Study on Analysis of Chenghe Fly Ash and Preparation of molecular sieve

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Abstract. In recent years, with the rapid development of coal industry, a large number of coal fly ash has been produced, while the recycling rate of the ash is rather low. It is not only a waste of the precious land resources, but also makes environment suffering severe pollution. As an important kind of new material in the national economy, the demand for molecular sieve is growing. It is possible to synthesis molecular sieve using fly ash. The way is not only energy conservation and environmental protection, but also waste reclamation, according with the theme of the sustainable development. This study is to synthesize the molecular sieve in different guide agent or addition agent conditions, which is on the basis of the analysis of chemical composition of fly ash and auxiliary guide agent and additional additives, and using inexpensive industrial waste material fly ash, which are from Cheng He mining area in Shanxi province, as basic raw material by the method of hydrothermal synthesis. It is also to find a approach for the use of fly ash with subtly. Through XRD expert zing phase, SEM observing appearance, the characterizing results show that excellent performance molecular sieve of 4A can be synthesized at conditions: calcined at 850℃and for 2 hours, then hydrothermal reacted with composition of reaction mixture $3Na_2O$:$1Al_2O_3$:$2SiO_2$: $185H_2O$ at temperature 90℃, crystallization time 6h with 5% guide agent or additives .

Introduction

Lecular sieve is a kind of aluminosilicate compounds which have cubic lattice. Its crystal structure have pore and cavity system which are uniform and regular, aperture is order of magnitude as molecular size, it only allows small molecules that is than the aperture to enter the diameter, so it can sieve mixture of molecular according to size, it derives its name [1] - [3]. Because zeolite has such advantages as high adsorption capacity, thermal stability, and so on, it has become an important new materials in the national economy. The molecular sieves are widely used in metallurgical, chemical, electronics, petrochemical, natural gas and other industries currently. But traditional zeolite synthesis method has high costs and limit its large-scale production. Therefore, to find a wide source and inexpensive synthetic materials is a research direction to prepare molecular sieves by more and more attention.

Fly ash is a fine-grained and dispersed remnants after coal or pulverized coal combustion, it is a main solid waste discharged from coal-fired power plants. Its emissions increase rapidly with the further development of the coal industry,. According to related statistics, the total annual consumption of coal in the world is 4.226 billion tons, annual emissions of fly ash in coal-fired power plant amounted to 290 million tons; Annual consumption of coal is about 1.106 billion tons in China, fly ash emissions amounted to 100 million tons [4]. The fly ash utilization is low, most deal with the landfill and stockpiling approach. These fly ash are not efficient use, increasingly restrict development of national economy and threaten people’s healthy living [5] - [6]. Therefore, exploiting high value-added products which has application and development value is a direction for the future development of fly ash. Fly ash and zeolite are very similar to the composition,this provide possible to use fly ash preparing molecular sieve. Molecular sieves are often synthesized by the chemical raw materials and cost is higher. If we use fly ash to synthesize molecular sieve, not only save resources, reduce costs, turn waste into use, provides a new idea for the utilization of fly ash and contribute to the improvement of economic and social benefits [7] - [8].

Cenghe mine in Shaanxi stacked lack of effective utilization of industrial waste fly ash, and not only take up valuable land resources, but also poses a major threat to the environment. In this regard, the study analysizes chemical composition of fly ash in the mine, and found it used to prepare zeolite as the basic raw material. On the basis of chemical analysis with fly ash to synthesize zeolite product, explore a new way in its waste reuse, waste to treasure and molecular sieve synthesis.

Experimental study

1.1 Chemical analysis of fly ash in chenghe mine area. The main component of the general fly ash is Al_2O_3, SiO_2, and also contains of Fe_2O_3, CaO, MgO, Na_2O, K_2O, P_2O_5, SO_3 and some of the trace rare elements. According to the needs of the synthetic zeolite, this study analyzed the percentage content of Al_2O_3, SiO_2, Fe_2O_3, CaO and MgO in Chenghe in fly ash. Component analysis method is in accordance with the implementation of the GB-T 1574-2007.

Study of fly ash from the Shaanxi Chenghe mine area, using 325 mesh sifter to sieve, chemical composition of fly ash sample shown in table 3:

Table 3 chemical composition of fly ash in chenghe mine area

Chemical compisition	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO
Content/%	40.40	21.29	16.24	6.68	0.60

Seen through the analysis from the table, the main chemical composition of fly ash are SiO_2 and Al_2O_3,two accounted for more than 60% of the total, and SiO_2 / Al_2O_3 (molar ratio) is 3.21. General requirements of SiO_2 / Al_2O_3 (molar ratio) for synthesis 4A molecular sieve is 1.3 ~ 2.4, so using this fly ash, when synthetic zeolite adding a certain amount of sodium aluminate in the reaction mixture to complement the aluminum source. High content of iron in it, because the iron ore of Chenghe mine is more, so percentage of Fe_2O_3 in fly ash is significantly higher than normal level, but is a normal phenomenon.

