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Research Article

Study on Thermal Insulation Zeolite by Coal Fly Ash

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This paper takes the coal fly ash as the material and makes zeolite with low thermal conductivity under a two-step synthesis for the purpose of thermal insulation. It studies main factors affecting zeolite such as the different concentration of NaOH, the solid-liquid ratio, the silica-alumina ratio, and the crystallization temperature. The optimal conditions were obtained that the NaOH concentration was 3 mol/L, the solid-liquid ratio was 10 : 1, the silica-alumina ratio was 2, and the crystallization temperature was 12°C. Zeolites have multiple pores and skeletal structures under SEM observation. The mean particle size was 2.78 um of concentrated distribution. The pore volume was 0.148 m^3/g measured by BET analysis, the specific surface was 118.6 m^2/g, and the thermal conductivity was 0.153 W/(m·K). Zeolite was proved to be a qualified insulation material which can be used in thermal insulation coating as a new material of energy conservation.

1. Introduction

Fly ash is the largest amount of industrial waste in the world. There is still a proportion of CFA that is discharged into ponds or landfills, which causes serious environmental problems and significant distress to local communities [1, 2]. Therefore, recycling CFA has important economic and environmental implications. The components of fly ash are some oxides derived from inorganic compounds, which remain after combustion of the coal. The main components of fly ash are SiO_2 and Al_2O_3, which are compositionally similar to natural zeolites [3]. Because of these similarities, more than 150 zeolites have been synthesized from CFA in the past few years [4].

Höller and Wirsching first reported how to create zeolites from fly ash in 1985 [5]. Then, many attempts have been made to derive zeolites from CFA using a one-stage hydrothermal method. The main obstacle to synthesizing zeolites from CFA is that, to speed up the reaction, temperatures in the range of 100–200°C must be applied in order to dissolve the silica and alumina [6, 7]. Over a decade later, Hollman et al. [8] pioneered the two-stage hydrothermal method, which reportedly yielded very pure zeolite. As a result, the two-stage hydrothermal method gained considerable interest in the following years [9]. The main disadvantages of the two-stage method are fairly long incubations times (~72 h) and the high temperatures (>500°C) required to prefuse the CFA with a solid alkali [10]. Studies in the literature suggest that it is possible to synthesize zeolites from natural materials and industrial residues, but all of these processes employ large quantities of sodium hydroxide (NaOH) and require high temperatures for performing the alkaline fusion [11]. Such processes have significant costs and are not always reproducible [12].

Zeolites were usually applied to environmental technology for ion exchange, soil improvement, and air purification [13, 14]. In addition, zeolites can be used in wastewater purification because they efficiently adsorb positively charged pollutants in wastewater, such as heavy metals [15–17]. But they have not been applied to thermal insulation. Zeolites have multiple pores filled with air of low thermal conductivity. There is a good reason to take them as a thermal insulation material.

In this study, a homogeneous-phase reactor was explored to reduce the temperatures and reaction times required to synthesize zeolites from deironed CFA. We selected qualified zeolites of low thermal conductivity by changing experimental conditions.

2. Materials and Methods

2.1. Raw Materials of Experiment. The main chemical components of CFA (sampled from Taiyuan First Thermal Power Plant) were SiO_2 (51.63%) and Al_2O_3 (35.00%). The main crystal phases of the ash included mullite ($3Al_2O_3{\cdot}2SiO_2$) and quartz (SiO_2) [18], the composition of which was very close to that of zeolite molecular sieves. These phases are very good raw materials for producing zeolite [5]. The raw material also includes 4.96% Fe_2O_3, which is not favorable for the preparation of zeolite molecular sieves. Thus, Fe_2O_3 must be removed from the materials prior to synthesizing zeolite.

2.2. Zeolites Synthesis. Based on the optimized experimental conditions determined earlier, the two-step synthesis of zeolites in this study was performed. In hot alkali solution, iron compound in the coal fly ash reacted with NaOH to produce $Fe(OH)_3$ sediment that reduced the alkali concentration and resulted in a reduction of crystallinity and whiteness [19]. Therefore, The CFA was pretreated several times using a permanent magnet (6000 Gs, Ningbo, China) to remove the iron in it. Then, CFA was added to reaction tanks in a JBJX-8 homogenous reactor (Jianbang, China) containing NaOH (analytical reagent, >96%) solutions. After the self-pressure alkali-leaching reaction, the supernatants in the reaction tanks were collected to determine the amount of silicon in the alkaline leaching solution by means of silicon molybdenum yellow spectrophotometry. The aluminum content in solution was also measured by means of test method for analysis of coal ash (GB/T 1547-2007). Sodium metaaluminate (analytical reagent, >99.5%) was added to adjust the molar ratio of SiO_2/Al_2O_3. The solution was then placed in the reactor again. The crystallized products were filtered and washed until pH 9-10. The products were dried at 100°C and stored overnight.

