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Influence of imidazolium-based ionic liquids on coal oxidation

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ABSTRACT

In order to find the ionic liquids (ILs) which can significantly suppress coal oxidation, nine imidazolium-based ILs, [EMIm][BF_4], [EMIm]Ac, [BMIm][BF_4], [BMIm]Ac, [AMIm][BF_4], [HOEtMIm][BF_4], [HOEtMIm][NTf_2], [AOEMIm][BF_4] and [EOMIm][BF_4], were used to treat lignite sample to reveal the inhibitory effect of ILs on coal oxidation activity. The TGA results showed that the ILs can reduce the mass loss of coal, of which the ILs [HOEtMIm][BF_4] and [HOEtMIm][NTf_2] showed the strongest reducing effect, while the IL [AMIm][BF_4] showed the weakest reducing effect. Differential thermal analysis (DTA) results indicated that the heat release of [HOEtMIm][BF_4] and [HOEtMIm][NTf_2]-treated coal were very less. At the same time, the oxidation reactions of the two coals were delayed. IR results showed that ILs treatment can effectively destroy the associated hydroxyl in coal and change the content of carbonyl and ether bonds. In the process of coal oxidation, the oxidation activity of hydrogen bonding, ether bonds in [HOEtMIm][BF_4] and [HOEtMIm][NTf_2]-treated coal were weakened significantly at the initial oxidation process. With the oxidation processing, the content of generated carbonyl was reduced. The micro mechanism of the reduced coal oxidation activity was ascribed to the weaker oxidation activity of the ether bonds and the inhibited formation of the carbonyl groups.

1. Introduction

Spontaneous combustion of coal after long term exposure to air is a well-known phenomenon [1–5]. This effect is mainly due to the heat release of the large number of surface active sites in coal which strongly interact with dioxygen, which results in significant temperature increases in coal piles [6,7]. As well as the obvious hazards involved with coal fires, there is also a large financial incentive to mitigate spontaneous combustion. In order to prevent spontaneous combustion from occurring, inhibitors are often used to suppress the coal oxidation [8–12]. The role of some physical inhibitors such as mud grout and three-phase foam [8], is to prevent oxygen from interacting with surface active sites on the coal. Other inhibitors, such as sodium chloride [9], calcium chloride [10,11], sodium phosphate [12], also play a chemical role by suppressing the autocatalytic coal oxidation process. Therefore, chemical inhibitors have been a main area of research in coal mine safety [13–17].

Room temperature ionic liquids (RTILs), as novel solvents, have excellent physicochemical characteristics such as low melting point, negligible volatility, non-flammable and dissolving a wide range of organic and inorganic materials [18–20]. Coal is a composite material composed of organics and inorganics and thus, the aforementioned properties of ILs as solvents in coal chemistry have attracted significant attention. Painter et al. demonstrated that a range of $[BMIm]^+$ ionic liquids with triflate ($[CF_3SO_3]^-$), tetrafluoroborate ($[BF_4]^-$), hexafluorophosphate ($[PF_6]^-$), Cl^- and I^- anions used as neat solvents or as co-solvents with *N*-methylpyrollidine or pyridine were capable of disintegrating, dispersing and solubilizing a range of coal samples at ambient temperatures [21,22]. Pulati et al. thermally treated Illinois No. 6 coal in IL [BMIm][CF_3SO_3] in the presence of tetralin and hydrogen leading to significant fragmentation and a dramatic increase in pyridine solubility of coal [23]. Jin et al. investigated the solubility of coal in three ILs composed by double imidazole ring anions and toluene sulfonate cation, and found that solubility property and light hydrocarbon products significantly increased with the increase of the alkyl ether bond length between imidazole rings [24]. Qi et al. investigated the solubility of Victorian brown coal in “distillable” IL DIMCARB and found that solubility from 10% to 23 wt% for the different coal samples from xyloid coal to bright coal could be obtained [25]. Lei and coworkers demonstrated that the solubility of the lignite in a range of $[BMIm]^+$ ILs was mainly related with the destruction of the hydrogen bonds in coal by ILs [26,27], and the pyrolysis property of lignite was

