Fuel Processing Technology 160 (2017) 170–177

Contents lists available at ScienceDirect

Fuel Processing Technology

journal homepage: www.elsevier.com/locate/fuproc

Research article

Characterization of organic nitrogen and sulfur in the oil shale kerogens

Qing Wang *, Qi Liu, Zhi-Chao Wang, Hong-Peng Liu, Jing-Ru Bai, Jiang-Bin Ye

Engineering Research Centre of Oil Shale Comprehensive Utilization, Ministry of Education, Northeast Dianli University, Jilin 132012, China

ARTICLE INFO

Article history:
Received 4 September 2016
Received in revised form 24 February 2017
Accepted 24 February 2017
Available online 7 March 2017

Keywords:
Kerogen
Organic nitrogen and sulfur
XPS

ABSTRACT

Organic nitrogen and sulfur species along with carbon structural features in the five different oil shale kerogens were characterized by solid-state ^{13}C NMR, XPS, and XRD techniques. Results indicate all the five kerogens contain aliphatic carbons in large amounts, aromatic carbons and small quantities of carbonyl and carboxyl carbons. Increased metamorphism results in increase in the number of aromatic carbons and corresponding decrease in that of aliphatic carbons. All kerogens contain five forms of organic nitrogen: pyridinic nitrogen, amine nitrogen, pyrrolic nitrogen, quaternary nitrogen, and nitrogen oxides. Relative amount of pyrrolic nitrogen is the highest and the majority of organic nitrogen exists as pyrrolic and quaternary nitrogens in comparable relative abundances, both accounting for >70%. With increase in the number of aromatic carbon, the relative number of pyridinic nitrogen increases and that of amine nitrogen decreases. Forms of organic sulfur include aliphatic sulfur, aromatic sulfur, sulfoxide, and sulfone in all the kerogens. A small amount of inorganic pyrite sulfur is also present. Most of the organic sulfur (>70%) exists as aromatic sulfur and sulfone. With increasing amount of aromatic carbon, the relative amount of aromatic sulfur increases significantly, whereas that of aliphatic sulfur decreases.

1. Introduction

Oil shale is a sedimentary rock containing organic matter, and generally belongs to the sapropelic coal, which has a high mineral content, making it a solid fossil fuel with a low calorific value [1]. Oil shale contains two kinds of organic matters: one is kerogen, which is insoluble in common organic solvents; another is bituminic, which is soluble in common organic solvent. However, the bituminic content in oil shales is very low [2]. In China, the main way to utilize oil shale is to extract shale oil by a common method of low temperature retorting. In the absence of air, oil shale is heated to about 500 °C, during which kerogen is transformed into shale oil [3]. In the oil shale retorting process, functional groups containing nitrogen and sulfur present in kerogens get transformed into various compounds, which are then distributed in semi-coke, shale oil and gases. This not only has a negative impact on the quality of shale oil products but also pollutes the environment, in a serious manner [4–7]. Moreover, nitrogen and sulfur are present in smaller amounts compared to that of carbon and hydrogen in kerogens. In spite of this, they are still associated with carbon atoms in various structural forms, which form the key components in the entire molecular structure of oil shale kerogens. Hence, it is necessary to investigate the structural forms and distribution characteristics of organic nitrogen and sulfur compounds, in order to understand the chemical structure of oil shale kerogens more comprehensively and develop the chemical structure model of kerogen. This also contributes to understanding the mechanism of formation of nitrogen-containing and sulfur-containing pollutants and finding ways to improve the quality of shale oil products and protect the environment. There is a close connection between the carbon skeleton structure and organic nitrogen, sulfur. The characterization of carbon skeleton structure further helps to recognize the structural features of organic nitrogen and sulfur present in oil shale kerogens.

XPS is a powerful method for identification and quantification of organic nitrogen [8–14] and sulfur [8,9,15–17] in solid carbonaceous materials, such as coals and kerogens. Kelemen et al. [8] used XPS to determine and quantify organic nitrogen and sulfur present in kerogens. The chemical speciation and distribution of organic nitrogen and sulfur were obtained. Pietrzak et al. [10] analyzed the changes taking place on the surface of pyrite-free coal oxidized with nitric acid by XPS. Kelemen et al. [15] employed XPS to identify and quantify organically bound forms of sulfur in non-volatile and solid hydrocarbons. Gorbaty et al. [17] studied the conversion and thermal reactivity of organic sulfur in coals during mild oxidation, using XPS. Previous researches were focused on coals and the comprehensive analysis of organic nitrogen and sulfur in kerogens was not sufficiently intensive. In particular, the study of organic nitrogen and sulfur in oil shale kerogens from China was obviously inadequate. Since organic nitrogen and sulfur are diverse and complex, it is necessary to characterize organic nitrogen and sulfur in oil shale kerogens. Solid-state ^{13}C NMR serves as an important tool to study the chemical and structural parameters of carbon compounds in oil shale kerogens [18–22]. Hillier et al. [23] used ^{13}C NMR and XPS to analyze the pyrolysis products of the oil shale and the demineralized

* Corresponding author.
E-mail address: rlx888@126.com (Q. Wang).

http://dx.doi.org/10.1016/j.fuproc.2017.02.031
0378-3820/

Nomenclature

HDK	Huadian kerogen
MMK	Maoming kerogen
FSK	Fushun kerogen
LKK	Longkou kerogen
YJK	Yaojie kerogen
NMR	nuclear magnetic resonance
XPS	X-ray photoelectron spectroscopy
fwhm	full width at half maximum
XRD	X-ray Diffraction
C_n	average aliphatic carbon chain length
X_b	fraction of bridgehead aromatic carbon in aromatic carbon
FAA	fraction of aromatic carbon with attachments

kerogen, including light gas, tar, and char. Information regarding the carbon structure can deepen the understanding of organic nitrogen and sulfur in oil shale kerogens.

