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Effect of stannous chloride on low-temperature oxidation reaction of coal

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ABSTRACT

Stannous chloride ($SnCl_2$) was firstly used as an inhibitor to prevent coal oxidation. Thermal analysis was used to study the influence of $SnCl_2$. Weight increase due to oxygen chemisorption, the ignition temperature, the burnout temperature and heat released during the whole process were evaluated as main parameters. The results indicated that the addition of $SnCl_2$ leads to significant reduction in the percentage of mass increase. The presence of $SnCl_2$ caused increase in the ignition temperature and decrease in the heat released. However, there is probably no effect of $SnCl_2$ on the burnout temperature. The mechanism of the $SnCl_2$ suggested that the addition of $SnCl_2$ to the coal oxidation mainly influence the oxygen chemisorption by consuming more oxygen. Thus, $SnCl_2$ can be recommended as effective inhibitor to coal oxidation.

1. Introduction

Coal oxidation problem has become more and more serious during the process of coal mining and storage [1–4]. Low-temperature oxidation of coal is the primary source of heat leading to uncontrolled spontaneous combustion which can result in damage and financial losses [5–9]. Impregnation of coal by some inhibitors can be one of the effective ways of preventing spontaneous combustion of coal [10–13]. The role of suction salts (such as NaCl, $MgCl_2$ and $CaCl_2$), and polymer inhibitors is absorbing moisture in air and form thin membrane on the surface of coal to hinder access of oxygen to reach the active centers on the coal surfaces [14–18]. However, these inhibitors exhibit both low efficiency and short active lifetimes. Meanwhile, these suction salts are corrosive on the metal parts of devices. Therefore, chemical reactions between coal and additives were also described by Smith et al. [19]. Some chemical inhibitors such as some oxidizing agents, ionic liquids, free radical scavenger and several inorganic salts including Na_3PO_4 and $Mg(Ac)_2$ which can react with active functional groups on the coal surface or eliminate free radicals so as to decrease the formation of active groups or reduce their activities of reaction with oxygen were also described [11,20–25]. For example, Zhan [21] studied the impact of Na_3PO_4 on coal oxidation process, and found that Na_3PO_4 plays a role in modifying the routes for decomposition of hydroxyl, and subsequently improving the coal thermal stability. Wang [22] used ionic liquids to inhibit the coal spontaneous combustion. Li [23] reported the inhibitory effect of free radical scavenger 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO). These compounds are highly efficient, although some of the chemical inhibitors exhibit disadvantages such as high cost and an unstable inhibitory effect when combined with certain types of coal. Therefore, the goal of the current work is to find a substrate with high inhibitory efficiency to prevent coal spontaneous combustion.

As we all know, stannous chloride ($SnCl_2$) is a stable and water tolerant Lewis acid, commercially available and less corrosive. Disparate studies in the literature suggest that stannous chloride is a good reducing agent which is widely used in different fields [26–29]. For example, $SnCl_2$ was shown to reduce grapheme oxide (GO) [30], and was also reported as precursor to synthesize SnO_2 nanoparticles [31]. Moreover, $SnCl_2$ was widely used in electrolytic baths for tin plating [32,33]. To the best of our knowledge, there is no report on $SnCl_2$ as an inhibitor used in prevention of coal oxidation. Therefore, in this paper, we firstly used $SnCl_2$ as a low-temperature inhibitor to prevent coal spontaneous combustion. The inhibition performance of stannous chloride was evaluated by thermal analysis.

2. Experimental

2.1. Preparation

A bituminous coal labeled as CJS was collected from Chenjiashan Colliery, Shanxi Province. The coal was crushed and ground into 0.1–0.15 mm particles. The basic characteristics of the coal are given in Table 1. The coal particles were dried at 40 °C in nitrogen till the mass of the coal was constant. Then it was collected and kept under seal for the experimental investigations.

$SnCl_2•2H_2O$ at a purity of 98% was selected as an additive for the experiments, which was purchased from a local medical station.

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Table 1
Properties of CJS coal.

Proximate analysis (air dried basis)	
Moisture/%	5.82
Ash/%	8.58
Volatile matter/%	28.74
Fixed carbon/%	56.86
Heat of combustion/kJ g^{-1}	30.03

Different amounts of $SnCl_2 \cdot 2H_2O$ were dispersed in deionized water with vigorously stirring to make the stannous chloride solutions. Sodium chloride at a purity of 99.5% was dissolved in deionized water to prepare 7 wt% NaCl aqueous solution, which was added to 2 g of coal samples together with the stannous chloride solutions. Then the mixtures were dried at 110 °C in nitrogen for 2 h to remove moisture, and finally, various amounts of $SnCl_2$ and 7 wt% NaCl treated bituminous coals were obtained.

