



Ion exchange of ammonium in natural and synthesized zeolites

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ARTICLE INFO

Article history:

Received 30 January 2007

Received in revised form 14 February 2008

Accepted 4 March 2008

Available online 18 March 2008

Keywords:

Ion exchange

Zeolite

Ammonium

Selectivity

Thermodynamic parameters

ABSTRACT

In this study, zeolite Na–P and Na–Y was prepared by hydrothermal treatment of the Chinese natural clinoptilolite with NaOH. The ion exchange of NH_4^+ into the three zeolites in the temperature range of 288–333 K was also investigated, and the thermodynamic parameters were calculated. The selectivity sequence for NH_4^+ entering the sodium form of the three materials was Na–clinoptilolite > Na–Y > Na–P, as indicated by values of ΔG° . The results demonstrated that the Si/Al molar ratio of zeolites determined the selectivity for NH_4^+ .

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1. Introduction

Zeolites are hydrated aluminosilicates that possess a three-dimensional framework structure. This structure is formed by AlO_4 and SiO_4 tetrahedra that are connected by sharing an oxygen atom. When an AlO_4 tetrahedron is substituted for a SiO_4 tetrahedron, a negative charge appears which is neutralized by the exchangeable cations (Na^+ , K^+ , Ca^{2+} , Mg^{2+}). The discovery of zeolites has eliminated, or at least reduced, many long-standing pollution problems [1–3].

Among Chinese natural zeolite deposits, clinoptilolite occurs most frequently. A range of studies have shown that clinoptilolite exhibits a high selectivity for NH_4^+ ion [3,4]. However, natural zeolites generally have high Si/Al ratio and contain quite a few impurities, and these factors greatly reduce their cation exchange capacity (CEC). Fusion with sodium hydroxide prior to hydrothermal reaction is the method to transform low-grade natural materials to high capacity cation exchangers. Several research groups have succeeded in synthesizing low Si/Al ratio zeolites, such as Na–P and zeolite Na–X from fly ash [5,6]. However, this method has not been used for transformation of natural zeolites [7].

Studies on the ion exchange properties of zeolites are critical to their uses as sorbents and catalysts, and much investigation has been carried out [8–11]. In the literature, it has been reported that the negative values of ΔG° indicated that the ion exchange reac-

tions of natural zeolites for NH_4^+ were spontaneous processes, and that the natural zeolites had good selectivity for NH_4^+ [12–14]. Furthermore, Karadag et al. reported that the exchange of NH_4^+ by clinoptilolite was an exothermic reaction with negative entropy change [14]. Despite these studies, the ion exchange behavior of ammonium in synthetic zeolites has received relatively little attention [15].

Recently, we succeeded in synthesizing zeolite Na–P and Na–Y by fusing the Chinese natural clinoptilolite with NaOH prior to hydrothermal reaction. The present work provides basic information on ion exchange of NH_4^+ in the synthetic and natural zeolites.

2. Materials and methods

2.1. Synthesis

Hard zeolite rock sample was collected at Jinyun, Zhejiang, the People's Republic of China. The sample was prepared as a starting material for the present study after crushing, air-drying and passing through a 74 μm sieve. Table 1 shows the chemical composition of the mineral [16].

Na–clinoptilolite was prepared by treating 15 g of natural zeolite with 100 ml 2 mol l⁻¹ NaCl at 100 °C for 2 h in a flask with reflux and stirring. The product was repeatedly washed with deionized water and dried at 150 °C.

