

Light Metals 2015

ALUMINA AND BAUXITE

**Alternative Raw Materials
and Processes, Industrial
Trends**

SESSION CHAIR

Linus M. Perander

Outotec GmbH

Oberursel, Germany

PREPARATION OF ZEOLITE 4A BY USING HIGH-ALUMINA COAL FLY ASH

Yan Shaoyong^{1,2}, Zhang Ting'an¹, Cheng Chu¹, Zhang Xianqi^{1,2}, Sun Junmin², Lv Guozhi¹, Yang Hui bin^{1,2}

ZHANG Ting-an, Professor, E-mail: zta2000@163.net, Shenyang, Liaoning 110819, China

SUN Junmin, Senior Engineer, E-mail: sunjmdt@163.com, Huhehaota, Neimenggu 010000, China

1. Key Laboratory of Ecological Utilization of Multi-metal Intergrown Ores of Ministry of Education, Northeastern University,

Shenyang 110819, China

2. High Alumina Coal R&D Center of Datang International Power Generation CO., Ltd.

Keywords: Zeolite 4A, High-alumina Coal Fly Ash, hydro-thermal method, specific surface area

Abstract

With the rapid development of the electric power industry in China, the amount of fly ash discharged is growing day by day, which brings great harm to the production industry and people's living conditions. In this article, hydro-thermal method and alkali fusion-hydro-thermal method have been used to prepare 4A zeolite from coal fly ash. The results indicate that the optimum conditions (calcination temperature 850 °C, ratio of silicon to aluminum in raw material 0.8, alkalinity of NaOH 2.5mol/L, the aging time 6h, crystal temperature 90 °C and crystal time 24h), the specific surface area of the prepared zeolite is 605.6m²/g. The synthesized 4A zeolite has a uniform particle size with a narrow distribution. Its shape is cube and in rules, and all its properties are close to 4A zeolite purchased in the market.

1. Introduction

Currently, China is the largest country of fly ash emissions in the world as coal is the main source of energy. Although in recent years, hydro, wind, nuclear power and other new type of power generation technology have got rapid progress, China's coal-fired power generation still occupies a major position. At present, fly ash has been applied in the construction, roads and many other fields, which belong to the type of extensive utilization with characteristics of low value addition and technical.[1-3]. Al₂O₃ content in the fly ash is usually 30~50% in most areas in China [4]. which equivalent to low grade bauxite in China. The total Al₂O₃ content and SiO₂ content can reach up to 80%. Therefore, this paper puts forward to using this kind of high alumina fly ash as material to prepare 4A zeolite [5-8].

4A zeolite has a unique shape-selective adsorption selectivity, choice of shape-selective

catalysis, special ion exchange selectivity and strong adsorption ability. 4A zeolite is widely used in areas such as catalysis, sewage treatment and detergent additives [9]. In addition, 4A zeolite has a strong calcium ions exchange capacity and has the advantages of non-toxic, no pollution and good stability. 4A zeolite has an irreplaceable role in the replacement of sodium tripolyphosphate as detergent additives in solving the pollution of the environment [10, 11].

This paper studied the preparation of 4A zeolite from high alumina fly ash by direct hydrothermal synthesis method and alkali fusion-hydrothermal synthesis method.

2. Experimental

Raw materials content for experiment is shown in Table 1. The material is come from China Inner Mongolia Datang International Power Generation Company, its loss on ignition is 2.89%.

Table 1 Chemical composition of coal fly ash

Com.	MgO	Al ₂ O ₃	SiO ₂	CaO	Fe	L.O.I.
Con.(%)	0.48	42.95	41.90	3.66	4.00	8.2

The SEM analysis of fly ash is shown in Figure 1 and Figure 2. XRD pattern of fly ash is shown in Figure 3. Particle size distribution of fly ash is shown in Figure 4. The morphology of fly ash is mainly scattered vitreous particles and spherical particles with smooth surface. There are some irregular shapes, porous micro carbon particles. Particle size distribution between 0.5µm~50µm. Beads of fly ash particles are mostly vitreous. The composition is mainly amorphous SiO₂ and Al₂O₃. XRD pattern shows mineral phases in the fly ash are mullite, quartz and corundum, amorphous phase also be identified.

