Synthesis of high capacity cation exchangers from a low-grade Chinese natural zeolite

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ABSTRACT

The Chinese natural zeolite, in which clinoptilolite coexists with quartz was treated hydrothermally with NaOH solutions, either with or without fusion with NaOH powder as pretreatment. Zeolite Na–P, Na–Y and analcime were identified as the reacted products, depending on the reaction conditions such as NaOH concentration, reaction time and hydrothermal temperature. The products were identified by X-ray diffraction, and characterized by Fourier transform IR and ICP. With hydrothermal treatment after fusion of natural zeolite with NaOH, high purity of zeolite Na–Y and Na–P can be selectively formed, their cation exchange capacity (CEC) are 275 and 355 meq/100 g respectively, which are greatly higher than that of the natural zeolite (97 meq/100 g). Furthermore, the ammonium removal by the synthetic zeolite Na–P in aqueous solution was also studied. The equilibrium isotherms have been got and the influence of other cations present in water upon the ammonia uptake suggested an order of preference $Ca^{2+} > K^+ > Mg^{2+}$.

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1. Introduction

Nature zeolites mined are abundant in China, but they are commercially low in price due to the exploitation mostly as raw materials. Generally, natural zeolite deposits have high Si/Al ratio and contain quite a few impurities. These factors greatly reduce their CEC, and limit their application to some high-value areas, especially as ion exchangers in the treatment of waste waters.

Synthetic zeolites are predominantly prepared from commercial reagents [1–3]. Less frequently, natural and waste materials such as fly ash [4,5], kaolin [6,7], diatomite [8] and smectite [9] have been used for the formation of zeolites under alkali hydrothermal conditions. However, after the direct hydrothermal treatment, some impurities in the starting materials, such as quartz and feldspar could still be detected in the solid phase [10,11].

Fusion with sodium hydroxide prior to hydrothermal reaction is the method to dissolve the impurities. Several research groups have adopted this method to making zeolites from fly ash [12–14]; high purity of zeolite Na–P or Na–X has been formed. However, only a few studies have been done for the zeolitic materials [15] and some factors affecting the hydrothermal process, such as the

hydrothermal temperature, aging time and stirring have not been investigated.

This study focuses on the transformation of a low-grade Chinese natural zeolite to high capacity cation exchangers by hydrothermal reaction with or without fusion with sodium hydroxide. Teflon-lined stainless-steel autoclaves were used in the hydrothermal process in order to get the high pressure condition. Different kinds of products were formed, depending on the reaction conditions such as NaOH concentration, reaction time and hydrothermal temperature. The CEC of the products was compared.

In addition, we previously reported the ammonium exchange in aqueous solution using the natural clinoptilolite and the zeolite Na–Y synthesized from natural zeolite [16]. Here, we studied the equilibrium uptake of ammonium onto the other product, zeolite Na–P. In addition the effect of the individual presence of potassium, calcium and magnesium ion upon ammonium uptake onto Na–P was also investigated.

2. Materials and methods

2.1. Materials

Hard zeolite rock sample (light grayish white) was collected at Jinyun, Zhejiang, P.R. China. The sample was prepared as a starting material for the present experiments after crushing, air-drying and passing through a 74 μm sieve. It is mostly composed of clinoptilolite and quartz by X-ray diffraction as shown in Fig. 1. Based on
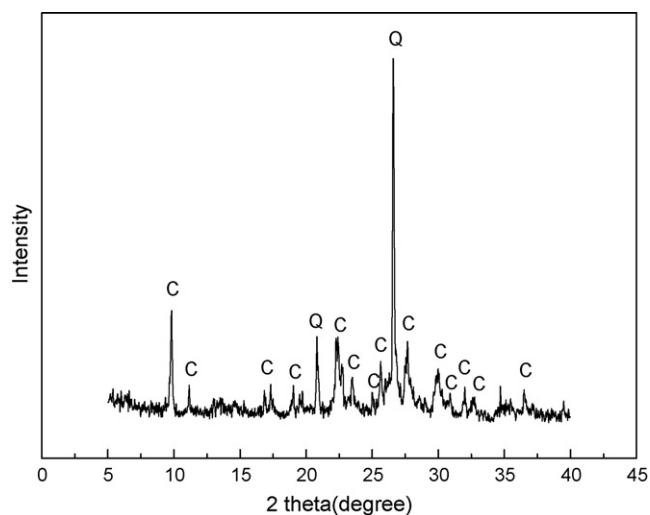
Fig. 1. XRD patterns of the Chinese natural zeolite. C: clinoptilolite, Q: quartz.

the intensity of the respective peaks, the content of quartz is high. Table 1 shows the chemical composition of the mineral [17].

