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The effects of poly(ethylene glycol) on the low-temperature oxidation reaction of coal as monitored using *in situ* series diffuse reflectance FTIR

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Abstract−*In situ* series diffuse reflectance FTIR was used to study the effects of poly(ethylene glycol) as a potential chemical additive inhibiting coal oxidation process at low temperatures. Two coals with different volatile content and, different ash percentages were examined following treatment with 5 wt% poly(ethylene glycol) 200. The surfaces of samples both with and without the additive were analyzed at temperature up to 200 °C in air using *in situ* diffuse reflectance FTIR. The results showed that poly(ethylene glycol) 200 is capable of inhibiting the oxidation of aliphatic moieties such as methyl and methylene groups, and also reducing the quantity of surface hydroxyl groups through reactions that form more stable ether linkages, thus improving the thermal stability of the coal. A mechanism by which the additive interacts with the coal surfaces is proposed.

Keywords: Poly(Ethylene Glycol), Coal Oxidation, *In Situ* Series Diffuse Reflectance FTIR, Mechanism

INTRODUCTION

Coal is a reactive organic material that may, when exposed to air, react with oxygen and generate heat, a process that sometimes results in spontaneous combustion with the release of hazardous gases and attendant risks to health and the environment [1-3]. The inhibition of the spontaneous combustion of coal is therefore highly desirable. The application of inhibiting agents is one possible means of preventing the spontaneous combustion of coal, and a wide range of inorganic and organic additives have were for this purpose [4-8]. Behaviors of samples both with and without these additive were examined on a macroscopic scale using TGA instrumentation, simultaneous TG-DSC measurement, and calorimetry [9-11]. However, these studies have not provided a clear picture of the mechanism by which additives retard spontaneous combustion. To further elucidate the action of chemical inhibitors of spontaneous coal combustion, other studies that monitored events on a microscopic scale were performed. The compounds present on coal surfaces during oxidation were examined by diffuse reflectance FIIR, which is an effective method of identifying functional groups. As an example, the FTIR spectra of raw and oxidized coal samples were compared by Wang [9], who demonstrated that the addition of Na_3PO_4 slows the oxidation of aromatics and alkanes. Lu [12] used diffuse reflectance FTIR to study differences in oxidation rates between raw and additive treated coal samples to elucidate the oxidation mechanism. There are other reports that describe the changes in functional groups during the thermolysis of coal with and without additives, using non-series FTIR [13-15]. Diffuse reflectance FTIR, however, is only able to collect the spectra of treated coal samples during oxidation over a narrow range of temperatures, and therefore the compounds appearing on the coal surface during oxidation cannot always be obtained in real time. As a result, it can be difficult to examine the interaction between additives and coal samples during the oxidation process to study the impact of the additives on a microscopic scale.

In situ series FTIR is an excellent means of monitoring real time reaction processes that is widely used in the study of electrochemistry and catalysis. In our past work, we used *in situ* series FTIR to investigate changes in surface functional groups during coal oxidation [16]. The present work is a continuation of our interest in coal self-heating, with the aim of developing a simple technique to study the mechanism by which inhibitors retard coal oxidation. We report the changes in surface functional groups on coal samples both with and without poly(ethylene glycol) (PEG), a potential oxidation inhibitor, using real time analysis by *in situ* series diffuse FTIR. Potential mechanism of interaction between the PEG 200 and coal during low-temperature oxidation was explored on the basis of the FTIR results.

MATERIALS AND METHODS

1. Coal Sample

Coal samples were collected from the Liangbaosi (LBS) Colliery in Shandong Province and the Pansan (PS) Colliery in Anhui Province. Table 1 summarizes the basic characteristics of these coal specimens. Lumps from the various coal samples were milled with an agate mortar under an inert atmosphere in a glove box and fragments ranging from 0.25 to 0.80 mm were used for the experimental investigations. The glove box helped to avoid spontaneous combus-

Table 1. Properties of the coal samples

Sample	Proximate analysis (air dried basis) (%)			
	M_{ad}	A_{ad}	V_{ad}	FC_{ad}
LBS coal	3.24	9.40	33.24	54.14
PS coal	1.62	24.86	27.45	46.18

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tion of the samples during the grinding procedure and minimized potential structural and surface reactivity changes. Following grinding, the samples were dried overnight under vacuum at 313 K prior to conducting experiments. Poly(ethylene glycol) (PEG) 200 (99% purity) was selected as the chemical inhibitor based on an assessment of the most suitable candidates.

