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RESEARCH ARTICLE

Influences of acid and heat treatments on the structure and water vapor adsorption property of natural zeolite

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Natural zeolite was first acid treated and then heat treated. The influences of acid and heat treatments on the structure and water vapor adsorption property of natural zeolite were investigated. X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), thermogravimetric analysis (TG), and Brunauer-Emmett-Teller (BET) surface areas were employed to investigate the structure changes of the zeolite samples. Water vapor adsorption property of the samples was investigated in order to determine wettability of the samples. The results showed that nitric acid treatment could remove Al from the structure, decrease relative crystallinity, and significantly increase specific surface area of the zeolite samples. Heat treatment could change or even destroy the structure, effectively remove water molecules from the surface/structure, and decrease the specific surface area of the zeolite samples. Water vapor adsorptions on the acid-treated zeolite samples were significantly lower than that for the zeolite sample, and the adsorptions further reduced for the heat-treated zeolite samples. The increase of Si/Al ratio, decreases of silanol groups, and specific surface area of the samples were major reasons related to the reductions of water vapor adsorptions on the zeolite samples.

KEYWORDS

acid treatment, heat treatment, natural zeolite, water vapor adsorption

1 | INTRODUCTION

Natural zeolite, as a kind of hydrated aluminosilicate porous mineral, has found a variety of applications in adsorption, catalysis, building industry, agriculture, soil remediation, and energy.[1] Structurally, it is mainly composed of a 3-dimensional framework structure bearing AlO_4 and SiO_4 tetrahedra linked by oxygen atoms. In the zeolite framework, each aluminum atom introduces 1 negative charge on the framework and balances by exchangeable alkalis and/or alkaline earth cation located together with water. The water molecules can be present in voids of large cavities and bonded between framework ions and exchangeable ions via aqueous.[1-3] Based on the above specific structure, zeolites exhibit high cation exchange property, polarity, and hydrophilicity and thus make them particularly suitable for removing NH_4^+, kinds of heave metal ions such as Hg, Pb, Ag, Cu, Cd, Cr, Zn, Ni, Co, Mn, etc.,[1,4] and polar organic contaminations such as phenol[5] and tetrahydrofuran.[6] The modifications of zeolites, such as ion exchange,[7] surfactant/organosilane modification,[2,8-10] acid treatment,[3,11-13] and heat treatment,[12,14] are applied to change the property of zeolites, which greatly influence the practical applications.

It has been reported that acid treatment can remove impurities blocked in the pores, eliminate cations to change into H-form, dealuminate the structure, increase the hydrophobicity, and finally increase the adsorption properties on hydrophobic contaminations.[1,12] However, the surface of the dealuminated zeolite still present some amount of silanol defect sites which renders its surface hydrophilic. Several techniques, such as organosilane modification[10] and heat treatment,[12] have been developed to solve the above problem, and the heat treatment seems to be a simple and effective method. Compared with the significant amount of severally researches on influences of acid treatment and heat treatment on zeolite, a little attention has been paid on influences of acid treatment followed by heat treatment on natural zeolite, especially for the influence of heat treatment on the structure and water vapor adsorption/hydrophobicity of acid-treated natural zeolite.

In this paper, we used acid treatment followed by heat treatment to treat natural clinoptilolite in purpose of increasing hydrophobicity of the sample. The objective is to investigate the influences of acid and heat treatments on the structure and water vapor adsorption/hydrophobicity of natural zeolite samples. X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), thermogravimetric (TG)

analysis, and Brunauer-Emmett-Teller (BET) were employed to investigate the structure changes of the samples. Water vapor adsorption method was used to determine wettability of the samples.

2 | EXPERIMENTAL

2.1 | Materials

The zeolite used in this study was purified natural clinoptilolite (<45 μm) obtained from Xinji, Hebei, China. Nitric acid (65%) was obtained from Aladdin, and sodium chloride was obtained from Sinopharm Chemical Reagent Co. Ltd. Acid treatment was carried out by treating 5.0 g of natural zeolite with 100 mL of 0.1, 1.0, 2.0, and 4.0 M nitric acid solutions and stirred at 25°C for 12 hours. Then, it was washed with deionized water for several times and dried at 75°C for 12 hours. Heat treatment was conducted by heat treating of zeolite and 2 M acid-treated zeolite at 400°C, 600°C, 800°C, and 1000°C for 6 hours.