2.2. Synthesis and products

In the method without fusion, 7.5 g of the natural zeolite powder was heated with 75 ml 2 or 4 mol l^{-1} NaOH solutions at 100 or 150 °C for 8–200 h. The products were repeatedly washed with deionized water, and dried at 150 °C.

In the method with fusion, 7.5 g of the natural zeolite powder was placed in a Ni crucible and fused with 3–12 g of NaOH powder at 550 °C for 2 h. The melt was ground and 75 ml water was added. The mixture was aged in a Teflon beaker for 0–36 h and then heated at 100 or 150 °C for 4–24 h. The product was repeatedly washed with deionized water, dried at 150 °C.

In the hydrothermal process of 100 °C, a 250 ml flask with reflux were used with or without magnetic stirring. While in the hydrothermal process of 150 °C, Teflon-lined stainless-steel autoclaves without stirring were used in order to get the high pressure condition.

2.3. Characterization

Identification of mineral species in the natural zeolite and the products was carried out by X-ray diffraction (XRD) of the random-oriented powder samples using Siemens X-ray diffractometer D5005 (Cu Kα radiation, λ = 0.15418 nm). The peak height was estimated at given diffraction faces: zeolite Na–Y (1 1 1) and zeolite Na–P (0 1 1).

Table 1
Chemical composition of the natural zeolite (wt%).

SiO$_2$	65.52
TiO$_2$	0.21
Al$_2$O$_3$	9.89
Fe$_2$O$_3$	1.04
MnO	0.06
MgO	0.61
CaO	3.17
Na$_2$O	2.31
K$_2$O	0.88
H$_2$O	7.25
LOI	10.02

An IRIS Intrepid IIXSP Inductively Coupled Plasma Atomic Emission Spectroscopy determined the content of Si and Al in the samples

IR spectrum was recorded on Nicolet Impact 410 FTIR Spectrophotometer using a KBr pellet. CEC of the samples was determined by extracting NH$_4^+$ with 1 mol l^{-1} KCl (pH 7) from NH$_4^+$-saturated sample prepared by equilibrating with 1 mol l^{-1} ammonium acetate (pH 7) at room temperature. The exact concentrations of ammonium ions in the solutions were determined by Nesslerization [18]. CEC was expressed as meq/100 g.

2.4. Equilibrium batch experiments

All sorption studies were carried out in beakers of 250 ml by subjecting a given dose of the synthetic zeolite Na–P to a period of stirring with ammonium solution on a magnetic stirrer (800 turns/min). Ammoniacal nitrogen is present in two forms when in water: ammonia (NH$_3$) or ammonium (NH$_4^+$), according to the following equation:

$$NH_3 + H_2O \Leftrightarrow NH_4^+ + OH^- \tag{1}$$

At higher pH, the NH$_4^+$ are transformed to aqueous ammonia; however, when the pH is lower, NH$_4^+$ have to compete with hydrogen ions among the exchange sites. So during all experimental work the pH was initially adjusted at a value of 6–7, the ammonia in this range should be expected to be nearly 100% in its ionic form. After adsorption, the Na–P was separated by centrifugal machine (2000 turns/min).

The exact concentrations of ammonium ions in the solutions were determined by Nesslerization. The solid-phase concentrations determined by mass balance, according to the following equation:

$$Q_e = \frac{V}{M}(C_0 - C_e) \tag{2}$$

where C_0 and C_e are the initial and equilibrium concentration of ammonium in the liquid phase (mg/l), respectively, Q_e is the solid-phase concentration of ammonium (mg/g), V is the volume of solution (l), and M is the mass of dry zeolite (g).

2.4.1. Equilibrium isotherms
0.5 g samples of Na–P were continuously stirred with 100 ml of ammonium chloride solution, having concentrations in the range 50–250 mg NH$_4^+$/l. The ammonia levels were measured every 1 h over a period of 8 h. Preliminary experiments showed that up to 5 h contact were required for equilibrium to be reached.

2.4.2. Influence of individual presence of K$^+$, Ca^{2+} and Mg^{2+} ions
In order to establish the extent to which the presence of potassium, calcium and magnesium ions influenced ammonium ion uptake, further equilibration experiments were conducted. These were confined to determination of the effect of each individual ion alone upon ammonium ion uptake. The starting solutions were dosed with the appropriate metal cation at a equivalent concentration of 5 meq/l and equilibration in the presence of ammonium ion 50–250 mg/l.