Zeolite Na–Y was prepared by placing 7.5 g of the natural zeolite powder in a Ni crucible and fused with 9 g NaOH powder at 550 °C for 2 h. The melt was ground and 75 ml water was added. The mixture was left in a Teflon beaker for 12 h, and then heated at 100 °C

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

SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	H ₂ O	LOI
65.52	0.21	9.89	1.04	0.06	0.61	3.17	2.31	0.88	7.25	10.02

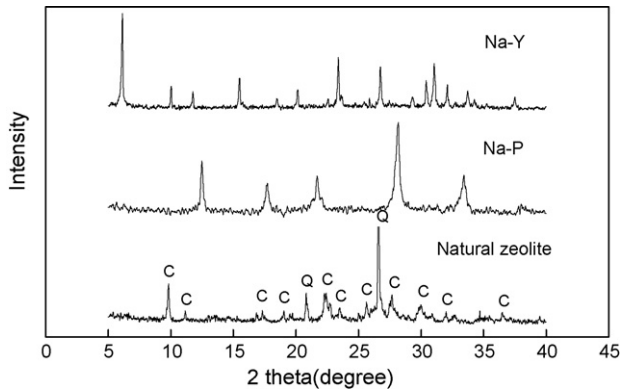


Fig. 1. XRD patterns of the natural and synthesized zeolites. C: clinoptilolite and Q: quartz.

for 8 h in a Teflon-lined stainless-steel autoclave without stirring. The products were filtrated, washed with acidic NaCl to remove the adsorbed alkali and dried at 150 °C.

For the preparation of Na-P, 7.5 g of the natural zeolite powder was placed in a Ni crucible and fused with 9 g NaOH powder at

550 °C for 2 h. The melt was ground and 75 ml water was added. The mixture was heated at 100 °C for 12 h in a flask with reflux and stirring. The products were filtrated, washed with acidic NaCl to remove the adsorbed alkali and dried at 150 °C.

2.2. Characterization

Identification of mineral species in the natural and synthesized zeolites was carried out by X-ray diffraction (XRD) of the random-oriented samples using Siemens X-ray diffractometer D5005 (Cu K α radiation, $\lambda = 0.15418$ nm). An IRIS Intrepid IIXSP Inductively Coupled Plasma Atomic Emission Spectroscopy was used to determined the content of Si and Al in the materials. SEM images were observed using a HITACHI model S-570 scanning electron microscope.

2.3. Construction of exchange isotherms

Initial kinetic experiments showed that all exchanges studied had reached equilibrium after 24 h. In subsequent experiments, 24 h was the time used for each exchange.

CEC of the zeolites was determined by extracting NH₄⁺ with 1 mol l⁻¹ KCl (pH 7) from NH₄⁺-saturated zeolites prepared by equilibrating with 1 mol l⁻¹ ammonium acetate (pH 7) at room temperature.

Ion exchange isotherms, at 288, 313, and 333 K, were constructed at constant ionic strength ($T_N = 0.01N$ for clinoptilolite; 0.025N for Na-P and Na-Y) using standard method [12]. The Na⁺ and NH₄⁺

