Asian Journal of Chemistry Vol. 21, No. 9 (2009), 7041-7048

Ultrasonic Assisted Synthesis of Nano-Sized NaY Zeolite Composite from Metakaolin by Hydrothermal Method

W. XUE JING
Chemistry and Chemical Engineering School, Henan Institute of Science and Technology, Xin Xiang 453003, He Nan, P.R. China
E-mail: xjw1206@163.com

Nano-sized NaY zeolite has been synthesized from metakaolin by hydrothermal method with ultrasonic assisted during aging time. Its structure was characterized by XRD, SEM, TEM, HREM and its physico-chemical properties and catalytic characteristics were studied. The results showed that the size of the product was about 100 nm, relative crystallinity being 80.12 %, Si/Al ratio being 5.12; compared with conventional zeolite, nano-sized zeolite has larger surface area and mesopore volume, better thermal stability, higher cracking activity, higher gasoline selectivity, lower coke and gas selectivity.

Key Words: Nano-sized NaY zeolite, Synthesis, Characterization, Catalytic characteristic.

INTRODUCTION

NaY zeolite is one of the important catalysts in petrochemical industries. Traditional synthesis methods of NaY zeolite involved crystallizing from a gel or clear solution under hydrothermal conditions and the size of NaY zeolite is micro-scaled. With the development of petrochemical, there are higher demands for NaY zeolite, such as larger surface area, more active sites, excellent attrition resistance, higher selective and so on. So many studies on the synthesis of nano-sized NaY zeolite had been done and some synthetic methods had been reported for example, changing the crystallization temperature, the sequence of adding foods[1,2] or increasing the density of alkali[3], adding thulium and organic solvent to the synthesis batch[4-6] and so on. However the products synthesized by these methods have following shortcomings *i.e.*, difficulty to be filtrated because of fine particles, bad thermal stability and hydrothermal stability. So synthesis of nano-sized NaY zeolite from metakaolin had aroused researchers' great interest. Xu mingcan[7] had synthesized nano-sized NaY from metakaolin by adding sodium citrate to the synthesis batch. Wang bo[8] had synthesized nano-sized NaY from metakaolin by adding starch to the synthesis batch. Because of using organic reagent, it was difficult to handle the mother liquor.

In this paper, Nano-sized NaY zeolite had been synthesized from metakaolin by hydrothermal method with ultrasonic assisted during aging time. Because of no organic reagent, there is no problem to handle the mother liquor.

EXPERIMENTAL

SuZhou kaolin, sodium aluminate, soluble silicate solution, sodium hydroxide, conventional NaY zeolite (1-2 μm) prepared without ultrasonic.

Characterization method

Relative crystallinity of zeolite was determined by X-ray diffraction (D5005 X-ray diffractometer) and SiO_2/Al_2O_3 was calculated according to the following relationship:

$$SiO_2/Al_2O_3 = (25.858\text{-}a_0) \times 2/(a_0\text{-}24.191).$$

The size and morphology of product was determined by 435VP scanning electron microscopy, HitachiH-7500 transmission electron microscopy and Tecnai F20 G2 high resolution electron microscopy.

The surface area, pore volume and pore distribution of zeolite was determined by N_2 adsorption and desorption techniques, using Micromeritics ASAP2400/2405 Automatic Adsorption Instrument.

The structure destroy temperature of zeolite was determined by TA5000, DSC2910 instrument.

Hydrothermal stability of nano-sized NaY zeolite was studied on the D5005 X-ray diffractometer. Hydrothermal treat condition: 800 ºC, 100 % water vapour aging.

The MAT of catalyst was studied on micro-fixed bed reactor. It was determined when DaGang light diesel reacted 70s at 460 ºC with catalytic which had been treated 4 h by 800 ºC, 100 % water vapour.

The catalytic characteristics were studied on small fixed bed. Determined condition: catalyst was used after treated 4 h by 800 ºC, 100 % water vapour, cracking temperature being 490 ºC, the ratio of catalytic and oil being 3.9.

RESULTS AND DISCUSSION

Synthesis of nano-sized NaY zeolite

Calcination of kaolin: Kaolin was dried at 120 ºC for 12 h, then crushed, sieved by 60 mesh sieve, finally calcined for 4 h at 650 ºC.

Synthesis of seed solution: Sodium silicate was added to the stirred sodium aluminate at 30 ºC. After stirring for 1 h, the solution was kept for 24 h at 20 ºC. The seed solution with molar ratios of $17SiO_2:Al_2O_3:20Na_2O:250H_2O$ had been obtained.