2. Experimental Procedures

Prior to analysis, all coal samples were dried overnight in a vacuum oven at 40 °C. PEG 200 was then blended with the raw coal particles in a beaker using mechanical stirring to produce coal samples containing 5 wt% of the PEG additive. All samples were stored in a desiccator while awaiting testing.

The distributions and changing concentrations of functional groups on the coal surfaces were determined *in situ* with a Nicolet 6700 FTIR spectrometer. A KBr powder background was collected prior to sample analysis as a baseline reference. During analysis, each ground coal sample was placed into the reaction chamber and the dome installed, following which a flow of dry air was introduced into the reaction chamber from its base at a rate of 100 mL/min, exiting from the top. A temperature controller was connected to the reaction chamber and the chamber was heated to 220 °C at a rate of 1 °C/min. The spectral region from 650 to 4,000 cm^{-1} was scanned with 4 cm^{-1} resolution, adding 64 scans per spectrum. For each sample, a series of spectra were collected at 30 second intervals. To linearize the relationship between functional group concentration and spectral response, the Kubelka-Munk function $f(R_\infty)$ was applied to the spectral data, as shown in Eq. (1).

$$f(R_\infty)=\frac{(1-R_\infty)^2}{2R_\infty}=\frac{2.303\varepsilon c}{s} \quad (1)$$

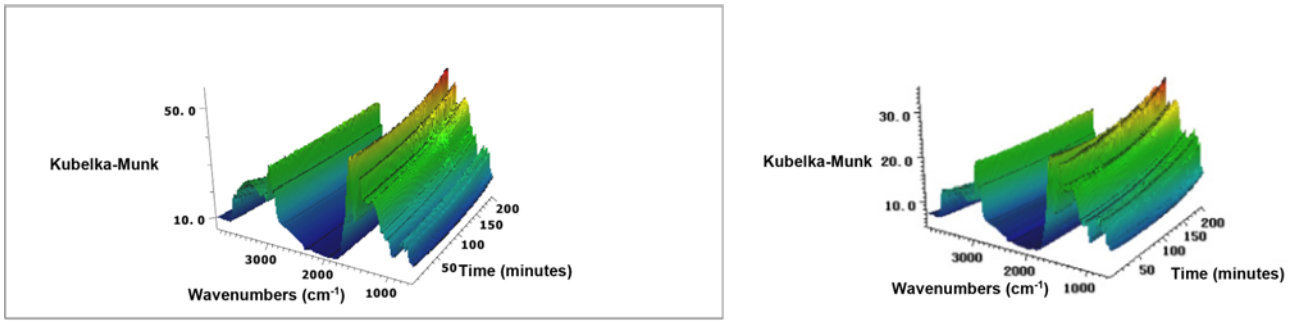
Here R_∞ represents the ratio of the single beam reflectance intensity of the sample to that of a non-absorbing standard (KBr in our work), ε is the molar absorptivity, c is the concentration of the sample and s is a scattering coefficient.

RESULTS AND DISCUSSION

1. *In-situ* Series Diffuse Reflection FTIR Measurements

The oxidation process of coal samples both with and without the addition of 5 wt% PEG was followed by collecting *in-situ* series diffuse reflectance FTIR spectra in the form of 3D (Kubelka Munk-time-wavenumber) data. The data obtained for raw LBS and PS coal are shown in Fig. 1.

The 3D data were analyzed to determine the peak intensity at specific wavenumbers as well as changes in intensity at several of these wavenumbers with variations in time or temperature. The wave-



(a) LBS coal (b) PS coal

Fig. 1. 3D *in situ* series FTIR data for raw LBS and PS coal.

