

DOI 10.1007/s11595-014-1049-6

# Influence of Calcination on the Physical Characteristics and Nitrogen Removal Performance of Clinoptilolites

LIN Hai, JIN Xin, DONG Yingbo\*, HUO Hanxin, LIU Quanli

(School of Civil and Environmental Engineering, University of Science and Technology Beijing, Beijing 100083, China)

**Abstract:** The influences of roasting activation on the particle morphology, microscopic structure, and adsorption properties of natural clinoptilolites were investigated. The experimental results show that the optimal modified conditions include a calcination temperature at 400 °C, a roasting time of 0.5 h, and furnace cooling. The ammonia nitrogen removal rate from analog renewable water of the modified clinoptilolites reached 72% in the optimized conditions, which is 12% higher than that of natural ones. Scanning electron microscopy analysis showed that the surface morphology changed, the micro-hole size increased, and the surface became smoother and more uniform after calcination. The single-point total adsorption average pore width increased from 7.74 nm to 10.64 nm.

**Key words:** calcination; clinoptilolites; adsorption properties; morphology; reclaimed water treatment

## 1 Introduction

Zeolites, a non-metallic mineral resource, have been widely developed and utilized in the fields of environmental protection and environmental materials because of their excellent physical and chemical properties<sup>[1]</sup>. Zeolites exhibit a relatively open crystal structure, excellent adsorption performance, ion exchange, catalytic cracking, resistance to heat, acid, and radiation, and small density<sup>[2]</sup>. Nowadays, studies have focused on further improving the performance of zeolites and developing new environment friendly materials for industrial applications<sup>[3]</sup>.

Zeolites, which are generally called zeolitic minerals, are aluminum-silicate minerals with a cage structure and contain alkali or alkaline earth metal ions and water<sup>[4]</sup>. Zeolites are different from activated carbon adsorbents because they have great dispersion and electrostatic forces. Their cavities and skeleton contain cations and negative charges,

respectively. Moreover, zeolites contain a silicon (Si)-oxy tetrahedron or aluminum (Al)-oxy tetrahedron structure, and their space frame is full of cavities and channels. The volume of their crystal caves account for about 40%-50% of their total volume, and their apertures are mostly below 10 nm. Zeolites have a wide diameter and a large internal surface area (400 m<sup>2</sup>/g-800 m<sup>2</sup>/g)<sup>[3]</sup>, which are second only to activated carbon.

However, the cavities and channels of natural zeolites can be easily clogged by other impurities and they exhibit a bad mutual communication degree, which lowers their adsorption capacity. The exchangeable ions of zeolites are not unified and have a variety of combination strengths, thereby lowering their ion exchange capacity. Cations are capable of hydrolysis, which makes the adsorption of anionic pollutants in water by zeolites difficult. Several zeolites have strong hydrophilic properties because of their Al-oxy tetrahedron structure on the surface, which decreases the adsorption performance of organic compounds<sup>[4]</sup>. In summary, zeolites need to be modified to improve their processing properties.

Studies have shown that water in the internal cavities and pores of zeolites can be removed at a specific temperature without destroying the zeolites' structure. In this study, zeolites were modified by calcination methods, and the effects of calcination

©Wuhan University of Technology and SpringerVerlag Berlin Heidelberg 2014

(Received: Sep. 19, 2013; Accepted: Jan. 20, 2014)

LIN Hai (林海): Prof.; Ph D; E-mail:linhai@ces.ustb.edu.cn

\*Corresponding author: DONG Yingbo(董颖博): Assoc. Prof.; Ph D; E-mail:ybdong@ustb.edu.cn

Funded by the National Natural Science Foundation of China (No. 51174017)

conditions on their morphology, microstructure, and adsorption property were discussed in detail.

## 2 Experimental

### 2.1 Original samples and preparation

Clinoptilolites were obtained from Shenyang. Clinoptilolites that were composed of grains with a diameter of 0.106 mm - 0.15 mm were dried, crushed, sieved<sup>[5]</sup> and washed with water. The zeolites were then filtrated, dried at 110 °C for 2 to 3 h, and stored in a dry place. The original sample was named Y.

### 2.2 Instruments and reagents

The testing instruments include a box atmosphere furnace (Tianhong Lituo Technology Co., Ltd.), an intelligent coagulation test mixing apparatus (MY3000-6, Qianjiang MeiYu Instruments Co., Ltd.), a UV-2100 UV-Vis spectrophotometer (Unicol Instruments Co., Ltd.), a blast temperature drying oven (DHG-9053A, Shanghai Yiheng Scientific Instruments Co., Ltd.), and so on.

