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Effect of Imidazolium Based Ionic Liquids on Coal Exothermic Oxidation by Thermal Analysis Experiments

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Abstract

In order to study the oxidation-inhibiting effect of ionic liquid (IL) on coal, this paper successfully used six imidazolium based ionic liquids, \([\text{AOEmim}][\text{BF}_4]\), \([\text{HOEmim}][\text{BF}_4]\), \([\text{Amim}][\text{Cl}]\), \([\text{Emim}][\text{AC}]\), \([\text{Bmim}][\text{AC}]\) and \([\text{Bmim}][\text{OTf}]\) to dissolve and disperse coal. The exothermic oxidation of the raw coal and those pretreated by ILs were separately tested by Simultaneous Thermal Analyzer. The tested results show that there were more active groups left in the \([\text{AOEmim}][\text{BF}_4]\) and \([\text{Amim}][\text{Cl}]\) pretreated coals. While, the \([\text{HOEmim}][\text{BF}_4]\), \([\text{Emim}][\text{AC}]\), \([\text{Bmim}][\text{AC}]\) and \([\text{Bmim}][\text{OTf}]\) pretreated coals lost less mass ratio and the process was short, which shows that these four ionic liquids dissolved or destroyed more active groups of coal and inhibited the coal oxidation better than the \([\text{AOEmim}][\text{BF}_4]\) and \([\text{Amim}][\text{Cl}]\) ionic liquids. Ionic liquid with a large anion and a cation substituted by simple chains and will improve the ionic liquid’s destroying ability for coal’s chemical structures.

Keywords: imidazolium based ionic liquids; coal; dissolution; exothermic oxidation

1. Introduction

Ionic liquids (ILs) can dissolve and swell the inorganic structures and organic structures such as fibers

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and polymers. There has been some investigation reporting that the [Bmim][Cl], [Emim][BF₄], [Emim][PF₆] can swell coals at the ambient temperatures for increasing the liquification and gasification yield [1-5]. And it was reported that the ILs can dissolve more aromatic structures than alkanes [6]. Many studies have confirmed that there exist kinds of active groups such as carboxyl, hydroxyl and hydrocarbon on the surface of coal reacting with oxygen leading to coal spontaneous combustion. If these functional groups are reduced, then the combustion property of coal will be weakened. However, there have been no relative reports so far. In this paper, we selected six ILs to mix with the coal and tested the macroscopical oxygenolysis loss mass and thermal discharge of the IL-pretreated coals using the Simultaneous Thermal Analyzer (TGA), deducing the regularity of ionic liquids affecting on coal’s oxidation ability.

2. Experiments and Analysis

2.1. Experimental Materials and Methods

The ILs used in this study were 1-acetoxyethyl-methyl imidazolium tetrafluoroborate [AOEmim][BF₄], 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-hydroxyethyl-3-methyl imidazolium tetrafluoroborate [HOEtmim][BF₄] with strong reductive property, 1-butyl-3-methylimidazolium trifluoromethanesulfonate [Bmim][OTf] with big anion. All solvents were 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 the used ionic liquids.

Bituminous coal is obtained from WenZhuang Coal Mine of Lu’An Group Corporation in China. This bituminous coal is reported have a moisture content of 0.97%, ash content of 17.62% and a volatile content of 15.19%. The coal sample was grinded into coal particles (<1.5 μm), and we removed the ash using 0.1mol/L HCl for avoiding the effects of inorganic minerals on spectra. After that the deashed coal samples were dried in the vacuum drying oven for avoiding effect of water. Then, we separately mixed equiponderant coal samples with isometric different ionic liquids. After 48 hours’ mixing under standard conditions, the IL-pretreated coals were put into a simultaneous thermal analyzer (TGA) for testing the macroscopical oxygenolysis loss mass and thermal discharge.

Fig.1 Structures of the used six ionic liquids [Bmim][AC], [Emim][AC], [Bmim][OTf], [AOEmim][BF₄], [HOEtmim][BF₄], [Amim][Cl]
conditions, we used distilled water to wash and filtrate the mixtures. Most of the detached structures soluble in water passed through the filter paper during the filtration washing. For entirely removing the IL in a mixture, we tested its pH value until it is neutral. Then the pre-treated coals were evaporated in the vacuum drying oven for the TG experiments.