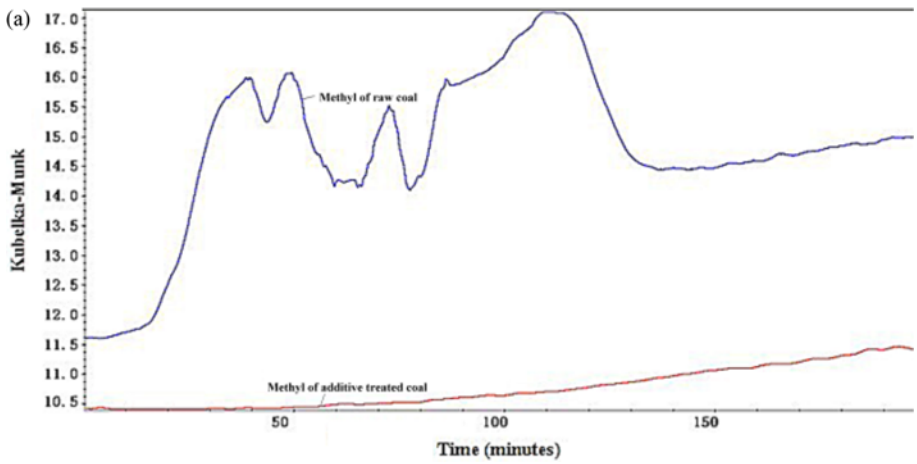


Fig. 2. Variations in the main active functional groups of LBS coal samples over time.
(a) Variations in CH_3 of LBS coal samples over time, (b) Variations in CH_2 of LBS coal samples over time, (c) Variations in OH of LBS coal samples over time, (d) Variations in ether bonds of LBS coal samples over time