2.2 | Sample characterization

XRD patterns of the samples were recorded using a D/max-2200PCX diffractometer (Rigaku Corporation, Japan), with Cu Kα radiation and a graphite monochromator, operating at 44 mA and 40 kV. The step size was 0.02° 2θ, and the exposure time was 1 second per step. The relative crystallinity of the treated zeolites was determined by measuring the intensity of the diffraction signal of the (400) peak and comparing it to that of the zeolite. TG-DTG analysis was performed on a STA409PC thermal analyzer (NETZSCH-Gerätebau GmbH, Germany) from room temperature to 1100°C at a heating rate of 10 K/min. The specific surface area and pore size distribution of the samples were determined using a Gemini VII2390 automated physisorption analyzer (Micromeritics Instrument Corp., USA) through N_2 adsorption/desorption. X-ray photoelectron spectroscopy (XPS) was recorded on a AXIS SUPRA (Kratos Company, England) system equipped with a Al/Mg dual anode X-ray source by using a AlK$_\alpha$ (1486.6 eV) anode and a hemispherical energy analyzer. All binding energies were calibrated with contaminant carbon (C1s = 284.6 eV) as a reference.

2.3 | Wettability determination

Water vapor adsorption method was employed to determine wettability of the zeolite samples. This method is an effective way to determine wettability of solids, and it can distinguish hydrophilicity/hydrophobicity with minor difference, eg, Saada etc.[15] adopted water vapor adsorption experiment (saturated salt solution was used to control humidity) to compare hydrophilicity/hydrophobicity of illite and kaolinite, and found that kaolinite was more hydrophobic than illite.

In this study, 1 g of solids and 200-mL saturated sodium chloride solution (75% relative humidity) were placed in a glass bottle and then sealed with a cap. The weight change of the samples was measured under atmospheric conditions and at room temperature every 24 hours until a constant weight was obtained.

3 | RESULTS AND DISCUSSIONS

3.1 | Influence of acid treatment

XPS survey spectra of zeolite and acid-treated zeolites in Figure 1 show the presence of O, Si, Al, C, and Ca characteristic peaks. However, Ca element cannot be detected for the acid-treated zeolite samples which are due to dissolution of Ca on the effect of nitric acid.

Figure 2 shows XPS high-resolution spectra for Si 2p, Al 2p, O 1s, and Si/Al ratio of zeolite and acid-treated zeolites. It is clear that the Si, Al, and O peaks for acid-treated zeolite samples shift to higher binding energy compared with these for zeolite sample. These binding energy shifts are closely related to the increase of Si/Al ratio of the samples from 3.6 to 7.1 with the increase of acid concentration from 0 to 4 mol/L. This result suggests that nitric acid treatment can remove Al from the structure of zeolite and thus increase the covalent nature of the Si—O bond and Al—O bond within the structure. Our XPS results are consistent with the results reported by Wang et al.[13]

Figure 3 shows the XRD patterns (A) and relative crystallinity (B) of zeolite and acid-treated zeolite samples. The patterns of zeolite indicate that the sample mainly composes of clinoptilolite with small amount of montmorillonite. It is interesting that cristobalite peaks appear in XRD patterns of the acid-treated samples and the peaks constantly increase with the increase of nitric acid concentration. This suggests that natural zeolite sample also contains some amount of cristobalite mineral. The cristobalite peak cannot be distinguished in the XRD patterns of zeolite sample due to overlapping of the strong clinoptilolite peaks.

The intensities of clinoptilolite peaks and their relative crystallinity for the aid-treated zeolites gradually decrease with the increase of the nitric acid concentration, which indicates that acid treatment changes the structure of clinoptilolite and thus decreases the crystallinity of clinoptilolite. This is attributed to dealumination of the clinoptilolite, and it has been proved by the XPS analysis.

3.2 | Influence of heat treatment

Figure 4 shows the XRD patterns of zeolite and its heat-treated samples (Figure 4A), 2 M nitric acid-treated zeolite, and its heat-treated
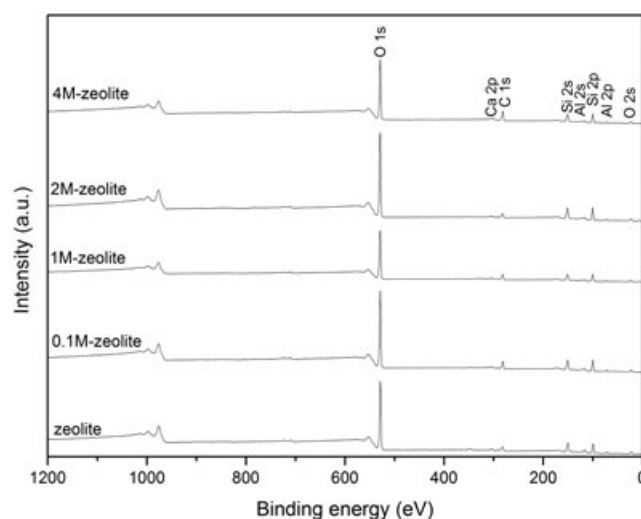

