Front. Chem. Eng. China 2009, 3(1): 8–11
DOI 10.1007/s11705-009-0094-8

RESEARCH ARTICLE

Synthesis of NaA zeolite from kaolin source

Qian MIAO, Zhihui ZHOU, Jianhua YANG, Jinming LU, Shiwei YAN, Jinqu WANG (✉)

State Key Laboratory of Fine Chemicals, Institute of Adsorption and Inorganic Membrane, Dalian University of Technology, Dalian 116012, China

Abstract In this work, zeolite NaA was successfully synthesized by a hydrothermal method using kaolin as a combined source for silica and alumina. Zeolite NaA with high static water adsorption was synthesized from the low-cost raw material, kaolin, and the reaction parameters were optimized. Metakaolin was obtained by calcining kaolin at temperatures ranged from 953 K to 1173 K. The synthesis mixture was pre-crystallized at 343 K and crystallized at 373 K successively. Zeolite NaA was obtained, which was confirmed by SEM, XRD and the water adsorption analysis. The optimized metakaolinization temperature was found at 973 K. The influence of Na_2O/SiO_2 molar ratio, pre-crystallization time and seed on the crystallization of NaA zeolite was investigated. A thorough mixing of metakaolin and NaOH solution was favourable for the nucleation/crystallization rate. The obtained NaA zeolite under the optimized conditions shows excellent crystallinity and static water adsorption of 28.0 wt-%, which was higher than 25.9 wt-% of the commercial NaA zeolite. Kaolin was suggested to be a feasible and economical raw material for the practical industrial applications for NaA zeolite.

Keywords NaA zeolite, kaolin, hydrothermal synthesis, static water adsorption

1 Introduction

NaA Zeolite is of great industrial importance due to its molecular sieving, ion exchange and water adsorption properties. NaA zeolite is generally synthesized from high-cost chemicals, which limits its commercial application. With the molar ratio Si/Al nearly equal to 1, kaolin is an ideal raw material for preparing NaA zeolite. Kaolin was one of the most versatile industrial minerals and was used extensively for many applications (Murray, 1986, 1991) [1]. The synthesis of NaA zeolite from kaolin source was started from the 1970s (Breck, 1974; Barrer, 1978) by the hydrothermal reaction of dehydroxylated kaolin with a sodium hydroxide solution. After a long exploration, kaolin has been accepted as the most appropriate raw materials. Belver et al. [2] prepared metakaolin by calcination of a natural Spanish kaolin at 600°C, 700°C, 800°C and 900°C. Their results indicated that metakaolin prepared at 900°C showed a lower reactivity than those synthesized at the other temperatures. For the synthesis of zeolites except NaA, other activated methods were also investigated [3–7].

In this work, NaA zeolite was hydrothermally synthesized from kaolin, and the effect of calcination temperature, molar ratio of Na_2O/SiO_2, pre-crystallization time and the content of seed was investigated, respectively. Under the optimized conditions, the NaA zeolite product exhibited an excellent relative crystallinity and better static water adsorption capacity of 28.0 wt-% than the industrial product provided by the Luoyang Jianlong Chemical Industrial Co., Ltd.

2 Experimental

2.1 Raw materials and chemical reagent

The chemical analysis of kaolin is shown in Table 1. Sodium hydroxide, calcium chloride, zinc oxide and EDTA were of analytical grade. Metakaolin was obtained by calcining kaolin at different temperatures ranging from 953 K to 1173 K, at a heating rate of 5 K/min in a muffle furnace with a temperature programmer.

2.2 Synthesis of NaA zeolite

Metakaolin was mixed with NaOH solution under fierce agitation at room temperature. After ageing for 12 h the reaction mixture was transferred into autoclaves to pre-crystallize at 343 K and crystallize at 373 K, successively. The NaA zeolite obtained was washed with deionized water until the pH = 8, and then dried at 318 K for 24 h.

Received August 3, 2008; accepted December 1, 2008

E-mail: Wjinqu@dlut.edu.cn

Table 1 Chemical composition of kaolin/wt-%

Al_2O_3	SiO_2	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O	MnO_2
44.5 ± 2.0	51.5 ± 2.0	< 0.5	< 1.5	< 0.5	< 0.3	< 0.1	< 0.2	< 0.004

2.3 Characterization

The NaA zeolite product was confirmed by X-ray diffraction (XRD) using Rigaku X/Max-2400 with Cu Kα (λ= 0.154 nm) radiation at 40 kV and 30 mA. The morphology was characterized by scanning electron microscopy (SEM) at 30 kV, using a KYKY-2800B instrument.

