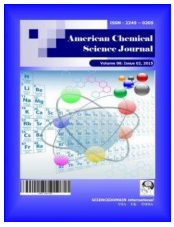

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Effects of Activation and Modification on the Microstructure and Composition of Fly Ash

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Authors' contributions

This work was carried out in collaboration between all authors. Author MQ designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Authors YW and MN managed the analyses of the study. Authors MQ and YW managed the literature searches. All authors read and approved the final manuscript.

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ABSTRACT

The fly ash was activated and modified respectively by acid and alkali- soluble method, BET, XRD, SEM and EDS were used to investigate the specific surface area, phase, surface microstructure and the major elements of the original coal fly ash and the modified sample. The results show that the acid or alkali can change the specific surface area, the microstructure and phase composition of fly ash obviously and the activation and modification by the sulfuric acid can improve the surface area significantly. Different modifiers have great effects on the relative content of the major elements in fly ash.

Keywords: Fly ash; activation; modification; microstructure.

1. INTRODUCTION

Fly ash is the waste or the coproduct of the coal-fired power plants and the centralized heating boilers. It is made up of various tiny particles of inorganic/organic components [1-2]. The microstructure, mineral composition and main composition decide its physical and chemical

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properties [3-4], which directly related to the comprehensive utilization and added value. The fly ash always show various physical properties and chemical structure due to the different coal source, the burning conditions as well as the burning of coal mining conditions [5-6]. Thus, it has great realistic significance to know how to make fly ash waste to treasure, improve the added value and the comprehensive utilization rate.

In recent years, the development and utilization of fly ash caused the attention of each country. Its utilization in Europe, the United States and other countries has reached 70%-80%, but in China only about 40% [7]. What is more, it is mainly used in road construction, packing, wall materials, cement and other aspects in China [8-10]. Its comprehensive utilization rate is far behind the developed countries in the West. The high carbon content, composition fluctuation and unstable quality lead to the low added value [11-13]. The main cause is the surface of fly ash particles were wrapped by dense stable glass shell, the potential activity of fly ash were influenced, so, it is very necessary to enhance the potential activity for the FA comprehensive utilization. Therefore, it is very necessary to enhance the potential activity and modified activation [14-15].

In this paper, the fly ash was modified and activated by sulfuric acid, hydrochloric acid, 1:3 acid and sulfuric acid mixed acid, sodium hydroxide solution and so on. The phase composition, surface microstructure and specific surface area before and after the modified were compared, based on XRD, SEM, EDS and BET to get some regular understanding, so as to provide experimental and theoretical basis for the comprehensive utilization.

2. EXPERIMENTAL SECTION

2.1 Reagent and Instrument

Main reagent: fly ash (original state, Baoding thermal power plant, Hebei province); sulfuric acid (H_2SO_4), hydrochloric acid (HCl), sodium hydroxide (NaOH) and ethanol (C_2H_5OH) were analytical reagents.

Main instrument:Y-2000 Automatic X-ray diffraction; JSM-7500F field emission scanning electron microscope (JEOL LTD./JAPAN X-ray energy dispersive spectrometer, American Noran Co.); Tristar II 3020 Automatic specific surfacearea analyzer, (American Micromeritics Co.).

2.2 Modification and Activation of Fly Ash

The fly ash modification and activation were achieved by the acid-leaching and alkali-leaching method. Firstly, four 3 g of the fly ash was placed in a beaker and then 50 mL sulfuric acid solution (1 mol/L), hydrochloric acid, sodium hydroxide and 1:3 hydrochloric acid and sulfuric acid mixed acid solution was added to each beaker following with stirring for 30 min. After the filter, washing, drying and grinding, the modified fly ash was obtained.

3. RESULTS AND DISCUSSION

3.1 The Specific Surface Area Analysis of Fly Ash

Table 1 displays the BET profiles of the origin ash and different modified fly ashes. From Table 1, we know that after the modification, activated fly ash specific surface area is increased. The sulfuric acid modified fly ash has the largest specific surface area, reached 13.4821 m^2/g, while the specific surface area of sodium hydroxide modified is relatively less increased. We hold that it is the mineral composition and microstructure on the surface to result this consequence. On one hand, there is a corresponding chemical reaction of the free inorganic composition with acid or alkali, consequently, fly ash particles act out the inherent surface hole in the formation process. On the other hand, acid or alkali damages silicon aluminium vitreous structure of particles surface and lead to the Si-O and Al-O bond tetrahedron structure flabby and fractured with soluble SiO_2 and Al_2O_3 increasing and forming new cavities, thereby the specific surface area increased. As the sample was treated after filtration and washing, the partially solubility product has been removed. So presumably, fly ash and alkali occurrence of condensation reaction in the process of sodium hydroxide modified fly ash, resulting in a lump, although changed the surface structure, the grain size in comparison with acid treatment increases, thus the specific surface area increased less.