2.3. Analyses Methods. X-Ray Powder Diffractometer (D8 Advance, Bruker, Germany) was used to analyze the phase of the zeolites synthesized from CFA. The sample was pressed into a tablet using a mold with a diameter of 2 cm. Cu-Ka radiation was adopted. The accelerating voltage was 40 kV, the electrical current was 40 mA, and the scans ranged from 10° to 80° at a speed of 6°/min. The thermal conductivities of samples were measured by the Thermal Conductivity Tester (DRL-II, Xiangtan, China). After the samples had been gold-sprayed, the surface topography of the samples was observed by the Field Emission Scanning Electron Microscope (S-4800, Hitachi, Japan). The size and distribution of the sample were measured by the Particle Size Analyser (Eyetech/CIS, Ankersmid B.V., Holland). Based on N_2 adsorption, BET method was used to measure specific surface area of the samples by the Surface Area and Pore Size Analyzer (ASAP 2020M, Micromeritics, USA).

3. Results and Discussion

3.1. The Influence of Sodium Hydroxide Concentration on Zeolite. In the process of synthesis, NaOH concentration determined the water-sodium ratio and the equilibrium state. As a result, the reaction headed to the synthesis of some kind of zeolite. The product's state changed with NaOH concentration. This paper studied the influence of coal fly ash on zeolite with four NaOH concentrations (1.5, 2, 3, and 4 mol/L). Experimental conditions were as follows: solid-liquid ratio was 10 : 1 (quality of NaOH solution and coal fly ash); alkaline-leaching temperature was 100°C; alkaline-leaching time was 2 h; the silica-alumina ratio was 2; the crystallization temperature was 100°C; the crystallization time was 3 h. Synthesized zeolites were applied to XRD analysis. The results are shown in Figure 1.

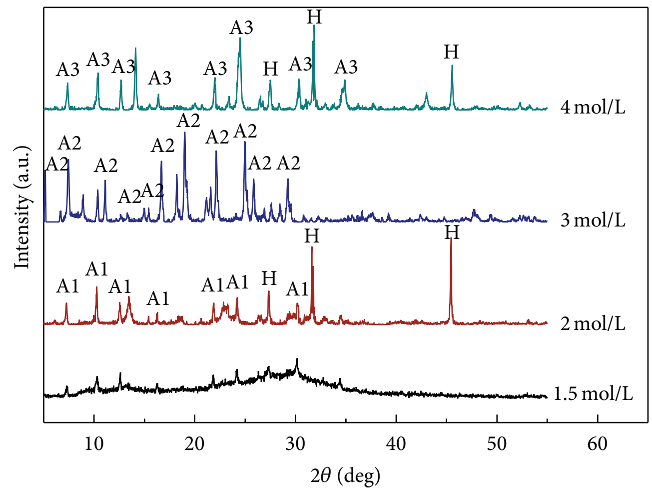

Figure 1: XRD pattern of samples synthesized with different concentration of sodium hydroxide. H-Halite, syn (PDF number 05-0628); A1-Zeolite A, [Na] (PDF number 39-0223), A2-Zeolite 4A (PDF number 43-0142); and A3-Zeolite A (PDF number 46-0564).

Qualitative phase analyses with the XRD data were performed. When NaOH concentration was 1.5 mol/L, the product was in the form of amorphous silica. When NaOH concentration was more than 2 mol/L, it became very pure NaA zeolite. Zeolite synthesis with hot water composed of two processes: first was the production of silica-alumina gel; then the gel turned into crystallized synthesized zeolites. When NaOH concentration was very low, silica and alumina could not react fully to produce the gel. As the concentration increased, silica and alumina could gradually react and reached the condition to synthesize zeolites [20].