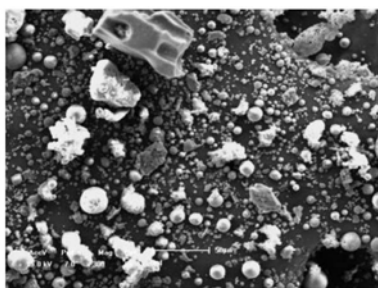


Figure.1 SEM Photograph of coal fly ash

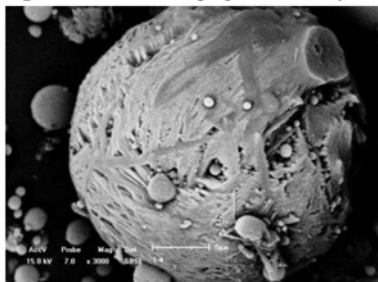


Figure.2 SEM Photograph of coal fly ash particle

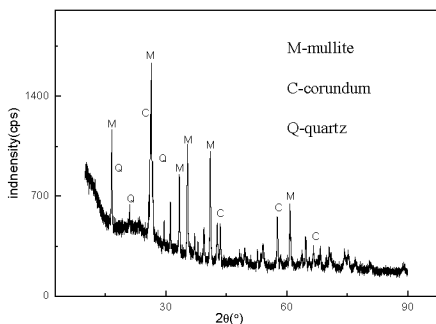


Figure. 3 XRD patterns of coal fly ash

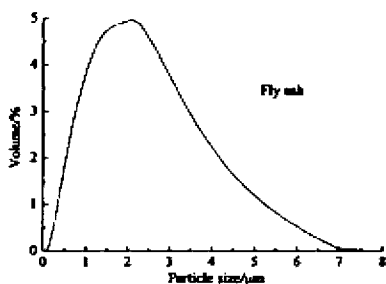


Figure. 4 Particle size distribution of coal fly ash

Instruments used in this experimental include muffle furnace, homogeneous reactor, separator, German Bruker D8 automatic rotating target X-ray diffractometer using Cu-K α radiation and Ni filter with the condition of Tube voltage of 40kV, a tube current 80mA, scanning range 10~90°, scanning speed of 8° / min, step size of 0.01°.

To measure the specific surface area and pore

volume, the BET specific surface area analyzer ASAP2020 type is used by nitrogen adsorption at -196 °C. BET specific surface area analyzer ASAP2020 type using nitrogen adsorption specific surface area of the product were measured and the pore volume at -196 °C.

3. Study of prepared 4A zeolite by direct hydrothermal synthesis

In order to synthesize zeolite from fly ash directly (50g fly ash with liquid-solid ratio 5:1), the NaOH solution was used as activator to decompose the mullite in fly ash, at the same time, NaAlO₂ was added in the solution to adjust ratio of alumina-silica (molar) close to 1. The effect of concentration of NaOH on synthesized products was investigated. After aging at room temperature for 6h, crystallized at 90°C for 12h, the products was washed with distilled water and dried at 90°C for 8h. XRD patterns of the synthesized products shown in Figure 5.

As Figure 5 shows, when the NaOH concentration is 2mol/L, 3mol/L and 4mol/L, the reaction product is mullite and aluminum silicate hydrate. It is noted that, with increasing of NaOH, peak intensity of hydrated aluminum silicate increase, meanwhile, peak of mullite decrease, however, zeolite phase was not generated. It's indicating that the higher concentration of NaOH promoted mullite transformed to hydrated aluminum silicate.

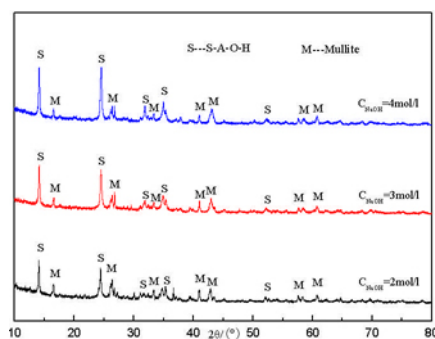


Figure. 5 XRD patterns of samples by different alkali concentration

4. Study of prepared 4A zeolite by alkali fusion – hydrothermal synthesis

10g fly ash and 12g NaOH was calcined in a muffle furnace at 850°C for 2h, and ground into powder after cooling. Then mixed with Distilled water

with the liquid-solid ratio 5:1, NaOH and NaAlO₂ was added to adjust the silica-alumina ratio (molar) of 0.8 and 2-4 mol/L NaOH, then aging for 6h, and crystallized at 90°C for 24h, washed with distilled water and dried at 80 °C for 6h. The mineralogy of products was characterized by X-ray diffraction as shown in Figure 6.