1.2 Pretreatment of fly ash. The presence of carbon and iron in fly ash would affect the whiteness of synthetic 4A molecular sieve, the vast majority of SiO_2 and Al_2O_3 of fly ash present in the vitreous, mullite and quartz, is non-activity. At first fly ash is removed carbon and activated, on the one hand to increase its whiteness, on the other hand to dissolve the vitreous, destruct structure of quartz and mullite crystal, release amorphous SiO_2 and Al_2O_3, in order to facilitate subsequent processing.

We take a high-temperature calcination method to remove carbon generally, fly ash take place a series of physical and chemical changes in the calcination process with the temperature and time extension, its loose, porous, and activity characteristics occur the corresponding change. Calcination time is too short, phase destruction is not complete, carbonaceous volatilization is incomplete, and thus activity is poor, is not conducive to prepare 4A molecular sieves; but time is too long, the reactivity is poor and energy consumption is great. Generally we choose favorable calcination temperature is 800 ~ 850℃. Additional acid activate amorphous SiO_2 in fly ash, make it to dissolve in alkalis easily, and does not affect the zeolite synthesis, we choose hydrochloric acid to achieve the purpose of activation in the pretreatment. The specific steps are as follows:

Weigh 10g original gray, mix 10% hydrochloric acid and the original fly ash as solid-liquid ratio of 1:25, seale in flask, stir with a thermostat magnetic stirrer under heating conditions with a temperature of 90℃ for 1h, then filter, wash to pH about 7, take into the ash pan after dry, then send into the muffle furnace, shut the door and make it slowly heated to 850℃ for 2 hours, remove and cool, reserve for future use.

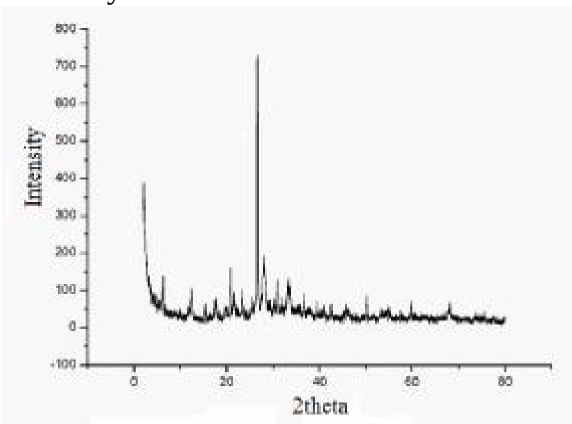
1.3 Zeolite synthesis and characterization. Synthesis process of molecular sieve is as follows.Structure type and quality of molecular sieve are understanded by the characterization. Characterization methods used in this study are:

(1) Molecular sieve type and degree of crystallinity are determinated by XRD, the conditions of X-ray diffraction instrument are: place of origin, Japanese Daojin;model,D/max-2700;the detection conditions, CuK radiation, Ni filter and the tube voltage / tube current, 40KV/30mA.

(2) Morphology and particle size of molecular sieve are observed by SEM, the conditions of scanning electron microscopy are: model,JSM-64460LV; scanning voltage is 20KV; magnification times is 5000-10000.

1.3.1 Preparation and characterization of conventional molecular sieve.(1) Perparation: take 5g fly ash that treated into 150mL flask, add 40mL 2mol / L sodium hydroxide solution, mix evenly and stir and age for 1 hour at room temperature. Then place the reaction system in a water bath pot, heat mix system to 90℃with evenly stir, hydrothermal reaction for 6 hours, put it aside for the night, get product after crystallization. And then proceed to filter, wash to pH = 9-10 with distilled water, dry at 110℃ for 6 hours, get molecular sieve products after ground.

