Research Article

Improving the ammonium ion uptake onto natural zeolite by using an integrated modification process

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ABSTRACT

Detailed investigation on the development of physical and chemical properties of a natural calcium-rich zeolite modified by an integrated process, as well as the relation between the development and ammonium ion uptake (AIU), was conducted. This process consisted of pretreatment (grinding and sieving), sodium salt modification and calcination. Both pretreatment and salt modification largely increased BET surface area, total pore volume and average pore diameter of the raw zeolite. Individual calcination at temperature above 150 °C caused framework collapse, losses of partial clinoptilolite and production of X-ray amorphous material, resulting in pore blockage and the decreases in pore volume and BET surface area. However, the introduction of sodium ion enhanced the heat resistance of the raw material from 150 to 400 °C, and Na+ ion treatment followed by calcination could effectively improved pore and surface properties of zeolite, thus leading to the significant enhancement in ammonium ion exchange and adsorption capabilities.

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1. Introduction

Ammonium ion (NH_4^+), one of the important pollutants in municipal sewage and many industrial wastewaters, can cause increase of oxygen demand and eutrophication in rivers and lakes. NH_4^+ can be removed by biological and physicochemical methods: nitrification–denitrification, precipitation, oxidation, adsorption, stripping, etc. [1–5]. Due to more strain energy sources and more stringent discharge regulations, new materials and technologies with high-purification efficiency and cost efficiency are more attractive. Natural zeolites have played important roles in many environmental applications, mainly due to their unique properties such as ion exchange and adsorption capabilities, selectivity and compatibility with the natural environment [6–8]. Among zeolite mineral family, clinoptilolite is the most abundant one and can effectively treat NH_4^+ by its high-ion-exchange selectivity [9–12]. Large deposits of natural zeolites in many countries can provide local industries cost efficiency. Therefore, high efficiency and low cost will lead to an increasing use of zeolite for the purpose of ammonium removal from wastewater.

Ammonium ion uptake (AIU) on zeolite is mainly attributed to ion-exchange process, and adsorption also plays an important role. However, mobile cations (calcium, magnesium, etc.), water molecules and organics in the pore channels of natural zeolite,

make negative influence on its purification capability. In addition, there are impurities like quartz and feldspars in most natural zeolites to reduce the content of clinoptilolite, resulting in the decrease in AIU. Therefore, the structure and physicochemical properties of natural zeolite should be activated and/or modified to improve ion exchange and sorption properties and clinoptilolite purity, before it is used to remove NH_4^+ effectively.

Natural zeolites can be modified by sole or combined treatment such as heating and chemical attacks (alkali, acids and salts of alkaline metals). Different methods are used to prepare zeolites with specific properties for different applications. Calcination and salt treatment may be more suitable to zeolite modification for ammonium ion removal. Calcination at high temperature, depending on the solid sample and temperature used can enhance pore volume by removing water molecules and organics in the pore channels [13]. The sodium salt treatment could improve the ion-exchange efficiencies of zeolite for lead and cadmium by nearly 8% and 30%, respectively [6], and distribution coefficient of cesium on Na+-enriched clinoptilolite is about two times that on Ca^{2+}-enriched clinoptilolite [14]. Seawater has been used to synthesize zeolitic products with large cavities and channels: large cations such as Na+ and K+ act as templates around which the aluminosilicate polymerizes, producing large pores in the structure [15]. These investigations have showed that there are significant increases in pollutants uptake when natural zeolites are pretreated with aqueous solutions containing sodium cation by improving pore property and enhancing cation-exchange capacity. Based on the different density and rigidity between impurities and clinoptilolite,

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Table 1
Mineralogical characteristics of the raw natural zeolite.

Minerals in raw samples	Content (wt%)
Clinoptilolite	55
Feldspars	19
Quartz	18
Montmorillonite	8
Muscovite	1

grinding and sieving by machine can remove part of feldspars and quartz from raw zeolites. As useful pretreatment, grinding and sieving can offer zeolites with improved structure and composition for subsequent modification processes. Activation/modification normally causes some degradation of properties and evolution of structure, and furthermore, physicochemical properties of natural zeolites vary significantly from sample to sample. Therefore it is necessary to know the degradation degree for given zeolite before modification method is put to practical use.

Even though considerable work has been carried out on the modification of natural zeolites, little detailed information is available on the development of physicochemical properties of modified zeolites, as well as the relation between the development and AIU. In the present work, for the purpose of AIU enhancement, an integrated modification process including pretreatment (grinding and sieving), calcination and salt (sodium chloride) treatment, was proposed to modify natural zeolite. The focuses of this publication were (1) to investigate the influences of each treatment stage in the process on surface and pore structure properties, phase transformation and element change of the natural zeolite, (2) to evaluate the improvement of AIU onto modified zeolite by each stage and entire process, and (3) to propose the optimum modification process and condition for the subjected zeolite.

2. Materials and methods

2.1. Raw material

The raw zeolite in this study, with particle size in the range of 10–20 mm, was obtained from a large deposit in Henan Province of China. Clinoptilolite was the major component with 55% content. As accessory minerals, feldspars and quartz were in relatively large quantities with contents of 19% and 18%, respectively (Table 1). According to the chemical composition of the raw zeolite (Tables 2 and 3), the molar ratio of $(Mg + Ca)/(Na + K)$ was 1.37, and mol percentages of calcium and sodium to the four cations were 44.9 and 15.2, respectively, indicating that calcium ion was the main exchangeable cation and that the raw material could be classified as Ca-rich zeolite. The raw zeolite was prepared as a starting material for the present experiment after washing and air-drying.

Table 2
Average chemical composition of the raw zeolite (wt%).

SiO_2	65.72
Al_2O_3	13.50
Fe_2O_3	1.30
CaO	3.10
MgO	0.63
K_2O	3.14
Na_2O	1.16
MnO	0.050
TiO_2	0.212
P_2O_5	0.040
LoI[a]	11.12
Total	99.96
Si/Al	4.13

[a] LoI represents loss of ignition.

2.2. Reagent

All chemicals used in this study were analytical grade reagents of the highest quality available, including reagents and high-purity ion-free water. We prepared stock solution of 1000 mg NH_4^+-N/L using ammonium chloride (NH_4Cl).