2.2. TG/DSC analysis

The oxidation behaviors of raw coal and those mixed with $SnCl_2$ were evaluated by thermo-gravimetric analysis (TG). The experiments were performed using a simultaneous TG-DSC measurement (TA-Q600). First, a sample of 5–10 mg in mass was quickly and loosely placed on the aluminum crucible. Each sample was heated at different heating rates (5, 10 and 15 K/min) up to 110 °C and held for 30 min to remove residual moisture, then was heated to 600 °C at different heating rates (5, 10 and 15 K/min). It is assumed that for such a small particle size the effect of temperature distribution within the sample particle is eliminated. 21% oxygen (dried air) was flowed as the reaction gas, and the flow rate of the air purging into the furnace was set as 100 mL/min. In order to study the stability of $SnCl_2$ over the studied temperature range, blank test was designed consisting of the same pretreatment procedure as mentioned above, however, instead of coal, α-Al_2O_3 was used as an inert supporting solid.

3. Results and discussion

3.1. TGA measurement

3.1.1. Determination of heating rate of TGA measurement

During the experiment, heating rate may affect the result, therefore, we first study the TGA-DSC profiles of $SnCl_2$ treated CJS coal sample at different heating rates. The results are shown in Fig. 1.

In our study, from the figure, during preliminary heating to 110 °C, as the temperature increased, the samples firstly undergo a slight decline in their masses, which is ascribed to the moisture loss. And we found that there was a little endothermic peak with very low heat consumption at about 110 °C in DSC curves, which is corresponding to the weight decline caused by moisture loss. It was observed that the maximum peak and burn-out temperatures are increased as the heating rate is increased from 5 to 15 K/min. This may be the result of longer reaction time allowed and slower combustion at lower heating rates. When lower heating rate is applied, coal and oxygen can interact well and reach higher conversion at lower temperature, thus reducing the thermal lag of a sample. Meanwhile, higher heating rate can cause the temperature gradient in the coal sample, thus resulting the TG curves deviates to higher temperature. Therefore, in order to reduce the thermal lag of a sample during its heating, lower heating rate (5 K/min) is determined.

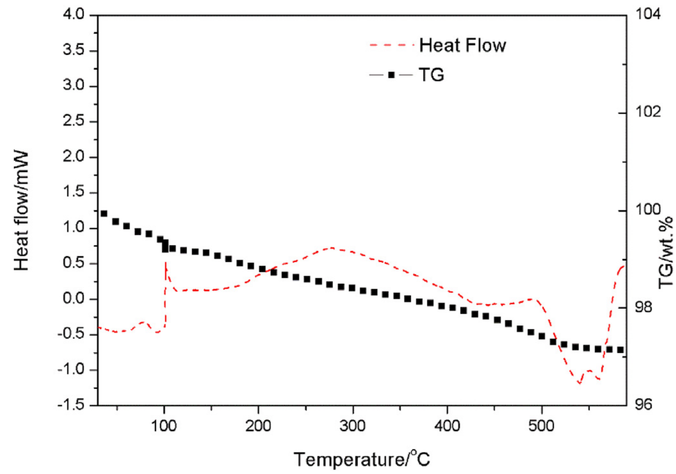
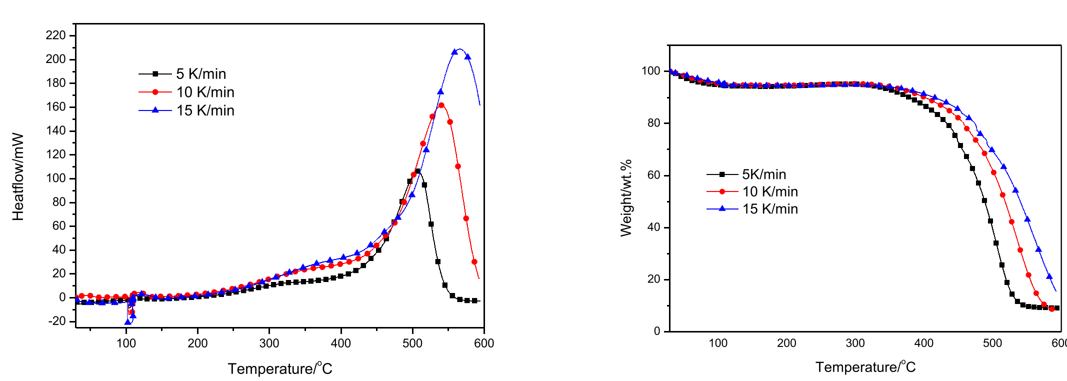


Fig. 2. TG-DSC curves of 7 wt% $SnCl_2$ in α-Al_2O_3.

3.1.2. Results from TGA analyses

With the best heating rate (5 K/min) in hand, blank tests with different amounts of pure $SnCl_2$ and α-Al_2O_3 was measured, and the TG-DSC curves of 7 wt% $SnCl_2$ in α-Al_2O_3 are shown in Fig. 2. The result indicated that the sample mainly loses weight between 100 and 450 °C, and this process is exothermic with low heat. This process may be attributed to the oxidation of $SnCl_2$ to form tin oxychloride, and following the decomposition of tin oxychloride. The DSC curve also showed that there's a little endothermic peak in about 100 °C, which is ascribed to the hydration water loss.

Typical TGA data were obtained from the aerial oxidation measurements for the coal sample containing various weight percent of $SnCl_2$. With this respect, corrections were made by subtraction of TG/



(a) DSC (b) TG

Fig. 1. Profiles from TG-DSC thermal analysis of CJS coal of different heating rate.