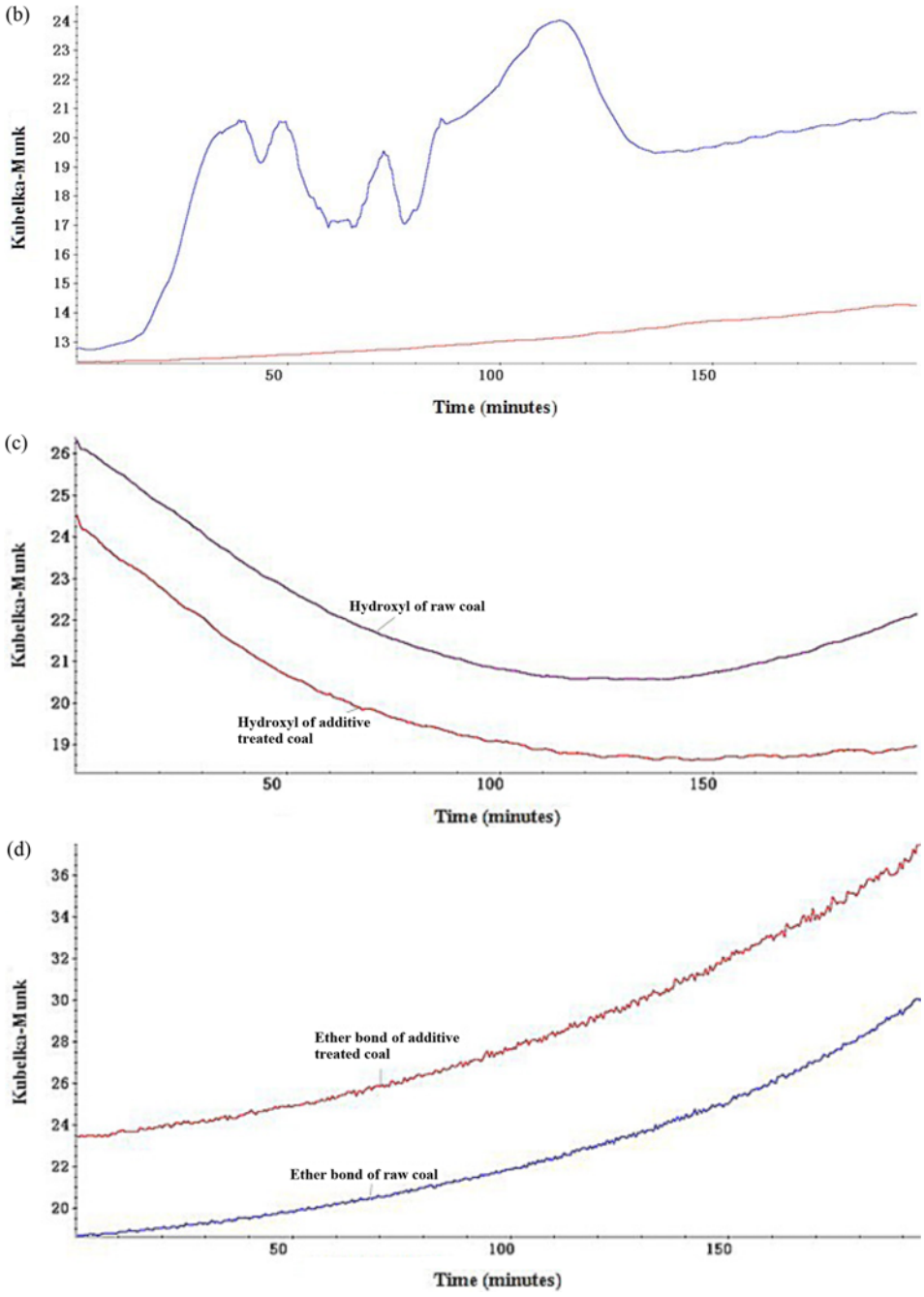


Fig. 2. Continued.

numbers that were monitored during these trials were 2,960 and 2,875 cm^{-1} (corresponding to the stretching vibrations (ν) of the CH_3 group), 2,925 and 2,855 cm^{-1} (assigned to CH_2 stretching), 1,125-1,110 cm^{-1} (corresponding to the antisymmetric stretching vibrations of ether (C-O-C) groups) and 3,650-3,200 cm^{-1} (specific to hydroxyl (-OH) stretching). The variations in the functional groups over time are summarized in Figs. 2 and 3. The upper and lower plots in panels a, b and c represent the time-dependent concentrations of CH_2, CH_3 and OH in the raw and inhibitor-treated coal samples, respectively. The upper and lower plots in the panel labeled "d" represent the corresponding concentration of ether bonds in the inhibitor-treated and raw coal samples, respectively.

The data collected by *in situ* series FTIR demonstrate that the concentration of alkyl groups on the surfaces of raw coal samples gradually increased during the oxidation process. It is well-known that alkyl groups at the coal surface react with oxygen at low temperatures to generate peroxides (-OO-) and hydroperoxides (-OOH) as intermediates, which should result in a decrease in the quantity of active alkyl groups. During oxidation, however, normally stable cycloalkanes and bridge bonds are broken to generate new active alkyl groups. During low-temperature oxidation of this coal, the rate at which new active alkyl groups were generated was therefore presumably higher than the rate at which they were consumed, leading to the observed increase in the concentration of active alkyl groups

