Influence of synthesis parameters on the crystallinity and Si/Al ratio of NaY zeolite synthesized from kaolin

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Abstract: Well-crystallized high-silica NaY zeolites (Si/Al>2.5) were prepared from a reaction mixture consisting of metakaolin, sodium silicate solution and seed solution via optimization of the mixture composition and reaction conditions. The transformation from kaolin to high-silica NaY zeolite was confirmed by XRD, SEM and IR techniques. Subsequently, the influence of synthesis parameters, i.e. initial SiO₂/Al₂O₃, initial Na₂O/SiO₂, initial H₂O/SiO₂, aging time of the seed solution, crystallization temperature and crystallization time, on the NaY growth was investigated in terms of crystallinity and Si/Al ratio. The results showed that the effects of initial SiO₂/Al₂O₃, initial Na₂O/SiO₂ and initial H₂O/SiO₂ on the crystallinity and Si/Al ratio of NaY zeolite are similar to those observed in the conventional syntheses of NaY zeolites only using sodium silicate solution as silicon source. However, due to the use of metakaolin as the main silicon and aluminum sources in the present study, a long crystallization induction period of 20 h was achieved, which can be attributed to the dissolution of metakaolin. In addition, different from the conventional syntheses of zeolite NaY, pure NaY zeolites (i.e. without NaP zeolite impurity) were still obtained even at 120 °C because of the use of a large quantity of seed solution (23 wt%) in the reaction mixture. As the aging time of the seed solution increased from 3.5 h to 22 h, the relative crystallinity of the NaY zeolite first increased sharply and then reached a plateau, while the Si/Al ratio first increased rapidly up to a maximum value of 2.75 corresponding to an aging time of 6.5 h, and then decreased sharply with the aging time.

Key words: Kaolin, NaY zeolite, high-silica, seed solution, aging time, crystallinity

1 Introduction

Porous materials such as zeolite, mesoporous silica and metal organic framework (MOF) are widely used in catalysis, adsorption, separation and bio-application (Czaja et al, 2009; Liu et al, 2009; Liu et al, 2008a; 2008b). Zeolite Y, an important high-silica zeolite, is extensively used as the active component of the fluid catalytic cracking (FCC) catalysts because of its unique catalytic properties (Wu et al, 2006). On the other hand, kaolin is one of the clay materials most widely used by human being since antiquity. It is an ideal raw material for syntheses of low-silica zeolites, such as zeolite A (Chandrasekhar et al, 1997; Chandrasekhar and Pramada, 2008), X (Colina and Llorens, 2007), JBW, CAN, SOD, and ABW (Lin et al, 2004), because the molar contents

of SiO₂ and Al₂O₃ are similar with each other. Some zeolites with higher Si/Al ratios, such as mordenite (Mignoni et al, 2008), ZSM-5 (Madhusoodana, et al, 2005) and Y have also been prepared by using kaolin and additional silica sources as starting materials.

However, as far as we know, only a few papers have focused on the synthesis of zeolite Y from kaolin. For example, Liu et al (2003) reported the in-situ synthesis of zeolite Y from coal-based kaolin. They investigated the effects of various factors on the properties and crystallinity of the Y samples, but the Si/Al ratios of zeolite Y were not mentioned in their paper. Chandrasekhar and Pramada (2004) reported the synthesis of zeolite Y with a Si/Al ratio of 1.8 from kaolin. They mainly aimed at the phase of products formed under various reaction conditions. Barrer (1978) synthesized zeolite Y with a high Si/Al ratio of 2.05, by using acid-leached metakaolin as the starting material, in a longer reaction time. Zhou et al (1981) enhanced the Si/Al ratio of the zeolite Y to 2.2-2.5 by adding sodium silicate solution as

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Received December 10, 2009

an additional silicon source besides kaolin.