The static water adsorption amount was measured as follows: NaA zeolite was calcined in a muffle at 823 K for one hour, then was sampled into a weighing bottle. The bottle with NaA zeolite was placed in a humidistat at 308 K whose humidity was controlled by NaCl saturated solution. After 24 h, the bottle was accurately weighed. The water static adsorption ω was calculated by the formulation below:

$$\omega = \frac{M3 - M2}{M2 - M1} \times 100\% ,$$

where $M1$ is weight of the weighing bottle, $M2$ is weight of the weighing bottle and the sample calcined, and $M3$ is weight of the weighing bottle and the sample after the water static adsorption.

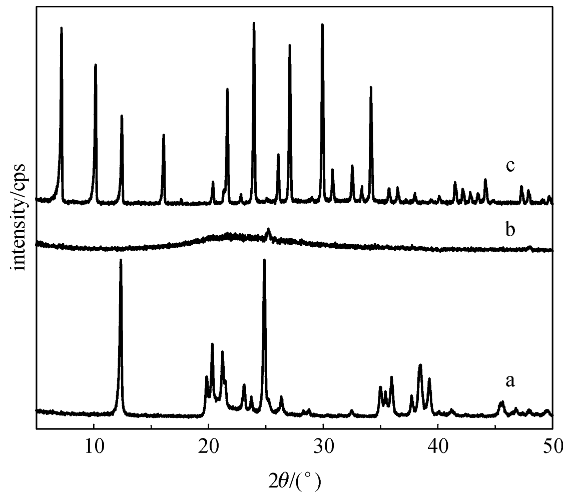

Fig. 1 XRD patterns of kaolin, metakaolin and NaA zeolite
a. kaolin; b. metakaolin; c. NaA zeolite

3 Results and discussion

3.1 Effect of calcination temperature

As seen from Fig. 1(c), the product shows characteristic peaks of NaA zeolite. The calcination temperature of kaolin was investigated and arranged from 953 K to 1173 K. From Fig. 2, the relative crystallinity and the static water adsorption both dropped slowly when the calcination temperature increased. However, there was a peak in the two curves at 973 K. The highest static water adsorption was up to 28.0 wt-%, which indicated that metakaolin calcined at 973 K was activated most sufficiently.

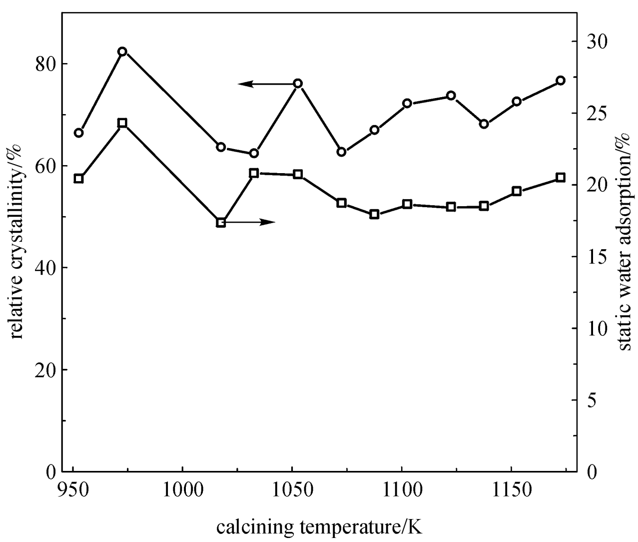

Fig. 2 Effect of calcination temperature on the relative crystallinity and static water adsorption (Na_2O/SiO_2 = 1.00, H_2O/Na_2O = 60, pre-crystallization time = 2 h, pre-crystallization temperature = 343 K, seed content = 0%)

3.2 Effect of material ratio

Since kaolin is a combined source for silica and alumina, when the molar ratio Na_2O/SiO_2 is larger, the content of kaolin in the unit volume of the reaction mixture becomes less and the concentration of the OH^- ion becomes larger. As seen in Fig. 3, the static water adsorption amount generally increased as the reaction time was prolonged, and reduced slowly with the increase of Na_2O/SiO_2 during the earlier crystallization stage (crystallization time 2–4 h) and then increased quickly to the highest 22.1 wt-% (crystallization time 6 h). The crystallization time on this condition was selected at 6 h, and a higher Na_2O/SiO_2 was favorable for synthesis of the NaA zeolite.