3. Results and discussion

3.1. Synthesis of zeolites from the low-grade natural zeolite by hydrothermal alkaline treatment

3.1.1. Hydrothermal process without stirring
The treatment conditions of the natural zeolite and the corresponding products were summarized in Table 2. We can find that three parameters influence the zeolitization. They are the concen-

Table 2
Summary of the conditions employed in the treatments of the natural zeolite with sodium hydroxide solutions and the corresponding products.

[NaOH(aq)] (mol dm^{-3})	Temperature (°C)	Reaction Time (h)	Product	CEC (meq/100 g)
2	100	8	Clinoptilolite + quartz	124
		16	Clinoptilolite + quartz	155
		24	Na–P + quartz	175
		32	Na–P + quartz	177
		40	Na–P + analcime + quartz	160
		80	Na–P + analcime + quartz	140
		200	Na–P + analcime + quartz	91
	150	8	Analcime + quartz	16
		16	Analcime	13
		24	Analcime	8
4	100	8	Clinoptilolite + quartz	121
		16	Na–P + quartz	161
		24	Na–P + analcime + quartz	140
	150	8	Analcime	21
		16	Analcime	25
		24	Analcime	20

tration of sodium hydroxide solution, reaction temperature and time.

It is apparent that at low NaOH solution concentrations (2 mol l^{-1}), zeolite Na–P was formed at 100 °C. In the first 32 h, clinoptilolite was gradually dissolved and transformed to Na–P, and the CEC of the products increased. When the hydrothermal time was extended, analcime appeared which reduced the exchange capacity. The alteration of CEC was consistent with the change in the peak heights of Na–P (Fig. 2). However, at 150 °C, analcime was the only new phase in the products. In addition, if the heating time was more than 16 h, quartz can completely dissolved and high purity of analcime can be synthesized.

The products at 4 mol l^{-1} NaOH solutions were similar to 2 mol l^{-1}, while the reaction time was obviously shortened. Furthermore, from the CEC of the products, we can conclude that the degree of crystallinity of Na–P was slightly decreased at 4 mol l^{-1} NaOH.

3.1.2. Hydrothermal process with stirring

A stirrer was also used in our experiments for comparison purpose. With stirring, Na–P and analcime were also selectively formed (Table 3). However, compared with the data in Table 2, CEC of the products were obviously higher.

With stirring, ions including Si^{4+} and Al^{3+} in the solution can be supplied ceaselessly to maintain growth of crystal and reaction. The

roles of using a stirrer are to keep a steady state vortex, decrease the solution viscosity, and to promise a good mixing of NaOH solution with the grains of natural zeolite to well dissolve the various components necessary for zeolite crystal growth [19].

3.2. Hydrothermal treatment after fusion of natural zeolite with NaOH

Alkali fusion is a conventional method for chemical analysis to decompose materials containing silicon and/or aluminum. The sodium hydroxide present in the reaction mixture acts as an activator during fusion to form soluble silicate and aluminate salts, which further takes part in zeolite formation during hydrothermal process.

3.2.1. Alkali requirement for fusion

The natural zeolite was fused with NaOH as the NaOH/natural zeolite weight ratio was varied from 0.4 to 1.6. We found that the quartz was not completely dissolved after fusion, if the NaOH/natural zeolite ratio is less than 1.2. The major product of fusion was a new Na aluminosilicate at ratio of 1.2–1.6.

If the Na aluminosilicate was stirred in water immediately after fusion, it turned into X-ray amorphous aluminosilicate gel. After the hydrothermal process at 100 °C for 8 h, Na–Y was formed from the gel. It can be seen from Fig. 3 that XRD peak height and CEC of Na–Y attained a maximum at NaOH/natural zeolite ratio = 1.2. So we regard 1.2 as the optimal ratio for fusion.

3.2.2. Effect of aging time

The influence of aging at room temperature on the characteristics of the synthesized zeolite was investigated in the present work. The aging is related to the development of crystal nuclei. It is observed from previous studies that the aging can considerably
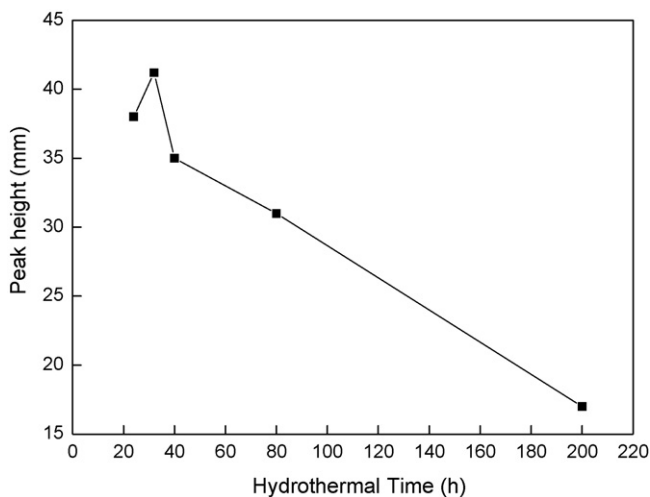

Fig. 2. Change in XRD peak heights of zeolite Na–P against hydrothermal time (conditions: concentration of NaOH, 2 mol dm^{-3}; hydrothermal temperature, 100 °C).