Zeolites were different under various NaOH concentrations. Their structure and performance varied for each kind. Their thermal conductivities were tested, as was shown in Figure 2. Within the selected NaOH concentration, the thermal conductivity was less than 0.25 W/(m·K), capable of being thermal materials. The thermal conductivity was the smallest, 0.179 W/(m·K), when NaOH concentration was 3.0 mol/L. Thus, 3.0 mol/L was the optimal concentration for NaOH.

3.2. The Influence of the Solid-Liquid Ratio on Zeolite. We explored the quality ratio of NaOH solution to coal fly ash (adjusted solid-liquid ratio was 3 : 1, 7 : 1, 10 : 1, 13 : 1, and 15 : 1).

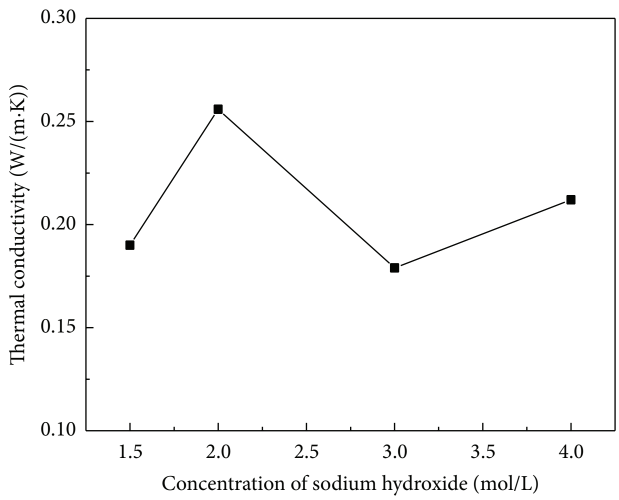

Figure 2: Thermal conductivity of samples synthesized with different concentration of sodium hydroxide.

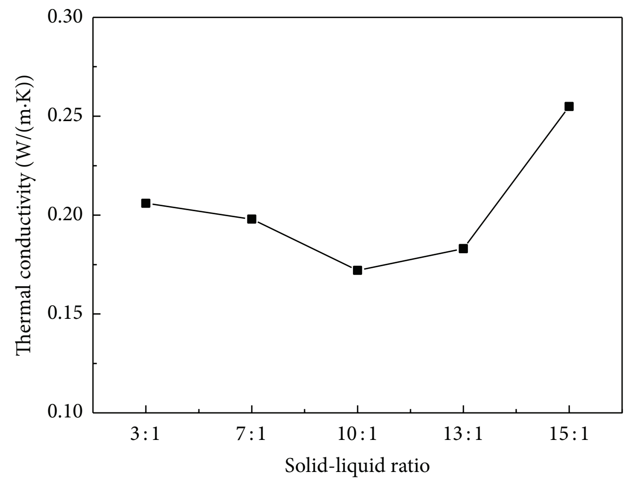

Figure 4: Thermal conductivity of samples synthesized with different solid-liquid ratio.

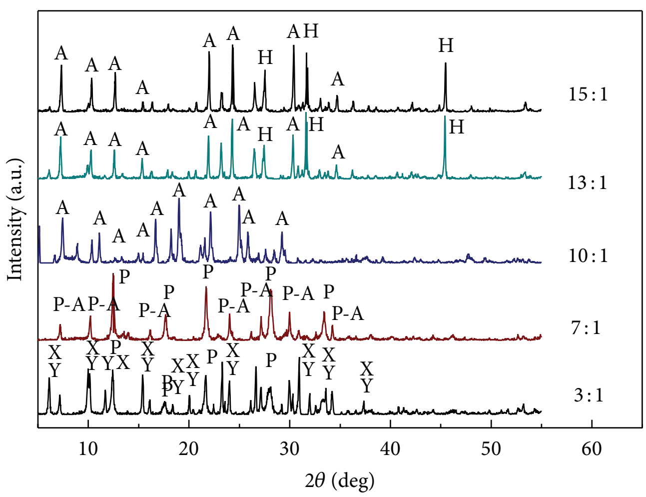

Figure 3: XRD pattern of samples synthesized with different solid-liquid ratio. Y-Faujasite Na, (PDF number 12-0246), X-Zeolite X (PDF number 41-0118), P-Zeolite P, [Na] (PDF number 44-0052), P-A-Zeolite P-A (PDF number 38-0323), A-Zeolite 4A (PDF number 43-0142), and H-Halite, syn (PDF number 05-0628).