Zeolite Y with high Si/Al ratio can retain a relatively high crystallinity during hydrothermal treatment, which strongly benefits the stability of zeolite Y, and is desirable for catalytic cracking catalysts (Wang et al, 2005). However, synthesis from kaolin of zeolite Y with a Si/Al ratio higher than 2.5 has not yet reported. In this paper, high-silica NaY zeolites with Si/Al ratios higher than 2.5 were synthesized from kaolin and the influence of synthesis variables on the crystallinity and Si/Al ratios of NaY zeolites is investigated and discussed.

2 Experimental

2.1 Synthesis

High-silica zeolite NaY was hydrothermally synthesized from a reaction mixture consisting of metakaolin, sodium silicate solution and seed solution. The metakaolin used as silica and alumina sources, was obtained by calcining Suzhou

kaolin at 720 °C for 4 h. The sodium silicate solution acted as a additional silica source. The seed solution was prepared by adding sodium hydroxide, sodium aluminate and sodium silicate solution to deionized water at the stoichiometry (molar ratio) of (15-18) Na₂O: Al₂O₃: (15-20) SiO₂: (320-400) H₂O with gentle stirring for 14 h, and then it was left to age at room temperature for 3.5-22 h.

The synthesis procedure of a typical zeolite NaY sample (run No.3 in Table 1) was as follows: First, metakaolin and deionized water were added to sodium silicate solution to obtain an initial mixture with a molar composition of 7.0SiO₂:Al₂O₃:2.6Na₂O:126.3H₂O. Then, 23 wt% of seed solution was added to this mixture to obtain the reaction mixture. Subsequently, the reaction mixture was aged at 54 °C for 1h and then transferred to a Teflon-lined stainless-steel autoclave to be crystallized for 28 h at 100 °C. The solid product was then filtered, washed repeatedly with deionized water and dried at 100 °C overnight. The most representative syntheses are listed in Table 1.

Table 1 Molar composition of the initial reaction mixtures, aging conditions of the seed solution and crystallization conditions for synthesis of zeolite NaY

Samples	SiO ₂ /Al ₂ O ₃	Na ₂ O/SiO ₂	H ₂ O/SiO ₂	Aging temperature °C	Aging time, h	Crystallization temperature °C	Crystallization time, h
Effect of initial SiO ₂ /Al ₂ O ₃							
No.1	6.0	0.37	18	25	6.5	100	28
No.2	6.5	0.37	18	25	6.5	100	28
No.3	7.0	0.37	18	25	6.5	100	28
No.4	7.5	0.37	18	25	6.5	100	28
No.5	8.0	0.37	18	25	6.5	100	28
Effect of initial Na ₂ O/SiO ₂							
No.6	7.0	0.40	18	25	6.5	100	28
No.7	7.0	0.43	18	25	6.5	100	28
No.8	7.0	0.45	18	25	6.5	100	28
Effect of initial H ₂ O/SiO ₂							
No.9	7.0	0.37	16	25	6.5	100	28
No.10	7.0	0.37	20	25	6.5	100	28
No.11	7.0	0.37	24	25	6.5	100	28
No.12	7.0	0.37	28	25	6.5	100	28
No.13	7.0	0.37	32	25	6.5	100	28
Effect of aging time of the seeds solution							
No.14	7.0	0.37	18	25	3.5	100	28
No.15	7.0	0.37	18	25	12	100	28
No.16	7.0	0.37	18	25	18	100	28
No.17	7.0	0.37	18	25	22	100	28
Effect of crystallization temperature							
No.18	7.0	0.37	18	25	6.5	90	28
No.19	7.0	0.37	18	25	6.5	110	28
No.20	7.0	0.37	18	25	6.5	120	28

2.2 Characterization

Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku D/MAX-2500 diffractometer using Ni filtered CuK α radiation. Fourier transform infrared spectra (FT-IR) were recorded by means of a DIGLAB FTS-3000 spectrophotometer using the KBr wafer technique. The morphology and size of zeolite Y were determined from images taken with a CAMBRIDGE S-360 scanning electron microscope (SEM).