Table 3
Effect of the hydrothermal time on the characteristics of the products, with stirring (conditions: concentration of NaOH, 2 mol dm^{-3}; hydrothermal temperature, 100 °C).

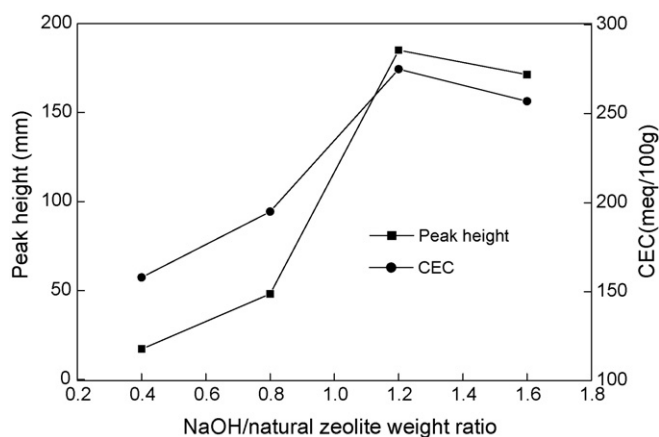| Reaction Time (h)	Product	CEC (meq/100 g)
8	Na–P + quartz	190
16	Na–P + quartz	215
24	Na–P + quartz	221
32	Na–P + quartz	222
40	Na–P + quartz	226
48	Na–P + quartz	231
72	Na–P + analcime + quartz	215

Fig. 3. Effect of NaOH/natural zeolite ratio on XRD peak height of Na–Y and CEC of the products (conditions: hydrothermal temperature, 100 °C; hydrothermal time, 8 h; without aging).
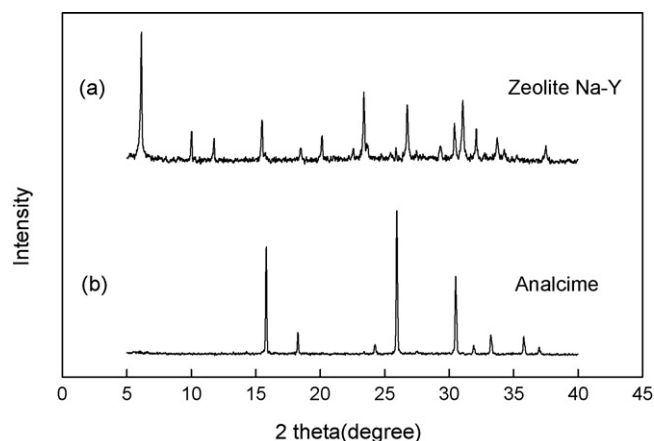

Fig. 4. XRD patterns of the products synthesized by hydrothermal process at (a) 100 °C and (b) 150 °C (conditions: NaOH/natural zeolite ratio, 1.2; aging time, 6 h; hydrothermal time, 8 h).

reduce the reaction time for crystallization at elevated temperatures [14].

The effects of aging time on characteristics of the zeolites were shown in Table 4. It is clear that aging time affected not only the crystallinity but also the species of the products. The crystallinity of Na–Y increased first and then decreased after attaining a maximum at the aging time of 12 h. High purity of Na–P was synthesized at 18 h with the highest CEC.

3.2.3. Effect of hydrothermal temperature

Previous studies reported that zeolites could be synthesized at any temperature in the range 333–573 K. The recommended crystallization temperature, which gives a reasonable rate and well developed crystals, is 373 K [20]. For the above-mentioned reasons, we chose 373 and 423 K as the heating temperature. In the process of 423 K, Teflon-lined stainless-steel autoclaves were used in order to get the high pressure condition. High purity of Na–Y and analcime were respectively formed at the two temperatures, as shown in Fig. 4. The observation is in good conformity with the Breck's description that the faujasite nucleate and crystallize more readily at lower temperature than those having more complicated structure [20].

