Research article

Synchronous thermal analyses and kinetic studies on a caged-wrapping and sustained-release type of composite inhibitor retarding the spontaneous combustion of low-rank coal

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ARTICLE INFO

ABSTRACT

In this paper, a novel type of composite inhibitor (PAA/SA-CC) was developed and characterized with the aim of achieving sustained and highly effective inhibition on spontaneous combustion of low-rank coal. A concept of realizing the caged-wrapping and sustained-releasing function of polymer as regard to high-activity chemical inhibitor was proposed, basing on which the composite inhibitor was prepared with poly(acrylic acid)/sodium alginate super absorbent and (+)-catechin. Subsequently, synchronous thermal analysis was carried out to investigate the influence of inhibitors on the tendency of coal to spontaneous combustion, which was characterized by four characteristic temperatures and three other characteristic parameters marked. Furthermore, hot-surface ignition tests were conducted to validate the inhibition on coal ignition behavior. Finally, non-isothermal isoconversional methods were performed by Starink model and Friedman-Reich-Levi model, respectively. The results demonstrate that PAA/SA-CC synergizes the inhibiting characteristics of the two distinctive inhibitors, especially exerts a continuously high-efficiency inhibition on the coal-oxygen chemisorption, which performs better than the case of mechanically blending. Besides, both the two kinetic analysis approaches agree on the results that the incorporation of 3 wt.% PAA/SA-CC shifts the apparent activation energy-temperature evolution to higher levels.

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1. Introduction

Self-oxidation and subsequent spontaneous combustion of low-rank coal is one of the major problems for coal mining industry, which remains quite common to occur in underground goafs [1], shallow-buried coalfields [2], coal stockpiles [3] and even coal gangue [4]. The associated detrimental effects involve huge personal casualties, loss of property and burnout of energy resources, which, in turn, produces serious environmental concerns [5]. To mitigate the hazards, various inhibitors [6–9] have been developed and applied in retarding the coal spontaneous combustion. For instance, suction salts such as $CaCl_2$, NaCl, $Mg(Ac)_2$[6], fly-ash stabilized foams [7], foamed hydrogels [8], and polymer emulsions [9] have been demonstrated to play the role of insulating the active sites on coal surface from oxygen with a physically-based principle of forming an isolation layer, which precisely determines low efficacy and poor environmental stability of this class of inhibitors. On the other hand, the chemically-based inhibitors [10–14] have also been described, aiming at either interrupting the free radical reactions or restraining the formation of reactive species. Ionic liquids such as imidazolium-based species [11] and phosphonium-based species [12] were added in coal samples proceeding to spontaneous

combustion, which have been demonstrated to be effective on dissolving the reductive groups, delaying the decomposition of aliphatic hydrocarbon groups and the formation of carbonyl groups during coal oxidation. Zhan et al. [13] reported the effects of Na_3PO_4 on inhibiting coal oxidation. This inorganic salt was discussed to take effect by promoting the conversion from hydroxyl into ether linkages, which improved the thermal stability of the coal. Additionally, the inhibiting behaviors of poly(ethylene glycol) were also investigated by Fourier transformation infrared spectroscopy, with results suggesting that the active groups on coal surface were suppressed while the formation of stable ether linkages was accelerated [14]. However, current chemical inhibitors exhibit common disadvantages of poor sustainability and short active lifetimes with temperature rising in that the burst-release pattern may cause huge waste by excess oxygen in initial period. Accordingly, the sustained and high-efficiency inhibition of coal spontaneous combustion remains a potential topic of inhibitor research.

In addition, several approaches and criteria have been developed for selecting and evaluating the inhibiting performance of various inhibitors [13–17]. Parameters such as the adiabatic oxidation rate [15], the oxygen consumption combined with the crossing point temperature [16], the greenhouse gases emission concentration [17] in industrial tests and variations of in-situ series FT-IR [14] in laboratory tests were utilized. In particular, synchronous thermal analyses, basing on the simultaneous TGA-DSC measurements of sample, can provide an

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interrelated mass/heat flow/temperature history of the reaction progress [18], which have been widely used to characterize the reactivity and compositional characteristics of coal, as well as assess the inhibition properties towards the tendency of coal to spontaneous combustion [19]. Avila's research group [20] proposed a reliable criterion for identifying coals prone to self-ignition with two defined parameters, i.e., the mass increase of oxygen adsorption and the spontaneous ignition index relying on TGA/DTG data collected from 27 typical coals. Moreover, thermal analyses were also performed in investigating the inhibition of urea and $CaCl_2$ on coal oxidation via the maximum-weight temperature, the weight increase of oxygen chemisorption and the corresponding heat release [21]. In addition, non-isothermal TGA-DSC tests with different heating rates allowed for the determination of activation energy, which also played a role of judging the inhibition [22,23]. However, current approaches only took into account partial reactivity but none have considered the inhibition on the complete stage evolution of coal proceeding to spontaneous combustion exerted by inhibitors.