2.3. Experiment setup

2.3.1. Pretreatment

The raw zeolite was firstly ground in a mill with three agate-heads (XPM-Φ120, China) and sieved to obtain samples with different sizes, and then AIUs of different samples were investigated to select appropriate size. Finally, enough zeolite with optimum size was prepared and stored in a vacuum desiccator for future modification. The pretreated zeolite with appropriate size was named Z-P.

2.3.2. Individual calcination

Z-P was calcined in a muffle furnace at different temperatures for 2 h, and then the optimal temperature was selected on the basis of AIU performance.

2.3.3. Individual salt modification

The modification consisted of the following three steps:

- *Step 1*: 10.000 g of Z-P was treated with 150 mL of 1.5 M NaCl solution for 24 h at given temperature in a stirrer with thermostat. After the mixture was allowed to settle and the supernatant was decanted, another 150 mL of 1.5 M NaCl solution was added into the mixture for another 24-h modification under the same condition.
- *Step 2*: The solid was repeatedly washed with deionized water and centrifugally filtered at 4000 rpm for 20 min.
- *Step 3*: The solid was dried firstly at 45 °C for 12 h and then 105 °C for 1 h in an oven, and the dried sample was ground in an agate mortar and sieved with 140-mesh sieve.

The produced material with 24-h modification was signed as once salt modified zeolite (Z-M(1)), and that with 48-h modification was twice salt modified zeolite (Z-M(2)). The effects of temperature and modification times on AIU were investigated, respectively.

2.3.4. Combined treatment with calcination and salt modification

Effects of two different procedures on AIU, calcination followed with salt modification and salt modification followed with calcination, were explored, respectively, and the resulting zeolites were named (Z-C-M) and (Z-M-C), respectively. Finally, the optimum modification condition and procedure were proposed.

2.3.5. Measurement of AIU and methods of isotherm and kinetic studies of ammonium ion exchange and adsorption

Measurement of AIU was performed as the following procedure: 1.000 g material was weighed into 150-mL conical flask, and then aliquot deionized water and ammonium stock solution were added so as to obtain mixture with total volume of 100 mL and initial NH_4^+-N concentration of 25 mg/L. After reacting for 2 h in a shaker at 220 rpm at 30 ± 1 °C, the suspension was centrifuged and then filtered with 0.45 μm membrane to remove the zeolite particles for analysis. AIU (mg NH_4^+-N/g zeolite) was calculated according to Eq. (1):

$$AIU = \frac{(C_0 - C_t)V}{1000m} \tag{1}$$

Table 3
Mol percentages of Na and Ca of four cations (Na, K, Ca and Mg) and Si/Al ratio for the different zeolite by unit cell composition EDX analyses.

Sample[a]	Z-R	Z-M(1)	Z-M(2)	Z-M(2)-C(400)
Na (mol%)	15.2	56.1	63.8	62.3
Ca (mol%)	44.9	14.0	0	0
(Mg + Ca)/(Na + K) molar ratio	1.37	0.16	0.09	0.10
Si/Al (mol ratio)	4.13	4.17	4.06	3.61

[a] Z-R, Z-M(1), Z-M(2) and Z-M(2)-C(400) represent the raw, once salt modified at 30 °C, twice salt modified at 30 °C and modified by twice salt modification followed with calcination at 400 °C zeolites, respectively.

where C_0 and C_t are the concentrations of initial and final NH_4^+-N in the solution at time t (mg/L), respectively, V is the solution volume (mL) and m is the weight of raw or modified zeolite (g).

The ammonium ion-exchange isotherms and kinetics of different zeolites were evaluated by using Langmuir isotherm model (Eq. (2)) and Bangham adsorption rate equation (Eq. (3)), respectively:

$$q_e = \frac{q_m b C_e}{1 + b C_e} \qquad (2)$$

$$q_t = k t^{1/m} \qquad (3)$$

where q_e is the equilibrium adsorption capacity (mg NH_4^+-N/g zeolite), q_m is the maximum adsorption capacity (mg NH_4^+-N/g zeolite), b (L/mg) is the equilibrium adsorption constant, and C_e is equilibrium liquid phase concentration (mg NH_4^+-N/L), q_t is the amount of NH_4^+-N adsorbed at time t (mg NH_4^+-N/g zeolite), and k (mg/(g min)) and m are the adsorption rate constants.

In all runs, the pH value of mixed solution was less than 7.1 and it was thus assumed that all ammonia existed in the ionic form [16] and was available for ion exchange and adsorption, and ionic strength was assumed to be equal to molar concentration of ammonium ion due to the usage of high-purity deionized water and without addition of other chemicals than NH_4Cl.

2.4. Mineralogical and chemical analyses

The mineralogical transformations of the raw and treated zeolites were monitored by X-ray diffraction (XRD), using an X'Pert Pro MPD diffractometer (Panalytjcal, Netherland) operating at 40 kV and 40 mA. A 0.017° (2θ) scanning step and 20 s scanning time per step was used. The diffraction patterns were identified using High-score Plus files.

The chemical composition of the raw zeolite was determined by X-ray fluorescence spectrophotometer (ARL ADVANT'XP⁺, Thermo Electron Corporation, USA). Si/Al molar ratio was calculated from the chemical composition.

The microstructure of the samples was observed by scanning electron microscope (SEM) using a Quanta 200FEG microscope (USA), and the unit cell average element composition of clinoptilolite crystals was analyzed by energy dispersive X-ray spectrometer.

BET surface area, pore volume and pore size were determined by nitrogen adsorption/desorption, using a Micromeritics ASAP 2010 apparatus.

According to the standard method issued by the Environmental Protection Agency (EPA) of China, the concentration of NH_4^+-N was determined by using the Nessler's reagent spectrophotometric method with a Unico spectrophotometer (model UV-2102PCS) at the corresponding wavelength ($\lambda = 540$ nm). All experiments were performed in duplicate and the average values were used for datum analyses.

