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Research article

Investigation of reducing ultrafine particulate matter formation by adding modified montmorillonite during coal combustion

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ABSTRACT

Up to now, nearly all sorbents used to reduce the formation of particulate matter (PM) during coal combustion are raw minerals in nature. In this work, a new idea is proposed to improve the control ability by modifying the natural minerals. First, hydrochloric acid (HCl) and hydroxyl polymeric aluminum were selected to modify raw montmorillonite, respectively. Then combustion experiment of pulverized coal alone and that mixed with the raw/modified montmorillonite was performed under O_2/N_2 atmosphere in a lab-scale drop tube furnace (DTF). The produced PM was collected via a low pressure impactor system (LPI). The results show that the raw montmorillonite reduced the $PM_{0.2}$ yield by 17.99%. Compared with raw montmorillonite, $PM_{0.2}$ yield further decreased by 29.00% and 13.11% when acid-treated montmorillonite and aluminum-treated aluminum were added. Further characterization show that the formation of ultrafine PM was reduced mainly because of the chemical reaction between the sorbent and the vaporized alkali metal. More importantly, the modification treatment optimized the surface characteristics of montmorillonite. Moreover, modification treatment increased the number of free oxygen active sites in montmorillonite due to the breakage or formation of certain metallic bonds. These changes promoted the process of capturing alkali metal and thereby the modified montmorillonite showed better performance in reducing $PM_{0.2}$ formation.

1. Introduction

Coal plays an important role in China's primary energy and coal-fired power plant is one of the major emission sources of PM. Usually, PM is enriched with heavy metals and seriously threatens human health [1–5]. Although the existing PM collection devices installed in coal-fired plants could capture most of fly ash particles, the penetration of particles with the diameter <0.2 μm ($PM_{0.2}$) is still relatively high [6]. $PM_{0.2}$ is more harmful to human health because of its higher toxicity and longer time staying in atmosphere [7–10]. Therefore, the control of $PM_{0.2}$ should be further strengthened.

Previous studies [7,11–15] indicate that the ultrafine PM produced during coal combustion is primarily derived from the alkali metals in coal. It is a good way to control the emission of ultrafine PM by adding sorbents and capturing the alkali metals during coal combustion. To find suitable sorbents, various minerals have been investigated under laboratory conditions [3,16–18]. Calcium-based, magnesium-based, silica-based and aluminosilicate-based minerals appeared to be some potential sorbents. Aluminosilicate-based clay mineral, such as kaolin, is considered as one of the most effective sorbent to control the formation of PM. Previous studies [19,20] show that kaolin is able to capture sodium vapor through complex processes, which involves both physical diffusion and surface reaction. The main product of the reaction between clay minerals and sodium vapor is different kinds of sodium aluminosilicate (Na-Al-Si) depending on the types of clay minerals. Coal combustion experiments [21–24] indicate that the yield of ultrafine PM will reduce by 30– 40% by adding kaolin. In summary, kaolin shows great potential to control ultrafine PM formation due to its distinctive physical and chemical characteristics.

As one of the most effective sorbents to capture alkali metals, kaolin has many specific properties, which provide much reference and guidance for searching new sorbents. Kaolin is a typical clay mineral with 1:1 layer aluminosilicate, containing silica tetrahedron layer and alumina octahedral layer linked with many hydroxyl groups [25,26]. When heated, kaolin would transform to meta-kaolin by dehydroxylation process. The meta-kaolin possesses more active physical and chemical properties, which play an important role in reaction between kaolin and alkali metals [19]. According to the characteristics of kaolin, another clay mineral, montmorillonite (MMT), is selected as new sorbent to capture alkali metal during coal combustion. MMT is naturally layered clay mineral and it has similar crystal structure with kaolin. The main structure unit is of 2:1 layer structure, containing double silicon tetrahedrons layers and one aluminum octahedron layer [27,28]. Also, there are many hydroxyl groups in both the surface of aluminum octahedron layer and the interlamination of MMT. When heated, a similar dehydroxylation

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process would happen, which provides potential ability to capture alkali metals just like kaolin [29,30]. Up to now, no work about using MMT as sorbent to control ultrafine PM formation during coal combustion has been done. What's more, the current sorbents are all limited to raw minerals and no modified minerals have ever been used. So, does MMT and modified MMT have good effect on reducing formation of ultrafine PM? If so, how does it work? These questions are not clear yet.

To figure out the questions mentioned above, we chose two typical methods to modify raw MMT and then obtains acid-modified MMT [31] and Al-modified MMT [32] respectively. Combustion experiment of pulverized coal with the raw MMT and the modified MMT sorbents was performed under O_2/N_2 atmosphere in a DTF to study their reduction ability to ultrafine PM. In order to reveal the reaction mechanism, combustion experiment of sodium acetate mixed with raw and modified MMT was conducted in another DTF under O_2/N_2 atmosphere. The reaction products with different residence times in the reactor are collected and characterized. This study not only introduces a new kind of sorbent but also propose a new idea to optimize the existing sorbents' physical and chemical characteristics through modification process and improve their ability to reduce ultrafine PM formation.