3.3 Effect of pre-crystallization time

The raw material, kaolin, influenced the crystallization of NaA zeolite due to: (1) kaolin was a natural mineral with

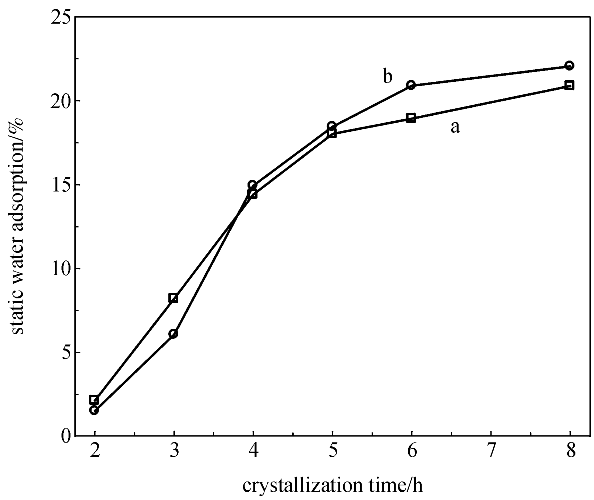

Fig. 3 Effect of Na_2O/SiO_2 on the static water adsorption
a. calcination temperature = 973 K, Na_2O/SiO_2= 1.50, H_2O/Na_2O = 45, pre-crystallization time = 2 h, pre-crystallization temperature = 343 K, seed content = 0%;
b. calcination temperature = 973 K, Na_2O/SiO_2= 1.71, H_2O/Na_2O = 45, pre-crystallization time = 2 h, pre-crystallization temperature = 343 K, seed content = 0%

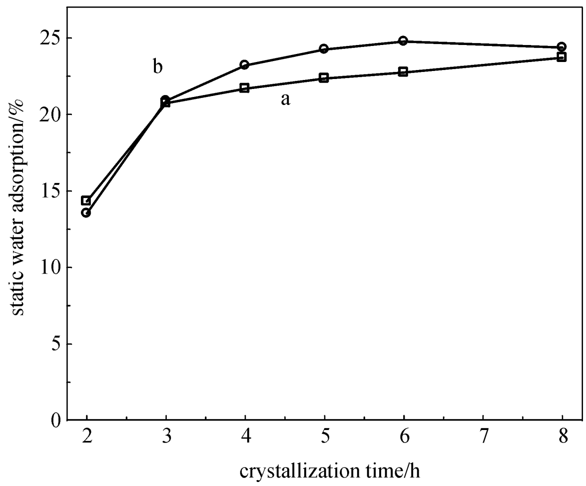

Fig. 4 Effect of pre-crystallization time on the static water adsorption
a. calcination temperature = 973 K, Na_2O/SiO_2= 1.71, H_2O/Na_2O = 40, pre-crystallization time = 2 h, pre-crystallization temperature = 343 K, seed content = 0%;
b. calcination temperature = 973 K, Na_2O/SiO_2= 1.71, H_2O/Na_2O = 40, pre-crystallization time = 3 h, pre-crystallization temperature = 343 K, seed content = 0%

low activity; (2) the particle size of kaolin used in this work was about 10 μm. Metakaolin did not completely dissolve under the same conditions compared with the synthesis from traditional chemical materials. The pre-crystallization course is applied to improve the nucleation and growth of NaA crystals. As illustrated in Fig. 4, the static water adsorption amount of pre-crystallizatin at 3 h (24.8 wt-%) was higher than that of 2 h (23.7 wt-%). The longer pre-crystallization time facilitated the crystallization growth of NaA zeolite.

3.4 Effect of seed

NaA zeolite would transform into other zeolites when the reaction time is longer than the synthesis required. The addition of seed would play an important role in the synthesis of NaA zeolite, especially when the raw material is kaolin, which is a natural mineral with impurity. The relative crystallinity increased with increasing amount of seed in the synthesis mixture as shown in Table 2. First, the seed did not have much influence on the crystallization rate, but was supposed to induce nucleation and thus to facilitate the next crystallization. The performance of NaA zeolite, including the relative crystallinity and the static water adsorption amount, was greatly improved, and this result was also in line with the XRD results (not shown). The morphology of NaA zeolite was shown in the Fig. 5. It could be seen that NaA zeolite well crystallized with cube shape.

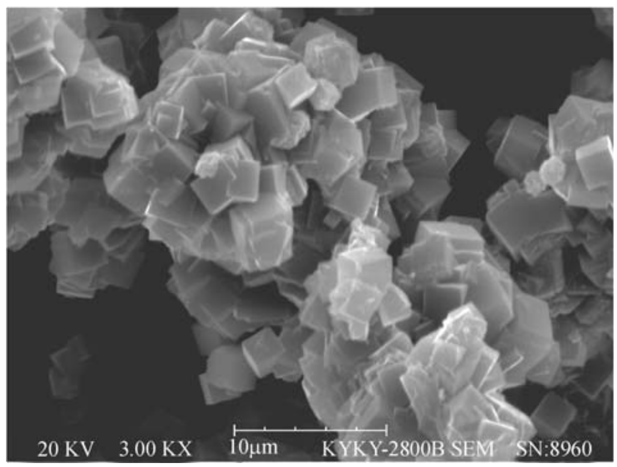

Fig. 5 SEM of NaA zeolite sample (calcination temperature = 973 K, Na_2O/SiO_2= 1.71, H_2O/Na_2O = 45, pre-crystallization time = 2 h, pre-crystallization temperature = 343 K, crystallization time = 6 h, seed content = 4%)