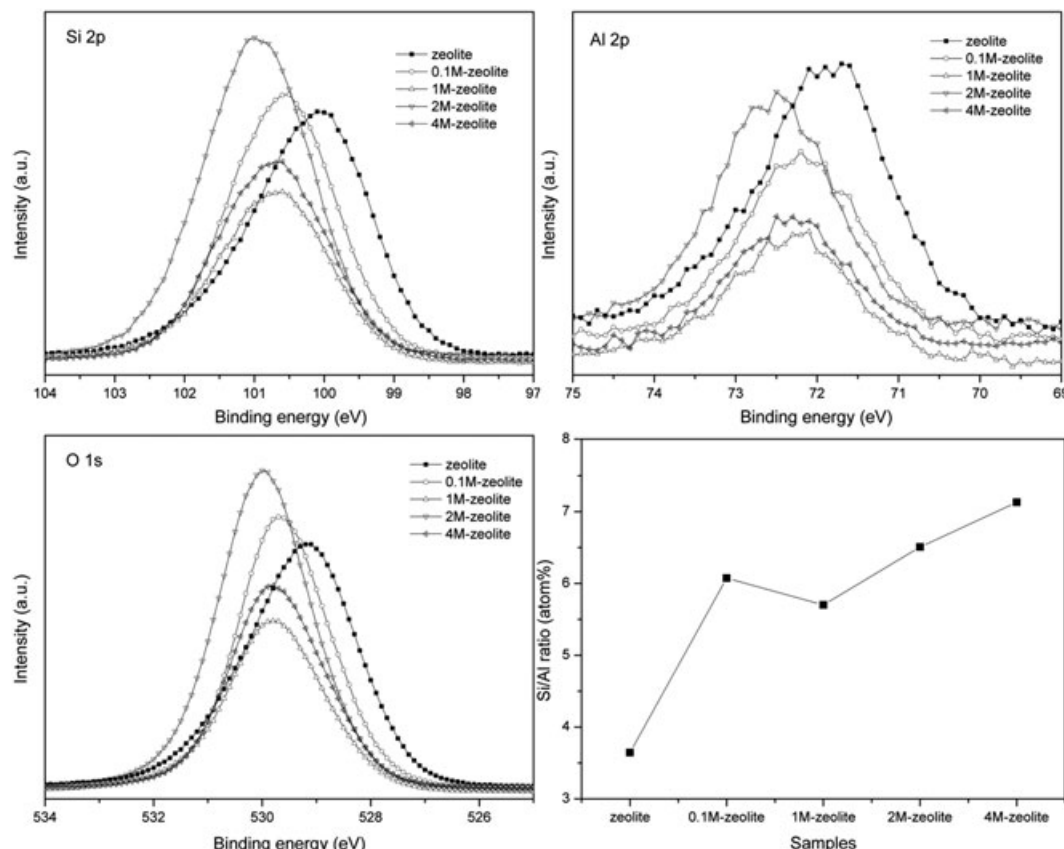**FIGURE 1** XPS survey spectra of zeolite and acid-treated zeolites

FIGURE 2 XPS high-resolution spectra for Si 2p, Al 2p, O 1s, and Si/Al ratio of zeolite and acid-treated zeolites
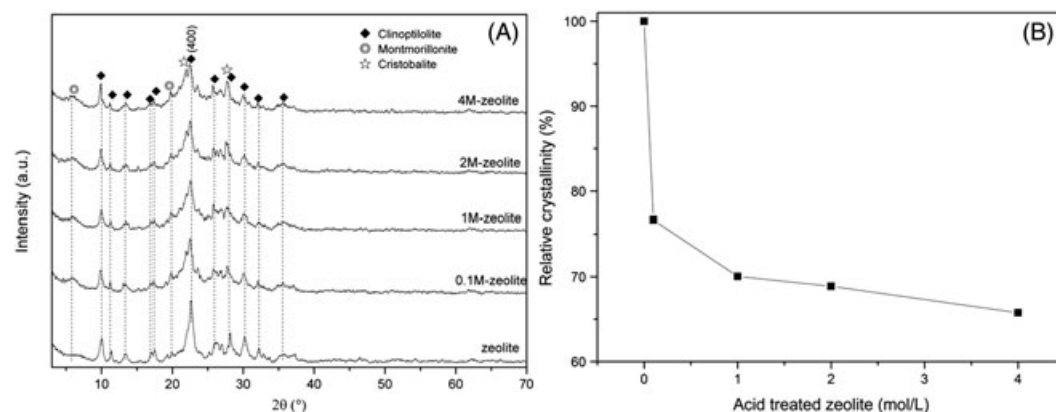

FIGURE 3 XRD patterns (A) and relative crystallinity (B) of zeolite and acid-treated zeolites

samples (Figure 4B). It is clear that intensity of the clinoptilolite peaks gradually decreases, while the cristobalite peaks increase with the increase of calcination temperature. No clinoptilolite peaks and only cristobalite peaks can be found for the 1000°C heat-treated samples. This indicates that heat treatment significantly changes the structure of the zeolite samples and the structure of clinoptilolite completely collapses under 1000°C.