3. Results and discussion

3.1. Pretreatment

As shown in Table 4, along with the reduction of particle size, AIU gradually increased, and changed slightly when size was less than 105 μm with AIU of 1.76 mg/g, which increased by 18% in comparison with 1.50 mg/g of the raw zeolite (Z-R). After grinding and sieving, the surface and pore properties of zeolite were developed largely, for example, BET surface area, pore volume and pore diameter of pretreated zeolite with size of 98–105 μm (Z-P), increased by 36.5%, 52.3%, and 11.6%, respectively, compared with those of Z-R (Table 5). It could be seen from Fig. 1 and Table 6 that, pretreatment brought significant increases in relative intensities (I/I_{max}) at 9.84°, 11.18°, 26.01° and 28.01° 2θ for clinoptilolite, and clear reduction at 36.51°, 42.46°, 50.1°, 54.91° and 59.94° 2θ for quartz, indicating that, with decreasing particle size, the content of quartz in zeolite decreased, resulting in the increase in clinoptilolite purity. Grinding and sieving did not only remove part of quartz, but also improved pore structure and surface properties, resulting in the enhancement of AIU to a certain extent. Considering pretreatment cost, a desirable particle size was in the range of 98–105 μm.

3.2. Individual calcination treatment

As illustrated in Fig. 2, AIU of calcined zeolite (Z-C) increased a little before temperature was above 150 °C and attained a maximum value of 1.80 mg/g at 150 °C, and then decreased a lot with increasing temperature, especially at 800 °C, AIU was only 8% of that of the raw material. So it was very obvious that thermal treatment at high temperature made against the improvement of AIU. According to Table 5, when Z-P was heated at 150 °C, pore volume and pore diameter increased by 16.4% and 19.6%, respectively. With increasing temperature, pore diameter maintained elevation, however, surface area and pore volume gradually decreased. The surface morphology analysis by SEM showed the raw zeolite had a rough surface and porous structure with definite channels/cavities (Fig. 3a). As compared with Z-R, zeolite calcined at 150 °C changed little with obvious pore (Fig. 3b) and however, heat treatment at higher temperature above 150 °C caused significant changes (Fig. 3c

Table 4
Effect of particle size of zeolite on AIU.

Particle size (μm)	AIU (mg NH_4^+-N/g zeolite)	Removal efficiency (%)
2000–1000	1.5	68.11
1000–450	1.62	73.64
450–280	1.67	75.92
280–180	1.7	77.22
180–154	1.74	79.17
154–105	1.75	79.50
105–98	1.76	80.15
98–74	1.78	81.13
<74	1.79	81.45

Table 5
BET surface, total pore volume and average pore size of the raw and activated/modified zeolites under different conditions.

| Sample[a]	BET surface area (m^2/g)	Total pore volume (cm^3/g)	Average pore diameter (nm)
Z-R	10.53	0.0383	14.54
Z-P	14.37	0.0583	16.23
Z-C(150)	13.79	0.0679	19.41
Z-C(400)	11.49	0.0558	19.42
Z-C(600)	10.96	0.0556	20.23
Z-M(2)	30.47	0.1551	20.36
Z-M(2)-C(400)	30.10	0.1846	25.00

[a] Z-P means pretreated material, and Z-C(150), Z-C(400), Z-C(600) mean calcined materials at 150, 400 and 600 °C, respectively. Other abbreviations are shown in Table 3.
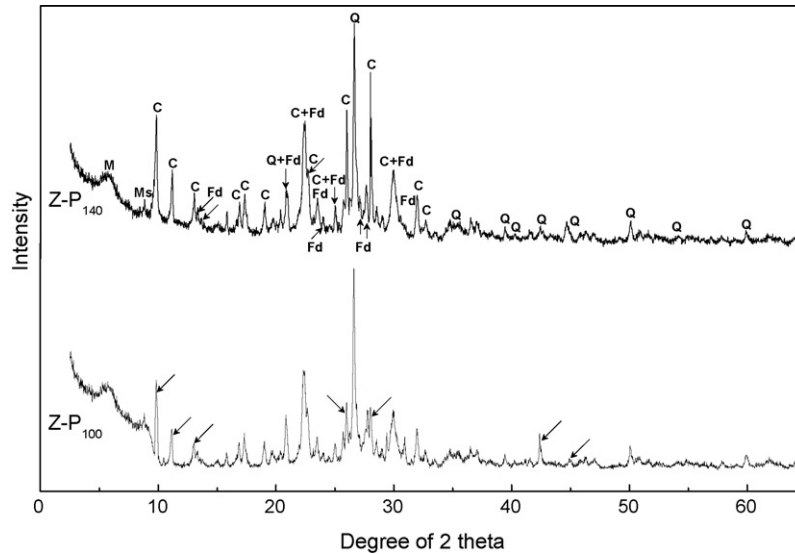
Fig. 1. XRD patterns of pretreated zeolites with 140-mesh sieve (Z-P$_{140}$) and 100-mesh sieve (Z-P$_{100}$). C, Fd, Q, M and Ms represent clinoptilolite, feldspars, quartz, montmorillonite and muscovite, respectively. The arrows for sample Z-P$_{100}$ indicate the same minerals as those in Z-P$_{140}$ at the same 2θ degrees, where the relative intensities were changed significantly.

Table 6
XRD data of different zeolites.