Experimental conditions were as follows: the concentration of NaOH is 3 mol/L; alkaline-leaching temperature was 100°C; alkaline-leaching time was 2 h; solid-liquid ratio was 10 : 1; silica-alumina ratio was 2.5; crystallization time was 3 h. Synthesized zeolites were applied to XRD analysis. The results were shown in Figure 3.

When the solid-liquid ratio was 3 : 1, the product concentration in coal fly ash solution was high. The crystallized speed was fast but the reaction was uneven. This brought about many mixed crystals, including Y-type zeolite, Faujasite Na (PDF number 12-0246), X-type zeolite (PDF number 41-0118), and P-type zeolite (PDF number 44-0052). As solid-liquid ratio increased, reactants were able to be dissolved with more silica and alumina. When solid-liquid ratio was 7 : 1, characteristic peak of NaA zeolite showed up with synthesized products of high crystallinity such as P-A-Zeolite P-A (PDF number 38-0323), A-Zeolite 4A (PDF number 43-0142), and H-Halite, syn (PDF number 05-0628). Zeolites were very pure when the ratio was 10 : 1.

To study the thermal insulation property, we tested the thermal conductivity of products with different solid-liquid ratios. The results were shown in Figure 4. When solid-liquid ratio was less than 15 : 1, the thermal conductivities were smaller than 0.25 W/(m·K), which fitted the standard of thermal insulation material. When the ratio was 10 : 1, the thermal conductivity was the smallest, 0.172 W/(m·K), which was the optimal ratio.

3.3. The Influence of the Silica-Alumina Ratio on Zeolite. The properties of synthesized zeolitic materials from coal fly ash are also affected by the silica-alumina ratio. The series experiments with different silica-alumina ratio were studied by adjusting the dose of sodium metaaluminate. Other experiment conditions were as follows: the concentration of NaOH is 3 mol/L; alkaline-leaching temperature was 100°C; alkaline-leaching time was 2 h; solid-liquid ratio was 10 : 1; crystallization time was 3 h; crystallization temperature was 100°C. Figure 5 shows the XRD pattern of samples synthesized with different silica-alumina ratio. Tanaka et al. [21] thought alumina affected the solubility of silica in the silica-alumina gel. They presented a negative correlation. Therefore, an adjusted silica-alumnia ratio was the key to produce qualified zeolite.

When silica-alumina ratio was 1.5, the synthesized product was mainly in the form of NaA-type zeolite. When it was adjusted to 2, 2.5, and 3, there were NaX-type zeolites and NaA-type. And these two types of zeolites are all with special pore and skeletal structure. After the test of thermal conductivity of synthesized zeolites with different silica-alumina ratio (as was shown in Figure 6), it was found out that the thermal conductivity was the smallest at 0.181 W/(m·K) when silica-alumina ratio was 2. Given soluble result of silica

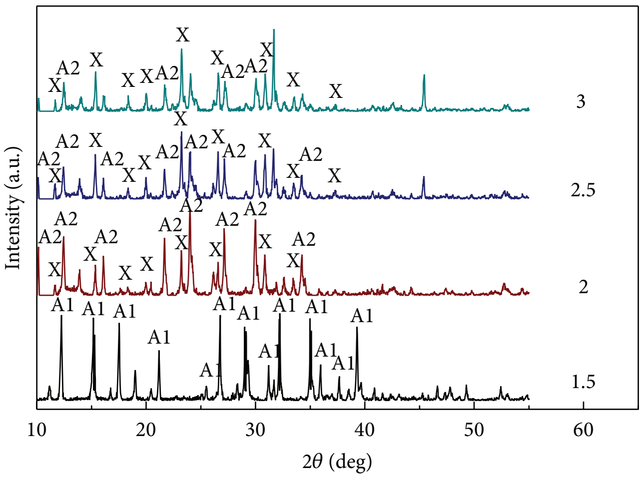

FIGURE 5: XRD pattern of samples synthesized with different silica-alumina ratio. A1-Zeolite A [Na] (PDF number 39-0222), A2-Zeolite 4A (PDF number 43-0142), and X-Zeolite (PDF number 41-0118).

