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Full Length Article

Effects of the modified kaolin sorbents on the reduction of ultrafine particulate matter ($PM_{0.2}$) emissions during pulverized coal combustion

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ABSTRACT

It is a good way to control the formation of particulate matter by adding sorbents during coal combustion. Kaolin is usually considered as the most effective sorbent. Modified kaolin was firstly used to reduce the formation of ultrafine particulate matter ($PM_{0.2}$, particles with the aerodynamic diameter less than 0.2 μm) in this work. Two kinds of typical modification methods were selected, namely, the acid modification and the sulfate modification. Then, pulverized coal was burned with raw and modified kaolin separately in an electrical heated drop-tube furnace, and the mass size distribution of the fly ash particulate was obtained. What's more, the different kaolin sorbents were heat-treated with alkali metal vapor in a quartz tube reactor and the products at different residence time were sampled and characterized. The results indicate that compared with raw kaolin, all the modified kaolin can significantly reduce the formation of $PM_{0.2}$. The yield of $PM_{0.2}$ decreased by 16.83% with the addition of raw kaolin, which was further reduced by 41.44% and 19.84% respectively with the addition of the acid and sulfate modified kaolin. It is found that the kaolin modified by hydrochloric acid owns more active sites and more free silicon dioxides, hence enhancing the reaction between kaolin and alkali metal and yielding less $PM_{0.2}$. The modification by aluminum sulfate not only obviously improved the surface characteristics, but also broke some functional groups of raw kaolin. Therefore more alkali metal were reacted by the kaolin and the formation of $PM_{0.2}$ were effectively reduced.

1. Introduction

Currently, heavy haze has become a serious environmental issue and caused the overwhelming public concerns in China [1,2]. As well known, one of the inducements to the haze is the particulate matter (PM), especially the PM with the aerodynamic diameter less than 2.5 μm ($PM_{2.5}$) [2]. $PM_{2.5}$ can adsorb organic pollutants and trace elements easily because of its small particle size and large specific surface area. Once being breathed into human's body, PM will cause great damages to human's respiratory system, nervous system and blood circulation system, etc. [3]. In China, one of the major sources of PM is the emission from coal combustion, especially the coal-fired power plants [4].

To reduce the emission of PM, current coal-fired power plants are generally equipped with various dust collectors [e.g., electrostatic precipitators (ESPs) and bag filters] at the downstream of the furnace [4,5]. However, the ultrafine PM, generally cannot be effectively removed in the dust collectors [4,5]. In order to reduce the formation and emission of ultrafine PM, the in-furnace sorbent addition technology has been proposed as a supplementary method to the dust collectors. The sorbents injected into the furnace are supposed to react with and fix the mineral matter vapors released during the combustion of coal, which otherwise generally transform into ultrafine PM via nucleation progress, and thereby inhibit the formation of the ultrafine PM [4].

A number of mineral sorbents that could be effective to reduce the PM emission have been reported. Based on the chemical composition, these sorbents can be categorized into Si-Al-based (e.g., kaolinite, montmorillonite, etc.) [6–10], Ca-based (e.g., limestone, hydrated lime, etc.) [11–14], Mg-based (e.g., magnesium hydroxide) [15–17] and Ti-based (e.g., TiO_2, etc.) [18,19] sorbents. The Si-Al-based sorbents, especially kaolin, have been studied extensively and generally could reduce the yield of PM_1 by 30–50%, which is one of the most effective sorbent material while still not sufficient enough for the industrial application [6,19,20]. The PM reduction mechanisms of them are relatively clear compared to other sorbents. Systemic experiments and modeling work on the capture mechanism of alkali metals by kaolin have been performed by Gale and Wendt [7,9], and their results showed that the reaction between the metal vapors (e.g., Na, Pb, etc.) and kaolinite included a temperature-activated eutectic-melting-enhanced capture progress and an excessive-melt deactivation progress, which

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was further verified in the studies of Takuwa and Naruse [21,22] and the latest research in our group [6,19,20]. The above-mentioned gas–solid reaction progress is the crux which controls the actual PM capture performance of the kaolin, while this progress is affected by both the combustion conditions (e.g., combustion temperature, atmosphere) and the inherent properties of sorbent particle (e.g., composition, surface characteristics, chemical reactivity) [6,19,20]. Although the Si/Al-based composition and the distinctive layered structure bring the natural kaolin a relative good PM reduction performance, some drawbacks in its physical and chemical properties, in particular the defective surface characteristics and chemical reactivity hinder the improvement of its performance at high temperature [7,9,19]. And more efforts are still needed to develop the effective and feasible sorbents. As far as we know, most of the current researches developing the PM sorbent persist in seeking and exploiting new sorbent materials, while few attempts are made to further improve the PM capture performance of the raw kaolin sorbent. Herein, for the first time, modification treatments were introduced into improving the performance of kaolin on capturing the PM. Could these modification methods improve their reduction efficiency of ultrafine PM? And if so, what is the action mechanism? All these questions remain unclear yet and are needed to be clarified.