Table 2 Effect of seed on the relative crystallinity of NaA zeolite[a)]

sample	seed/%	relative crystallinity/%
S1	1	68.83
S2	2	80.38
S3	4	99.68

a) calcination temperature = 973 K, Na_2O/SiO_2= 1.71, H_2O/Na_2O = 45, pre-crystallization time = 2 h, pre-crystallization temperature = 343 K, crystallization time = 6 h

3.5 Advantage of NaA zeolite by this method

Through the above discussions, the optimum conditions of NaA zeolite from a kaolin source were drawn as follows: calcination temperature = 973 K, Na_2O/SiO_2= 1.71, pre-crystallization time = 3 h, pre-crystallization temperature = 343 K, seed content = 4%. The static water adsorption analysis of the NaA zeolite obtained under the optimized conditions along the reaction time was conducted in comparison with that of the commercial product, and the result was exhibited in Fig. 6. The highest static water adsorption 28.0 wt-% of the synthesized sample exceeded that of the commercial product 25.9 wt-% which was indicated by the line in Fig. 6.

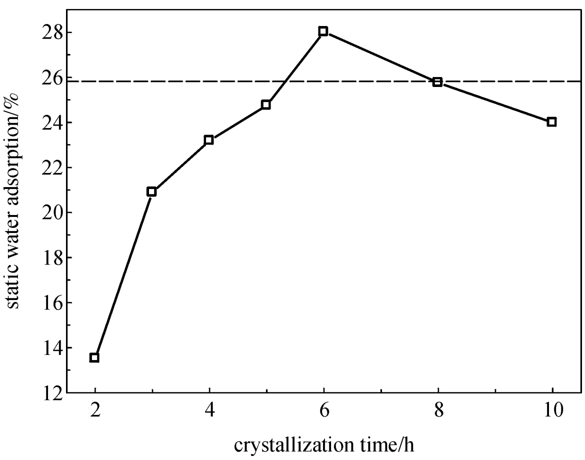

Fig. 6 Comparison of static water adsorption of sample and the commercial product

4 Conclusions

Pure zeolite NaA was hydrothermally synthesized using kaolin as the raw materials. XRD analysis confirmed an excellent relative crystallinity, and the static water adsorption exhibited good results. The surface morphology was proven to be cubic by SEM. The optimized conditions for the formation of zeolite NaA were found to be: (1) kaolin calcined at 973 K; (2) Na_2O/SiO_2= 1.71; (3) pre-crystallization time = 3 h at 343 K; (4) the content of seed was 4.0 wt-%, and the addition of seed facilitated crystallization. NaA zeolite obtained under the above conditions had better static water adsorption 28.0 wt-% than that of the industrial product (25.9Z wt-%) provided by the Luoyang Jianlong Chemical Industrial Co., Ltd. Kaolin was suggested to be a feasible and economical raw material for the practical industrial applications of NaA zeolite.

Acknowledgements The authors are grateful for the financial support from the National Natural Science Foundation of China (Grant No. 20606004).

References

1. Chandrasekhar S, Raghavan P, Sebastian, Damodaran A D. Brightness improvement studies on kaolin based zeolite 4A. Applied Clay Science, 1997, 12: 221–231
2. Jadambaa T, Kiyoshi O, Kenneth J D. MacKenzie. Zeolite formation by hydrothermal treatment of waste solution from selectively leached kaolinite. Materials Letters, 2002, 52: 91–95
3. Deepak A, Alan C, Russell F. Howe. The transformation of kaolin to low-silica X zeolite. Zeolites, 1997, 19: 359–365
4. Ghobarkar H, Schaf O. Hydrothermal synthesis of laumontite, a zeolite. Microporous and Mesoporous Materials, 1998, 23: 55–60
5. Vilma S, Ursula K, Ruby C. Synthesis of molecular sieves from Chilean kaolinites: 1. synthesis of NaA type zeolites. Journal of Chemical Technology and Biotechnology, 1999, 74: 358–363
6. Lin D C, Xu X W, Zuo F, Long Y C. Crystallization of JBW, CAN, SOD and ABW type zeolite from transformation of metakaolin. Microporous and Mesoporous Materials, 2004, 70: 63–70
7. Marcelo L M, Diego I P, Nadia R C. Fernandes Machado, Sibele B.C. Pergher. Synthesis of mordenite using kaolin as Si and Al source. Applied Clay Science, 2007, 41: 99–104