3.2 Phase Analysis of Modified Fly Ash

The XRD of origincoal fly ash and modified ashes are shown in Fig. 1. In Fig. 1 (a), after the peak searching by computer, the diffraction

peaks of 2θ = 16.39°, 26.01°, 26.27°, 33.23°, 35.22°, 40.83° all belong to the characteristic peaks of mulite (Al6Si2O13, standard PDF card number:15-0776); the diffraction peaks of 2θ = 26.58°, 20.86° all belong to the main characteristic peaks of quartz (SiO_2, standard PDF card number: 46-1045) and the diffraction peak of 29.42° is the characteristic peak of calcium carbonate. In addition, we can see from Fig. 1 (a), the peaks at the area of 2θ = 20~35° heaving, in the mean time, the background of diffraction graph is relative high, this indicate vitirous, unburned carbon particals and other uncrystallized oxidates exsit in fly ashes. It follows that the main compositions of fly ash are mulite, quartz and amorphous substance.

Fig. 1(b), (c), (d), (e) are XRD of sulfuric acid, hydrochloric acid, mixed acid, sodium hydroxide modified fly ash respectively. Through the comparative study, we see that after modified the phase occurs some change. In Fig. 1(b), there are the characteristic peaks of calcium sulfate ($CaSO_4$, PDF No is 83-0437) in the 2θ =14.72°, 31.90°, 33.18°, 49.29°; In Fig. 1 (c), diffraction peak of calcium carbonate disappeared; the position of diffraction peaks in Fig. 1 (d) are basically same as in Fig. 1 (b), but the strength is weaker; However, the diffraction peak position in Fig. 1 (e) is basically the same as in Fig. 1 (a), but the strength increases. Thus, the diffraction peak position and intensity of fly ash is changed after acid, alkali modified, so the phase composition changed. This is due to the addition of acid, basic not only destroy the structure of silicates in the fly ash, but also acid and alkali can react with the part of free metal oxides and salts in fly ash to form new salts. Water soluble substances are removed during filtration, leaving the insoluble substance. Because of the complex composition, the specific phases need a further study.

3.3 Microstructure and EDS Analysis of the Modified Fly Ash

The microstructure and chemical composition determine macro-physical and chemical properties, as well as relate to comprehensive utilization. We use the SEM with EDS analysis the surface micro structure and macro elements of them. Fig. 2 displays that.

It can be seen from Fig. 2(a), fly ash has two major kinds (spherical and amorphous) with unequal sized particles and rough surface, and adsorbs glass beads with small volume and smooth surface, which formed in the process of coal burning after high temperature melting of precipitation and the glass gathered together.

Table 1. Specific surface area of fly ashes

Fly ash	The origin fly ash	Hydrochloric acid modifide	Sulfuric acid modifide	Mixed acid modifide	Sodium hydroxide modifide
BET（m^2/g）	7.8059	10.4381	13.4821	10.5846	9.6391