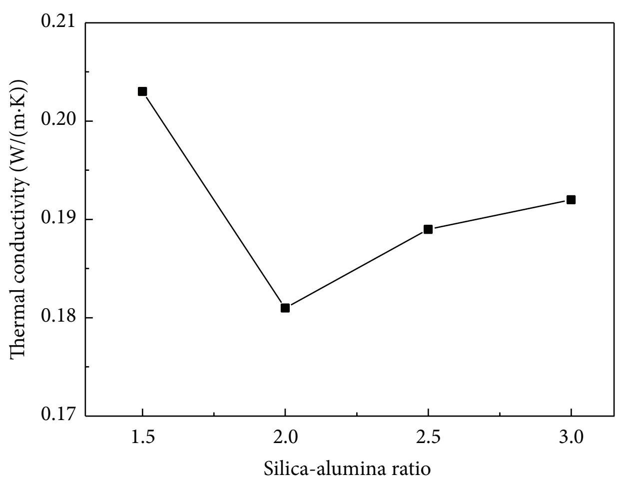

FIGURE 6: Thermal conductivity of samples synthesized with different silica-alumina ratio.

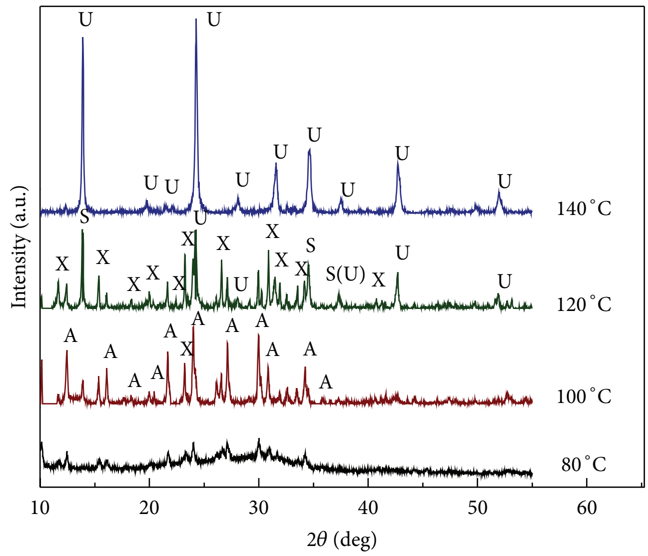

FIGURE 7: XRD pattern of samples synthesized with different crystallization temperature. A-Zeolite 4A (PDF number 43-0142), S-Sodalite (PDF number 41-0118), X-Zeolite (PDF number 41-0118), and U-Unnamed (PDF number 38-0221).

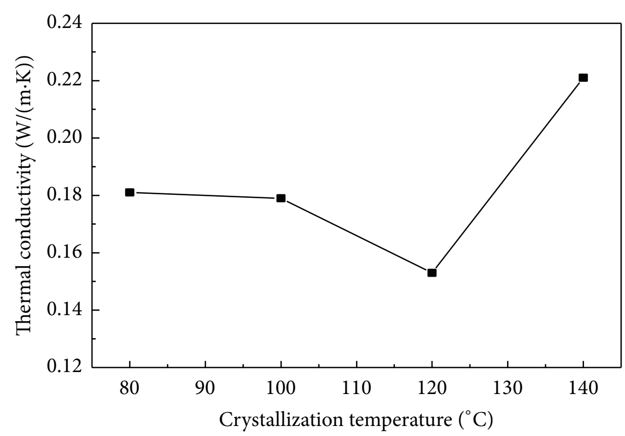

FIGURE 8: Thermal conductivity of samples synthesized with different crystallization temperature.

and alumina in the coal fly ash solution as well as the property of the product, the ratio was set as 2 in latter experiments.

3.4. The Influence of Crystallization Temperature on Zeolite. Crystallization temperature was important in the process of zeolite crystallization. Experiment conditions were as follows: the concentration of NaOH is 3 mol/L; alkaline-leaching temperature was 100°C; alkaline-leaching time was 2 h; solid-liquid ratio was 10 : 1; silica-alumina ratio was 2.5; crystallization time was 3 h; adjusted crystallization temperature was 80, 100, 120, and 140°C. Figure 7 shows the variation of samples synthesized with different crystallization temperatures. When the temperature was 80°C, the product was mainly in the form of amorphous silica and there was no zeolite. When it reached 100°C, the synthesized product was mainly in the form of NaA-type zeolite. When it reached 120°C, NaX-type zeolite with multiple pores was synthesized. When the temperature was 140°C, there was an unnamed zeolite with high crystallinity and purity. There was almost no characteristic peak of mixed crystal.

