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Characterization of organonitrogen species in Xianfeng lignite by sequential extraction and ruthenium ion-catalyzed oxidation

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ABSTRACT

A three-step degradation, including sequential ultrasonic extraction (UE), sequential thermal extraction (TE), and ruthenium ion-catalyzed oxidation (RICO), of Xianfeng lignite (XL) was performed to characterize the organonitrogen species (ONSs) in XL. More than 87.3% of organic matter in XL was converted into soluble portions through the degradation. The analysis with X-ray photoelectron spectrometer shows that pyrrolic, amino, and quaternary nitrogen species are the main nitrogen forms both in XL and its residue from UE, while nitroaromatics, chemisorbed *N*-oxides, and pyrrolic nitrogen are predominant in the residue from TE. A series of ONSs, including pyridines, quinolines, benzo[*d*]imidazoles, and arylamines, were identified in the extracts from TE of the UE residue according to GC/MS analysis. Among the ONSs, pyridines and quinolines are the most abundant. The ONSs could be released by thermally destroying noncovalent bonds, such as hydrogen bonds and aromatic $\pi-\pi$ interactions, during TE of the UE residue. Most of ONSs released from RICO of the TE residue could be generated from the degradation of nitrogen-containing macromolecular aromatics in XL matrix (XLM). Nitrobenzenecarboxylic acids are the most abundant ONSs released from RICO of the TE residue and should be released by the degradation of macromolecular nitroaromatics in XLM.

1. Introduction

When coals are used as fuel for power generation, organic nitrogen in coals is emitted as NO_x and N_2O during combustion, leading to severe environmental pollution, including acid rain, photochemical smog, greenhouse effects, and ozone-layer depletion [1–4]. Attempts have been made for reducing NO_x and N_2O emissions during coal combustion [3, 5–8]. Understanding the distribution and structures of organonitrogen species (ONSs) in coals is of great importance both for efficiently removing ONSs from coals and for providing important insights into coal structures. Many non-destructive techniques, such as nuclear magnetic resonance [9], X-ray photoelectron spectrometer (XPS) [10–18], and X-ray absorption near edge structure spectrometer [13,19–21], have been applied to clarify the occurrence forms of ONSs in coals and their derivatives. According to the investigations, the major ONSs identified in coals include pyrrolic, pyridonic, amino, quaternary, and pyrrolidonic nitrogen species [4]. However, most of the nondestructive methods did not afford the information on the structures of ONSs in coals at the molecular level. Therefore, the combination of nondestructive and selectively destructive methods for detailed characterization of ONSs in coals is needed.

Fractional extraction, especially Soxhlet extraction, along with subsequent analysis with a gas chromatography/mass spectrometer (GC/MS) was successfully used for separation and characterization of ONSs from coals and their derivatives [22–26]. Although this separable and nondestructive method provided some information on the molecular structures of ONSs in coals, the ONSs identified by this method can only represent a small portion of the ONSs in coals due to the low extract yields from fractional extraction. Since lignite is rich in oxygen functional groups [27], strong noncovalent bonds (NCVBs), e.g., hydrogen bonds (HBs), between oxygen functional groups and ONSs may lead to the difficulty in extracting ONSs from lignite matrix (LM) at room temperature. Moreover, some ONSs could be covalently bonded to the LM and are difficult to be released by fractional extraction at room temperature. Therefore, thermal extraction (TE) and subsequent oxidation could be a promising method to release the ONSs from LM as exhaustively as possible.

Extensive investigations have been performed on TE of coals to obtain more soluble portion used as clean fuel or precursor for producing carbon materials [28–31]. Organic nitrogen in the extracts from TE should have some influences in the extract properties. However, characterization of the ONSs in the extracts was rarely reported. Ruthenium ion-catalyzed oxidation (RICO) was widely used to characterize the types of alkyl groups on aromatic rings, methylene bridges connecting aromatic units, and aromatic rings themselves in coals combined with analyses of the resulting carboxylic acids [32–35]. Nevertheless, to our knowledge, few reports were issued on the detection of ONSs in the products from RICO of coals.

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In this study, Xianfeng lignite (XL) was first subjected to sequential ultrasonic extraction (UE) and TE to characterize the ONSs which are free in XL or bound in XL matrix (XLM) through NCVBs. Then, RICO of the residue from TE was performed under mild conditions to understand the ONSs bonded to XLM through strong covalent bonds (CVBs). XPS analysis was used to characterize the occurrence forms of ONSs in XL and residues from UE and TE.

2. Materials and methods

2.1. Materials

XL was collected from Xianfeng Coal Mine, Yunnan, China. It was pulverized to pass through a 200-mesh sieve (particle size of <74 μm) followed by desiccation in a vacuum at 80 °C for 24 h before use. The proximate and ultimate analyses of XL are listed in Table 1. Petroleum ether (PE), carbon disulfide (CDS), methanol, ethanol, acetone, cyclohexane, benzene, 1-methylnaphthalene (1-MN), ruthenium trichloride, sodium periodate, acetonitrile, perchloromethane, diethyl ether (DEE), and diazomethane (DAM) used in the experiments are analytical reagents, and all the organic solvents were distilled before use.

