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Imidazolium based ionic liquids affecting functional groups and oxidation properties of bituminous coal

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ABSTRACT

Low temperature oxidation of coal will result in coal spontaneous combustion in mined-out areas. We proposed to use ionic liquids to inhibit the coal spontaneous combustion in this paper. In order to study the inhibiting effect of ionic liquid (IL) on coal oxidation, we successfully dissolved bituminous coal samples in six kinds of imidazolium based ionic liquids, [AOEmim][BF_4], [HOEmim][BF_4], [Amim][Cl], [Emim][AC], [Bmim][AC] and [Bmim][OTf]. The functional groups in the coal samples pre-treated by different ILs were detected by Fourier Transform Infrared Spectroscopy (FTIR) in detail. It is found that the ILs are capable of breaking the associated hydroxyls into dissociated hydroxyls. And during the interaction between coal and ILs, the carboxyl groups have been created. Thermo Gravimetric experiment results show that the weight loss ratios of the IL-treated coals were less during 20–400 °C stage, compared with the IL-untreated coal, which indicates that most of the easily reductive groups effectively dissolved in the ionic liquids. According to the exothermic rate curves and the computed activation energy values, it is demonstrated that the [Bmim][OTf] and [Bmim][AC] make better effect than the other ILs for depressing the oxidation rate of bituminous coal.

1. Introduction

Coal has exothermic reactions with oxygen, even at ambient temperatures, and sometimes resulting in spontaneous combustion with certain hazardous gases released, which imposes a danger to life and the environment. Therefore, there is an obvious need to inhibit the coal spontaneous combustion in mined-out areas for mining safety. The existing fire-fighting materials, such as the three-phase foam and the inhibiting gels, make effect only by isolating oxygen from coal surface, and fail in preventing the combustion by changing or reducing the easily oxidative structures in coal. Accordingly, it is necessary to find a new material which can inhibit the spontaneous combustion by reducing the active chemical structures of coal.

Many studies have confirmed that there exist kinds of active groups, carboxyl, hydroxyl, hydrocarbon side-chains and so on, on the surface structure of coal, which may react with oxygen and even lead to spontaneous combustion. If these functional groups were reduced or changed, then the spontaneous combustion would be inhibited for lacking of reactants.

Some ionic liquids can swell and even dissolve the inorganic structures, fibers and polymers (Winterton, 2006; Wang et al., 2009a; Amitesh, 2009; Yuan et al., 2010; Fort et al., 2007). And the ionic liquids may dissolve more aromatic structures than alkanes (Hank et al., 2003). Ionic liquids also are mutually soluble with some solvents such as alcohol (Crosthwaite et al., 2004, 2005). As for the coal, it is reported that certain ionic liquids, such as [Bmim][Cl], [Emim][BF_4], [Emim][PF_6] can swell, disperse and partially fragment coal at the ambient temperatures, increasing the liquefaction and gasification yield. Geng et al. used [Bmim][BF_4] to pretreat coal to promote coal conversion ratio and oil–gas yield (Geng et al., 2010). Cao et al. used [Emim][BF_4] to swell coal and improved coal's fluid characteristics (Cao et al., 2009a,b). Paul Painter, and Neurxida Pulati et al. suggested that there be a rapid and large build up of stresses when two coals they studied were immersed in [Bmim][Cl] (Paul Painter et al., 2010a,b). And they inferred that the replacement of metal cations with bulky IL groups may play a role during the coal fracturing and dispersion in ionic liquids.

Although the ionic liquids can improve the swelling of coal to increase the liquefaction and gasification productivity, few attempts has been done to investigate the effect of ionic liquids on

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the coal spontaneous combustion properties. The author has put forward a new vision of using ionic liquids to inhibit the spontaneous combustion of coal in 2009, but gave no scientific investigations and conclusions (Wang et al., 2009b). Here, we will report our latest investigation results from two aspects, including dissolving the functional groups and affecting the exothermic oxidation of coal.

We selected some hydrophilic ILs to fragment, disperse, and dissolve the functional groups in a bituminous coal, and the oxidation ability of coal was weakened after ILs pretreatment. Also, we analyzed the microscopic functional groups change of IL-treated coals compared with the untreated coal by In situ Fourier transform infrared (In situ FTIR), and tested the macroscopic weight loss ratio and thermal discharge curves during oxygenolysis process using the Simultaneous Thermal Analyzer (STA). It is hoped that the question will be resolved with our proposed method. This paper also provides useful data for application of ionic liquid on coal liquefaction and gasification. We report out systematic results here.