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changed because of the effected oxygen-containing functional groups in coal by ILs pretreatment [28,29]. Cummings et al. also reported the change of the oxygen-containing functional groups in coal following ionic liquid treatment [30]. Nie and co-workers demonstrated that it was possible to use a range of protic, imidazolium, pyridinium and dialkylphosphate anion containing ILs to extract asphaltenes from direct coal liquefaction residue [31–34].

So far, the ILs have shown effective disintegrating, dispersing and solubilizing coal for the purpose of increasing the liquefied efficiency or extracting useful compounds from direct coal liquefaction residue. In coal oxidation properties, Wang et al. studied the dissolution of bituminous coal in six imidazolium-based ILs and found that ILs can partially change the functional groups in coal which affect the oxidation properties of the coal [35]. Zhang et al. also studied the low temperature oxidation of coal after being treated by 1-allyl-3-methyl imidazolium chloride ([AMIm]Cl) and concluded that the IL could inhibit the coal oxidation [36]. Zhang et al. investigated the effect of a range of phosphonium -based ILs on coal oxidation properties and found that the tributylethyl phosphonium diethylphosphate IL $[P_{4,4,4,2}]$[DEP] showed good inhibitory effect on coal oxidation over the temperature range studied [37]. These results showed that ILs can affect coal structure as well as suppress coal oxidation activity.

Herein, the authors further indicate the effect of a range of imidazolium-based ILs on coal oxidation. This paper reports the effect of ILs [EMIm][BF_4], [EMIm]Ac, [BMIm][BF_4], [BMIm]Ac, [AMIm][BF_4], [HOEtMIm][BF_4], [HOEtMIm][NTf_2], [AOEMIm][BF_4] and [EOMIm][BF_4] on coal thermogravimetry (TG), heat release and functional groups. The micro interaction process between coal and ILs was revealed. Such results are useful for developing a chemical inhibitor which can efficiently suppress coal oxidation.

2. Experimental

2.1. Coal sample and ILs

The coal sample was lignite according to the China Standard GB/T 5751-2009. The moisture, ash and volatility content of the sample on the air dry basis are 17.75, 20.86 and 36.22%, respectively.

The ILs samples of tetrafluoroborate anion $[BF_4]^-$ with 1-ethyl-3-methylimidazolium $[EMIm]^+$, 1-butyl-3-methylimidazolium $[BMIm]^+$, 1-allyl-3-methylimidazolium$[AMIm]^+$, 1-hydroxyethyl-3-methylimidazolium $[HOEtMIm]^+$, 1-((ethoxycarbonyl)methyl)-3-methylimidazolium $[AOEMIm][BF_4]^+$ and 1-methoxyethyl-3-methylimidazolium $[EOMIm]^+$ cations, the acetate Ac^- ILs with $[EMIm]^+$ and $[BMIm]^+$, and 1-hydroxyethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide, [HOEtMIm][NTf_2], were purchased from Lanzhou GreenChem ILS, LICP. CAS. (China) and used as received.

2.2. Sample preparation

The coal sample was ground in a mortar and pestle and sieved to a particle size of 150–250 μm and then vacuum dried IN oven for 24 h. The dried particulate coal (~0.5 g) was vigorously mixed with the nine ILs using a ratio of 1:2 (g:ml) separately and then sealed in an air bath at 50 °C over 8h. Thereafter, the nine mixtures were washed with distilled water (100 cm^3) and filtered to separate the coal. The coal was further washed with extra portions of distilled water (3 × 25 cm^3) until the filtrate was transparent. Then the washed coal was dried in a vacuum oven at 27 °C for 48 h, which is named as IL-treated coal. In addition to the IL-treated coal, a sample of the untreated particulate coal was washed with distilled water to enable a comparison to be made with the IL-treated coals, this sample is denoted as IL-untreated coal.