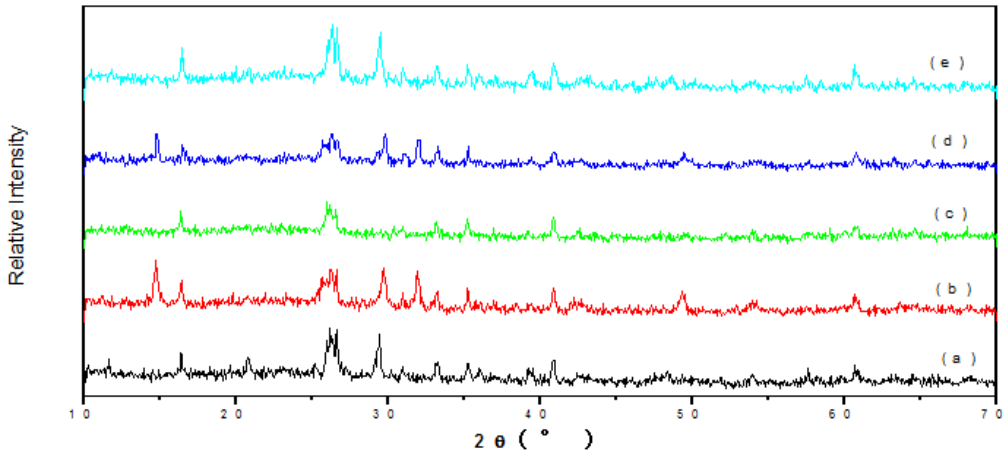

Fig. 1. XRD patterns of fly ashes
(a) Origin ash; (b) modified with sulfuric acid; (c) hydrochloric acid modified; (d) mixed acid modification; (e) sodium hydroxide modified

The grain size and surface structure has changed greatly after acid and alkali modification. Especially, great changes have taken place after the activated by the sulfuric acid. Not only the particles become smaller, but also the fly ash has a relatively uniform distribution. Form a lot of the acicular particles with diameter less than 1 μm. The EDS analysis of surface is mainly sulfate. Single particle surface becomes uneven, forming a lot of new micro holes and leading to the increase of specific surface. The result is same to the BET analysis, while after modified by the mixed acid, the particle size is between sulfuric acid and hydrochloric acid treatment. Relatively speaking, after NaOH modified, fly ash has a tendency to clot between particles and the surface roughness. In addition, we can also see from the particle surface micro structure that acid or alkali both can change the surface bonding state in different degree. It may be due to the acid and alkali modification, on the one hand silicon aluminum film on the particle surface was damaged that make more Si-O bond and Al-O bond broken; On the other hand, it due to the acid or alkali reaction with the free oxide on particle surface and generate new material.