2.2. Sequential UE and subsequent TE

As shown in Fig. 1, 10 g XL was extracted with PE to afford extract 1 (E_1) and residue 1 (R_1), followed by extraction of R_1 with CDS to afford extract 2 (E_2) and residue 2 (R_2), extraction of R_2 with methanol to afford extract 3 (E_3) and residue 3 (R_3), extraction of R_3 with acetone to afford extract 4 (E_4) and residue 4 (R_4), and extraction of R_4 with isometric CDS/acetone mixed solvent (IMCDSAMS) to afford extract 5 (E_5) and residue 5 (R_5), i.e., the UE residue (UER). Each extraction with the same solvent (200 mL) was conducted for 10 min and repeated at least 10 times under ultrasonication to extract the soluble species as exhaustively as possible. UER (2 g) was thermally extracted with cyclohexane in a 100 mL stainless-steel, magnetically stirred autoclave to afford extract 6 (E_6) and residue 6 (R_6) followed by TE with benzene to afford extract 7 (E_7) and residue 7 (R_7), TE with 1-MN to afford extract 8 (E_8) and residue 8 (R_8), TE with methanol to afford extract 9 (E_9) and residue 9 (R_9), and TE with ethanol to afford extract 10 (E_{10}) and residue 10 (R_{10}), i.e., the TE residue (TER). Each TE was performed with 20 mL of a solvent at 320 °C for 2 h. TER was dried in a vacuum at 100 °C for 2 h and then conserved in a desiccator for subsequent RICO.

2.3. RICO of TER

The procedure for RICO of TER was reported in previous investigations [36,37] except that aqueous phase separated from the reaction mixture was extracted with DEE rather than with dichloromethane. Then solvents in organic phase and aqueous phase were removed by rotary evaporation followed by esterification with DAM in DEE to afford corresponding methyl esterified organic phase (MEOP) and methyl esterified aqueous phase (MEAP).

Table 1
Proximate and ultimate analyses (wt.%) of XL, UER, and TER.

Sample	Proximate analysis			Ultimate analysis (daf)				$S_{t,d}$	H/C
	M_{ad}	A_d	V_{daf}	C	H	N	O_{diff}		
XL	25.67	18.45	36.52	63.07	6.01	1.79	>28.73	0.40	1.1356
UER				62.77	6.01	1.61	>29.15	0.46	1.1414
TER				70.09	3.54	3.05	>22.55	0.77	0.6012

diff: by difference; daf: dry and ash-free base; M_{ad}: moisture (air dried base); A_d: ash (dry base, i.e., moisture-free base); V_{daf}: volatile matter (dry and ash-free base); $S_{t,d}$: total sulfur (dry base).

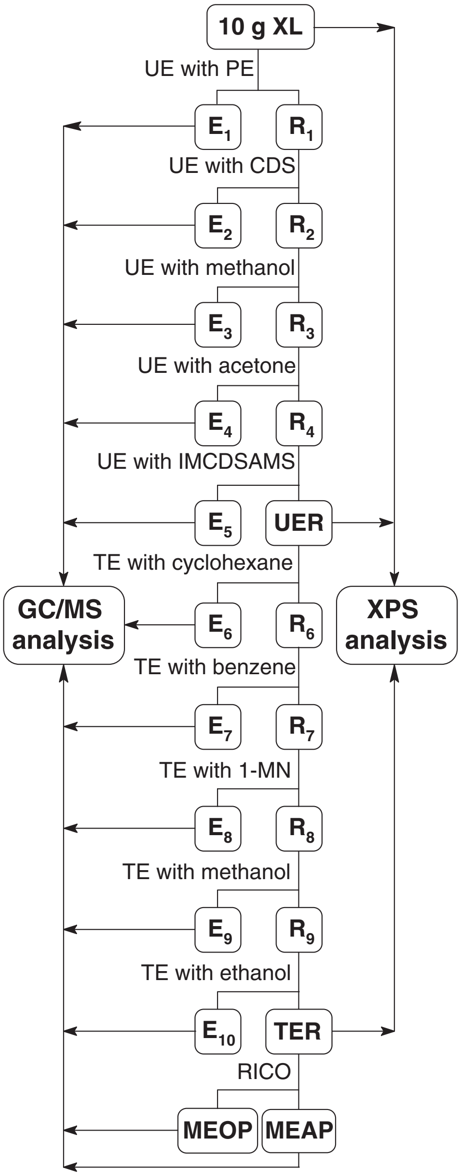

Fig. 1. Procedure for sequential extraction and subsequent RICO of XL, XPS and GC/MS analyses.

2.4. Analytical methods

The surface compositions of XL, UER, and TER were determined by a Thermo Fisher ESCALAB 250Xi XPS. The XPS was equipped with a microfocusing monochromator and a multi-technique system. A monochromatized Al Kα X-ray source was operated at 150 W. The spectra of XPS were conducted in a fixed analyzer transmission mode and the calibration was carried out to the main C 1 s peak at 284.8 eV. Each element content was calculated according to the intensity of an appropriate line and XPS cross sections. The fitting of XPS peaks was performed by least square using Gaussian–Lorentzian 50%–50% peak shapes. All the soluble portions were analyzed with a Hewlett-Packard 6890/5973 GC/MS, which is equipped with a capillary column coated with HP-5 (cross-link 5% PH ME siloxane, 60 m length, 0.25 mm inner diameter, 0.25 μm film thickness) and a quadrupole analyzer and operated in electron impact (70 eV) mode. The column temperature was raised from 60 to 300 °C at a rate of 6 °C/min and held at 300 °C for 15 min. ONSs were identified by comparing mass spectra with NIST05a library data and literatures. The reproducibility of quantitative analysis was performed by duplicated injection of the samples.