In this work, two kinds of modified kaolin (modified with hydrochloric acid and aluminum sulfate separately) were prepared firstly, and then combustion of coal separately with the raw/modified kaolin and PM collection were performed on a drop-tube furnace to test the effectiveness of the modification treatments. Furthermore, the different kaolin sorbents were heat-treated with alkali metal vapor in a quartz tube reactor and the products at different residence time were sampled and characterized. Finally, based on the systemic characterization of the kaolin, PM samples and the intermediate products of kaolin and mineral vapor, the effects of different modification methods on kaolin and their action mechanisms were investigated.

2. Experimental section

2.1. Experimental materials

The Shanxi anthracite was selected as the experimental coal sample due to two reasons [23]. Firstly, the ash melting point of this coal is 1554 °C, which implies that no serious slagging would happen during the combustion. Secondly, the relatively high Na + Mg + K/Si + Al ratio of this coal makes it suitable to determine the capture efficiency of the alkaline metals (major composition of the fine PM) by kaolin. The raw coal were crushed, grinded and sieved, and the parts in 45–90 μm were used in the experiments, and the detailed properties of the coal samples are presented in Table 1.

The raw kaolin used in the experiments was obtained from Sinopharm chemical reagent co., LTD, Shanghai and its composition is also presented in Table 2. All the modifying agents used in the modification study, namely, hydrochloric acid and aluminum sulfate are at analytical reagent grade.

Table 2
Composition analysis of kaolin and modified kaolin.

Samples	Composition (%)						
	Al_2O_3	SiO_2	TiO_2	K_2O	CaO	Fe_2O_3	SO_3
Raw Kaolin	47.07	51.42	0.86	0.14	0.12	0.39	0
HAMK	44.62	53.61	0.96	0.21	0.17	0.43	0
ASMK	44.25	46.63	0.83	0.14	0.19	0.42	7.54

2.2. Preparation of the modified kaolin

Two modified kaolin, including a hydrochloric acid modified kaolin (HAMK) and an aluminum sulfate modified kaolin (ASMK), were prepared [24–26]. Hydrochloric acid modification was adopted to remove the impurities in the raw kaolin and modify its reactivity. To prepare the HAMK, raw kaolin powder was firstly calcined at 650 °C for 3 h, and then mixed with hydrochloric acid solution (4 mol/L) at 90 °C for 2 h. The dosing ratio of hydrochloric acid to kaolin is 8 mL/g. Centrifugal separation was conducted to separate the kaolin from the acid solution. After the separation, the modified kaolin was washed by pure water for many times until no chloride ions remain, and finally dried at 50 °C for one night.

The preparation of the ASMK aims to improve the surface characteristics of kaolin [26]. To prepare the ASMK, 100 g kaolin, 25 g $Al_2(SO_4)_3{\cdot}18H_2O$, and 2 g activated carbon (30 nm) were mixed firstly with some distilled water. And then, the above mixture was stirred well at 25 °C until it becomes mushy, and then it was placed steadily for half an hour. Finally, the sample was dried at 100 °C for 1 h and then baked at 420 °C for 2 h [26]. Two modified kaolin were further dried overnight at 50 °C, grinded to powders with particle size of < 200 μm and saved for the following experiments.

2.3. Coal combustion and PM sampling

The PM reduction efficiency of raw and modified kaolin was firstly determined via the coal combustion experiments. Before the experiments, both the modified and the raw kaolin were mixed with raw coal at the mass ratio of 3 g-kaolin/100 g-coal mechanically [6,19]. During the experiments, coal or blend of coal and kaolin was burned in a simulated air atmosphere (21% vol O_2 balanced with 79% vol N_2) in a high temperature drop-tube furnace (DTF, shown in Fig. 1), the details of which have been described in the Ref. [6,27]. The combustion temperature was set at 1500 °C, the feeding rate of the coal/coal blend samples and the simulated air were 0.15 g/min and 5 L/min respectively. For evaluating the contribution of the particles produced by the pure sorbents to the total PM, the particle size distribution of each sorbent alone was also determined by burning the sorbents without coal in the DTF.

As shown in Fig. 1, PM generated during the combustion was sampled and collected via a LPI sampling system, which mainly consists of a Dekati low pressure impactor (LPI), a cyclone, a pressure gauge and a vacuum pump [6,19,27]. Briefly, the cyclone separates the PM larger

Table 1
Properties of coal.

Proximate analysis (wt%) (ar basis)				Ultimate analysis (wt%) (daf basis)				
M	A	V	FC	C	H	O[a]	N	S
3.14	16.57	11.95	68.34	53.87	3.77	36.84	0.87	4.65

XRF analysis of coal ash (wt%)									
Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	Fe_2O_3	TiO_2
1.64	1.43	34.25	49.02	0.45	4.22	0.98	3.69	3.44	0.88

[a] The content of O is calculated by subtraction.