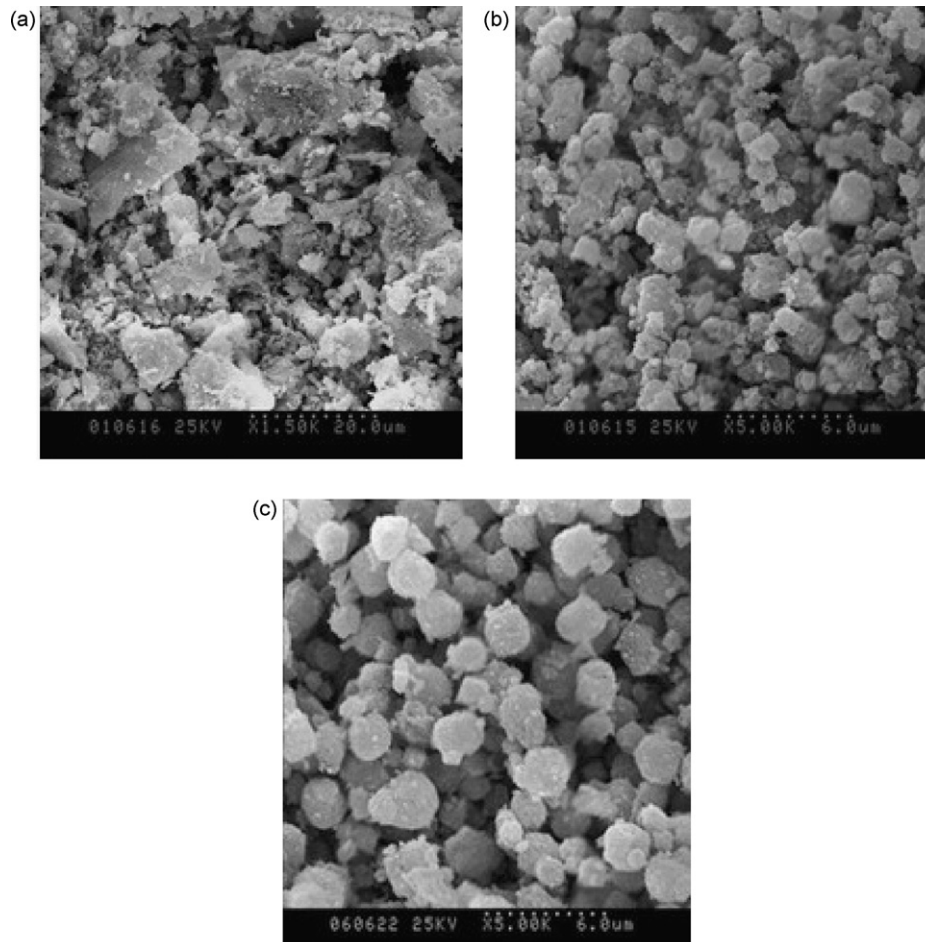
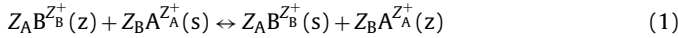


Fig. 2. Scanning electron micrographs of (a) natural clinoptilolite, (b) Na-Y and (c) Na-P.

in solution were analyzed by atomic emission spectrometry and Nesslerization [17], respectively.

2.4. Ion exchange [9]

The ion exchange process can be represented by



where Z_A , Z_B , respectively, are the charges of the cations A and B and the symbols 'z' and 's' refer to the zeolite and solution phases, respectively. The thermodynamic equilibrium constant (K_a) is evaluated from

$$\ln K_a = (Z_B - Z_A) + \int_0^1 \ln K_c dA_z \quad (2)$$

K_a can be obtained from the graphical integration of the plot of $\ln K_c$ against A_z , where K_c is the Kielland coefficient.

The free energy of exchange, ΔG° , then is determined by

$$\Delta G^\circ = \frac{-RT}{Z_A Z_B} \ln K_a \quad (3)$$

When exchanging of NH_4^+ in sodium form of zeolite, the equivalent fraction of NH_4^+ in the solution (A_s) and in the zeolite phase (A_z) can be defined by

$$A_s = \frac{C_e}{C_0} \quad (4)$$

$$A_z = \frac{V}{ME} (C_0 - C_e) \quad (5)$$

where C_0 and C_e are the initial and equilibrium concentrations of ammonium in the liquid phase (mg/l), respectively, E is the CEC of zeolite ($mg NH_4^+/g$), V is the volume of solution (l), and M is the mass of dry zeolite (g). And

$$\text{Kielland coefficient } K_c = \frac{A_z(1 - A_s)}{(1 - A_z)A_s} \quad (6)$$

Furthermore, Eqs. (2) and (3) can be expressed as

$$\ln K_a = \int_0^1 \ln K_c dA_z \quad (7)$$

$$\Delta G^\circ = -RT \ln K_a \quad (8)$$

3. Results and discussion

3.1. Materials characterization

Fig. 1 shows the XRD pattern of the three materials. In the natural zeolite, clinoptilolite was detected as coexisting with quartz. Based on the intensity of the respective peaks, the content of quartz was high. This may have contributed to the low CEC of the natural clinoptilolite ($21.68 mg NH_4^+/g$). After fusion with sodium hydroxide at $550^\circ C$ for 2 h, the natural zeolite, including the impurities was completely dissolved and changed into a dissoluble aluminosilicate. And then, with different hydrothermal process, high purity of Na-P or Na-Y was formed. Their CEC was determined to be 64.40 and $49.50 mg NH_4^+/g$, respectively. We found that frameworks of the hydrothermal products were