According to thermal conductivity test (as was shown in Figure 8), when the crystallization temperature was 140°C, the thermal conductivity was the biggest at 0.221 W/(m·K). When it was 120°C, the thermal conductivity was the smallest at 0.153 W/(m·K). Thus, crystallization temperature did have a great influence on the crystallinity of samples. If the crystallization temperature was too low, the reaction was hard to continue. As the temperature increased, the solubility of silica-alumina gel rose up. So did the number of crystal nucleus. The crystallization speed would be accelerated and the crystal was getting bigger, resulting in an increase of the thermal conductivity [22]. Therefore, the optimal crystallization temperature was 120°C.

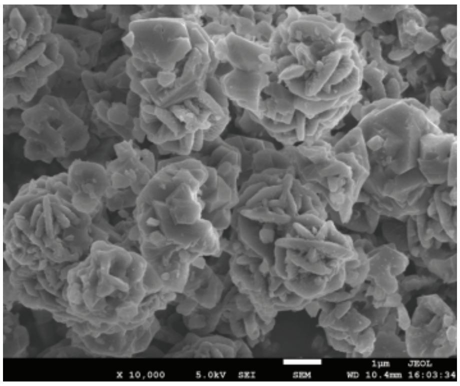

Figure 9: SEM observation for zeolite synthesized with different crystallization temperatures.

Therefore, with the coal fly ash as the material, the optimal condition for making zeolite with low thermal conductivity under a two-step synthesis was as follows: the concentration of NaOH was 3 mol/L with a solid-liquid ratio of 10 : 1, the silica-alumina ratio of 2, and the crystallization temperature of 120°C.

3.5. The Appearance Performance Analysis of Synthesized Zeolites. Make the zeolites under the optimal condition and observe their appearances by SEM observation. They had multiple pores and skeletal structures as were shown in Figure 9. According to laser particle size analyzer, mean particle size of zeolite was 2.78 um of concentrated distribution. About 70% of particles were from 700 nm to 2 um. By BET analysis, the pore volume of zeolite was 0.148 m^3/g, the specific surface is 118.6 m^2/g, and the thermal conductivity is 0.153 W/(m·K). Zeolite is proved to be a qualified insulation material, which can be used in thermal insulation coating as a new material of energy conservation.

4. Conclusion

This paper concludes the optimal condition for making zeolite with low thermal conductivity coefficient by deironing coal fly ash under two-step synthesis. The concentration of NaOH is 3 mol/L with a solid-liquid ratio of 10 : 1, silica-alumina ratio of 2, and crystallization temperature of 120°C. Zeolites have multiple pores and skeletal structures. The mean particle size is 2.78 um, the pore volume is 0.148 m^3/g, the specific surface is 118.6 m^2/g, and the thermal conductivity is 0.153 W/(m·K). Zeolite is proved to be a qualified insulation material which can be used in thermal insulation coating as a new material of energy conservation.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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References

[1] M. Ahmaruzzaman, "A review on the utilization of fly ash," *Progress in Energy and Combustion Science*, vol. 36, no. 3, pp. 327–363, 2010.

[2] P. Brown, T. Jones, and K. Bérubé, "The internal microstructure and fibrous mineralogy of fly ash from coal-burning power stations," *Environmental Pollution*, vol. 159, no. 12, pp. 3324–3333, 2011.

[3] J. Kugbe, N. Matsue, and T. Henmi, "Synthesis of Linde type A zeolite-goethite nanocomposite as an adsorbent for cationic and anionic pollutants," *Journal of Hazardous Materials*, vol. 164, no. 2-3, pp. 929–935, 2009.

[4] K. S. Hui, C. Y. H. Chao, and S. C. Kot, "Removal of mixed heavy metal ions in wastewater by zeolite 4A and residual products from recycled coal fly ash," *Journal of Hazardous Materials*, vol. 127, no. 1–3, pp. 89–101, 2005.

[5] H. Höller and U. Wirsching, "Zeolites formation from fly ash," *Fortschr Mineral*, vol. 63, pp. 21–43, 1985.