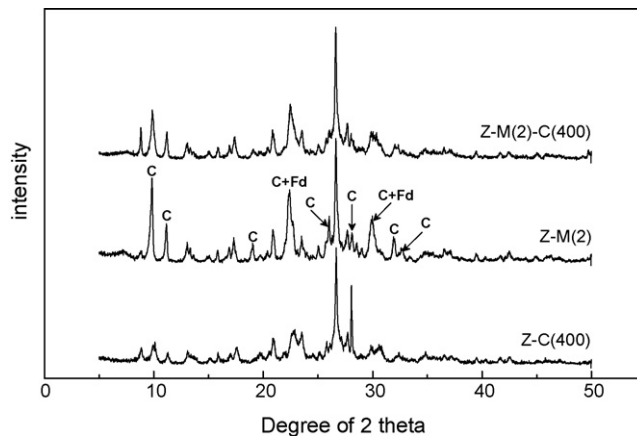| 2θ (°)	d-Spacing (Å)	Relative intensities (I/I_{max}) of different treated zeolites[a]					Mineral
		Z-P$_{140}$	Z-P$_{100}$	Z-C(400)	Z-M(2)	Z-M(2)-C(400)	
9.8482	8.974	44.2	33	20	67	35	C
11.1885	7.901	23.5	21	13	31	21	C
13.0555	6.775	14.9	14	14	16	13	C
13.329	6.637	13.2	10	11	14	10	C + Fd
16.8685	5.251	11.5	14	13	14	12	C
17.3224	5.115	16.6	17	19	20	17	C
19.0231	4.661	11.3	12	Undetected	16	9	C
22.4455	3.957	46.1	47	Undetected	57	38	C + Fd
22.7391	3.907	24.4	30	33	33	25	C
23.5092	3.781	13.2	17	31	20	22	Fd
25.0098	3.557	12.2	14	13	16	12	C + Fd
25.7251	3.460	25.4	18	21	18	17	Fd
26.0051	3.423	66.3	32	9	38	23	C
26.6399	3.343	100.0	100	100	100	100	Q
27.0991	3.287	27.6	18	24	28	22	Fd
27.6307	3.225	20.2	20	31	27	26	Fd
28.0128	3.182	99.7	33	64	25	21	C
29.975	2.978	27.0	29	19	35	21	C + Fd
30.5758	2.921	15.0	17	19	11	19	Fd
31.9945	2.795	17.8	22	14	22	13	C
32.6947	2.736	14.6	11	Undetected	13	8	C
36.5176	2.458	7.2	12	12	14	11	Q
39.4231	2.283	11.6	9	9	9	8	Q
42.4619	2.127	4.3	22	10	11	8	Q
50.103	1.819	11.3	14	11	10	10	Q
54.9054	1.670	3.8	7	3	4	4	Q
59.9454	1.541	5.0	10	5	6	5	Q

[a] Z-P$_{140}$ and Z-P$_{100}$ represent the pretreated zeolites with 140-mesh and 100-mesh sieves, respectively, and other abbreviations are shown in Tables 3 and 5.
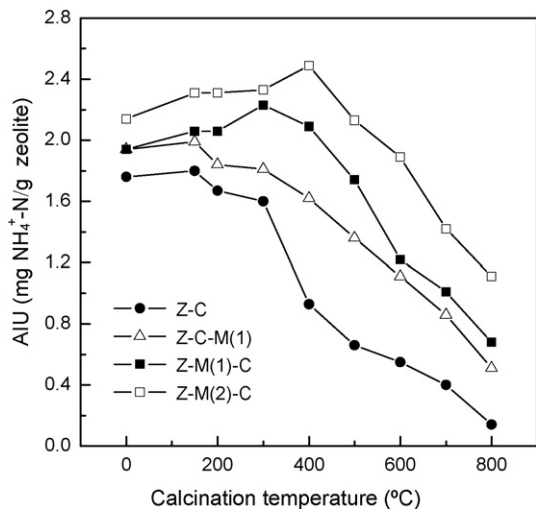
Fig. 2. Effects of individual calcination and combined calcination with salt modification on AIU. See Tables 3 and 5 for abbreviations.

Fig. 4. XRD spectra of Z-C(400), Z-M(2) and Z-M(2)-C(400). See Tables 3 and 5 for abbreviations.

and d): (1) something was formed and aggregated on the surface and in the channels of zeolite, leading to the pore blockage; (2) more aggregate was produced and the channels were blocked up more seriously at 600 °C than 400 °C. Despite the enhanced pore diameter, treatment at high temperature resulted in blockage of pore channels, which was responsible for the decreases in pore volume and BET surface area. As reported by Xu et al., a remarkable aggregation of something in the channels of zeolite catalyst caused by high-calcination temperatures, brought on the pore blockage and the loss of reactivity, and moreover, a decrease in surface area and an increase in average pore size were found [17]. It was obvious that, therefore, high-temperature calcination always exerted negative influences on the surface and pore volume of zeolites.
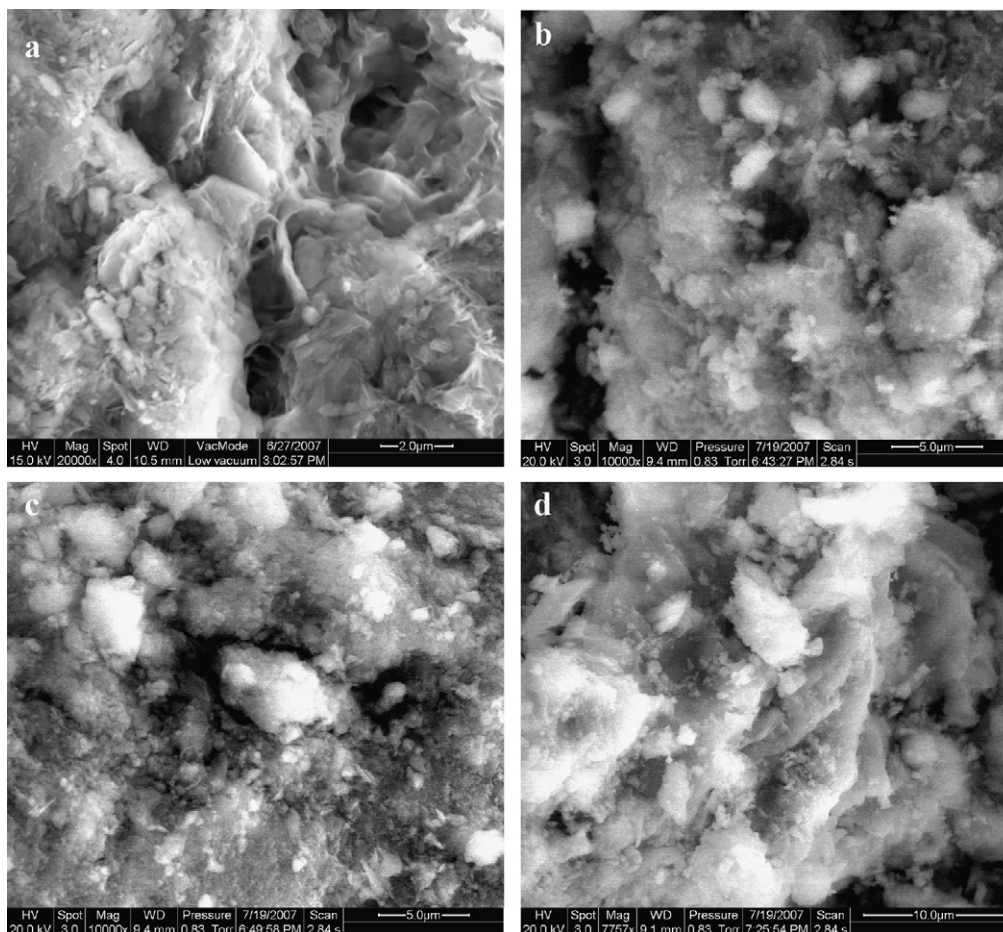
Fig. 3. SEM patterns of the raw and calcined zeolites at different temperatures (a: Z-R; b: Z-C at 150 °C; c: Z-C at 400 °C; d: Z-C at 600 °C). See Tables 3 and 5 for abbreviations.