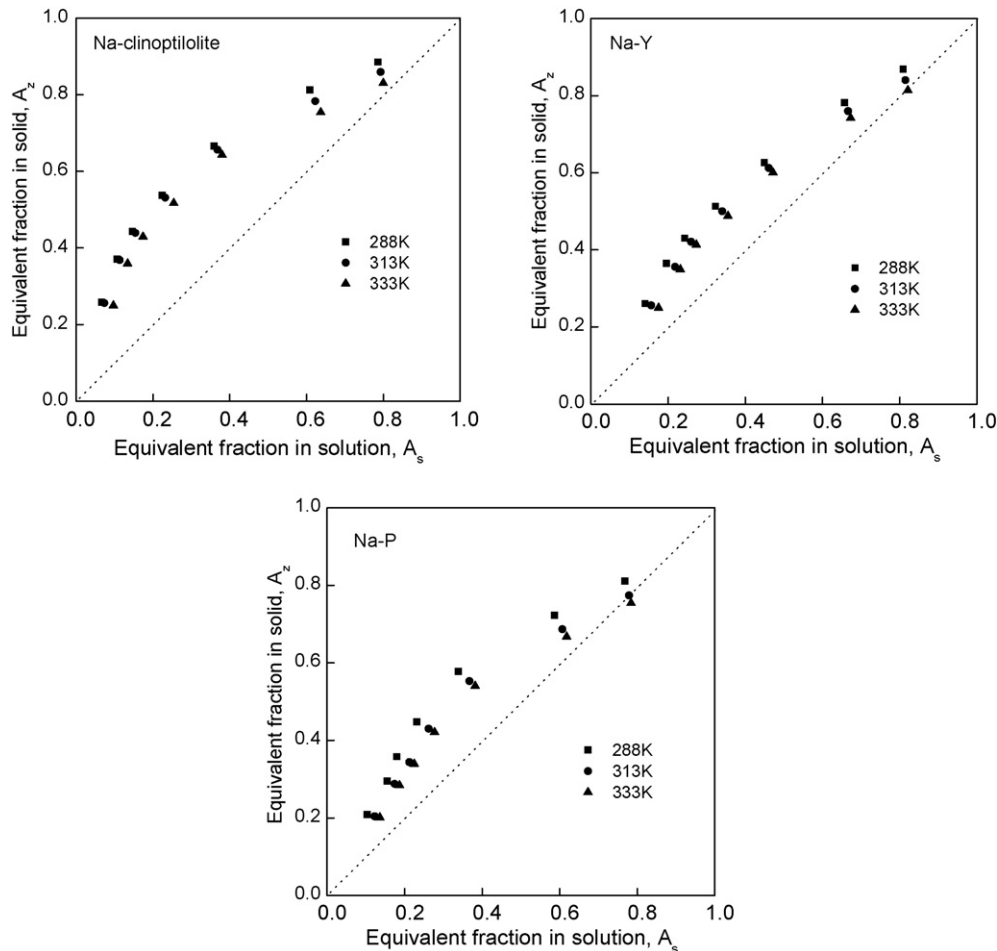


Fig. 3. Na^+/NH_4^+ cation exchange isotherms.

Table 2
Values of the Langmuir coefficients for the three zeolites

	Na-clinoptilolite	Na-Y	Na-P
288 K			
<i>b</i>	1.124	1.590	1.346
<i>K</i>	4.332	1.478	2.022
<i>r</i> ²	0.996	0.999	0.991
313 K			
<i>b</i>	1.094	1.673	1.431
<i>K</i>	4.229	1.247	1.548
<i>r</i> ²	0.997	0.998	0.990
333 K			
<i>b</i>	1.132	1.758	1.480
<i>K</i>	3.335	1.074	1.355
<i>r</i> ²	0.995	0.995	0.989

greatly affected by stir, which can entirely change the crystallization.