Synthesis of nano-sized NaY zeolit: The molar ratios of material: $4Na_2O:Al_2O_2:8SiO_2:200H_2O$.

Synthesis: Added seed solution to soluble silicate solution and metakaolin to sodium hydroxide solution at 40 ºC. After 2 h at 40 ºC with ultrasonic assisted, the mixture was hydrothermally treated at 90 ºC for 12 h. After cooled to room temperature, the slurry was filtered and the cake was washed with deionized water, finally dried for 8 h at 110 ºC, then nano-sized NaY zeolite has been separated out.

Characterization of nano-sized NaY zeolite: The phase of the product was determined by D5005 X-ray diffractometer. The content of zeolite in the product, defined as relative crystallinity, was determined by comparing the peak intensities with those of a pure standard. $SiO_2/A1_2O_3$ ratio in the final product was estimated from the measurements of the cell constants. The result was shown as Fig. 1. It shows clearly the characteristic peak of NaY zeolite. The peak become wider because of fine particle. The relative crystallinity is 80.12 % and Si/Al ratio being 5.12.

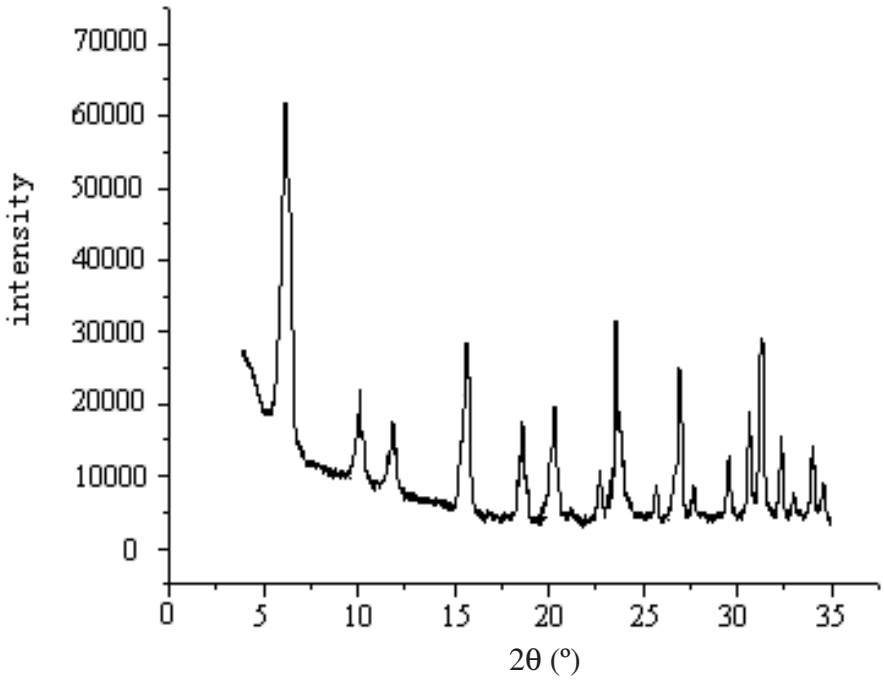


Fig. 1. XRD pattern of nano-sized NaY zeolite

Fig. 2 is SEM image of product. Fig. 3 is TEM image of product. They show that the size of product is about 100-150 nm. Fig.4 is HREM image of product. It shows clearly that several nanometer sized NaY zeolite particles are distributed evenly in the noncrystal matrix. So the product is a kind of composite, rather than pure NaY zeolite. Fig. 5 is SEM image of conventional NaY zeolite prepared without ultrasonic assisted during aging time. The size is 1-2 μm.