In addition, it can be observed that most of clinoptilolite peaks for the 400°C acid-treated sample disappear, while those for the 400°C zeolite sample still reserve with a certain reduction. It suggests that the structure of the acid-treated zeolite sample is much easier to be changed/destroyed than that of zeolite sample after heat treatment.

This is owing to the dealumination and decrease of structure stability of the zeolite sample after nitric acid treatment.

Figure 5 shows the TG-DTG curves of zeolite and zeolite treated with 2 mol/L nitric acid and their heat-treated samples. The TG curves exhibit continuous mass loss as a function of temperature which is attributed to the dehydration of the samples. Based on the 3 forms of water molecules in zeolite,[16] ie, physisorbed water (100°C), water associated with extra-framework cations and aluminum (100–400°C), and water associated with silanol nests (>400°C), the relative weight loss percentage of water molecules from samples at each dehydration stage for the above samples are plotted in Figure 6. For zeolite samples, it is clear that the total weight loss, and water molecules weight
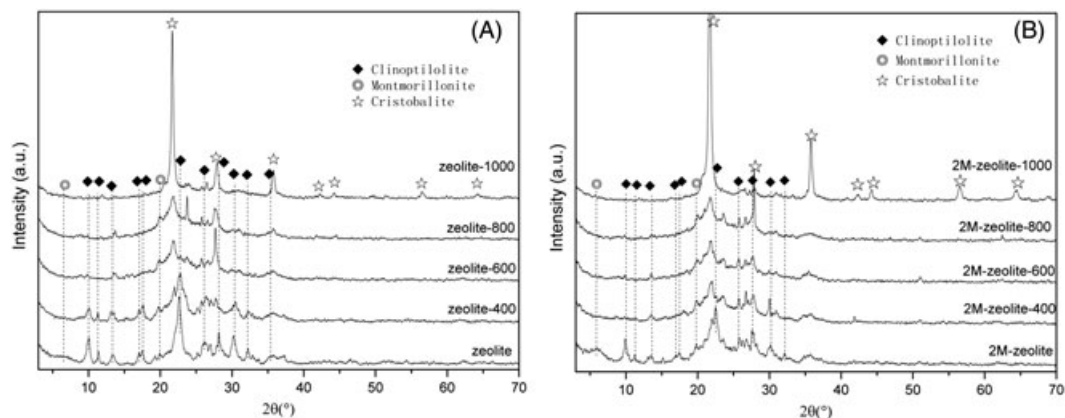
FIGURE 4 XRD patterns of heat-treated zeolite (A) and 2 M acid-treated zeolite (B)
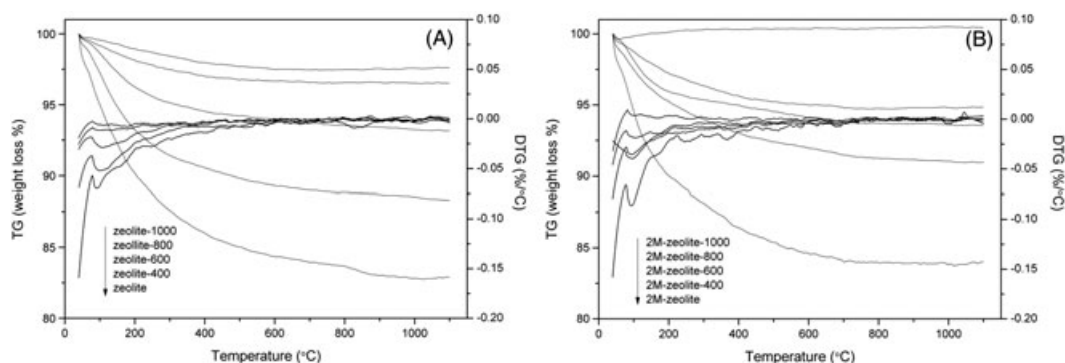

