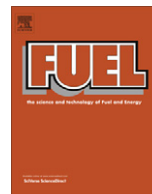




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Study on the structure and association of asphaltene derived from liquefaction of lignite by fluorescence spectroscopy

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HIGHLIGHTS

- ▶ The aromatic system of ASs derived at different liquefaction temperatures mainly consists of 2–3 rings aromatic nucleuses.
- ▶ The associations of AS originate mostly from the π – π interaction rather than the hydrogen bonding interaction.
- ▶ The size of AS nano-aggregates observed in AS solution is independent of AS concentration.

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ABSTRACT

Asphaltene (AS) is one of important heavy intermediates of direct coal liquefaction (DCL). It has significant influences on the technology of liquefaction, such as the coking property and the liquefaction efficiency. In this paper, the structure of AS derived from the liquefaction of Xiaolongtan lignite (XLT, a Chinese lignite) was characterized by element analysis, FTIR, UV and fluorescence spectroscopy, and its association was studied by the fluorescence spectroscopy. Results indicate that the aromatic system of AS derived at different liquefaction temperatures mainly consists of 2–3 rings aromatic nucleuses. With the increase of liquefaction temperature, the aliphatic structure is gradually cracked, and the aromaticity of AS and the proportion of large size aromatic nucleus increase. AS molecules easily form the nano-aggregates in a certain concentration of THF solution. The size of the nano-aggregates is independent of the liquefaction temperature and the AS concentration. The associations of ASs, which including intermolecular association and intramolecular association, originate mostly from the π – π interactions between aromatic nucleuses of AS rather than the hydrogen bonding interaction.

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1. Introduction

Direct coal liquefaction (DCL) is one of the most important techniques to obtain transportation fuel from coal. As inevitable heavy intermediates, asphaltene (AS) and preasphaltene (PA) have very important influences on the DCL [1,2]. Since these heavy intermediates contain many hetero-atoms and aromatic structures, they are easy to associate and aggregate resulting in the sedimentation and/or coking on the surface of catalyst and the devices in the process of DCL, and further hydro-refining of liquefied oil. The investigations of the composition, structure and the association of these heavy products will play an important role in the optimization of DCL technology.

As is well-known, the compositions of PA and AS are very complex and heterogeneous, which are similar to coal. Meanwhile, it is very difficult to separate these heavy products into individual compounds due to their poor solubility. Conventional analytic tech-

niques without prior fractionation, such as element analysis, FTIR and NMR spectroscopy, can only provide the average composition of element and the functional groups of these heavy intermediates. For example, Kanda et al. [1] analyzed statistically the average structure of AS from coal liquefaction by NMR and element analysis results, suggesting that one molecule of original AS consists of 1–3 structural units on average, which consist of 2 or 3 aromatic rings with 1 or 2 naphthenic rings, 0 or 1 alkyl carbon atoms, 0 or 1 OH groups and 0 or 1 hetero-rings. Seshadri et al. [3] characterized the ASs and PAs of SRC-I and SRC-II by NMR and FTIR spectroscopy, suggesting that they are 'oligomeric' in structure, with aromatic clusters linked by carbon bridge. However, these analytic techniques above-mentioned are difficult in the investigation of AS and PA associations, which always present in the liquefaction products and deteriorate the virtual operation.

Fluorescence spectroscopy is not only a very sensitive method for the analysis of aromatic compounds (containing fluorophore) but also a vigorous technique to study the association of the organic compounds with the aromatic structure in very dilute solution. It has been used, for example, to study the structure of coal derived

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liquid such as the pyrolysis tars [4,5], the coal–tar pitches [6,7], the coal liquefaction products [8], and the solvent extracts of coal [9] without fractionation. Zander and Haenel [6] found that there is a quantitative linear relation between the logarithms of molecular weights and the fluorescence maxima of coal–tar pitch fractions. Compared with the fluorescence analysis of individual compound, that of coal-derived liquid is always interfered by the re-adsorption of fluorescence emission, the intermolecular and intramolecular energy transfers [4,5,10], so that the fluorescence analysis of the coal-derived liquid composition can only be considered as qualitative or semiquantitative [5]. Since fluorescence originates presumably from the (π – π^*) state [7], in which the π – π^* transition energy is susceptible to the association between aromatic rings, the fluorescence spectroscopy has lately been becoming a conventional method to study the association of asphalt in crude oil [11]. According to literatures, AS associates even at very low concentrations [12,13], so this technique might be more sensitive to the onset of aggregation than other methods [14]. It has been widely used to elucidate the fundamental properties of crude oil and AS [15–20]. For example, Yokota et al. [15] suggested that the aggregation of Athabasca AS commences at concentrations above 5 mg/L. Groenzin and Mullins [16] proposed that AS forms dimers at 60 mg/L in toluene by the fluorescence depolarization measurements. Pietraru and Cramb [11] found that AS has a critical aggregation concentration (CAC) in the range of 0.2–1.5 g/L, and the fluorescence spectral shift occurs at the CAC. Goncalves et al. [21] observed that the tendency of octylated AS to form the aggregates diminishes by examining the changes of absorbance and fluorescence spectra of original AS and its corresponding octylated AS in toluene solvent. In addition, Ghosh et al. [7] investigated the aggregation of a coal-derived AS from Barari coke plant by fluorescence spectroscopy, suggesting that the aggregation is a gradual process with a critical aggregation constant of ca. 90–100 and 180–200 mg/L in different solvents.