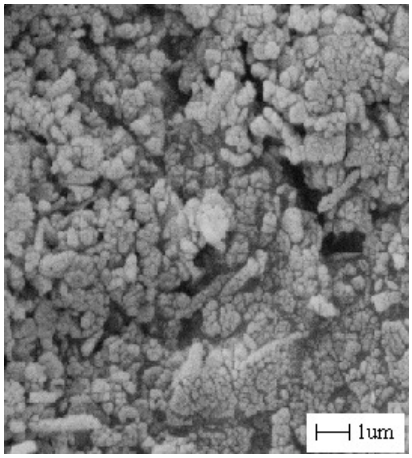


Fig. 2. SEM image of nano-sized NaY zeolite

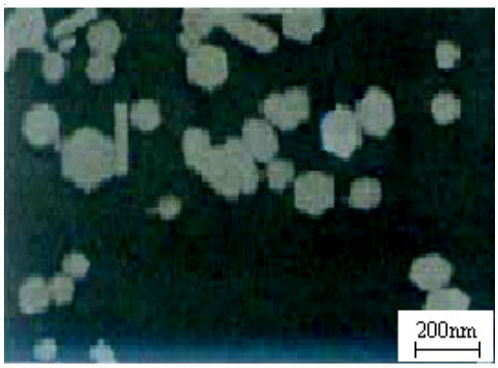


Fig. 3. TEM image of nano-sized NaY zeolite

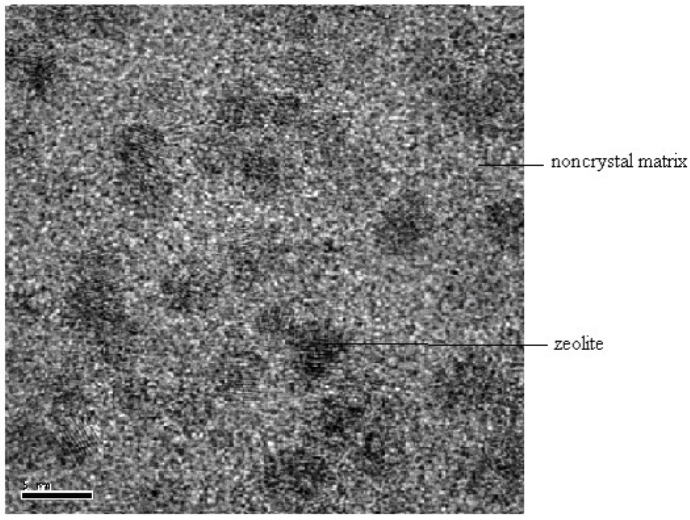


Fig. 4. HREM image of nano-sized NaY zeolite

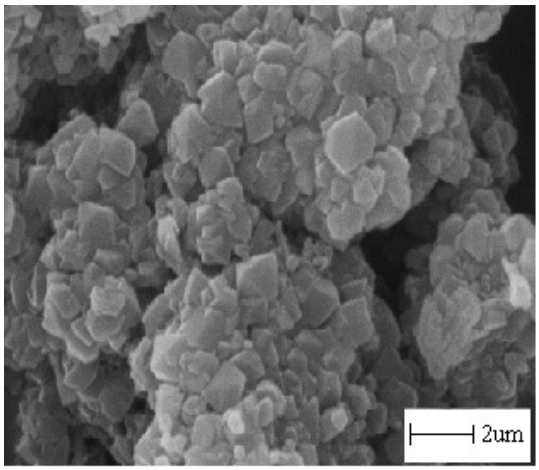


Fig. 5. SEM image of conventional NaY zeolite

Physico-chemical properties of NaY zeolite exchanged by rare earth

Preparation of sample: Mixed nanosized NaY, conventional NaY, respectively with $NH_4Cl{\cdot}H_2O$ at weight ratio of $NaY:NH_4Cl:H_2O = 1:1:10$, stirred mixture 1.5 h at 90 ºC, filtered slurry, dried cake, then got NH_4Y.

Mixed NH_4Y with H_2O, $ReCl_3$ at ratio of $NH_4Y:H_2O:ReCl_3 = 1:10:0.1$. Stired mixture 1.5 h at 90 ºC, filtered slurry, calcined the cake 1 h at 550 ºC, Finally exchanged it with NH_4Cl solution two times. Nano-sized NaY composite and conventional NaY composite that contain 10 % rare earth.

Physico-chemical properties: The physico-chemical properties of nano-sized NaY composite and conventional NaY composite exchanged with rare earth are shown in Tables 1 and 2.