The crystallinity of zeolite Y was determined by X-ray diffraction and the crystallinity of the as-synthesized typical sample (No.3 in Table 1) was designated as 100%. The relative crystallinity of the other samples was calculated by comparing the total area of five strong diffraction peaks in the 2θ region of 5° - 35° with that of the typical sample. The XRD peak location at $2\theta \approx 31^\circ$ was used to determine the unit cell parameter a_0 of the zeolite Y sample. The Si/Al ratio of zeolite Y was determined according to the following equation (Wang and Ma, 1998): $\text{Si/Al} = (25.858 - a_0)/(a_0 - 24.191)$.

3 Results and discussion

3.1 XRD, SEM and FT-IR analyses

The parent kaolin is not suitable for preparation of zeolites because of its chemical stability, so it is dehydrated by calcination at 720°C for 4 h and converted to metakaolin, which is semicrystalline and much more reactive than kaolin. Fig. 1 shows the X-ray diffraction patterns of kaolin, metakaolin and a typical zeolite product. The parent kaolin (XRD pattern *a* in Fig. 1) shows two intense diffraction peaks at $2\theta = 12.5^\circ$ and 25.2° and a hump at $2\theta = 19.8^\circ$ - 21.9° , all of which correspond to kaolinite. There are no obvious peaks at about 5.9° , 8.6° and 26.7° , respectively corresponding to smectite, mica and quartz (Belver et al, 2002). This suggests that the Suzhou kaolin used in this study is composed of kaolinite with no detectable impurities. As mentioned above, after calcination at 720°C , kaolin is transformed into metakaolin, which shows an amorphous pattern (pattern *b* in Fig. 1) with the disappearance of the kaolinite diffraction peaks. These changes are completely consistent with the previous literature (Belver et al, 2002) on the kaolin-metakaolin transformation. The resulting product synthesized from metakaolin shows an XRD pattern (pattern *c* in Fig. 1) identical to the X-ray diffractogram of the zeolite Y given in the literature (Treacy and Higgins, 2007), indicating a

crystalline structure of the faujasite-type zeolite.

The SEM micrographs in Fig. 2 show the transformation of metakaolin into NaY zeolite. The parent kaolin (Fig. 2a) and metakaolin (Fig. 2b) both show stacks of large plates while the typical NaY sample (Fig. 2c) shows completely grown crystals of cubic morphology with diameter of 700-800 nm. This transformation process from kaolin to metakaolin, and then to the NaY product can be monitored by infrared spectroscopy. In Fig. 3 the infrared spectrum of kaolin (*a*) shows the typical 10 characteristic bands in the region of $1,400$ - 400 cm^{-1} of this material (Belver et al, 2002). The metakaolin (*b*) shows a very simple spectrum composed of three wide bands centered at 1100 , 800 and 470 cm^{-1} , respectively corresponding to the vibrations of the tetrahedral sheet, the free silica and the structural bending. As is expected, the spectrum of the NaY sample (*c*) shows the characteristic bands of zeolite Y (Sang et al, 2006). Furthermore, the characteristic asymmetric ($1,144\text{ cm}^{-1}$, $1,021\text{ cm}^{-1}$) and symmetric (789 cm^{-1} , 719 cm^{-1}) stretching T-O-T bond vibrations of the as-synthesized NaY sample are shifted to higher wavenumbers compared to its lower Si/Al ratio counterpart ($1,130\text{ cm}^{-1}$, $1,005\text{ cm}^{-1}$ and 784 cm^{-1} , 714 cm^{-1} , respectively, for Si/Al=2.43) reported in the literature (Chandrasekhar and Pramada, 2004). This suggests that the typical NaY sample synthesized from kaolin had a Si/Al ratio higher than 2.43. The exact Si/Al ratio of the typical NaY sample was determined as 2.75 by XRD technique.