As Figure 6 shows, when the concentration of NaOH is low, the dissolution rate of alumina-containing components is low, and the peak intensity of generated zeolite is low relatively. With increasing concentration of NaOH, the dissolution of the active alumina-containing components increases, the supersaturated solution is to increase the soluble alumina species, facilitate the creation of metastable 4A zeolite, therefore, 4A zeolite diffraction peak intensity increased gradually, with a max at a NaOH concentration of 2.5mol/L.

With further increase in the concentration of NaOH, 4A zeolite diffraction peak intensity gradually weakened, and the sodalite phase was generated, which indicates that the high concentration of NaOH can promote the transformation of 4A zeolite to sodalite. This is mainly due to the high concentration of alkali lead to low polymerization of the silicate ions in the solution, and resulting in the generation of sodalite, which is more stable in the solution [13]. Therefore, fly ash 4A zeolite synthesis, NaOH concentration should be controlled at 2.5mol/L.

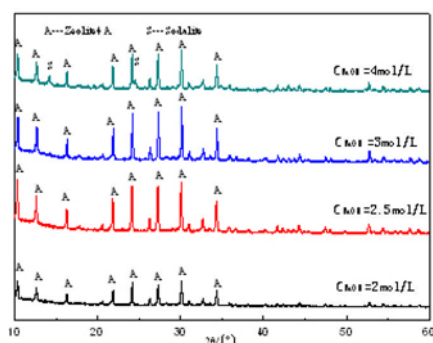


Figure. 6 XRD patterns of samples by different alkali concentration

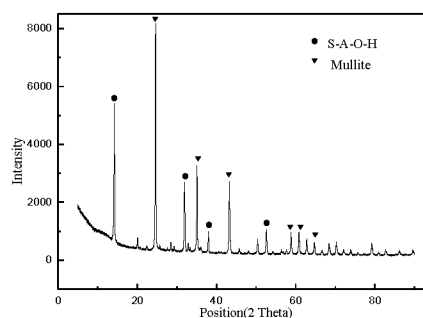
5. Characterization of the product

XRD pattern analysis

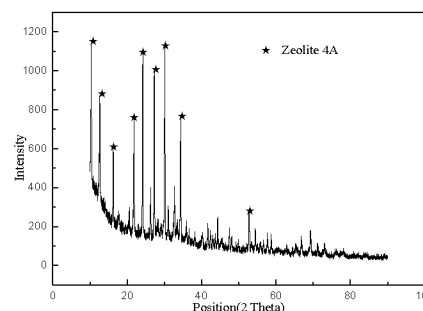
Figure 7 (a) is silica to alumina ratio 1, NaOH

concentration of 2mol/L under the direct synthesis of the XRD pattern of sample. Figure 7 (b) is temperature 850°C for 2h, silica-alumina ratio of 0.8, NaOH concentration of 2.5mol/L at the alkali fusion-hydrothermal synthesis of 4A zeolite XRD patterns of the samples.

As shown in the Figure 7(a), the reaction product is mullite phase and hydrated aluminum silicate phase for 4A zeolite synthesis experiments and there is no zeolite phase. However, in alkali fusion-4A zeolite hydrothermal synthesis experiments, the reaction products is only 4A zeolite phase. Therefore, under conditions of low concentration of alkali, alkali melt-hydrothermal synthesis method is easy for synthetic 4A zeolite.



(a) direct synthesis of 4A zeolite



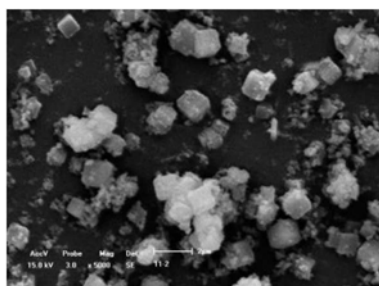
(b) alkali fusion-hydrothermal synthesis of 4A zeolite

Figure. 7 XRD patterns of products synthesized by different method

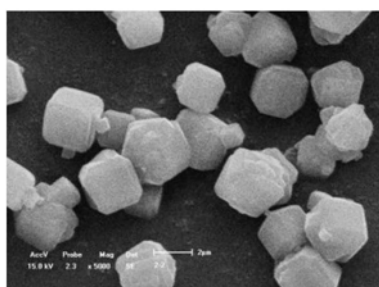
Morphology of 4A zeolite

Figure 8 shows the morphology difference between the synthesized 4A (the same conditions as Figure 7 (b)) zeolite and the commercially available zeolite sample. As can be seen from the images, the synthesized 4A zeolite and the sample 4A zeolite is similar. But the synthesized 4A zeolite contains small amounts of impurity with uneven and smaller particle size. Which mainly because the ash contains more

impurities than the 4A zeolite sample. In the laboratory synthesis process, the alkalinity greater depolymerization and the formation of silica-alumina gel more nuclei, so that the crystal growth rate is higher than the nucleation rate, thereby reducing the particle size of crystals.