(2) XRD analysis:



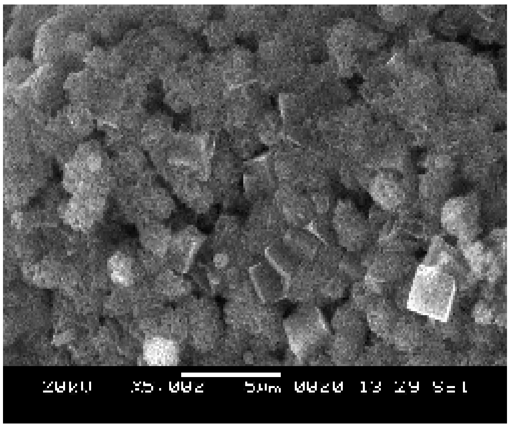


Fig 1 XRD chart of synthesis product Fig 2 SEM picture of synthesis product

Strong diffraction peaks can be seen only in the 20-30 diffraction angle region from figure 1, while the number of diffraction peaks is little in the other angles and the intensity is very small, almost do not see the formation of 4A molecular sieve. This indicates that large numbers of vitreous exit which does not transform, crystallinity degree of product is low.

(3) SEM observation:Seen by scanning electron micrographs, synthetic product shows rarely of the cube-shaped, only presence sporadically, distribution is not uniform, but the floc irregular miscellaneous crystal is more. Results of SEM observation and XRD analysis show that the conventional hydrothermal synthesis method is not ideal.

Described above, the conventional hydrothermal synthesis method is not easy to prepare molecular sieve products. In order to prepare qualified molecular sieve product, directing agent should be added in the reaction system. It can greatly short induction period of zeolite synthesis with adding high dispersion nucleation directing agent, the crystal can grow rapidly and reach a higher degree of crystallization in the case of relatively lower temperatures and shorter time. In view of this, the next experiment directing agent is added to accelerate the crystallization speed while supplementary sodium aluminate, so that the crystal crystallize prefectly. In addition, we investigated adding varying amounts of the directing agent how to affect preparation of molecular sieve.

1.3.2 Synthesis and characterization of molecular sieve by adding the directing agent.(1) synthesis: oriented agent is prepared beforehand. Directing agent were prepared by pre-crystallization method, reference [9], mix various ingredients evenly according to ratio of molecular sieve, age certain time, then add it to synthesis system as directing agent involved in the synthesis. We compound according to the ratio of Al_2O_3: SiO_2: Na_2O: H_2O = 1:2:3:185 (molar ratio),mix water, sodium hydroxide, aluminum hydroxide and sodium silicate in boiling state, generate gel, stir evenly and age more than 24 hours at room temperature, ie form amorphous seed.

Weigh 5g fly ash which treated in a 150mL flask, add 40mL 2 mol/L sodium hydroxide solution, , then add 1.5g sodium aluminate and mix evenly, age with stirring an hours at room temperature. Then place reaction system at a constant temperature water bath, add 5% to 10% (mass fraction) directing agent in reaction mixture, heat mixing system to 90 ℃ with uniform mixing to carry out hydrothermal reaction, continued for 6 hours, crystallize staticly overnight and get the product. Then filter, and wash with distilled water to pH = 9 ~ 10, dry 6 hours at 110℃, get molecular sieve product after grind.

(2)XRD analysis :Synthetic samples were characterized by XRD, and the results shown in Figure 3:

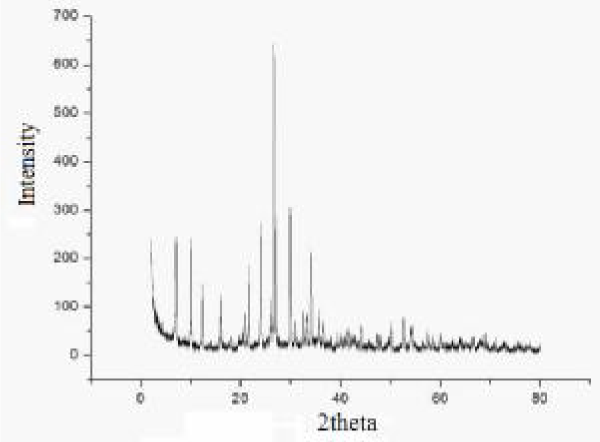


Fig 3 XRD chart of synthesis product

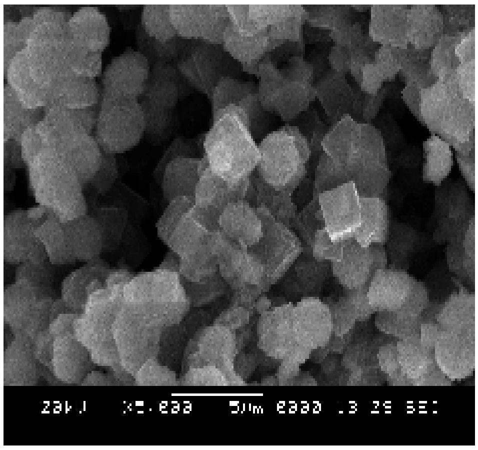


Fig 4 SEM picture of synthesis product

Figure 3 is X-ray diffraction diagram of synthetic sample by adding 8% directing agent. The figure shows, the number of product peaks is numerous, the intensity of diffraction peaks is strong, consistent with the standard map data of 4A molecular sieve. Adding directing agent helps to prepare 4A molecular sieve by using fly ash.

