. Simultaneously, the coke formation of the modified samples ware obviously inhibited, and the yield of lighter olefins have partially increased. This is due to the acid sites of the modified samples decrease in number, but enhance in strength. Generally, the lighter olefins should be preferably produced on stronger acid sites in micropores or small cavity, while the diesel distillate is mainly formed on the medium and weaker of acid sites in mesopores or supercages. The modified zeolites have the gradient distribution of acid sites and nanopores. The gradient distribution of acid sites in mesoporres or large cavity might effectively inhibits the occurrence of the hydrogen transfer reaction and deep cracking and coke formation, which result in the increase of the yield of lighter olefin and diesel, decrease of the coke yield. Furthermore, the result of the fixed bed evaluation using amplificatory modified samples is in good agreement with that of laboratory test (MAT). Thus optimization of nanopores and acid sites of USY modified with tartaric acid and citric acid in unbuffered system might result in an industrial process to design novel FCC catalysts.

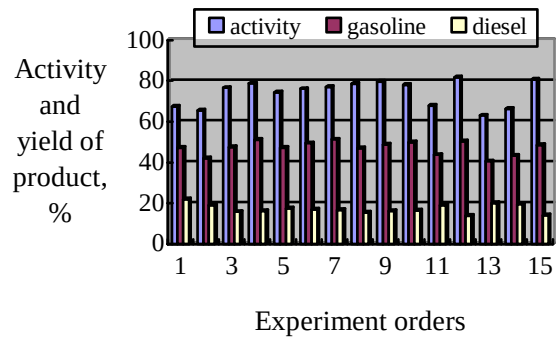

Figure 4. The activity and the yield of gasoline and diesel (where 15 is untreated sample).

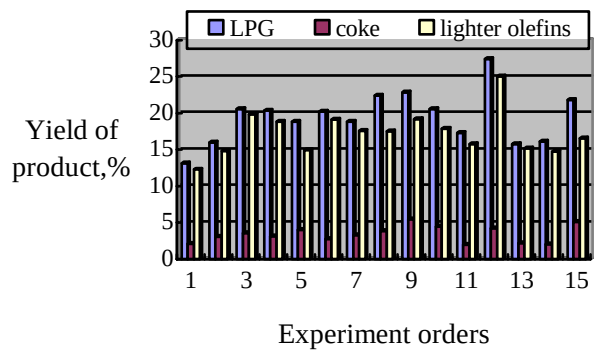

Figure 5. Profile of the product yield (where 15 is untreated sample).

Acknowledgments

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References

1. Fleisch, T.H., Meyers, B.L., Ray, G. J., Hall, J. B., Marshall, C. L., *J. Catal.*, **1986**, 99, 11.
2. Zhou, P., *Petrol. Proc. Petrochem. (China)*. **1997**, 28, 52.
3. Liu, X. M.; Qian, L.; Yan, Z. F., *J. Petrochem. Univ. (China)*, **1997**, *10*, 4-26.
4. Nguyen, C., Sonwane, C.G., *Langmuir*, **1998**, 14, 4950