3.2.4. Effect of hydrothermal treatment time

When the heating temperature was 100 °C, the effect of hydrothermal time on the characteristics of the synthesized zeolite was similar to that of the aging time. Na–Y and Na–P were formed in the products alternately (Table 5). However, at 150 °C, the crystallization of analcime was completed within 8 h of treatment, no further transformations were observed.

3.2.5. Effect of magnetic stirring in hydrothermal process

The product of fusion of the natural zeolite with NaOH transformed into zeolite Y when hydrothermal treated at 100 °C after

Table 4
Effect of aging time on characteristics of the products (conditions: NaOH/natural zeolite ratio, 1.2; hydrothermal temperature, 100 °C; hydrothermal time, 8 h).

Aging time (h)	Species of the products	Peak height (mm)	CEC (meq/100 g)
0	Na–Y	162	253
6	Na–Y	170	257
12	Na–Y	185	275
18	Na–P	37	353
24	Na–Y	183	274
30	Na–Y, Na–P	Na–Y, 55; Na–P, 22	289
36	Na–Y, Na–P	Na–Y, 49; Na–P, 31	317

Table 5
Effect of hydrothermal time on characteristics of the zeolites (conditions: NaOH/natural zeolite ratio, 1.2; hydrothermal temperature, 100 °C; without aging).

Hydrothermal time (h)	Species of the products	Peak height (mm)	CEC (meq/100g)
4	Na–Y	39	183
8	Na–Y	170	257
12	Na–P	34	352
16	Na–Y, Na–P	Na–Y, 47; Na–P, 25	327
20	Na–P	46	355
24	Na–Y, Na–P	Na–Y, 91; Na–P, 32	272

aging the gel at room temperature for 6 h without stirring. Without aging and when stirring was applied during the treatment, zeolite P formed instead (Fig. 5). The crystallization of Na–P was completed within 12 h of treatment, and no further transformations were observed. These results were similar with the findings of Shigemoto, who synthesized Na–X from fly ash [12].

In summary, the optimal conditions to synthesize the high capacity cation exchangers are as follow: 7.5 g of the natural zeolite were fused with 9 g NaOH at 550 °C for 2 h. The melt was mixed with 75 ml water. If the mixture was aged for 12 h, and heated at 100 °C for 8 h without stirring, high purity of Na–Y were formed.
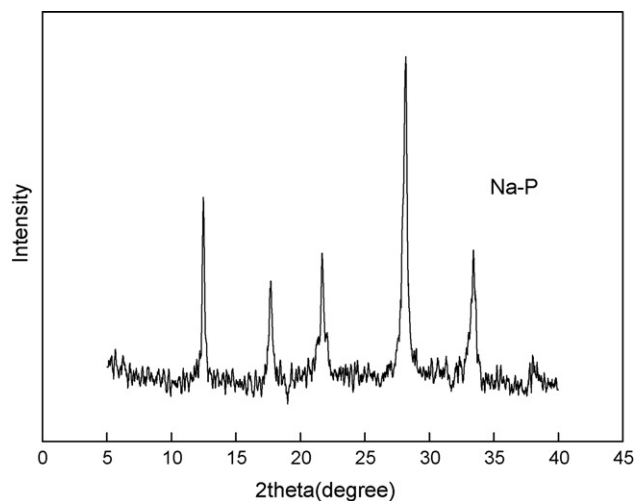

Fig. 5. XRD patterns of the product prepared from hydrothermal process with stirring (conditions: NaOH/natural zeolite ratio, 1.2; aging time, 0 h; hydrothermal temperature, 100 °C; hydrothermal time, 12 h).
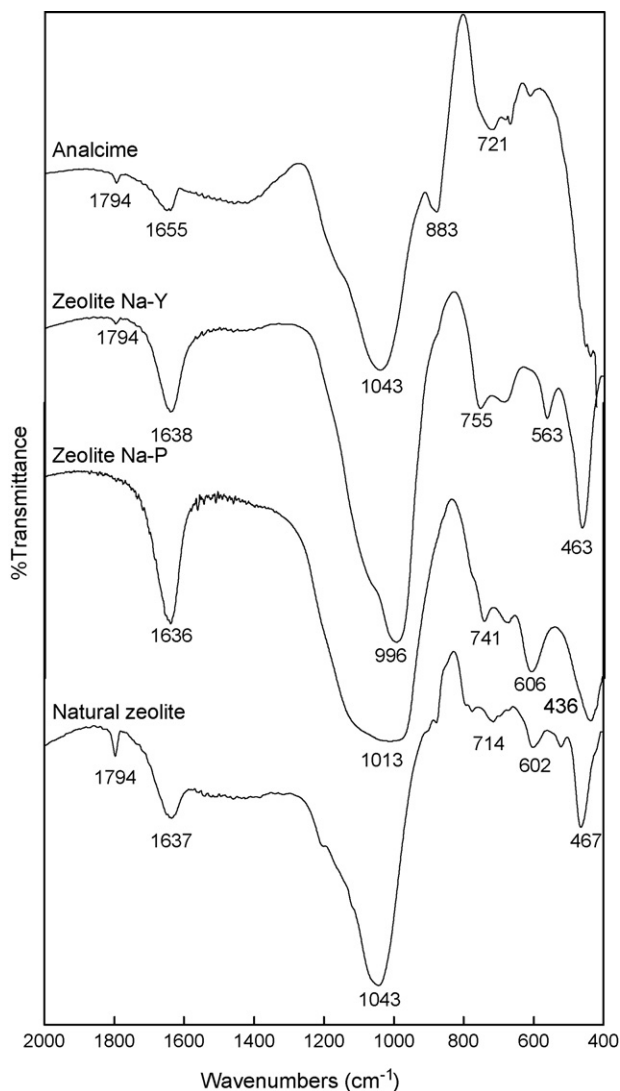
Fig. 6. IR spectra of the natural and synthesized zeolites.