The reagents that were mainly used for ammonia adsorption experiments include an ammonium standard stock solution, a potassium sodium tartrate solution, and Nessler's reagent A liquid.

### 2.3 Experimental methods

#### 2.3.1 Adsorption performance test

The removal performance of ammonia nitrogen from analog renewable water was evaluated through static adsorption tests<sup>[6,7]</sup>. The test procedures are as follows: a measuring cylinder was used to add 200 ml analog renewable water into the 400 mL beaker, whose ammonia nitrogen concentration was 6 mg/L. The resulting solution was then mixed at 300 r/min for 3 h with 0.4 g of zeolites at room temperature. The ammonia nitrogen concentration of water was determined by the Nessler's reagent spectrophotometry, and the ammonia nitrogen removal efficiency and residual content were calculated with the absorbance values.

#### 2.3.2 Roasting temperature and time test

Several grams of the original sample Y were roasted at different temperatures and times in the box atmosphere furnace. The samples were calcined at a constant temperature after the heating stage and were naturally cooled in the furnace. The modified samples were subjected to the ammonia adsorption test, and the results were compared with the ammonia nitrogen removal efficiency of the original sample. Based on the test results, the optimal roasting temperature ( $T$ ) and time ( $H$ ) were obtained.

#### 2.3.3 Cooling method

The calcination experiments were conducted at the optimal roasting conditions  $T$  and  $H$ . After roasting, the cooling tests were conducted in three ways, namely, cooling inside the furnace, cooling outside the furnace, and cooling in the closed container. After treatment, the modified samples were subjected to the ammonia adsorption test, and the experimental results revealed the best cooling method.

### 2.4 Characterization

Static adsorption tests were conducted to determine the ammonia nitrogen removal capacity of zeolites before and after roasting. The differences in the single-point total adsorption average pore width between zeolites before and after roasting were measured using the specific surface area and a pore size analyzer (V-Sorb X4800)<sup>[8]</sup>. The surface morphology and structural changes were observed and analyzed by a scanning electron microscope (SEM; JSM-6510A). The changes in micro area composition characteristics were described using energy dispersive spectrometry (EDS)<sup>[9-11]</sup>.

## 3 Results and discussion

### 3.1 Effect of roasting temperature

Roasting operation can affect the surface morphology and adsorption performance of the sample at a particular temperature<sup>[12,13]</sup>. In the present study, six different roasting temperatures are tested as follows: 200, 300, 400, 500, 600, and 700 °C.

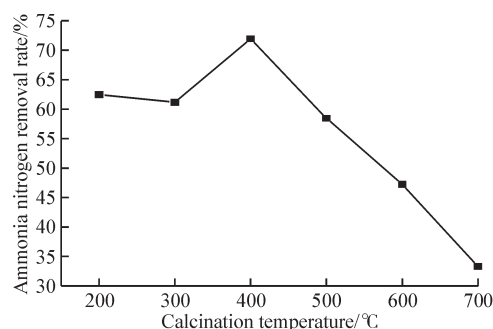


Fig.1 Effect of roasting temperature on ammonia nitrogen removal rate

Fig.1 shows the effect of roasting temperature on the ammonia nitrogen removal efficiency of zeolites. As presented in the chart, the adsorption performance of the zeolites increased and then decreased with increasing roasting temperature. The static adsorption test results on the analog renewable water show that the ammonia nitrogen removal rate of zeolites increased by 11.21% from 60.72% to 71.93% after roasting at 400 °C.

Roasting can remove part of the excess water and air in the internal cavities and pores of the zeolites<sup>[14]</sup>; thus, the specific surface area increases and the adsorption ability is improved. However, when the roasting temperature reaches 500 °C and above, the performance of the sample worsens compared with those of the original samples. Overheating can internally destroy the crystal lattice, reduce the micro-pore size, and change the structure of the zeolites. Thus, their exchange capacity decreases, surface convolution is deformed, and the pores become covered or clogged, thereby reducing the adsorption capacity of the material<sup>[14]</sup>. Therefore, the optimal roasting temperature is 400 °C.

### 3.2 Effect of roasting time

The length of roasting time greatly influences the adsorption performance of the as-prepared zeolites. A study has shown that modification methods can destroy the structure of zeolites if the roasting time is too long<sup>[15]</sup>. In the present study, the effects of different roasting times on the properties of zeolites were discussed.