Compared with the report by Kang [7], where only high purity of Na-P (CEC: 73.8 mg NH₄⁺/g) could be formed, the CEC of our products are relatively low. A possible explanation for this is that the natural zeolite used in the present study has different chemical composition from that used by Kang.

The changes in crystal shape and size by the hydrothermal treatment are shown in Fig. 2. The SEM micrographs show that the natural clinoptilolite was irregular, while the high purity of Na-Y and Na-P were small aggregates, with diameter of 1.5–2 μm.

3.2. Ion exchange isotherms

The isotherms for Na⁺ → NH₄⁺ in the three zeolites are given in Fig. 3, which show the equivalent fraction of NH₄⁺ in the zeolite phase (*A_z*) against the equivalent NH₄⁺ fraction in the solution (*A_s*). The isotherms appeared to be sigmoid-type curves, which are often observed in the cation exchange isotherms of inorganic ion-exchange materials [18]. The isotherms have been fitted to the Langmuir model ($A_z = KbA_s/(1 + KA_s)$), and the values of coefficients are given in Table 2. Most of the experimental points in the figure lie above the diagonal; this indicates a good selectivity for NH₄⁺ entering the three materials.

3.3. Thermodynamic parameters

Fig. 4 shows the Kielland plots for the NH₄⁺ exchange. The curves have been fitted to polynomials and the values of ln*K_a* have been calculated from Eq. (7), as shown in Table 3. Thermodynamic function Δ*G*[°] was obtained from Eq. (8) (Table 3). The negative values of Δ*G*[°] confirmed the spontaneity of the exchange processes and indicated that the selectivity sequence for NH₄⁺ entering the three zeolites was Na-clinoptilolite > Na-Y > Na-P. The results demonstrated that the Si/Al molar ratio of zeolites determined the

Table 3
Thermodynamic parameters for Na⁺/NH₄⁺ ion exchange in the zeolites at various temperatures

Zeolite	<i>T</i> (K)	ln <i>K_a</i>	<i>K_a</i>	Δ <i>G</i> [°] (kJ mol ⁻¹)	Δ <i>H</i> [°] (kJ mol ⁻¹)	Δ <i>S</i> [°] (J mol ⁻¹ K ⁻¹)
Na-clinoptilolite	288	1.301	3.7	-3.1	-9.9	-23.4
	313	1.088	3.0	-2.8	-9.9	-22.5
	333	0.727	2.1	-2.0	-9.9	-23.6
Na-P	288	0.570	1.8	-1.4	-9.0	-26.4
	313	0.249	1.3	-0.6	-9.0	-26.6
	333	0.066	1.1	-0.2	-9.0	-26.4
Na-Y	288	0.672	2.0	-1.6	-7.9	-21.8
	313	0.447	1.6	-1.2	-7.9	-21.5
	333	0.220	1.2	-0.6	-7.9	-21.9

selectivity of NH₄⁺. Previous studies have found that zeolites with high Si/Al ratio resulted in low anionic field that gave rise to good selectivity toward cations of lower charge [8,12]. As a kind of monovalent ions, NH₄⁺ prefers the high silica zeolite, clinoptilolite (Si/Al molar ratio = 5.6). The Na-P and Na-Y are all synthetic zeolites with relatively low Si/Al molar ratio (Na-P: 1.8; Na-Y: 2.3), and it is clear that the selectivity sequence for NH₄⁺ is consistent with the digression of the Si/Al ratio of zeolites.