And if the mixture was heated at 100 °C for 12 h with stirring, high purity of Na–P were formed.

3.3. IR spectrum of the zeolites

The presence of aluminosilicate framework in the zeolited solids was confirmed using IR spectroscopic technique. Every zeolite shows similar IR spectrum in Fig. 6. The vibrational bands at 710–760 cm^{-1} corresponding to the vibration of Al-O fragment and at about 1000 cm^{-1}, characteristic bands for SiO_4 and AlO_4. The bands observed at about 1640 cm^{-1} correspond to the deformation mode of vibration of HOH [21].

3.4. CEC of the zeolites

The CEC and Si/Al molar ratio of the synthesized zeolites are shown in Table 6. It's well known that CEC is determined by the framework and Si/Al molar ratio of the materials. With high content of quartz, CEC of the natural zeolite is low. In the hydrothermal process without fusion, clinoptilolite was dissolved completely to be altered to zeolite Na–P, which has low Si/Al molar ratio and high CEC. However, the impurity quartz hardly changed, that restricted the increase in the CEC of the products. Fusion with NaOH powder prior to hydrothermal reaction, we got high purity of Na–Y and Na–P

Table 6
CEC and Si/Al molar ratio of the natural and synthesized zeolites.

Zeolite	CEC (meq/100g)	Si/Al molar ratio
Natural zeolite	97	5.4
Na–P (mixed with quartz)	231	2.7
Na–P	355	1.8
Na–Y	275	2.3
Analcime	36	2.2

without quartz. With comparatively low Si/Al molar ratio, the CEC was greatly increased. The aperture in the framework of analcime is too small (pore diameter: 2.6 Å) to let the cation in. So although the high purity of analcime has the lower Si/Al molar ratio, the CEC of it is the quite low.

3.5. Ammonium exchange in aqueous solution using the synthetic zeolite Na–P

3.5.1. Equilibrium isotherms

The Langmuir model assumes only one solute molecule per site, and also assumes a fixed number of sites. The Langmuir isotherm relates Q_e (mg of ammonia absorbed per gram of zeolite) and C_e (the equilibrium ammonium concentration in solution) as shown in Eq. (3)

$$Q_e = \frac{KbC_e}{1 + KC_e} \qquad (3)$$

Q_e was calculated from the volume of ammonia solution, the mass of the material exposed to the solution and the equilibrium ammonium concentration in the solution (C_e).

The Freundlich isotherm relates the uptake of solute onto the exchanger to the solution concentration, as shown in Eq. (4)

$$Q_e = kC_e^{1/n} \qquad (4)$$

Fig. 7 shows the equilibrium isotherm data for ammonium uptake onto the synthetic zeolite Na–P, fitted to the Langmuir and Freundlich uptake models. Values for the coefficients are given in Table 7. It seems that the Freundlich model provides a more consistent fit to the data compared with the Langmuir.