FIGURE 5 TG-DTG curves of zeolite, heat-treated zeolites (A) and 2 M acid-treated zeolite, heat-treated 2 M–zeolites (B)
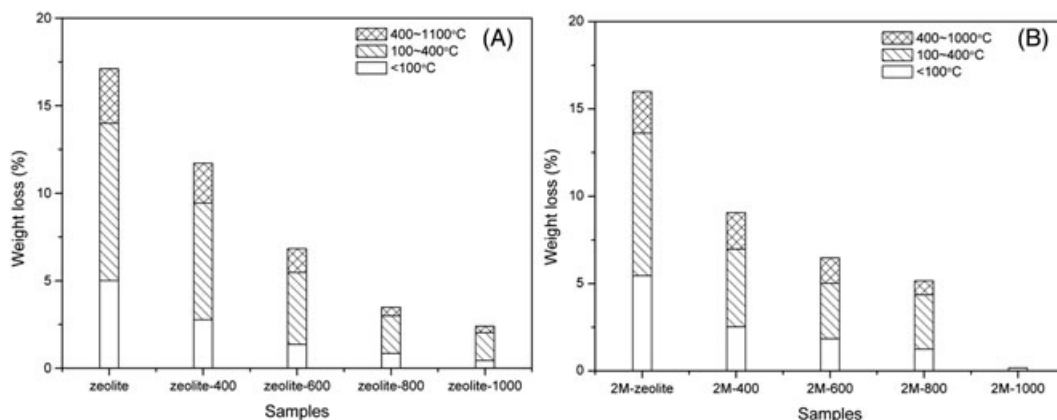

FIGURE 6 Relative weight loss percentage of water molecules from samples at each dehydration stage

loss at each dehydration stage continuously decrease with the increase of calcination temperature. Weight loss behaviors of the acid-treated zeolite samples have the similar trend as those for the zeolite samples. The results indicate that heat treatment can effectively remove water molecules from the surface/structure of zeolite samples. In addition, weight losses of acid-treated zeolite samples at 100–400°C stages appear to be lower than the zeolite samples except for the 2 M–zeolite-800 sample. This suggests that acid treatment decreases extra-framework cation and alumination associated water in the zeolite, which is probably due to dealumination of zeolite after acid treatment. It can be also found that weight losses of heat-treated samples at >400°C stage are lower than the corresponding zeolite and acid-

treated samples and the weight losses (>400°C stage) gradually decrease with the increase of calcination temperature. This indicates that heat treatment decreases the silonal nest associated water in the zeolite sample.

Figure 7 shows the adsorption-desorption isotherms of N_2 at liquid N_2 (−197.3°C) temperature and pore size distributions of zeolite and its heat-treated zeolites. The isotherm shape indicates that zeolite sample is dominately mesopores. However, no hysteresis loop can be seen for the 1000°C zeolite sample which suggests that no pores exist in this sample.

The specific surface areas calculated from the adsorption isotherms using BET theory show that specific surface area of the zeolite
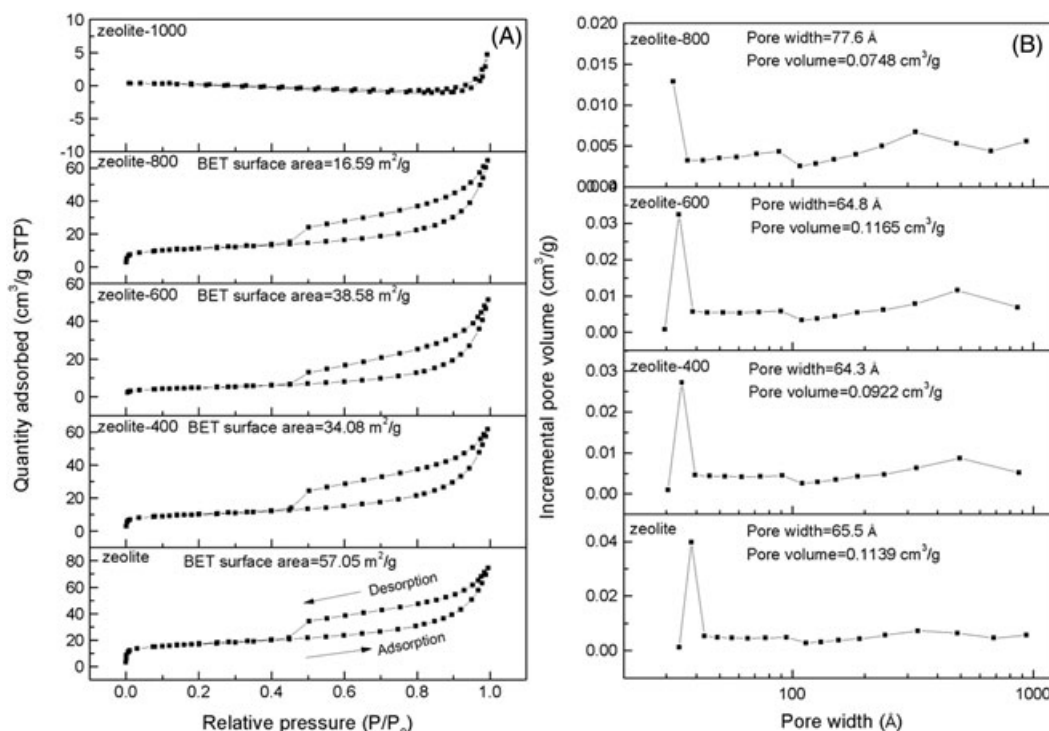
FIGURE 7 Adsorption-desorption isotherms of N_2 at liquid N_2 (−197.3°C) temperature and pore size distributions of zeolite and its heat-treated zeolites