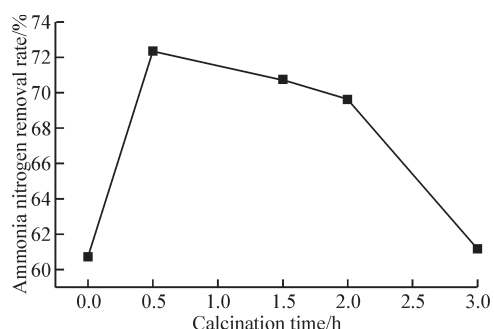


Fig. 2 Effect of calcination time on ammonia nitrogen removal rate

The effect of roasting time on the adsorption performance of the zeolites is shown in Fig.2. As shown in the chart, the roasting time significantly influences the performance of the zeolites. When the roasting time is further extended, the adsorption performance of the zeolites is reduced to a particular extent. After roasting for 0.5 h, the ammonia nitrogen removal rate of the zeolites significantly improved and increased from 60.72% to 72.36%. When the roasting was prolonged, the removal performance rate decreased and sharply changed, which resulted in a decrease to the original zeolite rate after 3 h. When the zeolites were exposed in a high temperature environment for a prolonged period of time, the micro hole and channel structure collapse, thereby decreasing their adsorption ability<sup>[14]</sup>. Therefore, the optimal roasting time is 0.5 h.

### 3.3 Effect of cooling methods

As shown in Fig.1, the adsorption performances of zeolites strongly fluctuate between 200 °C to 400 °C. The optimal roasting temperature is 400 °C. Thus, cooling to room temperature has a particular impact on the performance of the modified zeolites. In this study, the effects of cooling methods on the performance of the zeolites were discussed.

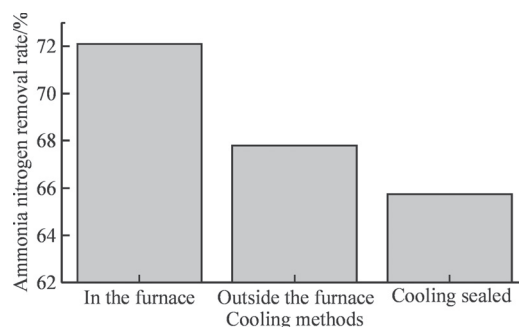


Fig.3 Effect of cooling methods on ammonia nitrogen removal rate

Fig.3 shows the changes in the ammonia nitrogen removal rate with different cooling methods. The results show that the adsorption performances of the samples prepared using three kinds of cooling methods were 72%, 67%, and 65%, respectively. The performance of the sample cooled in the furnace was higher than those of the other samples. When the sample was cooled outside the furnace, the opened micro-hole may close again because of moisture adsorption in air. When cooling was performed in a sealed container, the samples rapidly cooled because of the cold environment. Thus, the structure changed and the adsorption properties worsened. Cooling in the furnace can guarantee a high adsorption performance of the roasted samples. Thus, cooling in the furnace is the optimal cooling method.

### 3.4 Effect of roasting on zeolites' physical characteristics

#### 3.4.1 Changes of physical characteristics

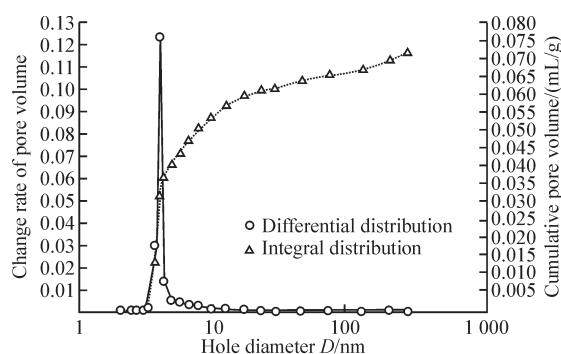


Fig.4 BJH-desorption-pore size distribution curves of original zeolites

The differences in the single-point total adsorption average pore width between zeolites before and after roasting were measured using the specific surface area and a pore size analyzer (V-Sorb X4800). The results show that the pore sizes of the zeolites were mainly distributed between 2 and 10 nm (BJH method) [8]. The BJH-desorption-pore size distribution curves of the zeolites before and after calcination are shown in Figs.4 and 5, respectively. The single-point total adsorption average pore width (BET method) increased from 7.74 nm to 10.64 nm after roasting.

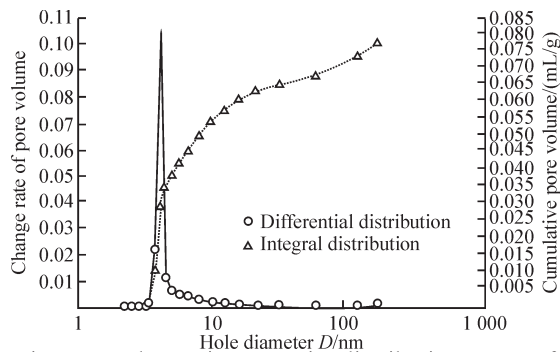


Fig.5 BJH-desorption-pore size distribution curves of modified zeolites

The surface morphology and structural changes were observed and analyzed by SEM (JSM-6510A). The obtained images are shown in Figs.6 and 7.