3.5.2. The effect of the individual presence of other metals

The experimental uptake equilibrium data for Na–P are shown in Fig. 8. The relationships between exchanger-phase concentration and solution-phase concentration are shown for the case of ammo-
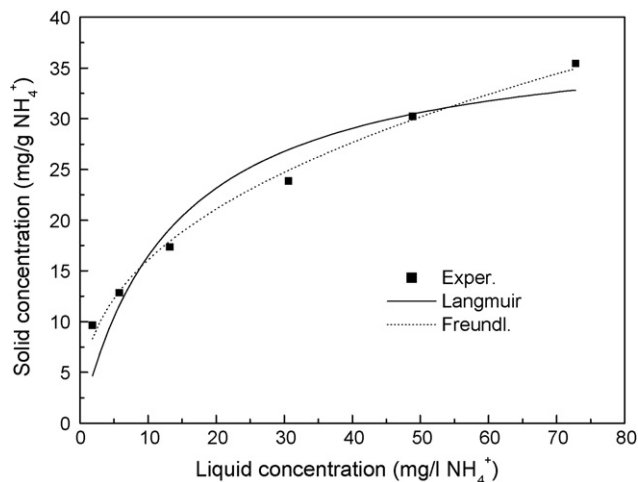

Fig. 7. Equilibrium isotherm data for ammonium uptake onto the zeolite Na–P fitted to the Langmuir and the Freundlich uptake models.

Table 7
Values for the Langmuir and Freundlich coefficients for the zeolite Na–P.

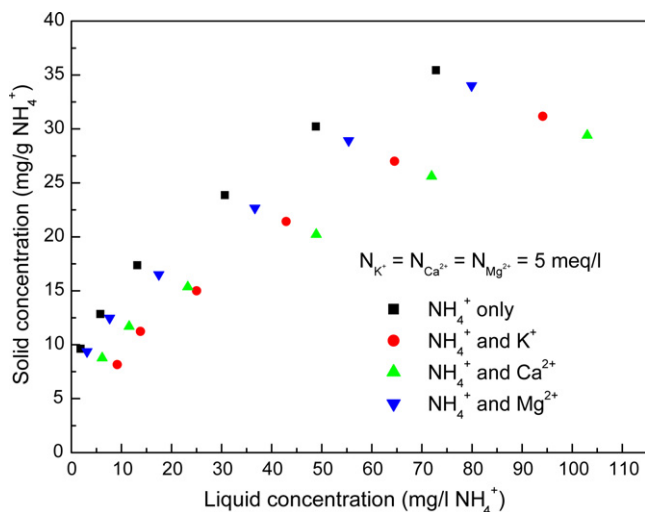| Langmuir parameter	
b (mg/g)	39.057
K (l/mg)	0.073
r^2	0.910
Freundlich parameter	
k	6.536
$1/n$	0.391
r^2	0.993

Fig. 8. Ammonium ion uptake onto the zeolite Na–P, in the presence of potassium, calcium and magnesium ions. (For interpretation of the references to color in this artwork, the reader is referred to the web version of the article.)

nium ion only, and for ammonium ion in the individual presence of potassium, calcium and magnesium ions.

From the results we can notice that in each case there is a significant reduction in the equilibrium uptake of ammonium ion in the presence of the other ion. The effect of the metal ions suggests an order of preference $Ca^{2+} > K^+ > Mg^{2+}$. This order was determined by electrostatic free energy and cation-hydration free energy. Compared with the natural clinoptilolite and Na–Y, Na–P has low Si/Al ratio, which resulted in high anionic field that gave rise to good selectivity toward cations of higher charge. However, Mg^{2+} is a small and more hydrated ion, so it tended to remain in solution [22].

4. Conclusions

The sodium zeolites were successfully synthesized from Chinese natural zeolite by hydrothermal reaction with or without fusion with sodium hydroxide. Zeolite Na–P or analcime was selectively formed by directly hydrothermal treatment. The products depend on NaOH concentration of solution, reaction temperature and time. By fusion with NaOH powder, high purity of zeolite Na–Y, Na–P and analcime can also be selectively synthesized.

CEC of the materials was restricted by the existence of quartz. So it is crucial to transform quartz to an active phase for zeolitization. Without fusion, quartz can only be dissolved at high temperature

and pressure. While at those conditions only the low capacity cation exchanger, analcime could be synthesized. Fusion by NaOH powder with NaOH/zeolite = 1.2 (weight ratio) at 550 °C for 2 h, quartz can be completely changed into a Na aluminosilicate. And after hydrothermal process at 100 °C, the high cation exchanger, Na–Y, Na–P could be formed.

The ammonium uptake behavior of zeolite Na–P was also studied. Compared with the Langmuir model, the Freundlich model provides a more consistent fit to the equilibrium isotherm data. The influence of other cations (K^+, Ca^{2+} and Mg^{2+}) present in water upon the ammonia uptake was remarkable. The effects suggest the orders of preference: $K^+ > Ca^{2+} > Mg^{2+}$.