The plots of ln*K_a* vs. 1/*T* were found to be linear and these are shown in Fig. 5. The values of Δ*H*[°] were determined from the slopes of the lines. The negative values of Δ*H*[°] in Table 3 indicated that the

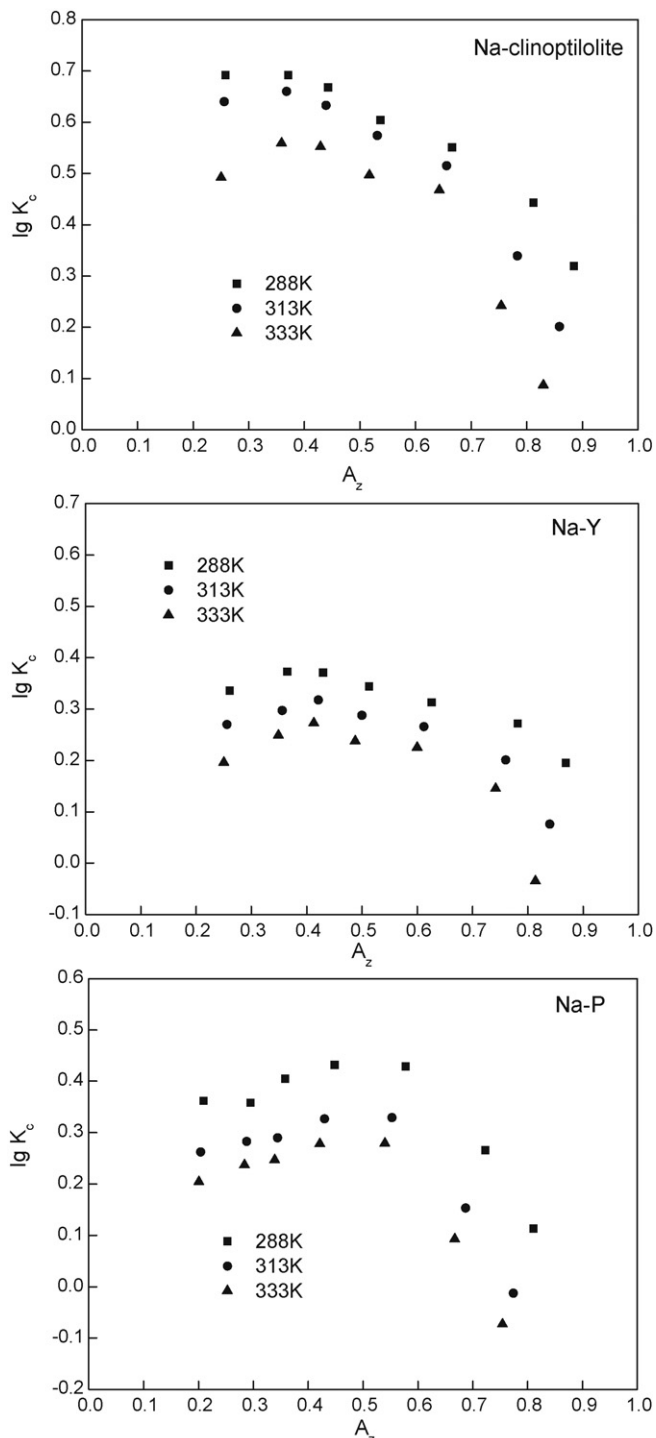


Fig. 4. Na⁺/NH₄⁺ Kielland plots.