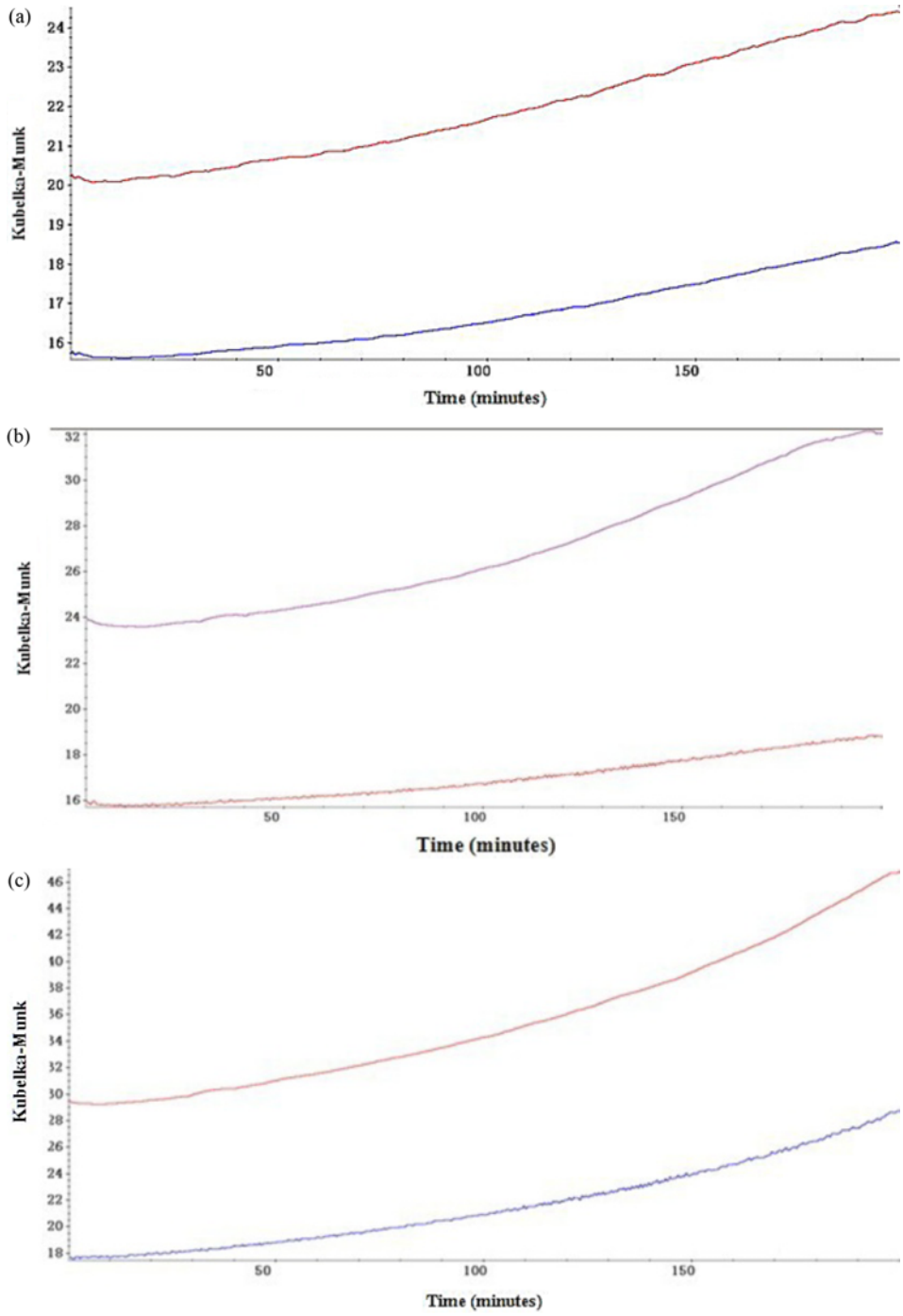


Fig. 3. Variations in the main active functional groups of PS coal samples over time.
(a) Variations in CH_3 of PS coal samples over time, (b) Variations in CH_2 of PS coal samples over time, (c) Variations in OH of PS coal samples over time, (d) Variations in ether bonds of PS coal samples over time

with time. Owing to the similar activities of the CH_2 and CH_3 groups, the intensities of the corresponding peaks exhibit the same variation trend over time. Although the concentrations of CH_2 and CH_3 on the PEG 200-treated coals increased during the oxidation period, the concentrations of these groups were lower on the treated coal than on the raw coal sample. It is also evident that the Kubelka-Munk values of the hydroxyl groups on the coal samples both with and without the additives decreased in the initial stage of oxidation. This trend presumably resulted from the decomposition of hydroxyl groups, generating carbonyl groups (-C=O) and water. Subsequent to these reactions, carboxyl groups (-COOH) were formed [17,18], thus producing more surface -OH. Similar to the results obtained concerning the alkyl groups, the concentrations of -OH groups on the PEG 200 treated-coals were much lower than the concentrations on the raw coal specimens. Conversely, the concentration of ether bonds on the additive treated coal was much higher than on