It was observed from Fig. 4 that, when Z-P was heated at 400 °C, new X-ray crystal peaks did not arise, accompanied with great weakening of many peaks. Compared with Z-P (Fig. 1 and Table 6), Z-C(400) changed a lot in I/I_{max}, including significant decreases at 9.84°, 11.18°, 26.01°, 28.01°, 29.97° and 31.99° 2θ for clinoptilolite, and complete disappearances at 19.02°, 22.44° and 32.69° 2θ for clinoptilolite. As a result, it was certain that high-temperature calcination brought on the losses of part of clinoptilolite in the raw material, finally leading to the fall of clinoptilolite content. On one hand, based on the facts that new material with distinct crystalline structure was not formed and X-ray amorphous and small peaks appeared, lost clinoptilolite was certainly transformed into amorphous matter; on the other hand, calcination at 400 °C made little influence on quartz and feldspars, and thereby, produced X-ray amorphous material was dominantly from lost clinoptilolite. Higher temperature and heating rate may cause larger expansion of pellets due to a rapid derivation of thermally unstable gas releasing phases and water vapor derived from dehydration [18]. By using this feature, zeolitic tuffs with high-water content could be used in the production of lightweight aggregates [18,19], and the phase composition of lightweight aggregates is mainly glass, whose amount generally depends on the starting zeolite [18]. In this work, the thermal gravimetric analysis (TGA) results of the Z-P showed 4.1% weight loss at 150 °C and 8.6% at 600 °C (data not shown here). The weight loss of heated zeolites can be ascribed to the loss of water [20]. It could be concluded that, thereby, those amorphous materials from clinoptilolite mainly formed the lightweight aggregates during the course of high-temperature treatment, as illustrated in Fig. 3c and d. Calcination at high temperature exerted adverse effects on crystalline phase of zeolites: losses of quite a part of clinoptilolite and production of amorphous materials. Furthermore, it was conceivable that it was produced amorphous material to bloke pore channels, and that more amorphous material, heavier blockage.

In addition, EDX analyses demonstrated that the content of carbon in the Z-P decreased with calcination temperature and fell to zero at 300 °C. Therefore, blockage of pore and channels/cavities, decreases in pore volume and BET surface area and the reduction of clinoptilolite content should be the main reasons for the fall of AIUs of calcined zeolites at high temperatures, and the elevation of AIU at 150 °C was mainly attributed to the removal of part of water molecules and organics from the raw zeolite and increases in pore diameter and pore volume.

Calcination can decompose organics and remove water on surface or in pores of zeolites, and enlarge pore diameter [21]. However, due to thermal stabilities of zeolites, high-temperature treatment can also induce dealumination and dehydroxylation of zeolites, and change the surface function groups and cause framework collapse, resulting in lower surface area and pore volume and leading to lower adsorption capacity [13,19,22–24]. Furthermore, with increasing time and temperature of thermal treatment, the degree of crystallinity of original zeolite may decrease, and amorphous phase may be yielded [25,26]. The calcination-test results in this study were in agreement with these studies. However, the subjected zeolite seemed to have lower thermal stability based on the sharp decline of AIU at temperature above 150 °C. Thermal stability of zeolite depends on the physicochemical composition and water content, such as Si/Al ratio, cation form and correlation between cation and framework [18,24,27]. Natural zeolite with almost the same SiO_2/Al_2O_3 ratio as that of the subjected zeolite can resist calcinations at 550 °C [13]. It might be the cation form rather than Si/Al ratio to be the main reason for the lower heat resistance of the subjected zeolite, as discussed in Section 3.4.
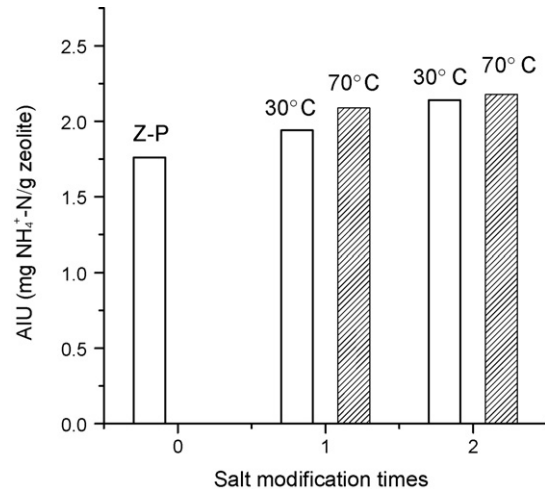

Fig. 5. Effects of temperature and modification times on AIU of salt-modified zeolites.

3.3. Individual salt modification with sodium chloride

Fig. 5 showed that salt modification effectively improved AIU of Z-P. AIU increased from 1.94 to 2.14 mg/g with modification times at 30 °C (modification temperature), and from 2.09 to 2.18 mg/g at 70 °C. According to Table 3, AIU was closely related to the contents of Na^+ and Ca^{2+}, that is, zeolite with more Na^+ and less Ca^{2+} acquired higher AIU. Additionally, with increasing modification times, mol percentage of Ca and (Mg + Ca)/(Na + K) molar ratio decreased from 44.9 to 14, and then to zero, from 1.37 to 0.16, and then to 0.09, respectively, and correspondingly, mol percentage of Na^+ was raised greatly from 15.2 to 56.1, and then to 63.8, indicating that Ca-zeolite was completely transformed into Na-zeolite by twice salt treatment. In addition, the increase of modification times resulted in an evident decline of Si/Al from 4.17 to 4.06. In comparison with Z-P (Fig. 2), there were not obvious changes in crystalline phase of Z-M(2) (Fig. 4), but relative intensities at 9.84°, 11.18°, 13.1°, 16.86°, 17.32°, 19.02°, 22.44°, 22.74° and 31.99°, were elevated, accompanied by evident decreases at 26.00° and 28.01° 2θ for clinoptilolite. Both Table 5 and Fig. 6a clearly demonstrated that salt-modified zeolite had very significant changes in the surface and pore properties, compared with Z-P: (1) BET surface area, pore volume and pore diameter of Z-M(2) increased by 112%, 166% and 25.4%, respectively; and (2) Z-M(2) showed a relatively homogeneous pore system.