2. Experimental

2.1. Experimental materials and coal samples

The ILs used here were 1-acetoxyethyl-methyl imidazolium tetrafluoroborate [AOEmim][BF_4], 1-allyl-3-methyl imidazolium chloride [Amim][Cl], 1-butyl-3-methylimidazolium acetate [Bmim] [AC], and 1-ethyl-3-methylimidazolium acetate [Emim][AC] which can dissolve fiber structures, 1-hydroxylethyl-3-methyl imidazolium tetrafluoroborate [HOEtmim][BF_4] having strong reductive property, 1-butyl-3-methylimidazolium trifluoromethanesulfonate [Bmim][OTf] with big anion, purchased from the Lanzhou Greenchem ILS, LICP. CAS., China. Purity of all used ionic liquids is more than 99%. Fig. 1 gives the chemical structures of these ionic liquids.

A bituminous coal sample was obtained from WenZhuang Coal Mine of Lu'An Group Corporation in China. This bituminous coal has a moisture content of 0.97%, ash content of 17.62% and a volatile content of 15.19%.

2.2. Experimental procedures

A freshly picked coal sample was crushed and sieved, and the 0.1–0.15 mm size fraction was retained for preparation. The coal sample was dried in a vacuum drying oven overnight at 30 °C. Then we mixed it with 0.1 N HCl in order to remove most of the dissociated mineral ions from the coal to avoid their interference on spectra. After being mixed with HCl for 4 h, the HCl was washed by the distilled water until the retained coal sample presented the neutral pH. Then, the acid-treated coal sample was dried in the vacuum drying oven for 48 h. We shared the dried coal sample into seven, and separately mixed six shares well with six kinds of isometric ionic liquids. After 48 h mixing under ambient conditions, we used distilled water to wash away the ionic liquids and filtrate the mixtures. For entirely removing the ionic liquids in the coal samples, we tested the pH value until it was neutral. Then the residues were evaporated in the vacuum drying oven. The acid-washed coal sample which is not pre-treated by the ionic liquids is named as the IL-untreated coal, and the contrasts are the IL-treated coal samples.

Functional groups of the IL-untreated coal and IL-treated coal were detected by an In situ Fourier Transform Infrared Spectrometer of NICOLET 6700. Solid dried coal samples were prepared by grinding with KBr (mass ratio of coal to KBr is 1:150) in a Wig-L-Bug. Every sample was scanned 64 times ranged from 450 to 4000 cm^{-1} with the resolution of 4 cm^{-1}. All tested spectra were transformed based on the Kubelka–Munk function for making absorption intensity proportional to the quantity of functional groups.

The weight loss and thermal release of the IL-untreated coal and IL-treated coals were detected by the STA449C Simultaneous Thermal Analyzer produced by Germany NETZSCH. Seven coal samples with the initial mass of about 30 mg were prepared for experiments. Heating rate was set as 10 °C/min from 20 °C to 850 °C. 21% oxygen was flowed as the reaction gas, and the air flow was set as 250 ml/min. Before heating, we displayed the tested sample in the sample room for 5 min, and then the non-isothermal heating process started.

3. Results and discussion

3.1. The effect of ionic liquids on the functional groups

For the convenience of the readers, we show the FTIR results in Fig. 2 showing the typical functional groups spectra.

As shown in Fig. 2, the ionic liquids do not greatly change the functional group variety of coal, but some groups such as the hydroxyl, carbonyl and carboxyl present some obvious shift in their FTIR spectra.

1) The hydroxyls in the IL-untreated sample include the dissociated ones at about 3655 cm^{-1} and 3629 cm^{-1}, and the associated ones at about 3531 cm^{-1}, 3406 cm^{-1} and 3341 cm^{-1}. But only dissociated hydroxyl absorption peaks are shown in the spectra of the IL-treated coals. It indicates that the ionic liquids can break the

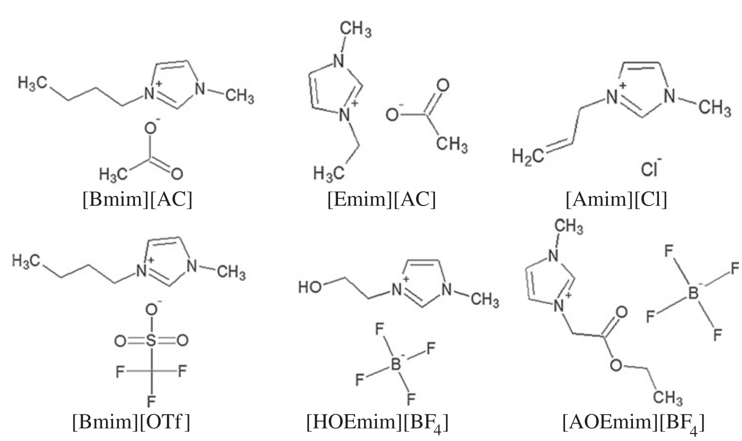

Fig. 1. Structures of the used six ionic liquids [AOEmim][BF_4], [HOEmim][BF_4], [Amim][Cl], [Bmim][AC], [Emim][AC], [Bmim][OTf].