(a) synthesized 4A zeolite by alkali fusion-hydrothermal



(b) 4A zeolite sample

Figure. 8 SEM images of 4A zeolite

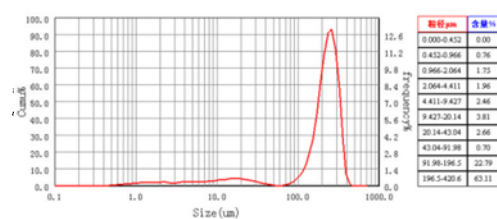
Particle size analysis

For the samples prepared under the following conditions: calcination temperature of 850°C for 2h; Si/Al ratio is 0.8, and a concentration of NaOH of 2.5mol/L, we measured the particle size distribution patterns of alkali fusion-hydrothermal synthesized 4A samples shows in Figure 9(a), and Figure 9(b) is the particle size distribution patterns of 4A zeolite sample. As can be seen from Figure 9, particle size of synthesized 4A zeolite are mainly distributed between 240.4~534.7μm. In contrast, the 4A zeolite sample has a relatively narrow particle size distribution between 247.8~347.7μm. In addition, the prepared 4A zeolite has a small portion of particle size distributed around 10μm.

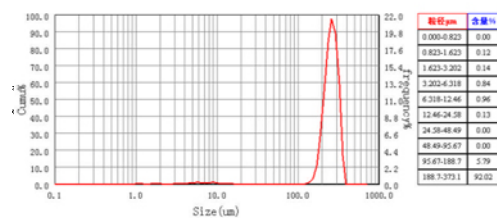
Analysis of N₂ Adsorption-desorption

Figure 10 shows N₂ Adsorption-desorption isotherms of the prepared and the commercially

available 4A zeolite. Table 2 shows specific surface area and porosity of prepared and sold 4A zeolite.



(a) synthesized 4A zeolite by alkali fusion-hydrothermal



(b) 4A zeolite sample

Figure. 9 Particle size distribution patterns of 4A zeolite

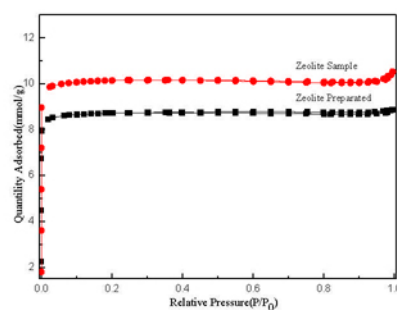


Figure. 10 N₂ adsorption-desorption isotherms of prepared and sold 4A zeolite

Figure 13 shows N₂ adsorption-desorption isotherm curves of the prepared and 4A zeolite sample, both of them have a sharp rise part from the origin, then close to the level, having a horizontal section of a clear inflection point. It belongs to I-type isotherm. But we can see from the N₂ Adsorption-desorption isotherms that, there is a H₃-type hysteresis loop after absolute pressure greater than 60kPa. This indicates that there exists mid size pores in the zeolite.

It may be due to the second poles formed between unconverted ash and synthetic zeolite, or Impurities in coal ash.

It appeared H₃ hysteresis loop in the temperature line where the absolute pressure is more than 60KPa with some mesoporous specific surface area which

may be due to impurities in fly ash and secondary zeolite. holes generated from remaining fly ash and prepared

Table 2 Specific surface area and porosity of prepared and purchased 4A zeolite

Samples	$S_{BET}(m^2/g)$	$S_{Langmuir}(m^2/g)$	$S_{t-plot}(m^2/g)$	$V_{t-plot}(cm^3/g)$	$V_{BSH}(cm^3/g)$
sold zeolite	723.513	953.4901	693.3659	0.0337535	0.01913637
prepared zeolite	590.437	695.6045	560.8167	0.0313585	0.01043671

As can be seen from Table 2, the BET specific surface area of 4A zeolite prepared from fly ash is very high, almost reaching for the requirements of industrial application of 4A zeolite molecular sieves of $600m^2/g$ [14, 15]. In addition, the specific surface area and pore volume of 4A zeolite prepared are both smaller than those of industrial zeolite bought from markets, which is mainly due to the 4A zeolite

synthesized from fly ash with less impurities or mixed crystal. At the same time, it also shows that the synthesis process of zeolite can effectively convert fly ash into 4A zeolite.