Therefore, salt modification could not transform Ca-zeolite into Na-zeolite by exchanging Ca^{2+} ion in the raw zeolite for Na^+ ion, but raise pore volume, pore diameter and surface area by dredging pore channels and voids of the raw zeolite, and these changes could improve material reactivity to acquire higher AIU. It could be inferred that Na-zeolite had higher ammonium ion exchange capability and better surface and pore properties than the raw zeolite, Ca-zeolite. The original and the Na^+-exchanged zeolites showed that the crystallinities of the samples were basically maintained, suggesting that salt modification exerted influence on the crystallinity of neither clinoptilolite nor impurities (quartz and feldspars), which was consistent with report from Abusafa and Yucel [14]. AIU of the twice-modification zeolite at 70 °C was almost the same as that at 30 °C, and moreover, twice modification at 30 °C achieved the complete Ca^{2+} exchange with Na^+. Therefore, twice modification at 30 °C was the feasible condition to salt modification. Partial exchange levels for many cation forms are generally observed [6], and full replacement of Ca^{2+} by Na^+ in this work might be associated with Ca^{2+} in the clinoptilolite instead of impurities.
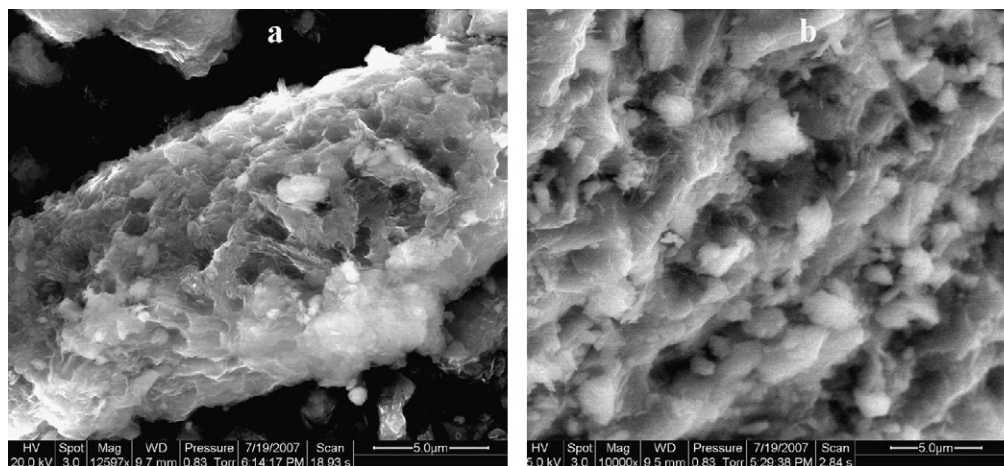
Fig. 6. SEM patterns of zeolites treated by individual salt modification and combined modification with salt and calcination (a: Z-M(2); b: Z-M(2)-C(400)). See Tables 3 and 5 for abbreviations.

3.4. Combined modification with sodium salt and calcinations

Investigation results about AIUs of Z-M-C and Z-C-M at different temperatures were shown in Fig. 2, revealing the following information: (1) compared with Z-C, AIU of Z-C-M was improved with the maximum value of 1.99 mg/g at 150 °C; and (2) AIUs of both Z-M(1)-C and Z-M(2)-C were more than that of Z-C-M, and increased with temperature with the maximum values of 2.23 and 2.49 mg/g at 300 and 400 °C, respectively, indicating salt modification prior to calcination could enhance resistance of the raw zeolite to calcination shock at high temperature, and more salt modification times, higher resistant temperature.

Figs. 4 and 6b, Tables 5 and 6 gave us a lot of information about Z-M(2)-C(400) as follows: (1) compared with Z-M(2), Z-M(2)-C(400) had the same decrease in peak intensity of at 28.01° 2θ for clinoptilolite, where Z-C(400) had not the change; pore volume and pore diameter were elevated by 19.1% and 22.8%, respectively, accompanied with a slight decrease of BET surface area of 1.2%; Si/Al ratio decreased by 11.1% from 4.06 to 3.61; mol percentage of Na$^+$ slightly fell from 63.8 to 62.3; (2) compared with Z-C(400), Z-M(2)-C(400) had the same decreases in the peak intensities at 26.01° 2θ for clinoptilolite, and however, complete disappearances at 19.02° and 32.99° 2θ for clinoptilolite for Z-C(400) did not take place for Z-M(2)-C(400), where these peak intensities were just reduced, and moreover, significant decreases at 9.84°, 11.18°, 22.44°, and 31.99° 2θ for clinoptilolite for Z-C(400), were replaced by small decreases for Z-M(2)-C(400). In the meanwhile, there was also no new crystal matter generated in the Z-M(2)-C(400). Therefore, the degree of crystallinity of Z-M(2)-C(400) was changed much less than that of Z-C(400). BET surface area, pore volume and pore diameter increased largely and were 2.6, 3.3 and 1.3 times as many as those of Z-C(400), respectively. Direct calcination at 400 °C resulted in the decrease of pore volume; however, calcination after salt treatment did not do the same way. SEM diagram of Z-M(2)-C(400) also showed the pore blockage in the surface of zeolite, however, that was mild when compared with Z-C(400) (Fig. 3c).

Based on above information, the followings could be inferred: (1) salt modification followed with calcination could further improve pore volume and pore diameter to increase activity of ammonium ion exchange and adsorption; (2) salt treatment prior to calcination could enhance resistance of the raw zeolite to higher temperature, thereby avoiding the disappearance and weakening

of part of X-ray peaks for clinoptilolite, that is, greater loss of clinoptilolite and more production of amorphous material, suggesting that Na-zeolite had higher thermal stability than Ca-zeolite, which could be also proved by the enhancement in optimum calcination-temperature from 300 to 400 °C with increasing Na$^+$ mol percentage (Fig. 2). Consequently, it could be explained that low resistance to heat shock of the raw zeolite was mainly ascribed to the high-calcium content, and that Na$^+$ exchange modification raised the calcination temperature effectively.