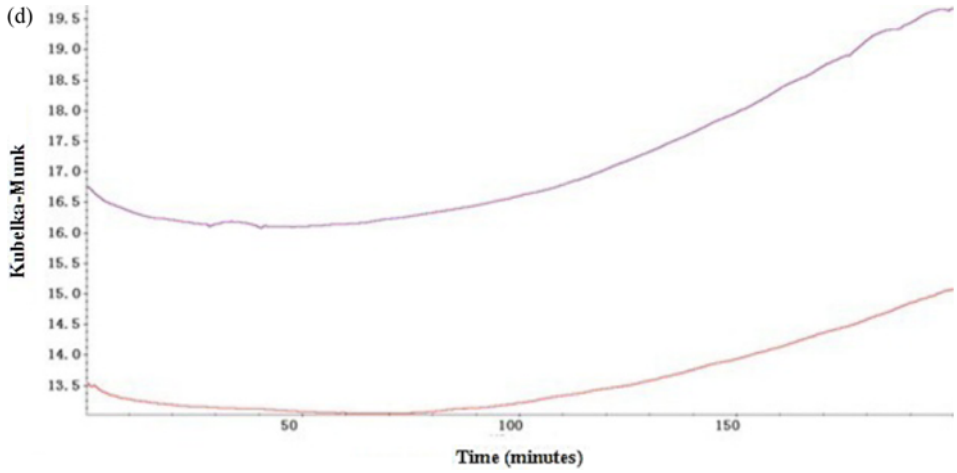


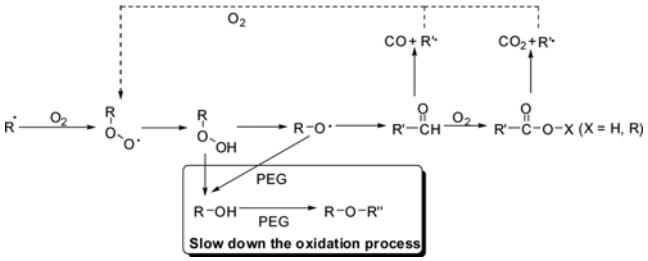
Fig. 3. Continued.

the raw coal. In general, the addition of PEG 200 appears to reduce the concentration of alkyl groups (CH_2 and CH_3) and hydroxyl groups (OH) during the oxidation process while assisting in the formation of ether linkages.

Considering the results of prior investigations in conjunction with our *in situ* FTIR data, we believe that the low-temperature oxidation of alkyl and hydroxyl groups is the primary cause of the self-heating and subsequent spontaneous combustion of coal. According to the basic principles of chemical reactions, once the oxidation of such active groups is interrupted, the associated heat release of the exothermic reactions will be markedly decreased in the early oxidation stage, such that fewer of the active functional groups that require higher energies to react will be able to do so. On this basis, the *in situ* FTIR spectra indicate that the addition of PEG 200 inhibits the oxidation process.

3. Mechanism by which PEG Inhibits Coal Oxidation

As determined from the *in situ* FTIR analysis, the initial concentration of aliphatic groups was much lower in coal samples containing PEG 200 and these groups also increased at a slower rate during the heating process when the sample contained the additive. Additionally, a large quantity of ether bonds was generated in the treated samples during the oxidation process. The ether bond is a relatively stable group within the coal structure: Kidena et al. [19] confirmed that ethers represent the most highly stable oxygen-containing groups during pyrolysis and other studies have shown that compounds containing ether linkages comprise the majority of end products following the low-temperature oxidation of coal [20-22]. The formation of ether bonds is therefore a key factor in the retardation of the oxidation process associated with the addition of PEG. PEG is a hydrophilic ethylene oxide polymer that has many desirable properties. It is inexpensive, nontoxic, biodegradable, thermally stable and water soluble. Consideration of the structure of PEG suggests that this polymer, when added to water, is capable of generating hydrogen ions that will react with the alkoxy and peroxy radicals resulting from the oxidation of alkyl groups, thus interrupting the chain reaction involved in oxidation of these groups. PEG also contains hydroxyl groups that can react with the abundant hydroxyl groups present on the coal surface, generating ethers that are more resistant to oxidation. In theory, therefore, PEG can either remove



Scheme 1. Proposed mechanism by which the inhibitor system retards coal oxidation.

the active functional groups on the coal surface or prevent their oxidation and thus is well suited to inhibit the oxidation of these groups (Scheme 1). This mechanism explains the phenomena observed during our *in situ* FTIR observations.

CONCLUSION

In situ series FTIR has been found to be a useful method for monitoring the overall processes of coal oxidation. Analysis of our 3D FTIR data shows that the concentrations of all functional groups on the surfaces of the coal samples, both with and without the additives, vary with each 1 °C rise in temperature, which reflects the slight changes in functional groups that can be followed and thus the sensitivity of this technique. The *in situ* FTIR spectra of coal samples acquired during the oxidation process show that the oxidation of aliphatic groups such as methyl and methylene groups, is inhibited by PEG 200, while the concentrations of these same groups along with the concentration of hydroxyl groups are reduced, and the concentration of ether bonds is increased subsequent to the addition of PEG 200. The mechanism by which the PEG and coal interact at low temperatures was also explored. *In situ* series diffuse FTIR is an effective means of studying the interactions between coals and inhibitors.

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