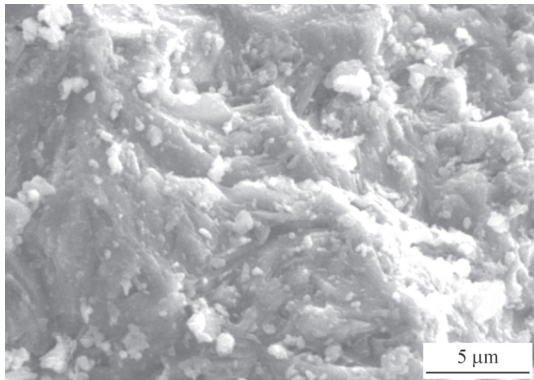


Fig.6 SEM image of original zeolites

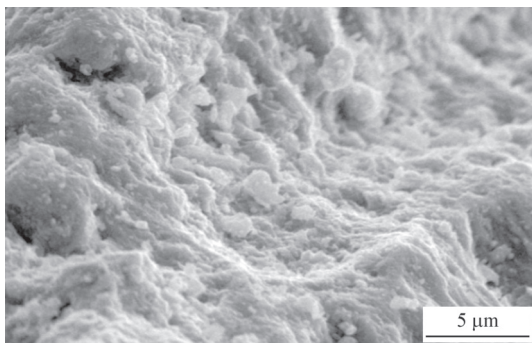


Fig.7 SEM image of modified zeolites

The images show the closely spaced grain structure of the original zeolites and the surface covered with a clutter of small particles, which are rough and uneven. The morphology of the modified samples were significantly different from those of the original samples. The surface morphology of the roasted samples appears flocculated, the lines are gentle and smooth, and the micro-pore sizes increased and were uniformly arranged. The change in the surface area of the zeolite particles, the expansion of the aperture and amount, and the pore size distribution can change the physical adsorption capacity of the material [16]. The test results indicate that the ammonia nitrogen removal performance of the modified samples was 72%, which is 12% higher than that of the original samples. Thus, roasting activation can change the physical characteristics and improve the adsorption performance of the zeolites.

### 3.4.2 Changes of micro area component

EDS was performed to describe and analyze the changes in the inorganic element composition and content of the zeolites before and after roasting. The EDS photographs are shown in Figs.8 and 9.

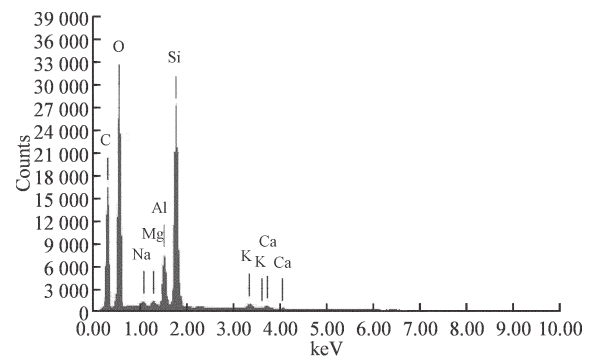


Fig.8 The EDS image of original zeolites

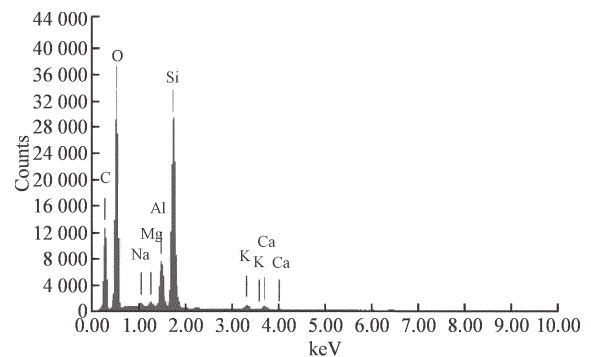


Fig.9 The EDS image of modified zeolites

Table 1 Mass fraction of the main elements

	O/%	Na/%	Mg/%	Al/%	Si/%	K/%	Ca/%
Original	38.81	0.24	0.30	3.66	17.46	1.28	0.92
Modified	42.56	0.32	0.36	3.84	19.20	1.33	1.04



As shown in the images, the main compositions of the modified zeolites are Si, Al, and O. The mass fraction of the main elements is listed in Table 1.