TABLE-1
PHYSICO-CHEMICAL PROPERTIES OF NANO-SIZED NaY ZEOLITE

Sample	Relative crystallinity (%)	$10^{-10}a_0$ (m)	$T_{structure\ destroy}$ (ºC)	S_{BET} (m^2g^{-1})	V_{pore} (mL g^{-1})	$V_{micropore}$ (mL g^{-1})	$V_{mesopore}$ (mL g^{-1})
Nanosized zeolite	80.12	24.68	901	762	0.36	0.26	15.33
Conventional zeolite	81.26	24.67	879	565	0.35	0.28	4.62

Note: a_0-unit cell

TABLE-2
HYDROTHERMAL STABILITY OF NANO-SIZED NaY ZEOLITE

Sample	Novel zeolite Crystallinity (%)	Hydrothermal aging 8 h		Hydrothermal aging 16 h	
		Crystallinity (%)	Crystallinity preserve (%)	Crystallinity (%)	Crystallinity preserve (%)
Nano-sized zeolite	80.12	24.31	30.34	19.75	24.65
Conventional zeolite	81.26	25.72	31.65	20.56	25.30

Table-1 shows that the structure destroy temperature of nanosized NaY composite is a little higher than that of conventional NaY composite and surface area, pore volume and mesopore volume of nanosized NaY composite is more than that of conventional NaY composite. Table-2 shows that hydrothermal stability of both composites is almost same.

Catalytic characteristics of zeolites: Mixed NaY composite containing rare earth, kaolin, deionized water, aluminum gel and diaspore at appropriate ratio, then dried the mixture, calcined the cake at 600 ºC, finally got FCC catalyst containing 30 % zeolite.

The catalytic characteristics properties of zeolites such as (1) higher micro reaction activity; (2) more gasoline; (3) less gas and coke; (4) higher conversion per cent are shown as Table-3.

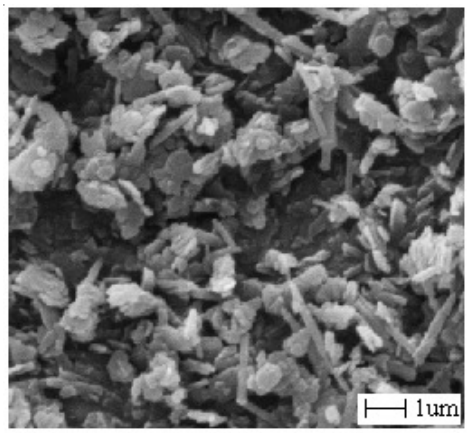
TABLE-3
TEST RESULTS OF CATALYSTS IN SMALL FIXED-BED REACTOR

Sample	MAT (%)	W (%)					Conversion (%)
		Gas	Gasoline	Diesel	Coke	Heavy oil	
Nano-sized zeolite	74	11.9	65.7	14.8	2.3	5.3	79.9
Conventional zeolite	71	12.7	62.3	13.1	3.2	8.7	78.2

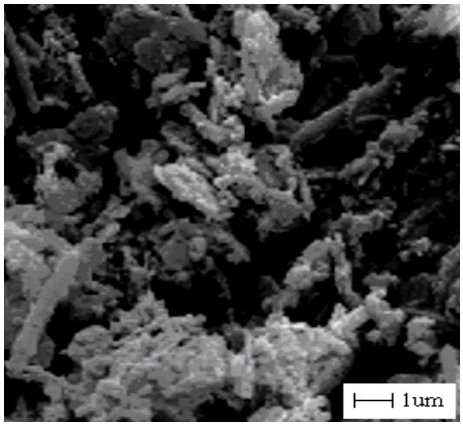
MAT = Micro-reaction activity; W (%) = Mass fraction in product.

Nanosize NaY composite has larger surface area, more active sites, shorter diffuse channel that make oil easy to get the active centre, so it has higher micro reaction activity. Because of large size, it is difficult for heavy oil to get in the microchannel of catalyst to get cracked. Nano-size NaY composite has bigger mesopore volume that is benefit for heavy oil to get in, so improve the ability of cracking heavy oil and decrease the yield of heavy oil. Meanwhile, nanosized zeolite particle distributes evenly in the non-crystal matrix, decrease the chance of olefin to be cracked excessively somewhere, so the yield of coke is lower.