sample is 57.05 m^2/g, and the number decreases to 16.59 m^2/g for the 800°C zeolite sample. The specific surface area of 1000°C zeolite sample cannot be obtained using BET theory because of the isotherm of 1000°C zeolite sample close to a horizontal line. The result indicates that heat treatment significantly decreases specific surface area of the zeolite samples. This is caused by the structure charge or collapse of zeolite samples after heat treament which has been proved by XRD and TG-DTG analyses.

The average pore widths and pore volumes from the desorption isotherms using BJH theroy show that the pore width and pore volume of zeolite sample are 65.5 Å and 0.1139 cm^3/g, respectively, and these numbers slightly change for the 400 and 600°C samples. For the 800°C sample, the pore width increases and the pore volume decreases as compared with the zeolite, 400°C and 600°C samples. This result suggests that heat treatment at relatively low calcination temperature has a negligible effect on the pore structure of zeolite samples. However, the pore structure of zeolite significantly changes or is even completely destroyed at relatively high calcination temperature.

The adsorption-desorption isotherms of N_2 at liquid N_2 temperature and pore size distributions of 2 M acid-treated zeolite and its heat-treated zeolite samples in Figure 8 exhibit the same trend as those for the zeolite samples in Figure 7. Comparison of Figures 7 and 8 shows that the specific surface area, pore width, and pore volume of acid-treated zeolite are apparently higher than those for the zeolite sample. In addtion, the specific surface area of 2 M acid-treated zeolite is 109.61 m^2/g which is much higher than that of the zeolite sample for 57.05 m^2/g. The results suggest that acid treatment can change the pore structure of zeolite sample and significantly increase the specific surface area of the sample, which is due to the creation of aluminum vacancies in the clinoptilolite framework. This result is

similar to the previous report.[11] In addition, the dissolution of Ca on the effect of nitric acid may be another factor leading to the increase of the specific surface area of zeolite sample which has been proved by the XPS analysis.

3.3 | Water vapor adsorption

Figure 9 shows the water vapor adsorptions of zeolite, acid-treated zeolites (A) and their heat-treated samples (B). It can be observed that water vapor adsorption on the zeolite sample is 49.3 mg/g and the adsorption significantly decreases after the sample treated with nitric acid solution. The 0.1 M acid-treated zeolite sample only adsorbs approximately half amount of water vapor as compared with the zeolite sample. The reduction of water vapor adsorptions on the zeolite samples is mainly due to increase of Si/Al ratio. In addition, water vapor adsorptions appear to slowly increase with the increase of acid concentration. It may be attributed to the increase of specific surface areas of the samples accompanied by the increase of nitric acid concentration, which has been proved by Burris et al.[17]