As shown in Table 1, roasting activation removes and burns water and impurities from the zeolites. The mass fraction of the main elements of the modified zeolites is higher than those of the original samples, and the Si/Al ratio has increased from 4.77 to 5. The results also show that modification does not essentially change the entire skeletal and pore structures of the zeolites. Therefore, calcination under appropriate conditions can enhance the adsorption performance without damaging the zeolites.

## 4 Conclusions

Calcination activation significantly influences the physical characteristics and adsorption properties of zeolites. The samples modified at a roasting temperature of 400 °C, a roasting time of 0.5 h, and cooling in the furnace have better adsorption performance. The ammonia nitrogen removal rate from analog renewable water of the modified zeolites reached 72%, which is nearly 12% higher than that of the original zeolites.

SEM and EDS analysis results show that calcination activation removes and burns water and impurities from zeolites without changing the entire skeletal and pore structure of the zeolites. After roasting, the surface morphology of the samples appears flocculated, the lines are gentle and smooth, and the micro-pore size increases and are uniformly arranged. The single-point total adsorption average pore width has increased from 7.74 nm to 10.64 nm. The change is significant. Therefore, roasting activation is an effective modification method.

### References

- [1] Liu TT, Zhang ST. Distribution, Utilization and Development Directions of the Zeolite Resources Nationwide[J]. *China Mining Magazine*, 2011, 20(4):41-45
- [2] Serrano DP, Garcia RA, Linares M. Influence of the Calcination Treatment on the Catalytic Properties of Hierarchical ZSM-5[J]. *Catalysis Today*, 2012, 179: 91-101
- [3] Liang K. Application of Nonmetallic Materials in Environmental Protection[J]. *Geology and Resources*, 2011, 20(12): 458-461
- [4] Ye MM, Luo XP. Application of Non-metallic Minerals Materials Used in Wastewater Treatment[J]. *China Non-Metallic Minerals Industry*, 2012, 2: 71-73
- [5] Jiang LY, Lin H, Song QW, et al. Study on Nitrogen and Phosphate Removal by Using Compound Zeolite[J]. *Industrial Safety and Environmental Protection*, 2011, 37(2):7-9
- [6] Elimbi A, Tchakoute HK, Njopwouo D. Effects of Calcination Temperature of Kaolinite Clays on the Properties of Geopolymer Cements[J]. *Construction and Building Materials*, 2011, 25: 2 805-2 812
- [7] Huo HX, Lin H, Dong YB, et al. Ammonia-nitrogen and Phosphates Sorption from Simulated Reclaimed Waters by Modified Clinoptilolite[J]. *Journal of Hazardous Materials*, 2012, 229:292-297
- [8] Zhao BB, Xu CC, Tang T, et al. Preparation of SiO<sub>2</sub> Microspheres by Two-step Catalytic Sol-gel Method[J]. *Journal of Inorganic Materials*, 2011, 10: 1 090-1 094
- [9] Yan CF, Grace JR, Jim C. Effects of Rapid Calcination on Properties of Calcium-based Sorbents[J]. *Fuel Processing Technology*, 2010, 91: 1 678-1 686
- [10] Costa ACFM, Diniz AP, Silva VJ. Influence of Calcination Temperature on the Morphology and Magnetic Properties of Ni-Zn Ferrite Applied as an Electromagnetic Energy Absorber[J]. *Journal of Alloys and Compounds*, 2009, 48: 563-565
- [11] Jang SH, Lim JH, Lee JS. Effect of Calcination Conditions on Microstructures and Jc of YBCO Films Fabricated by TFA-MOD Method[J]. *Physica. C.*, 2008, 179: 1 550-1 553
- [12] He DS, Xu XY, Qin F, et al. Experimental Study on Roasting of Stone Coal Vanadium Ore[J]. *Modern Mining*, 2011, 10(10): 15-17
- [13] Shen WQ, Qin S. Effect of Roast Conditions on the Adsorption Rate of Organic Matter in Municipal Domestic Sewage by Using Coal-Measures Kaoline[J]. *Industrial Water Treatment*, 2012, 32(2): 38-40
- [14] Gao ZZ, Gao XB, Li TP, et al. Research on Activation Modification of the Bentonite with High Temperature[J]. *Science Technology and Engineering*, 2010, 10(1): 766-768
- [15] Yang H, Han C, Li QW, et al. Effect of Baking Temperature on Photocatalytic Properties of Titanium Calcium[J]. *Journal of Functional Materials*, 2010, 11: 1 888-1 891
- [16] Chen JT, Ding SF, Bai CH, et al. Effect of Roasting on Pore Distribution and Adsorption Performance of Fly Ash[J]. *Journal of Heilongjiang Institute of Science & Technology*, 2011, 21(9): 357-359