Poly(acrylic acid)/sodium alginate super absorbent (PAA/SA) has been regarded as a promising material for application in pharmacology such as controlled drug delivery due to its excellent properties, e.g., controlled water release ability, biodegradability and non-toxicity [24,25], which also make PAA/SA potential to be examined as an ideal carrier as well as sustained-release pump for chemical inhibitors of coal spontaneous combustion. Catechin (CC), the natural polyphenol extracted from green tea plants, presents valuable in a variety of research fields including biomedicine [26], anti-aging [27] and food science [28] due to its potent antioxidant activity. In addition, as reported in previous research, (+)-catechin can function as a highly effective chemical inhibitor towards coal spontaneous combustion by eliminating crucial peroxy radicals during oxidation [29]. Taking full account of characteristics of both PAA/SA and CC, a sustained-release type of composite inhibitor is proposed. In this paper, PAA/SA-CC was synthetized, aiming at achieving the continuously high-efficiency inhibition on coal spontaneous combustion, accompanied with characterization by SEM. Furthermore, a comprehensive methodology for evaluation of the inhibiting behavior of PAA/SA-CC on the complete stage evolution of coal proceeding to spontaneous combustion was established on the bases of synchronous thermal analyses and corresponding kinetic analyses.

2. Experimental and methods

2.1. Coal samples preparation and characterization

Two typical Chinese low-rank coals prone to spontaneous combustion were sampled from Xiashijie (XSJ) Colliery in Shanxi province and Shengli (SL) Colliery in Inner Mongolia, respectively, the former had recently suffered a fire accident caused by the spontaneous combustion of coal [30]. The coal lumps were mechanically crushed and sieved to the size ranging from 0.075 to 0.15 mm in a vacuum glove box and then dried for 24 h at 40 °C under vacuum. Proximate and ultimate analyses were carried out with the results summarized in Table 1.

2.2. Composite inhibitors preparation and characterization

2.2.1. Preparation of PAA/SA-CC composite inhibitors

Poly(acrylic acid)/sodium alginate super absorbent (denoted as 'PAA/SA') and (+)-catechin (denoted as 'CC') were selected as raw materials to prepare the composite inhibitor (denoted as 'PAA/SA-CC') for the experiments. PAA/SA was synthesized depending on the means of solution polymerization [31]. Specifically, 5 g of acrylic acid was weighed and added into a 100-mL beaker and then the prepared NaOH solution (25 wt.%) was dripped under stirring into the beaker until the pH value reached 6.5. After cooling, the neutralized solution was transferred to a 250-mL four-neck flask equipped with a stirrer, a reflux condenser, a thermometer and N_2 inlet. Subsequently, 100 g of 5.0 wt.% sodium alginate aqueous solution was added into the flask and stirred well. The reactor was placed in a water bath at a constant temperature (80 °C). N,N′-methylenebisacrylamide (32 mg) as the cross linker and ammonium persulfate (120 mg) as the initiator were successively added into the reactor, stirring constantly, polymerization and graft copolymerization were carried out for 3 h under nitrogen condition. The product was dried at 80 °C and then pulverized to particles of 0.15–0.20 mm.

Afterwards, obtained PAA/SA particles were mixed with CC at a mass ratio of 1:2. A certain amount of distilled water was added into the mixture and the obtained suspension was magnetically stirred at 150 rpm for 1 h at room temperature, during which the PAA/SA particles swelled and CC molecules penetrated into the three-dimensional cross-linked network structure of PAA/SA hydrogel. The product was filtered, then vacuum dried at 40 °C to a constant weight and pulverized to particles of 0.15–0.20 mm and the desired PAA/SA-CC was obtained. Prior to measurements, different proportions of inhibitors were added to coal samples, mechanically homogenized, and then stored in a thermostat at 25 °C for 48 h.

2.2.2. Characterization of the sustained-release property

The composite inhibitor of PAA/SA-CC was designed with the aim of achieving synergism by realizing the caged-wrapping and sustained-releasing function of polymer as regard to high-activity chemical inhibitor, as depicted in Fig. 1. Concerning the multi-component interaction forms, we can see that CC is homogeneously embedded in the dense three-dimensional network structure cross-linked by chains of PAA and chains of SA, which may protect the inhibiting activity of CC against being depleted by the excess dynamic oxygen. With the increase of temperature, the three-dimensional cross-linked network gradually depolymerizes and becomes sparse [25], as a result, the internal active CC is sustained-released to the surrounding coal-oxygen interaction system, which can continuously afford reactive hydroxyl groups and further hydrogen free radicals for inactivating the active sites of coal oxidation by eliminating the crucial linking radicals (i.e. ROO•, RO•, •OH), cutting off the free radical chain reaction of coal oxidation and reducing the formation of secondary active sites, and as a result, realizing the continuous inhibition of coal spontaneous combustion [29]. On the basis of the sustained-release property of PAA/SA-CC, it can not only combine the inhibition characteristics of PAA/SA and CC, but also achieve synergism by improving the effective utilization rate as well as the inhibitory efficiency of CC.

In order to characterize the sustained-release property visually, a Quanta 250 scanning electron microscope (SEM) was employed to observe the micromorphology of PAA/SA-CC and the coal samples with and without inhibition. Samples were coated with Au using a sputtering coater which endowed sample surfaces with electroconductivity prior to observation.

Table 1
Basic parameters of the coal samples.

Species	Moisture (wt.%), air dried basis	Ash	Volatiles	Fixed carbon	Carbon (wt.%), dry ash free basis	Hydrogen	Ro (%)[a]	Coal rank
XSJ	10.33	16.21	30.10	43.36	75.72	4.18	0.49	Sub-bituminous
SL	16.05	12.69	34.56	36.70	71.03	4.54	0.38	Lignite B

[a] Ro, vitrinite reflectance index.