For the heat-treated zeolite and acid-treated zeolite samples, water vapor adsorptions on the samples continuously decrease with the increase of calcination temperature. It is interesting that the zeolite and acid-treated zeolite samples adsorb almost the same amount of water vapor at the same calcination temperature. The untreated zeolite and 2 M acid-treated zeolite sample adsorb 49.3 and 27.4 mg/g of water vapor, while their 1000°C-treated samples both adsorb 12.4 mg/g of water vapor. The reductions of water vapor adsorption can be caused by 2 reasons, ie, (1) heat treatment decreases the silanol groups and thus decreases the water vapor adsorption on the zeolite samples; (2) the decrease of specific surface area of the samples is
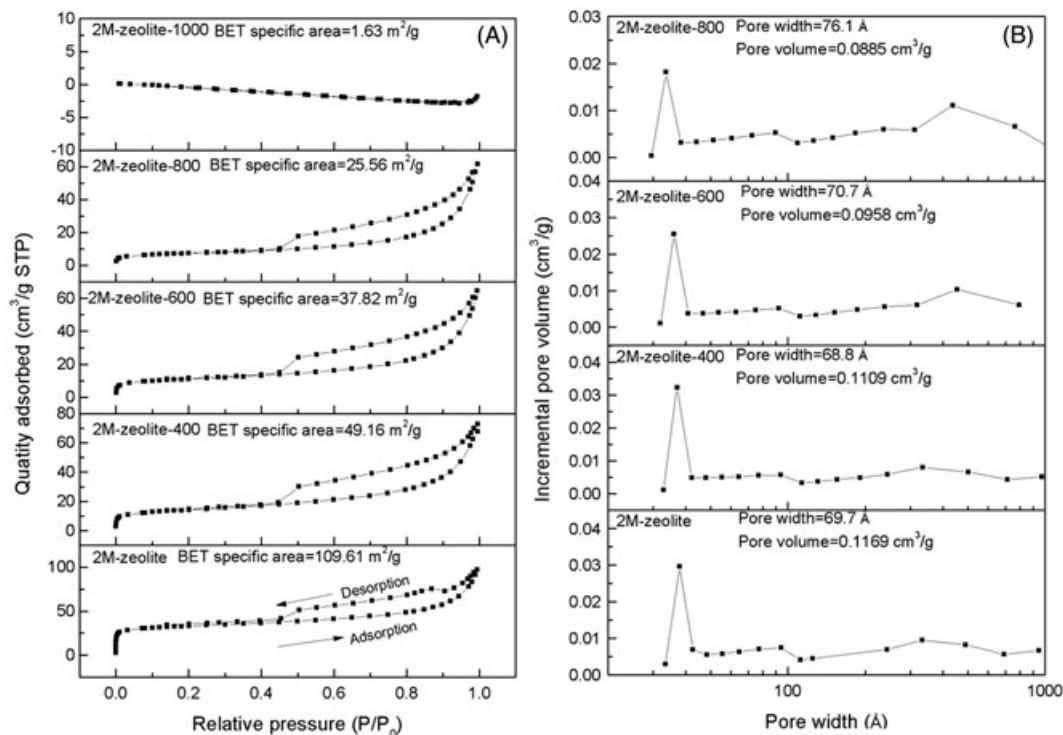
FIGURE 8 Adsorption-desorption isotherms of N_2 at liquid N_2 (−197.3°C) temperature and pore size distributions of 2 M acid-treated zeolite and its heat-treated zeolites
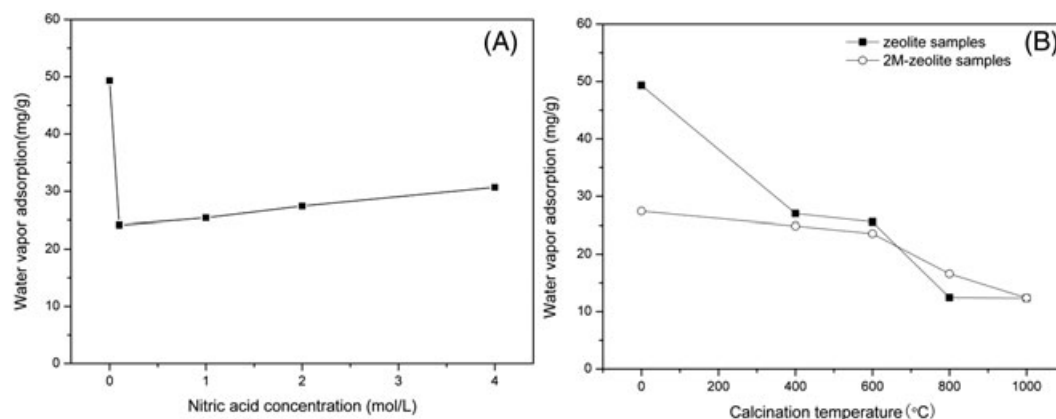

FIGURE 9 Water vapor adsorption of zeolite, acid-treated zeolites (A) and their heat-treated samples (B)

another major reason related to the reductions of water vapor adsorption on the zeolite samples.

4 | CONCLUSIONS

Natural zeolite was successively treated using nitric acid solutions with different concentrations and heat treated at different temperatures. The influences of acid and heat treatments on the structure and water vapor adsorption property of the samples were investigated.

It shows that the Si/Al ratio of the zeolite samples increases, the relative crystallinity for the aid-treated zeolite samples decreases with the increase of nitric acid concentrations. Acid treatment changes the pore structure of zeolite sample and increases the specific surface area of the sample. Heat treatment effectively removes water molecules

from the surface/structure of zeolite samples. The specific surface area of the zeolite sample increases from 57.05 to 109.61 m²/g after treated with 2 M nitric acid. Heat treatment significantly changes the structure of the zeolite samples, and the structure of clinoptilolite completely collapses under 1000°C. Heat treatment at relative low calcination temperature has a negligible effect on the pore structure of zeolite samples, while the pore structure of zeolite significantly changes or is even completely destroyed at relatively high calcination temperature.