(3) SEM observation:Shown in Figure 4, after adding 8% directing agent, the shape of the synthetic products is regular, crystals are uniform, profile is clear, purity is high, while the grain size reduced and synthesis effect is better.

1.3.3 Synthesis and characterization of molecular sieve by adding citric acid. (1) Synthesis: take 5g fly ash that treated in a 150mL flask, add 40mL 2 mol/L sodium hydroxide solution, then add 1.5g sodium aluminate, mix evenly, age with stirring for 1 hour at room temperature. Then place the reaction system at a water bath with constant temperature, add different amounts of citric acid in the reaction mixture, heat hybrid system to 90 ℃ and hydrothermal react for 6 hours under the uniform mixing, obtain product after stand overnight. Finally filter, wash with distilled water to pH = 9 ~ 10, dry 6 hours at 110 ℃ , get molecular sieve product after grind.

(2)XRD analysis: Can be seen from Figure 5, after add 5% citric acid, the number of X-ray diffraction pattern peak of product is numerors, the intensity of diffraction peak is strong, consistent with 4A molecular sieve standard map data, indicate that the crystallization of the synthetic products is very good.

(3) SEM observation:Can be seen from Figure 6, the crystal uniform of synthetic molecular sieve is uniform and neat, high crystallinity, small particle size, a small number of miscellaneous crystal, show that adding citric acid is conducive to synthesize molecular sieve, and synthesis effect is the best when add 5% citric acid.

Conclusion

In this study, we use chemical analysis method to determine ingredients Chenghe fly ash, and on this basis, add the directing agent and citric acid to prepare molecular sieve by hydrothermal synthesis method,and synthetic products are characterized by XRD, SEM, get following conclusions:

(1) Silica content of fly ash in Chenghe mine area is more than 40%, the total amount of silica and alumina are also more than 60%, it can be directly used in the preparation of molecular sieves.

(2) 4A molecular sieve product has almost not been prepared by conventional hydrothermal method with no adding aluminum source and any additives.

(3) 8% directing agent, or 5% citric acid is conducive to prepare 4A molecular sieve, which shape is regular, high crystallinity and the effect of crystallization is very good through the X-ray diffraction, scanning electron microscopy characterization.

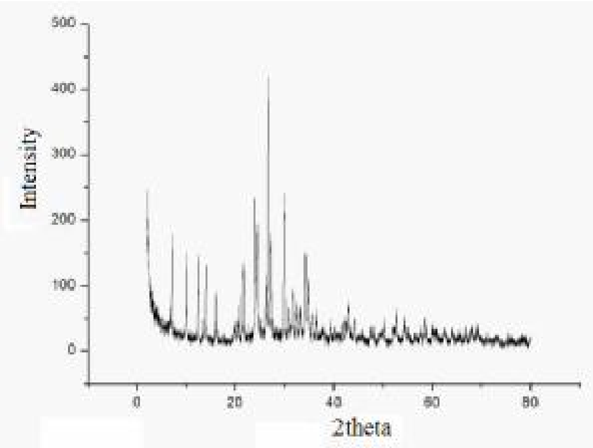


Fig 5 XRD chart of synthesis product

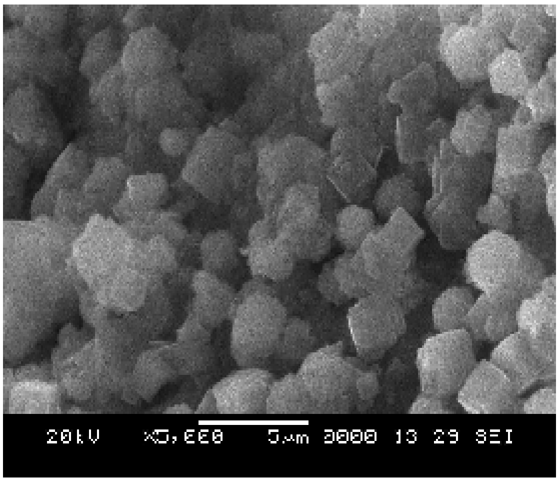


Fig 6 SEM picture of synthesis product

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