Fig. 1 XRD patterns of the parent kaolin (*a*), metakaolin (*b*) and a typical NaY sample (*c*)

Fig. 2 SEM micrographs of the parent kaolin(*a*), metakaolin (*b*) and a typical NaY sample (*c*)

Fig. 3 IR spectra of the parent kaolin (a), metakaolin (b) and the typical NaY sample (c)

3.2 The crystallization curve

Fig. 4 gives the crystallization curve of a typical NaY sample, which shows an S-shape. The characteristic S-shaped crystallization curve of the sample can be divided into three periods: induction period (I), crystallization period (II) and stable period (III). During the induction period (I), i.e. the first 20 h, crystalline nuclei formed but a crystalline product was not observed by XRD. During the crystallization period (II), crystal nuclei grew rapidly in size. Finally, during the stable period (III), the crystallization was over after 33 h at 100 °C.

Fig. 4 The crystallization curve of the typical NaY sample at 100 °C

Interestingly, there appears a long induction period of 20 h shown in the crystallization curve of the NaY sample. As described in section 2.1, the typical NaY sample was synthesized from a reaction mixture containing metakaolin as the main silicon source and 23 wt% of seed solution. The seed solution introduced proto-nuclei into the synthesis system, and the proto-nuclei were later developed into nuclei during the nucleation step (Cundy and Paul, 2005). The conversion of proto-nuclei to viable nuclei (nucleation) corresponds to the establishment of a sufficiently ordered and sufficiently

extensive element of the zeolite structure to initiate systematic periodic propagation, i.e. crystal growth. The occurrence of such conversion requires the supply of nutrient composed of soluble silica and/or alumina species. Different from the conventional synthesis of NaY sample, in this study, metakaolin serves as the main silicon source. During the hydrothermal synthesis, the metakaolin first dissolved to form soluble four-fold coordinated silicon and aluminium species. These are the main sources of nutrient during the nucleation (Chandrasekhar and Pramada, 2004; Colina and Llorens, 2007). So the prolongation of the induction step can be attributed to the dissolution of metakaolin.

3.3 Effect of aging time of seed solution on NaY zeolite

The seeding potential of seed solution has been reported to be time-dependent although the seed solution is usually found to be X-ray amorphous (Cundy and Paul, 2005). This time-dependent effect was well demonstrated in our experiments, as shown in Fig. 5. As the aging time of the seed solution increased from 3.5 h to 22 h (run No.3 and No.14-17 in Table 1), the relative crystallinity of the NaY zeolite first increased sharply to 100 % corresponding to aging time of 6.5 h, then reached a plateau with the aging time, while the Si/Al ratio first increased rapidly up to a maximum value of 2.75, also corresponding to the aging time of 6.5 h, then decreased sharply to 2.65. It is clear that when the aging time was more than 6.5 h, the relative crystallinity was no longer improved, but the Si/Al ratio decreased greatly. Therefore, the optimal aging time of the seed solution is 6.5 h under these experimental conditions.

Fig. 5 The crystallinity and Si/Al ratios of the NaY samples as a function of aging time of the seed solution

The seed solution is believed to contain proto-nuclei, which are primary particle agglomerates to generate zeolite nuclei. It plays a direct role on the crystallization rate and homogeneity of final products (Lee et al, 2007). Longer aging time of the seed solution results in higher concentration of primary particle aggregates, and thus more mass gain through the higher surface area of these aggregates, which leads to faster crystallization rates. This is consistent with our observation that a high degree of crystallinity was obtained with increasing aging time. However, when the aging time

was more than 6.5 h, the relative crystallinity changed only a little. The reason might be that the equilibration process leading to the intermediate semi-ordered state reached a thermodynamic pseudo-equilibrium, i.e. the concentration of proto-nuclei reached a steady state. Therefore, the seeding effects of the seed solution after the time period of 6.5 h were no longer time-dependent.