References

[1] J. Zhu, S. Qiu, J. Yu, Y. Sakamoto, F. Xiao, R. Xu, O. Terasaki, Synthesis and characterization of high-quality zeolite LTA and FAU single nanocrystals, Chem. Mater. 10 (1998) 1483–1486.
[2] Y. Sun, T. Song, S. Qiu, W. Pang, Synthesis of mordenite single crystals using two silica sources, Zeolites 15 (1995) 745–753.
[3] E.N. Coker, J.C. Jansen, F. Direnzo, F. Fajula, J.A. Martens, P.A. Jacobs, A. Sacco Jr., Zeolite ZSM-5 synthesized in space: catalysts with reduced external surface activity, Micropor. Mesopor. Mater. 46 (2001) 223–236.
[4] H. Tanaka, S. Matsumura, S. Furusawa, R. Hino, Conversion of coal fly ash to Na-X zeolites, J. Mater. Sci. Lett. 22 (2003) 323–325.
[5] K.S. Hui, C.Y.H. Chao, Pure, single phase, high crystalline, chamfered-edge zeolite 4A synthesized from coal fly ash for use as a builder in detergents, J. Hazard. Mater. B137 (2006) 401–409.
[6] D. Akolekar, A. Chaffee, R.F. Howe, The transformation of kaolin to low-silica X zeolite, Zeolites 19 (1997) 359–365.
[7] D. Lin, X. Xu, F. Zuo, Y. Long, Crystallization of JBW, CAN, SOD and ABW type zeolite from transformation of meta-kaolin, Micropor. Mesopor. Mater. 70 (2004) 63–70.
[8] V. Sanhueza, U. Kelm, R. Cid, L. López-Escobar, Synthesis of ZSM-5 from diatomite: a case of zeolite synthesis from a natural material, J. Chem. Technol. Biotechnol. 79 (2004) 686–690.
[9] K. Abdmeziem, B. Siffert, Synthesis of large crystals of ZSM-5 zeolite from smectite clay mineral, Appl. Clay Sci. 8 (1994) 437–447.
[10] S.J. Kang, K. Egashira, Modification of different grades of Korean natural zeolites for increasing cation exchange capacity, Appl. Clay Sci. 12 (1997) 131–144.
[11] Y. Watanabe, H. Yamada, J. Tanaka, Y. Moriyoshi, Hydrothermal modification of natural zeolites to improve uptake of ammonium ions, J. Chem. Technol. Biotechnol. 80 (2005) 376–380.
[12] N. Shigemoto, H. Hayashi, K. Miyaura, Selective formation of Na-X zeolite from coal fly ash by fusion with sodium hydroxide prior to hydrothermal reaction, J. Mater. Sci. 28 (1993) 4781–4786.
[13] V. Berkgaut, A. Singer, High capacity cation exchanger by hydrothermal zeolitization of coal fly ash, Appl. Clay Sci. 10 (1996) 369–378.
[14] K. Ojha, N.C. Pradhan, A.N. Samanta, Zeolite from fly ash: synthesis and characterization, Bull. Mater. Sci. 27 (2004) 555–564.
[15] S.J. Kang, K. Egashira, A. Yoshida, Transformation of a low-grade Korean natural zeolite to high cation exchanger by hydrothermal reaction with or without fusion with sodium hydroxide, Appl. Clay Sci. 13 (1998) 117–135.
[16] Y.F. Wang, F. Lin, W.Q. Pang, Ammonium exchange in aqueous solution using Chinese natural clinoptilolite and modified zeolite, J. Hazard. Mater. 142 (2007) 160–164.
[17] Q. Du, S.J. Liu, Z.H. Cao, Y.Q. Wang, Ammonia removal from aqueous solution using natural Chinese clinoptilolite, Sep. Purif. Technol. 44 (2005) 229–234.
[18] WPCF, APHA, AWWA, Standard methods for the examination of water and wastewater, 17th ed., Method 4500C, 1989, pp. 4-–117.
[19] Y. Wang, Y. Guo, Z. Yang, H. Cai, Q. Xavier, Synthesis of zeolites using fly ash and their application in removing heavy metals from waters, Sci. China (Ser. D) 46 (2003) 967–976.
[20] D.W. Breck, Zeolite Molecular Sieves, John Wiley and Sons, New York, 1974.
[21] A. Rujiwatra, A selective preparation of phillipsite and sodalite from perlite, Mater. Lett. 58 (2004) 2012–2015.
[22] S. Tangkawanit, K. Rangsriwatananon, A. Dyer, Ion exchange of Cu^{2+}, Ni^{2+}, Pb^{2+} and Zn^{2+} in analcime (ANA) synthesized from Thai perlite, Micropor. Mesopor. Mater. 79 (2005) 171–175.