It should be pointed out that calcination after salt treatment still aroused the loss of clinoptilolite in a small quantity. In addition, it was interesting that Si/Al ratio of Z-M(2) further decreased after calcination, which was not in agreement with general conclusion on the increase in Si/Al after calcination due to dealumination. Enhancement of resistant temperature might be one of reasons. It was necessary that further experimental and theoretical works should be done to explain it.

Finally, it could be confirmed that twice salt modification at 30 °C followed with calcination at 400 °C was the optimum modification condition.

3.5. Comparison of ammonium ion exchange isotherms and kinetics for different zeolites

Fig. 7 and Table 7 presented the ammonium ion-exchange isotherms and kinetics of different zeolites. The data were fitted to Langmuir isotherm model (Eq. (2)) and Bangham adsorption rate equation (Eq. (3)) very well. Both the theoretical maximum adsorption capacities (q_m) and equilibrium adsorption constant (b) of modified zeolites were higher than those of the natural one. Adsorption equilibrium was achieved at about 60, 180 and 280 min for Z-M(2)-C(400), Z-P and Z-R, respectively, and the adsorption rate constants (k and m) were also largely enhanced from 0.5 and 3.3 to 5.3 and 303, respectively. These observations indicated that the integrated modification process effectively improved the ion exchange and adsorption capabilities of the raw zeolite, consequently leading to the increase of AIU, as pointed in pertinent reports [28,29]. Therefore, it could be proposed that the optimal modification process as well as condition was as follows: pretreatment using grinding and sieving to obtain zeolite with particle size in the range of 98–105 μm, and then twice salt modification with 1.5 M NaCl at 30 °C followed with calcination at 400 °C for 2 h.
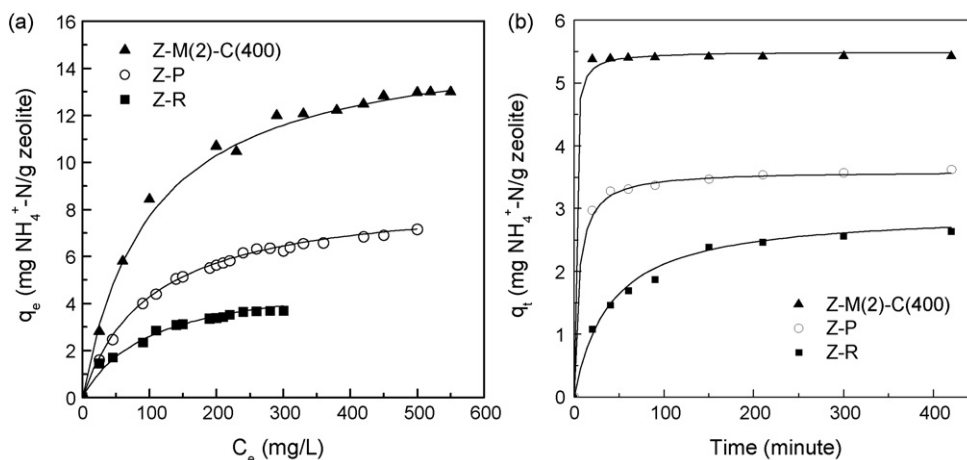
Fig. 7. Ammonium ion exchange isotherms and kinetics for the raw and modified zeolites: (a) m (zeolite) = 1.000 g, V (solution) = 100 mL, t(reaction time) = 2 h, T (temperature) = 30 ± 1 °C. (b) m (zeolite) = 1.000 g, V (solution) = 100 mL, C (initial concentration of NH_4^+-N in solution) = 55 mg/L, T (temperature) = 30 ± 1 °C. See Tables 3 and 5 for abbreviations.

Table 7
Langmuir adsorption isotherm parameters and Bangham adsorption rate parameters of different zeolites.

Zeolite[a]	Langmuir isotherm parameter			Bangham adsorption rate parameter		
	q_m (mg/g)	b (L/mg)	R^2	k (mg/(g min))	m	R^2
Z-R	5.22	0.0096	0.9829	0.4771	3.34	0.9532
Z-P	9.72	0.0098	0.9955	2.4177	14.1	0.9227
Z-M(2)-C(400)	15.44	0.01	0.9867	5.3271	303.03	0.9515

[a] See Tables 3 and 5 for abbreviations.

Table 8
Cost comparisons between the raw and modified zeolites (Yuan RMB/g).

Sample[a]	Raw material	Energy consumption during grinding	NaCl cost	Energy consumption during calcination	Total cost
Z-R	0.0003	0	0	0	0.0003
Z-M(2)-C(400)	0.0003	0.0002	0.0016	0.0012	0.0033

[a] See Table 3 for abbreviations.

3.6. Cost comparison of different zeolites

Based on the energy consumption and used chemicals during the course of modification, the cost comparison between the natural and modified zeolites under the optimal conditions was made in the Table 8, from which we could see that the cost of modified material was the 11 times of that of the raw one, and that the modification cost was mainly ascribed to the chemicals and the energy consumption during calcination. Of course, the cost estimate was rough and moreover based on data from the small scale test, so we believed that the modification cost would be much more less in the factual industrial application.

4. Conclusions

With the aim to improve AIU, an integrated process was used to activate a natural calcium-rich zeolite, and the test results revealed the following information:

(1) Grinding and sieving improved BET surface area, pore volume and pore diameter, and removed part quartz from zeolite, leading to the increase in AIU from 1.50 to 1.76 mg/g.
(2) Individual calcination could not benefit significant improvement of AIU, on the contrary, calcination at high-temperature above 150 °C brought on losses of part of clinoptilolite and production of amorphous material, leading to pore blockage and decreases in pore volume and BET surface area. High content of calcium was the main reason for the low-thermal stability.
(3) Individual salt treatment transformed Ca-zeolite into Na-zeolite, and moreover caused significant increases in BET surface area, pore volume and pore diameter with 112%, 166% and 25.4%, respectively, which was responsible for the improvement of AIU.
(4) Calcination after salt treatment could not only enhance resistant temperature from 150 to 400 °C, but also improve pore volume and pore diameter.
(5) By the optimum modification process, NH_4^+ ion exchange capacity was largely enhanced, and the maximum AIU (17.24 mg/g) of the modified zeolite was 4.3 times that of the raw zeolite (4.04 mg/g).
(6) Neither salt treatment nor calcination caused the production of new crystal materials. Only pretreatment could reduce the content of quartz.