2.3. Experimental procedures

The IL-untreated coal and nine IL-treated coals were subjected to thermogravimetric analysis (TGA), differential thermal analysis (DTA) and Fourier transform infrared spectroscopy (FTIR) measurements. TGA and DTA measurements were carried out using a thermogravimetric analyzer (Diamond TG/DTA 6300, PerkinElmer, UK) in dry air flow of 50 cm^3/min at a heating rate of 5 °C/min over the temperature range 30–400 °C. FTIR spectra were recorded between 3800 and 650 cm^{-1} and were accumulated for 32 scans at a resolution of 4 cm^{-1} on a FTIR Spectroscopy (Vertex 80v, Bruker, Germany). The IL-untreated coal and nine IL-treated coals were further measured using FTIR after oxidation of the sample at 110 °C and 180 °C. To obtain these oxidation samples, 0.1 g of the coal was heated in a programmed temperature oven at heating rate of 0.5 °C/min from 30 °C to 110 °C, and 30 °C to 180 °C in a dry air flow of 50 cm^3/min. At the end of the oxidation treatment, the 20 samples were cooled to room temperature in N_2 and then measured using FTIR. All the spectra were auto-baseline corrected using software Omnic 8.0. Similar analytical procedure were previously divulgated by others authors [38–47,3,48].

3. Results and discussion

3.1. TG-DTG results

Fig. 1 showed the TG results for the IL-untreated and IL-treated coal samples. It is clear that all the coals showed similar mass loss trends, but different degrees of mass loss for each IL-treated coal, indicating that the coal oxidation activity was strongly affected by IL treatment.

From Fig. 1, at temperatures below 125 °C all the coal samples initially undergoes a small decrease in mass (~1.0–3.5 wt%), mainly

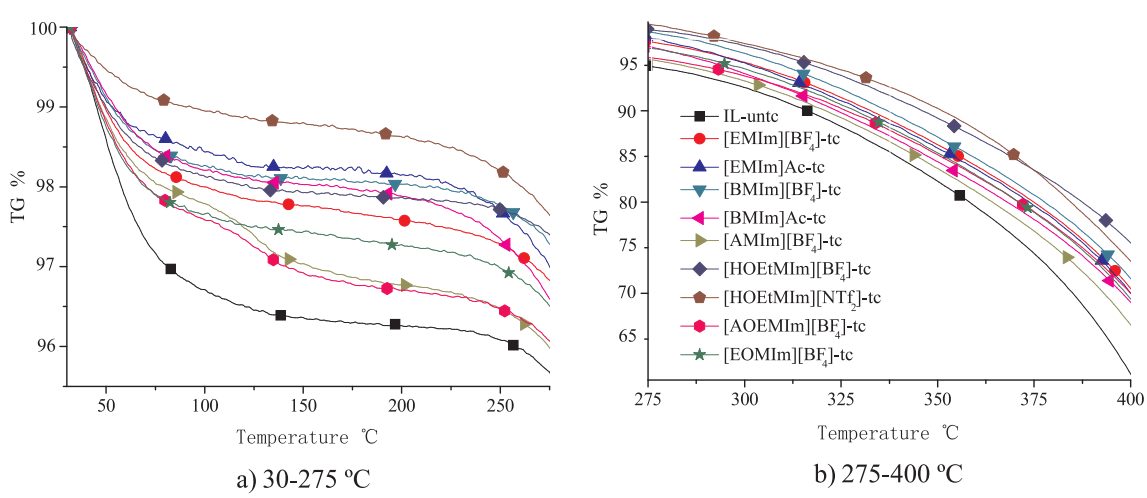

Fig. 1. TG profiles of IL-untreated coal and IL-treated coals: (a) 30–275 °C and (b) 275–400 °C. (Note: "tc" denotes "treated coal" in the following figures and tables.)