Water vapor adsorptions on the acid-treated zeolite samples are lower than that for the zeolite sample. The 0.1 M acid-treated zeolite sample adsorbs approximately half amount of water vapor as compared with the zeolite sample. Water vapor adsorptions slowly increase with the increase of acid concentration which is attributed to the increase of specific surface areas of the samples accompanied

by the increase of acid concentration. Water vapor adsorptions on the zeolite samples decrease with the increase of calcination temperature. The untreated zeolite and 2 M-zeolite sample adsorb 49.3 and 27.4 mg/g of water vapor, while their 1000°C-treated samples both adsorb 12.4 mg/g of water vapor.

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REFERENCES

1. Wang S, Peng Y. Natural zeolites as effective adsorbents in water and wastewater treatment. *Chem Eng J*. 2010;156:11-24.

2. Jin X, Jiang MQ, Shan XQ, Pei ZG, Chen Z. Adsorption of methylene blue and orange II onto unmodified and surfactant-modified zeolite. *J Colloid Interface Sci*. 2008;328:243-247.

3. Cakicioglu-Ozkan F, Ulku S. The effect of HCl treatment on water vapor adsorption characteristics of clinoptilolite rich natural zeolite. *Micopor Mesopor Mat*. 2005;77:47-53.

4. Korkuna O, Leboda R, Skubiszewska-Zie ba J, Vrublevs ka T, Gun ko VM, Ryczkowski J. Structural and physicochemical properties of natural zeolites: clinoptilolite and mordenite. *Micropor. Mesopor. Mat.* 2006;87:243-254.

5. Yousef RI, El-Eswed B, Al-Muhtaseb AH. Adsorption characteristics of natural zeolites as solid adsorbents for phenol removal from aqueous solutions: kinetics, mechanism, and thermodynamics studies. *Chem Eng J*. 2011;171:1143-1149.

6. Liang HJ, Gao H, Kong QQ, Chen ZX. Adsorption equilibrium and kinetics of tetrahydrofuran + water solution. *J Chem Eng Data*. 2006;51:119-122.

7. Gómez-Hortigüela L, Pinar AB, Pérez-Pariente J, Sani T, Chebude Y, Díaz I. Ion-exchange in natural zeolite stilbite and significance in defluoridation ability. *Micropor. Mesopor. Mat.* 2014;193:93-102.

8. Jin X, Yu B, Chen Z, Arocena JM, Thring RW. Adsorption of Orange II dye in aqueous solution onto surfactant-coated zeolite: characterization, kinetic and thermodynamic studies. *J Colloid Interface Sci*. 2014;435:15-20.

9. Wang C, Li Y, Shi HS, Huang JF. Preparation and characterization of natural zeolite supported nano TiO_2 photocatalysts by a modified electrostatic self-assembly method. *Suf Interface Anal*. 2015;47:142-147.

10. Bonaccorsi L, Bruzzaniti P, Calabrese L, Proverbio E. Organosilanes functionalization of alumino-silica zeolites for water adsorption applications. *Micropor. Mesopor. Mat.* 2016;234:113-119.

11. Garcia-Basabe Y, Rodriguez-Iznaga I, De Menorval LC, et al. Step-wise dealumination of natural clinoptilolite: structural and physicochemical characterization. *Micropor Mesopor Mat*. 2010;135:187-196.

12. Kuwahara Y, Aoyama J, Miyakubo K, et al. TiO_2 photocatalyst for degradation of organic compounds in water and air supported on highly hydrophobic FAU zeolite: structural, sorptive,and photocatalytic studies. *J Catal*. 2012;285:223-234.

13. Wang X, Plackowski CA, Nguyen AV. X-ray photoelectron spectroscopic investigation into the surface effects of sulphuric acid treated natural zeolite. *Powder Technol*. 2016;295:27-34.

14. Duvarcı ÖÇ, Akdeniz Y, Özmıhçı F, Ülkü S, Balköse D, Çiftçioğlu M. Thermal behaviour of a zeolitic tuff. *Ceram Int*. 2007;33:795-801.

15. Saada A, Siffert B, Papirer E. Comparison of the hydrophilicity/hydrophobicity of illites and kaolinites. *J Colloid Interface Sci*. 1995;174:185-190.

16. Ates A. Role of modification of natural zeolite in removal of manganese from aqueous solutions. *Powder Technol*. 2014;264:86-95.

17. Burris LE, Juenger MCG. The effect of acid treatment on the reactivity of natural zeolites used as supplementary cementitious materials. *Cem Concr Res*. 2016;79:185-193.