Although the analytic technique of fluorescence has been applied to study the coal derived liquid, to our knowledge, little information was available about the association of AS and PA derived from coal liquefied product. In our previous works, the fluorescence spectroscopy had been successfully applied to study of the aggregation of AS and PA derived from sub-bituminous coal. It was found that the PA shows strong aggregation tendency in tetrahydrofuran (THF) solvent and can form nano-aggregates even in the very dilute solution such as 6.25 mg/L [22,23]. Recently, we also studied the aromatic nucleuses distribution in the sub-fractions of AS and PA derived from coal liquefaction by synchronous fluorescence [24]. In this paper, the structure of AS derived from Xiaolongtan lignite (a Chinese lignite) liquefaction was characterized, and the associations was studied by the fluorescence spectroscopy.

2. Experimental

2.1. Sample preparation

AS samples, which are defined as the toluene soluble and n-hexane insoluble fraction of liquefaction product, were obtained by the hydro-liquefaction of Xiaolongtan (XLT) lignite in tetralin solvent, with FeS as catalyst under 5 MPa H_2 (initial) at different temperatures, and the subsequent soxhlet extraction. A detailed description can be found elsewhere [25]. The results of XLT lignite liquefaction and the ultimate analysis of AS samples were listed in Table 1.

2.2. Characterization methods

AS stock solution was prepared by dissolving the dried AS in THF solvent. In order to assure complete dissolution, the stock

solution was left in ultrasonic bath for 30 min and then set overnight. Finally, the stock solution was diluted with THF into specific concentrations.

In this paper, AS solution was used to determine the absorption and fluorescence spectra and GPC curve. Fluorescence spectra were recorded on a Hitachi F-4600 spectrophotometer. Fluorescence measurements were made using a classic optic mount at 90° signal observation. Emission and excitation slits were set at 5 nm. The scanning speed was kept constant (1200 nm/min). Absorption spectra were taken using a diode array spectrometer (Lambda 35 UV-vis) of 1 nm spectral resolutions. All the measurements were made at room temperature. Quartz sample cell with optical path 1 cm was used. A Shimadzu LC-20AT liquid chromatography, equipped with a SPD-20A UV/vis detector, was used to measure the GPC curve of AS. The GPC columns were a Shim-pack GPC-8025 (8×300 mm, 10 μ m). THF was selected as eluent at 1 mL/min flow rate, and the injection volume was 50 μ L. The detective wavelength was set at 254 nm and the column temperature was usually controlled at 20 °C. All graphs were plotted using Origin 7.0 software. A detailed description can be availed in Ref. [23].

A dried AS sample was used in the FT-IR measurement and the ultimate analysis. FTIR spectrum was recorded by a Nicolet 6790 IR spectrometer at ambient temperature using KBr disc. The element analysis was carried out by Elementar Vario EL III using the mode of CHNS.

3. Results and discussion

3.1. Characterization of AS structure

Table 1 shows that the temperature has a significant influence on the liquefaction of XLT lignite. With the increase of temperature, the conversion and AS yield obviously increase, and the O%, H%, H/C, and O/C of AS decrease gradually. It suggested that the aromaticity of AS increases and the containing oxygen functional groups content of AS decreases with the increase of liquefaction temperature. Further, it can also be seen from Table 1 that H/C and O/C of XLT lignite are 0.96 and 0.28, but those of ASs are in the range of 0.94–1.08 and 0.09–0.12, respectively. So we speculated that the XLT lignite liquefaction catalyzed by FeS is dominated by the pyrolytic reaction along with pronounced deoxygenation.

FTIR spectra of ASs as shown in Fig. 1 display that the ASs derived from lignite liquefaction contain abundant hydrogen-bonded (HB) OH groups (3700 – 2500 cm^{-1}), carbonyl groups (1653 cm^{-1}) and aromatic systems (1611 cm^{-1}). It can be observed that the position of OH peak increases with the increase of liquefaction temperature, suggesting that the liquefaction temperature influences the distribution of HB OH groups in AS. According to the spectrum-resolving method suggested by Miura et al. [26], the OH absorption bands of ASs were successfully resolved with six types of OH peaks, which can be assigned to free OH groups (3630 cm^{-1}), OH– π HB OH (OH– π , 3535 cm^{-1}), self-associated n -mers ($n > 3$) OH (OH–OH, 3410 cm^{-1}), OH–ether HB OH (RO–OH, 3280 cm^{-1}), tightly bound cyclic OH tetramers (cyc–OH, 3165 cm^{-1}) and OH–N HB OH (OH–N, 3020 cm^{-1}), respectively [27]. The distributions of above OH groups as shown in Fig. 2 indicates that the percents of stronger HB OH groups including RO–OH, cyc–OH and OH–N decrease, and those of other weaker HB OH groups increase with the increase of liquefaction temperature. It suggested that the intensity of HB interaction in AS decreased with the increase of liquefaction temperature. In addition, Fig. 1 also shows that the absorption intensity of carboxylic group (near to 1708 cm^{-1}) and the intensity ratio of CH_2 (2922 cm^{-1}) to CH_3 (2956 cm^{-1}) clearly decreases with the increase of liquefaction temperature. It was proposed that the

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