The mass loss and thermal releasing regularity of the raw coal and ILs pre-treated coals were detected by the STA449C simultaneous thermal analyzer produced by Germany NETZSCH. The size of coal particles was 0.1~0.15mm with 30 mg of mass. Heating rate was set as 10℃/min from 20℃ to about 900℃. The reaction gas was oxygen and nitrogen mixtures with 21% oxygen and the air flow was 250 ml/min. Before heating, we displayed the sample in the sample room for 5 minutes, then, the non-isothermal heating process started.

2.2. Lostmass Analysis

The TG curves of the IL-pretreated coals and the raw coal

![Fig.2 The TG curves of the IL-pretreated coals and the raw coal](image)

The TG curves describe the coal mass ratio change with the rising temperatures[7]. The TG curves of the raw coal and the six IL-pretreated coals were shown in Fig.2. Comparing the lost mass ratio of the ILs pre-treated coals with that of the raw coal, it was found that the weight loss ratios of the IL-pretreated coals were always less than that of the raw coal, which maybe ascribe to the dissolution of the easily oxidized functional groups such as hydroxyls, carbonyls, carboxyls and alkanes in the six ionic liquids. [HOEmim][BF₄] pre-treated coal lost the least weight ratio, followed by the [Bmim][AC] and [Emim][AC] pre-treated coals. The [AOEmim][BF₄] and [Amim][Cl] pre-treated coals lost weight sharply during 30~200℃.

The DTG curves shown in Fig.3 demonstrated the thermogravimetric rates of the all coal samples. Form the trends of the thermogravimetric rates change, it was observed that the weight loss rate of the raw coal reached peak at the temperature of 65℃, and gradually decreased after 100℃. In the whole stage, the weight changing rates of ILs pre-treated coals were slower than that of the raw coal.

Synthesizing the TG-DTG curves, it was observed that the [AOEmim][BF₄] pretreated coal contained more strong active groups, and its oxidation mainly happened at the low temperature stage.
2.3. Exothermic rates analysis

The DSC results shown in Fig.4 indicated that not all used ionic liquids could reduce the heat releasing during the coal oxidation. The [AOEmim][BF₄], [Amim][Cl] and [Emim][AC] ionic liquid pre-treated coals released heat more quickly than the raw coal did, which showed that these three ionic liquids made poor dissolution for coal active groups. The heat releasing rates of the [Bmim][AC], [Bmim][OTf] pre-treated coals were the least, indicating that the two ionic liquids dissolved more active structures leading to less functional groups reacting during the low temperature oxidation of coal.

From the TG-DTG-DSC curves, we obtained the results that the [HOEmim][BF₄], [Emim][AC], [Bmim][AC] and [Bmim][OTf] ionic liquids can dissolve or destroy more active groups of coal and inhibited the coal oxidation better than the [AOEmim][BF₄] and [Amim][Cl] ionic liquids. Accordingly, the complex cation and small anion will reduce the dissolution ability of ionic liquid, while, the long and simple cation and large anion will improve the ionic liquid’s destroying ability for coal structure groups.
3. Conclusion

This paper investigated the oxidation-inhibiting effect of six hydrophilic ionic liquids on coal by the Simultaneous Thermal Analyzer. According to TG-DTG-DSC testing results, it was learned that there were more active groups left in [AOEmim][BF₄] and [Amim][Cl] pretreated coals. The [HOEmim][BF₄], [Emim][AC], [Bmim][AC] and [Bmim][OTf] ionic liquids could dissolve or destroy more active groups of coal and inhibit the coal oxidation better than the [AOEmim][BF₄] and [Amim][Cl] ionic liquids. The dissolution ability of ionic liquids is related to the cation and anion structures. Cation with long and simple substituted chains and large anion will improve the ability of ionic liquid for dissolving the structures of coal.

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References