Notably, the Si/Al ratios of NaY samples depended strongly on the aging time of the seed solution within the whole experimental time span. During the initial period of aging time before 6.5 h, the Si/Al ratio increased with increasing aging time, indicating that it was more ease to incorporate Si than Al species into the zeolite framework. With the aging time further increased from 6.5 h to 22 h, the Si/Al ratio of the NaY product fell greatly although the concentration of proto-nuclei kept steady. It seems that during the thermodynamic pseudo-equilibrium, the dissolution and polymerization of the silica and alumina precursors in proto-nuclei were in kinetic equilibrium. With an aging time longer than 6.5 h, aluminum species were preferentially incorporated into the framework, leading to the decrease of Si/Al ratio.

3.4 Effect of initial $\text{Na}_2\text{O}/\text{SiO}_2$ ratio on NaY zeolite

In this study, NaOH solid powder was used as alkali and so the $\text{Na}_2\text{O}/\text{SiO}_2$ ratio was related to the alkalinity of the synthesis system. The alkalinity in a synthesis batch is one of the most important parameters for the control of the crystallization of zeolites. It determines their composition and is, to a great extent, responsible for the type of the crystallizing zeolite (Lechert, 1998). The effect of $\text{Na}_2\text{O}/\text{SiO}_2$ ratio in the initial solution (or the alkalinity) on the crystallinity and Si/Al ratio of the NaY sample is shown in Fig. 6 (run No.3 and No.6-8 in Table 1). With an increase of the $\text{Na}_2\text{O}/\text{SiO}_2$ ratio, the relative crystallinity first increased, then decreased. While the Si/Al ratio decreased gradually with the increase of the $\text{Na}_2\text{O}/\text{SiO}_2$ ratio. These results are similar to those reported in the literature (Occelli and Robson, 1989). In general, lowering the alkalinity of the synthesis solution could prolong the dissolution time of silica-alumina sources, reduce the overall reactivity, increase the polymerization degree of silicon species and thus result in higher silicon incorporation into the zeolite Y framework. However, when

Fig. 6 The crystallinity and Si/Al ratios of the NaY samples as a function of initial $\text{Na}_2\text{O}/\text{SiO}_2$ ratio

the alkalinity is excessively high, the crystalline structure of zeolite Y, in the metastable state, is liable to dissolve and the crystallinity will decrease. The $\text{Na}_2\text{O}/\text{SiO}_2$ ratio of 0.4 appeared to be the optimum in terms of crystallinity in our experimental conditions.

3.5 Effect of initial $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio on NaY zeolite

In order to study the effect of the initial $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio on NaY zeolite, several reaction mixtures were prepared with $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios varying between 6.0 and 8.0 while the other reaction parameters were held constant (Run No.1-5 in Table 1). The crystallinity and Si/Al ratios of the NaY samples prepared from these reaction mixtures are shown in Fig. 7. With the increase of the initial $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio, the Si/Al ratio of the NaY sample gradually increased, which was also observed by Samia et al (2001). However, the crystallinity of these samples first remained approximately constant, and then decreased sharply with the further increase of the initial $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio.

An increase of the initial $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio can stimulate the dissolution equilibration of silica sources and result in high concentration of silicon species in the solution. Lechert et al (1996) reported the quantitative correlation of the Si/Al ratio of faujasites with the composition of the solution phase expressed by an equation: $(\text{Si}/\text{Al})_{\text{product}} = 1 + b \cdot \left\{ \frac{[\text{SiO}_2]}{[\text{OH}^-]} \right\}_{\text{solution}}$, where $b \approx 2$. From the equation, it can be seen clearly that with the increase of the concentration of silicon species, the Si/Al ratio of NaY product also increases. This is in good accordance with our observation. However, with the increase of the concentration of silicon species in the solution, the excess amount of silicon species could not be incorporated into the NaY framework but precipitated as amorphous silicates, which dilute the crystalline NaY samples and causes the decrease of relative crystallinity.