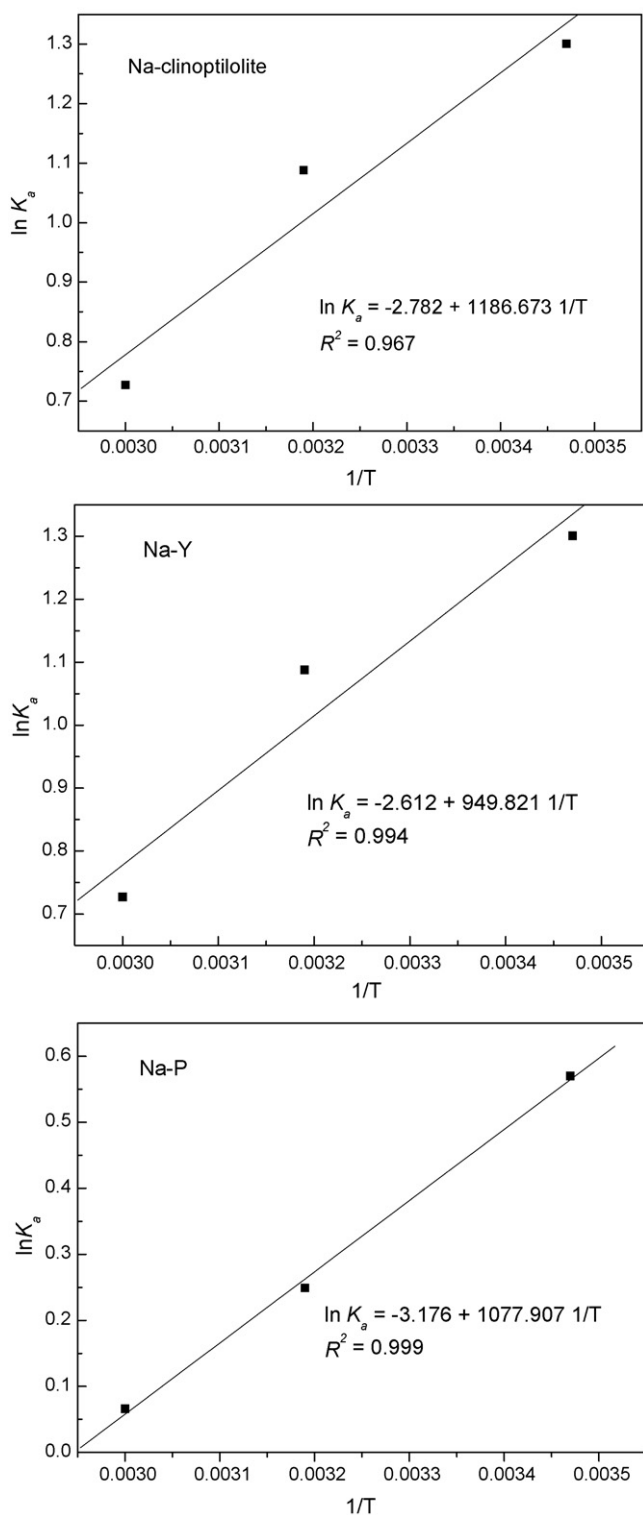


Fig. 5. $\ln K_a$ vs. $1/T$.

exchange reactions were all exothermic. This may have been caused by the increase in ammonium desorption from the adsorption sites with temperature.

The values of ΔS° as shown in Table 3 were calculated from the following equation $(9)\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T}$

The cation solvation may have contributed to the values of ΔS° shown in Table 3. It has been suggested that entropy changes as a

result of water–cation environment created during exchange when cations with differing hydration spheres move between the solution and solid phases [19]. Negative entropy changes tend to reflect a net release of water molecules to the aqueous phase when cations are fixed to exchange sites in the zeolite phase [9]. Here the relatively lightly hydrated sodium cation is being replaced by NH_4^+ which is more hydrated in nature, giving rise to an overall negative change in entropy was created.

4. Conclusion

By fusing the Chinese natural clinoptilolite with NaOH prior to hydrothermal reaction, high purity of zeolite Na–P or Na–Y could be synthesized. Although the two synthetic zeolites have much higher CEC than the natural clinoptilolite, the latter has the highest selectivity for NH_4^+ among the three materials, as indicated by the values of ΔG° . As a monovalent cation, NH_4^+ prefers the zeolite with a low anionic field. ΔH° and ΔS° were also calculated, and these indicated that the exchange of NH_4^+ was an exothermic reaction with negative entropy change. This study is of relevance in transformation of low-grade materials to high cation exchanger and ammonia waste water treatment.

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