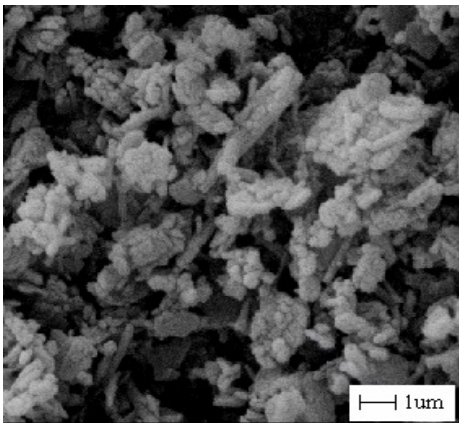
Formation mechanism of nano-sized NaY zeolite: Fig. 6 is the SEM images of samples at different crystallization time. At the end of aging time, the metakaolin particles become smaller. There are two reasons: First, because of break action of ultrasonic, the metakaolin particles become smaller. Second, because of cavitation of ultrasonic, there are many air bubbles in synthesis system. When these bubbles break, they produce great energy, which make alkali quickly disperse to the surface and inside of metakaolin, accelerate metakaolin to dissolve, so the particle become lessening. At the same time, more aluminum silicate ions in the liquid disperse to the surface and inside of metakaolin, forming gel layer in which aluminum silicate ion has larger supersaturation. After heated, on the one hand, metakaolin continue dissolving, on the other hand, NaY zeolite begin to grow. These two processes exist in the synthesis system. Larger supersaturation of aluminum silicate ion increase nucleation speed, produce more nucleus of NaY zeolite, so the size of products decrease. Meanwhile ultrasonic can make the aluminum silicate ions and gel distribute more



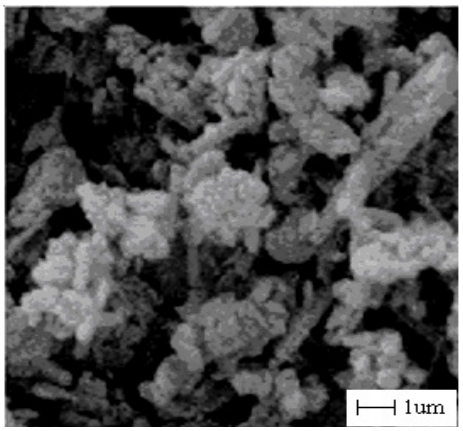
Metakaolin



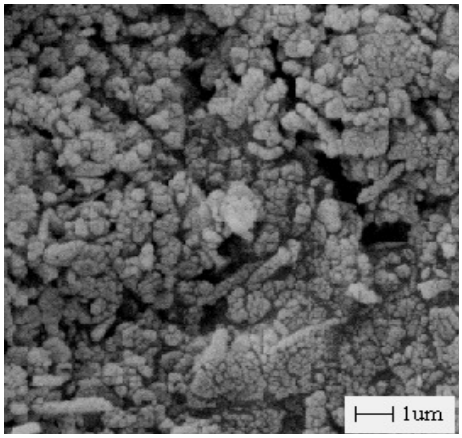
0 h



4 h



8 h



12 h

Fig. 6. SEM images of products at different crystal time

evenly on the surface and inside of metakaolin, so the size of products is homogeneous. The image of product crystallizing after 12 h shows that the size of product is homogeneous and nano-scaled.

Conclusion

Nano-sized NaY zeolite has been synthesized from metakaolin by hydrothermal method with ultrasonic assisted during aging time. Compared with conventional zeolite, nano-sized zeolite has larger surface area and mesopore volume, better thermal stability, higher cracking activity, higher gasoline selectivity, lower coke and gas selectivity. So it has good industrial application prospects.

ACKNOWLEDGEMENT

The authors thank Henan Institute of Science and Technology provide financial support, fund number 0703.

REFERENCES

1. Z.-S. Chao, H.-Q. Lin, G.-Z. Shen, T.-H. Wu and H.-L. Wan, *Chem. J. Chin. Univ.*, **22**, 10 (2001).
2. R.-F. Li, H.-X. Yang, F. Song, K.-C. Xie and M.-F. Hou, The Synthesis Method of Nano-Zeolite, CN 1296915A[p] (2001).
3. B.J. Scheman, J. Sterte and J.E. Otterstedt, *Chem. Soc. Chem. Commun.*, **12**, 994 (1993).
4. W.A. Ambs and Pa. Warthmore, U.S. Patent 4372931 (1983).
5. T. Linder and H. Lechert, *Zeolites*, **16**, 196 (1996).
6. P.K. Mather and J. Scherzer, U.S. Patent 3516786 (1970).
7. M.-C. Xu, M.-J. Cheng and X.-H. Bao, The Synthesis Method of NaY Zeolite from Metakaolin Sphere. CN1393402A[p] (1983).
8. B. Wang, H.Z. Ma and Z.S. Qi, *Chin. Chem. Lett.*, **13**, 385 (2002).

(*Received*: 29 November 2008; *Accepted*: 7 August 2009) AJC-7728