Fig. 7 The crystallinity and Si/Al ratios of the NaY samples as a function of initial $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio

3.6 Effect of initial $\text{H}_2\text{O}/\text{SiO}_2$ ratio

Syntheses of NaY zeolites, in which SiO_2 , Al_2O_3 and Na_2O content was held constant for all the batches while the H_2O content was varied, was carried out (run No. 9-13 in Table 1). The effect of $\text{H}_2\text{O}/\text{SiO}_2$ ratio in the initial solution

on the crystallinity of the NaY sample is shown in Fig. 8. It can be seen that the relative crystallinity of the NaY sample decreased sharply with increasing water content in the reaction mixture. The reason might be that an increase of water amount can dilute the solution, lower the concentration of primary species and finally slow the crystallization rate and reduce the crystallinity of the NaY sample due to the decrease in nucleation rate from fewer collisions between primary species. However, the Si/Al ratio of the NaY samples almost maintained the same value of 2.7 when the initial $\text{H}_2\text{O}/\text{SiO}_2$ ratio varied from 16 to 36. Compared with the effects of initial $\text{Na}_2\text{O}/\text{SiO}_2$ and $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios, the effect of the water amount was small on the Si/Al ratio of the NaY sample.

Fig. 8 The crystallinity of NaY samples as a function of initial $\text{H}_2\text{O}/\text{SiO}_2$ ratio

3.7 Effect of crystallization temperature

Nucleation and crystallization in the solution are commonly governed by a driving force related to the supersaturation and reaction temperature under autogenous pressure, so the effect of crystallization temperature was investigated. Fig. 9 shows the influence of the reaction temperature on the crystallinity and Si/Al ratio of the typical NaY sample (run No.3 and No.18-20 in Table 1).

It can be seen from Fig. 9 that the crystallinity of the NaY product synthesized at 90 °C was relatively low. When the

Fig. 9 The crystallinity and Si/Al ratios of the NaY samples as a function of the reaction temperature

temperature was increased to 100 °C, the pure NaY zeolite with the highest relative crystallinity was obtained. However, further increasing of the temperature to 110 °C and 120 °C, led to a sharp decrease in crystallinity. The initial increase of the crystallinity with temperature from 90 °C to 100 °C can be explained by the fact that a higher reaction temperature can increase zeolite growth and thus accelerate the crystallization. On the other hand, during the crystallization period, there exists a kinetic equilibration between crystal formation and dissolution, and too high a temperature can facilitate the dissolution of crystals. Therefore, the further increasing of temperature to 110 °C and 120 °C resulted in the decrease of the crystallinity. The variation of Si/Al ratio of the NaY product at different crystallization temperatures may be explained by the difference in the supersaturation and polycondensation of silicon and aluminium species.

In addition, it has been reported that 4A and NaP zeolites are the competitive phases present in the NaY products (Liu et al, 2003) at low and high crystallization temperature, respectively. In our study, even in the synthesis at 120 °C, NaP zeolite impurity did not appear in the NaY products. This may be attributed to the use of a large quantity of seeds solution (23 wt%) in the reaction mixture.

4 Conclusions

In the current work, well-crystallized high-silica Y zeolites were hydrothermally synthesized from reaction mixtures consisting of metakaolin, sodium silicate solution and seed solution. The final product was characterized by XRD, SEM and IR techniques, which showed the transformation from kaolin to high-silica NaY sample. Some important experimental parameters, including the aging time of the seed solution, the crystallization temperature, the crystallization time, and the molar composition of the starting mixture, were investigated in detail. The optimal synthesis variables for the preparation of well-crystallized high-silica NaY ($\text{Si}/\text{Al} > 2.5$, relative crystallinity > 90) are: $\text{SiO}_2/\text{Al}_2\text{O}_3=6.0-7.0$, $\text{Na}_2\text{O}/\text{SiO}_2=0.37-0.40$, $\text{H}_2\text{O}/\text{SiO}_2=16-20$, aging of the seed solution for 6.5-22 h and crystallization at 100 °C for 28 h.

Acknowledgements

This work was financially supported by Beijing Natural Science Foundation (Grant No.2093043) and the National Natural Science Foundation of China (Grant No.20606038).

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(Edited by Zhu Xiuqin)