[6] R. S. Blissett and N. A. Rowson, "A review of the multi-component utilisation of coal fly ash," *Fuel*, vol. 97, pp. 1–23, 2012.

[7] C.-F. Wang, J.-S. Li, L.-J. Wang, and X.-Y. Sun, "Influence of NaOH concentrations on synthesis of pure-form zeolite A from fly ash using two-stage method," *Journal of Hazardous Materials*, vol. 155, no. 1-2, pp. 58–64, 2008.

[8] G. G. Hollman, G. Steenbruggen, and M. Janssen-Jurkovičová, "Two-step process for the synthesis of zeolites from coal fly ash," *Fuel*, vol. 78, no. 10, pp. 1225–1230, 1999.

[9] H. Tanaka and A. Fujii, "Effect of stirring on the dissolution of coal fly ash and synthesis of pure-form Na-A and -X zeolites by two-step process," *Advanced Powder Technology*, vol. 20, no. 5, pp. 473–479, 2009.

[10] N. Shigemoto, S. Sugiyama, H. Hayashi, and K. Miyaura, "Characterization of Na-X, Na-A, and coal fly ash zeolites and their amorphous precursors by IR, MAS NMR and XPS," *Journal of Materials Science*, vol. 30, no. 22, pp. 5777–5783, 1995.

[11] Y. Yaping, Z. Xiaoqiang, Q. Weilan, and W. Mingwen, "Synthesis of pure zeolites from supersaturated silicon and aluminum alkali extracts from fused coal fly ash," *Fuel*, vol. 87, no. 10-11, pp. 1880–1886, 2008.

[12] L. Bieseki, F. G. Penha, and S. B. C. Pergher, "Zeolite a synthesis employing a brazilian coal ash as the silicon and aluminum source and its applications in adsorption and pigment formulation," *Materials Research*, vol. 16, no. 1, pp. 38–43, 2013.

[13] X. Querol, N. Moreno, J. C. Umaña et al., "Synthesis of zeolites from coal fly ash: an overview," *International Journal of Coal Geology*, vol. 50, no. 1–4, pp. 413–423, 2002.

[14] R. Juan, S. Hernández, X. Querol, J. M. Andrés, and N. Moreno, "Zeolitic material synthesised from fly ash: use as cationic exchanger," *Journal of Chemical Technology and Biotechnology*, vol. 77, no. 3, pp. 299–304, 2002.

[15] S. Babel and T. A. Kurniawan, "Low-cost adsorbents for heavy metals uptake from contaminated water: a review," *Journal of Hazardous Materials*, vol. 97, no. 1–3, pp. 219–243, 2003.

[16] V. K. Jha, M. Matsuda, and M. Miyake, "Sorption properties of the activated carbon-zeolite composite prepared from coal fly ash for Ni^{2+}, Cu^{2+}, Cd^{2+} and Pb^{2+}," *Journal of Hazardous Materials*, vol. 160, no. 1, pp. 148–153, 2008.

[17] R. Apiratikul and P. Pavasant, "Sorption of Cu^{2+}, Cd^{2+}, and Pb^{2+} using modified zeolite from coal fly ash," *Chemical Engineering Journal*, vol. 144, no. 2, pp. 245–258, 2008.

[18] X. J. Chen, *Research on the modified methods of fly ash for ammonia-nitrogen wastewater treatment [M.S. thesis]*, Shanxi University, 2011 (Chinese).

[19] A. Molina and C. Poole, "A comparative study using two methods to produce zeolites from fly ash," *Minerals Engineering*, vol. 17, no. 2, pp. 167–173, 2004.

[20] R. R. Xu, W. Q. Pang, and J. H. Yu, *Chemistry—Zeolites and Porous Materials*, Science press, Beijing, China, 2004 (Chinese).

[21] H. Tanaka, H. Eguchi, S. Fujimoto, and R. Hino, "Two-step process for synthesis of a single phase Na-A zeolite from coal fly ash by dialysis," *Fuel*, vol. 85, no. 10-11, pp. 1329–1334, 2006.

[22] Z. H. Wei, L. S. Jin, and W. X. Cao, "The optimum transport process of synthesis of 4(A)-zeolite with coal fly ash," *China Resources Comprehensive Utilization*, vol. 25, pp. 9–12, 2007 (Chinese).