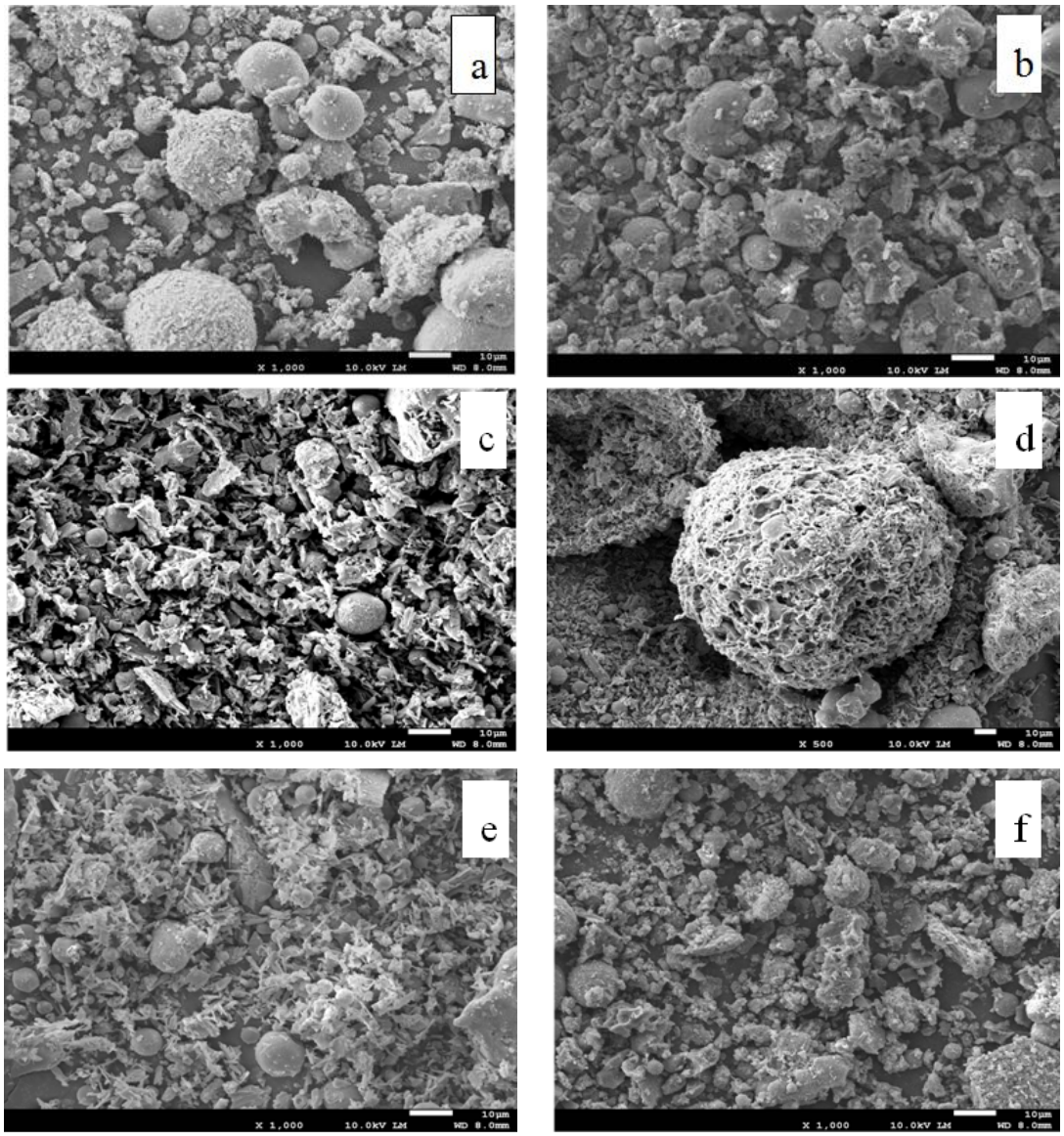

Fig. 2. SEM photographs of samples

(a) origin fly (b) hydrochloric acid modified (c) sulfuric acid modified (d) Sulfuric acid modified (e) Mixed acid modified (f) NaOH modified

Table 2. EDS analysis result of relative average content of the major elements in fly ash

Element / Fly ash	W (element)%								
	K	Ca	Ti	Fe	Al	Si	S	Mg	Na
The original fly ash	1.35	23.00	1.24	5.86	25.78	34.16	4.6	2.78	0.95
Hydrochloric acid modification	2.03	1.69	2.04	6.42	34.28	52.10	0.69	0.74	0.0
Sulfuric acid modified	0.87	24.31	1.22	4.93	20.33	26.34	21.67	0.32	0.0
Mixed acid modified	1.24	18.24	1.29	6.53	23.58	31.52	17.22	0.35	0.0
Sodium hydroxide modified	1.12	24.42	1.15	5.87	25.53	34.19	1.4	5.33	0.97

We also use the SEM equipped with X ray energy dispersive spectrometer to make the major element analysis, the activated and modified samples. The sample after the spraying carbon conductive treatment and then get the average value of the each sample after tested five times. The average results were shown in Table 2.

From Table 2, the major elements in fly ash are Al、Si、K、Ca、Ti、Fe、Mg and so on, which mainly exist in the form of oxide or silicate, because the content of the original ash calcium is high, the fly ash is a kind of the high calcium coal ash. After the modification of hydrochloric acid, the relative content of calcium decreased significantly. That a majority of calcium reacted with hydrochloric acid, become the water soluble salt and mostly removed with the filtration process. After the treatment of sulfuric acid, the calcium content is equal to the original ash basically, and the content of sulfur elements significantly increased. It showed that the slightly soluble calcium sulfate was produced. But the iron content had a slightly decrease that there was only a few parts reaction of iron element in fly ash. While after modified by the mixed acid, the relative contents of elements was between them. When modified by the NaOH, the relative content of magnesium elements significantly increased. Illustrate the free magnesium with alkali to form magnesium hydroxide precipitate. Other components were similar with the original ash.

It can be seen from Table 2, Sodium hydroxide, hydrochloric acid modification of fly ash to remove the sulfur in coal ash. And for the relatively high content of silicon, aluminum element, sulfuric acid modified processing has great influence on it. In general little changes in iron, titanium element, because it is mainly exist in the form of perovskite and ilmenite. This finding is consistent with XRD and SEM research results.

4. CONCLUSION

Treatment of acid or alkali can obviously change the fly ash surface area, microstructure and phase composition. In terms of the microstructure, the effect of sulfuric acid modified activated is best, many new holes are formed, specific surface area increases significantly. While the alkali solution effect is the worst, it is confirmed by EDS analysis that different activation modifier have great influence on the relative content of fly ash elements, which provides a scientific basis for choosing the appropriate activation modification method according to different purposes and requirements in the development and utilization of fly ash.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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