2. Material and methods

2.1. Modified MMT samples preparation

Raw MMT (denoted as R-M) from Inner Mongolia Chifeng was used in this work and its purity was over 95%. Two typical methods, acid-treatment and aluminum-treatment, were adopted to modify MMT. The reagents used to modify MMT are HCl, sodium hydroxide (NaOH) and aluminum chloride ($AlCl_3$), and all reagents are chemical pure.

As shown in Fig. 1, treating MMT by HCl was conducted as follows: (1) raw MMT was mixed with HCl solution (1 mol/L) at a solid to liquid ratio of 30 g/L; (2) the liquid-solid suspension was constantly stirred in magnetic stirrer for 12 h at the temperature of 80 °C; (3) the sample was cooled to room temperature and washed with deionized water at least 5 times to rinse out the excess acid; (4) finally, the sample was pulverized and sieved into a size fraction of 38.5–90 μm, denoted as Ac-M.

The method of modifying MMT by hydroxyl polymeric aluminum solution was similar to the former, the modified process was carried out as follows: (1) hydroxyl polyhydroxy aluminum solution was prepared by dropwise adding NaOH (0.3 mol/L) solution to the $AlCl_3$ (0.4 mol/L) solution at volume ratio of 16/5; (2) raw MMT was mixed with the hydroxyl polyhydroxy aluminum solution at a solid to liquid ratio of 20 g/L; (3) the mixture was then stirred for 4 h at the temperature at 100 °C; (4) the following steps were the same with acid treatment and the sample was denoted as Al-M.

Table 1
Proximate and ultimate analysis of coal samples.

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

[a] By difference.

2.2. Combustion experiments

2.2.1. Coal combustion and PM sampling

A typical anthracite (Shanxi coal) was used in our study. The coal was pulverized and sieved into a size fraction of 45–90 μm, denoted as R-coal. The raw coal was physically mixed with each sorbents (R-M, Ac-M, and Al-M) at a mass ratio of 3% and the blends were denoted as R-M-coal, Ac-M-coal and Al-M-coal, respectively. The properties of coal samples are listed in Tables 1 and 2.

The combustion experiment of pulverized coal mixed with MMT and modified MMT sorbets was conducted in a DTF at the temperature of 1500 °C. As shown in Fig. 2, the reactor is 1440 mm in length and 40 mm in inner diameter [33]. The combustion atmosphere was 21 vol.% O_2 balanced with N_2 and the gas flow rate was set as 5 L/min to guarantee that the residence time of particle was ~1.2 s. The feed rate of coal, with and without sorbents, all maintained at 0.15 g/min. During experiment, the combustion product got into cyclone and LPI in turn after quenched with pure N_2 (5 L/min). In cyclone, the coarse particles with aerodynamic diameter larger than 10 μm were removed. The rest of PM was collected and segregated into 13 stages from 10 μm down to 0.0281 μm by LPI. To avoid the condensation of vapor, the sample devices and the connections kept heating at the temperature ~135 °C. It is noted that sample amount was proper when sampling time was set as 4 min. To ensure the accuracy and repeatability of the experiment results, PM sampling was repeated at least 3 times for each combustion case.

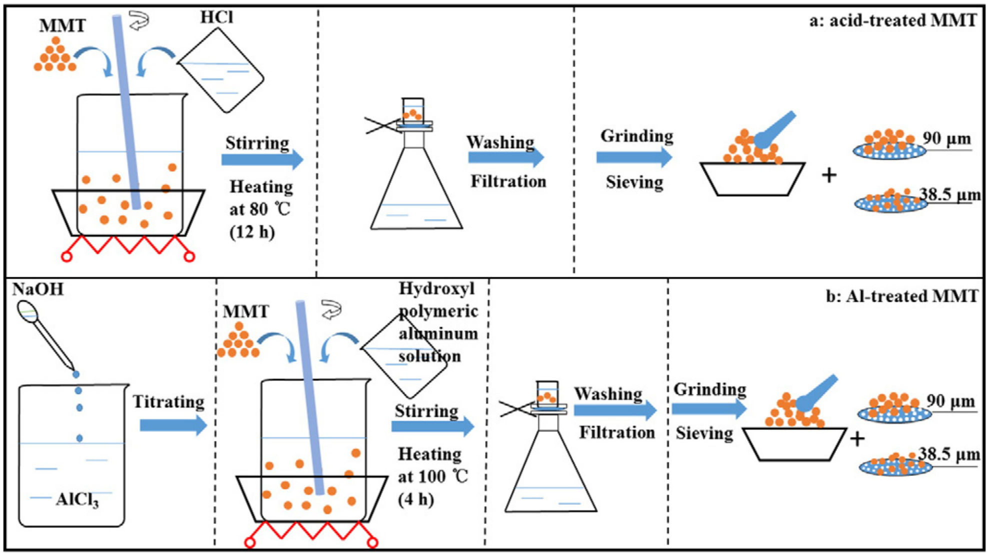

Fig. 1. Schematic sketch of the methods of producing the modified MMT.