Chemical component analysis

The chemical composition of prepared and purchased 4A zeolite was determined by XRF, shown in Table 3.

Table 3 Chemical composition of prepared and purchased 4A zeolite

Samples	SiO_2	Al_2O_3	Na	CaO	Fe_2O_3
sold zeolite	32.48	28.17	9.18	-	-
prepared zeolite	31.28	25.66	9.50	3.94	2.80

As can be seen from Table 3, the main chemical compositions of synthesized 4A zeolite and commercially available 4A zeolite are basically same, but the prepared 4A zeolite 4A contains impurities such as iron oxide and calcium oxide, which are mainly due to impurities in raw fly ash.

6. Conclusions

Low temperature activation dissolve of mullite in high alumina fly ash is the main problem of direct synthesis of zeolite from fly ash. High temperature and alkalinity will promote the decomposition of the mullite by NaOH solution, however, the sodalite was generated rather than zeolite under the conditions of high temperature and alkalinity by direct synthesis.

The alkali fusion hydrothermal synthesis experiment shows that alkali fusion temperature has a great influence on the synthesis of 4A zeolite. The optimum process conditions are: alkali melting temperature of $850\text{ }^\circ\text{C}$, $SiO_2-Al_2O_3$ ratio of 0.8 (molar), NaOH concentration of 2.5mol/L, aging time of 6h, crystallization time of 24h and crystallization temperature of $90\text{ }^\circ\text{C}$.

The adsorption-desorption isotherms of 4A zeolite synthesized from coal fly ash belong to Type I isotherms. In zeolite samples, microporous distribution is highly concentrated and there is regular

microporous structure. The main chemical compositions of synthesis 4A zeolite and commercially available 4A zeolite are basically the same, but the laboratory prepared 4A zeolite contains a small quantity of impurities such as iron oxide and calcium oxide.

Acknowledgements

This research was supported by the National Natural Science Foundation of China (Nos. U1202274, 51004033, 51204040), National 863 Plan (2012AA062303) and The Research Fund for the Doctoral Program of Higher Education of China (20120042110011).

References

1. G. Q. Yang and K. H. Liu, Solid waste treatment engineering (Beijing, China: Science Press, 2000).
2. B. X. Bian, Q. Xie and Y. C. Zhao, Coal Solid Waste Recycling Technology (Beijing, China: Chemical Industry Press, 2005).
3. H. B. Song, F. R. Zhai and L. L. Zhang, J. KU. Sci. Tech. 5, 31 (2006).
4. J. S. Qian, C. M. Wu and Z. Wang, Compre. Utiliz. Fly Ash. 1 (2001).
5. H. L. Chang and W. S. Shi, Ing. Eng. Chem. Res. 11, 39 (2000).

6. Molina A and Poole C, *Miner. Eng.* 2, 17 (2004).
7. Hollan G G, Steenbruggen G and Janssen-Jurkovicova M, *FUEL*. 10, 78 (1999).
8. Querol X, Moreno N and Lope. Soler A. *Int. J. Coal. Geol.* 1-4, 50 (2002).
9. X. Y. Yang, G. Y. Zhang and Q. X. Li, *Daily Chem. Ind.* 1, 33 (2003).
10. Mario L, Occelli, *Zeolite synthesis* (Washington DC, America: American Chemical Society, 1989).
11. J. Y. Li, *Chem. Eng. Equip.* 4, 6 (2010).
12. J. D. Zhang, *Oil Refin. Che. Ind.* 5, 21 (1978).
13. K. S. Hui and Y. H. Chao, *Micropor. Mesopor. Mater.* 1-3, 88 (2006).
14. Y. P. Ye, X. Q. Zeng, W. L. Qian and M. W. Wang, *Fuel.* 10-11, 87 (2008).
15. Y. Fan, F. S. Zhang, J. X. Zhu and Z. G. Liu, *J. Hazard. Mater.* 153 (2008).