References

[1] P.H. Liao, A. Chen, K.V. Lo, Removal of nitrogen from swine manure wastewater by ammonia stripping, Bioresour. Technol. 54 (1995) 17–20.

[2] H. Christine, K. Sabine, Simultaneous nitrification/denitrification in an aerobic biofilm system, Water Sci. Technol. 37 (1998) 183–187.

[3] X.Z. Li, Q.L. Zhao, X.D. Hao, Ammonium removal from landfill leachate by chemical precipitation, Waste Manage. 19 (1999) 409–415.

[4] S. Balci, Y. Dincel, Ammonium ion adsorption with sepiolite: use of transient uptake method, Chem. Eng. Process. 41 (2002) 79–85.

[5] C.M. Hung, J.C. Lou, C.H. Lin, Removal of ammonia solutions used in catalytic wet oxidation processes, Chemosphere 52 (2003) 989–995.

[6] L. Curkovic, S.C. Stefanovic, T. Filipan, Metal ion exchange by natural and modified zeolites, Water Res. 31 (1997) 1379–1382.

[7] T. Sismanoglu, S. Pura, Adsorption of aqueous nitrophenols on clinoptilolite, Colloids Surf. A180 (2001) 1–6.

[8] S. Aiyuka, J. Amoakoa, L. Raskinb, A. van Haandelc, W. Verstraetea, Removal of carbon and nutrients from domestic wastewater using a low investment, integrated treatment concept, Water Res. 38 (2004) 3031–3042.

[9] Comparison of the ion exchange uptake of ammonium ion onto New Zealand clinoptilolite and mordenite, Water Res. 38 (2004) 4305–4312.

[10] 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.

[11] A. Farkas, M. Rozic, Z.B. Mikocevic, Ammonium exchange in leakage waters of waste dumps using natural zeolite from the Krapina region, Croatia, J. Hazard. Mater. B117 (2005) 25–33.

[12] M. Sprynskyy, M. Lebedynets, R. Zbytniewski, J. Namiesnik, B. Buszewski, Ammonium removal from aqueous solution by natural zeolite, Transcarpathian mordenite, kinetics, equilibrium and column tests, Sep. Purif. Technol. 46 (2005) 155–160.

[13] S.B. Wang, Z.H. Zhu, Characterisation and environmental application of an Australian natural zeolite for basic dye removal from aqueous solution, J. Hazard. Mater. B136 (2006) 946–952.

[14] A. Abusafa, H. Yucel, Removal of 137Cs from aqueous solutions using different cationic forms of a natural zeolite: clinoptilolite, Sep. Purif. Technol. 28 (2002) 103–116.

[15] R. Ruiz, C. Blanco, C. Pesquera, F. Gonzilez, I. Benito, J.L. Lopez, Zeolitization of a bentonite and its application to the removal of ammonium ion from waste water, Appl. Clay Sci. 12 (1997) 73–83.

[16] K.R. Emmerson, R.C. Russo, R.E. Lund, R.V. Thurston, Aqueous ammonia equilibrium calculation; effect of pH and temperature, Can. J. Fish. Aquat. Sci. 32 (1981) 2379–2382.

[17] Y.D. Xu, S.T. Liu, L.S. Wang, M.S. Xie, X.X. Guo, Methane activation without using oxidants over Mo/HZSM-5 zeolite catalysts, Catal. Lett. 30 (1995) 135–149.

[18] M. Dondi, P. Cappelletti, G. Cerri, M. de Gennaro, R. de Gennaro, A. Langella, Zeolitc tuffs as raw materials for lightweight aggregates, Appl. Clay Sci. 25 (2004) 71–81.

[19] O.C. Duvarci, Y. Akdeniz, F. Ozmihci, S. Ulku, D. Balkose, M. Ciftcioglu, Thermal behaviour of a zeolitic tuff, Ceram. Int. 33 (2007) 795–801.

[20] S. Chandrasekhar, P.N. Pramada, Sintering behaviour of calcium exchanged low silica zeolites synthesized from kaolin, Ceram. Int. 27 (2001) 105–114.

[21] R.L. Mao, L. Lu, N.T. Vu, Q. Zhao, H.T. Yan, N. Al-Yassir, Silica nanoboxes from alumina rich zeolites: thermal and chemical stability of the monomodal and bimodal materials, Catal. Lett. 114 (2007) 129–134.

[22] A.L. Klyachko, G.I. Kapustiu, T.R. Brueva, A.M. Rubinstein, Relationship between acidity and catalytic activity of high-silica zeolites in cracking, Zeolites 7 (1987) 119–122.

[23] D.T. Chen, S.B. Sharm, I. Filimonov, J.A. Dumesic, Microcalorimetric studies of zeolite acidity, Catal. Lett. 12 (1992) 201–212.

[24] M.J.B. Cardoso, D.O. Rosas, L.Y. Lau, Surface P and Al distribution in P-modified ZSM-5 zeolites, Adsorption 11 (2005) 577–580.

[25] Y.V. Shumovskii, S.N. Khadzhiev, M.I. Levinbuk, T.V. Limova, Influence of thermal and hydrothermal activation on the adsorptive, acidic and catalytic properties of high-silica zeolites, React. Kinet. Catal. Lett. 24 (1984) 277–280.

[26] H.J. Lee, Y.M. Kima, O.S. Kweonb, I.J. Kima, Structural and morphological transformation of NaX zeolite crystals at high temperature, J. Eur. Ceram. Soc. 27 (2007) 561–564.

[27] W.J. Mortier, J.R. Pearce, Thermal stability of the heulandite-type framework: crystal structure of the calcium/ammonium from dehydrated at 483 K, Am. Mineral. 66 (1981) 309–314.

[28] 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.

[29] C.R. Oliveira, J. Rubio, New basis for adsorption of ionic pollutants onto modified zeolites, Miner. Eng. 20 (2007) 552–558.