In this study, five oil shale kerogens with different types of organic matter and metamorphic grades were characterized. Solid-state ^{13}C NMR was used for the qualitative and quantitative analyses of the carbon structures in these kerogens. XPS was used to identify and quantify organic nitrogen and sulfur forms, and was supplemented with XRD analysis.

2. Experimental

2.1. Materials

Five typical Chinese oil shales having different types of organic matter and metamorphic grades, namely Huadian oil shale, Maoming oil shale, Fushun oil shale, Longkou oil shale, Yaojie oil shale, were chosen for the present study. These oil shales were ground and sieved to mesh sizes of 200 mesh. Kerogens were isolated from the oil shales by demineralization with HCl and HF, according to the standard procedure described by Durand and Nicaise [24]. The kerogens were marked as HDK, MMK, FSK, LKK and YJK, respectively and stored in a vacuum desiccator for further analyses. Ultimate analysis of samples was operated in Euro Vector EA3000 Automatic Elemental Analyzer and two models of CHNS and O were used separately during the experiment. The furnace temperatures were 980 °C (CHNS) and 1060 °C (O), respectively. The flow rate of oxygen was 80 ml/min in this experiment. As Table 1 lists, base on the atomic ratios of H/C and O/C on 100 carbon atoms basis and van Krevelen diagram [25], it is clear that HDK belongs to type I kerogen with low metamorphic grade. MMK, FSK, and LKK are all between types I and II. YJK belongs to type II kerogen with high metamorphic grade. Prior to the loss on ignition test, the samples were dried in a vacuum oven at the temperature of 100 °C until the mass constant. Loss on ignition tests were carried out, in which kerogens were burned in a furnace at 800 °C, until the mass of residue remained constant. Obtained results of five kerogens are found to be >97%, which indicates that the purity of five kerogens is high.

Table 1
Ultimate analysis and loss on ignition of the five oil shale kerogens.

Sample	Ultimate analysis (w_{daf}/%)				Oxygen* (wt%)		Atomic ratio		Loss on ignition (wt%)
	C	H	N	S	UA	XPS	H/C	O/C	
HDK	68.20	9.13	2.77	2.93	16.91	18.26	1.61	0.19	98.21
MMK	65.56	7.54	5.14	2.30	20.24	22.09	1.38	0.23	97.26
FSK	68.73	8.04	5.31	1.87	16.14	18.76	1.40	0.18	97.18
LKK	63.48	6.96	5.30	2.87	20.30	21.18	1.32	0.24	97.12
YJK	71.43	7.10	4.94	1.71	14.67	17.70	1.19	0.15	98.22

daf: dry and ash free; *: obtained by direct method, based on C + N + S + O; UA: ultimate analysis, bulk oxygen content; XPS: X-ray photoelectron spectroscopy, surface oxygen content.
The error of ultimate analysis and loss on ignition were both ±0.1% by weight.

2.2. Solid-state ^{13}C NMR

Solid-state ^{13}C NMR spectroscopic analyses of all the five oil shale kerogens were performed on a Bruker Advance III spectrometer, operating at 100.63 MHz. The samples were packed in 5-mm zirconia rotors and spun at 5 kHz. The kerogens were characterized by cross-polarization magic-angle spinning (CP/MAS) experiments performed with a contact time of 2 ms, and a pulse repetition delay of 6 s. Data were obtained by a total accumulation of over 9000 transients. ^{13}C NMR spectra of five kerogens were curve-resolved to quantify the relative proportions of the different carbon types. The structural parameters and chemical shift ranges were compared to literature references [18,26–28] for interpretation of the ^{13}C NMR spectra and the data is are presented in Table 2.

2.3. XPS

XPS analyses of five oil shale kerogens were performed with a Thermo VG Scientific ESCALAB 250Xi spectrometer, equipped with a microfocusing monochromator and a charge compensation system. The monochromatic Al Kα (1486.6 eV) X-ray source was used, which was operated at 150 W and the spot size was 500 μm (diameter). While obtaining the spectra of kerogens, all corrections for binding energies arising from charging were made by assigning a binding energy of 284.8 eV to the principal C (1 s) component. Spectra were acquired in a constant analyzer energy mode. Pass energies of the survey and narrow spectra were fixed at 100 and 30 eV, respectively. For improved effects, powder samples were converted to tablettings for XPS analyses.

XPS was used to identify and quantify nitrogen and sulfur functionalities in all the five oil shale kerogens. XPS N (1 s) spectra and S (2p) spectra of these kerogens were curve-resolved using Casa XPS processing software. These spectra were curve-resolved using components with fixed binding energy positions and fwhm values. A mixed 70% Gaussian 30% Lorentzian line shape was used and the Shirley-type background was subtracted prior to fitting. The binding energies and forms of N (1 s) functional groups, after referring to the parameters reported in the literatures [8,11–14], are presented in Table 3. In each case, the N (1 s) spectrum was curve-resolved using the fwhm of 1.4 (±0.1) eV. It should be noted that the binding energies of pyridone or its isomers are close to that of the pyrrolic nitrogen, and hence could not be distinguished by XPS. The fitting peaks located at 400.3 (±0.3) eV represent pyrrolic nitrogen and pyridone or its isomers. The binding energies and forms of S (2p) functional groups, after referring to the parameters reported in the literatures [8,15–17], are shown in Table 4. Ma et al. [29] found that the XPS S (2p) spectrum from an individual component was comprised of a pair of spin-orbit splitting peaks: $2p_{3/2}$ and $2p_{1/2}$. The ratio of the intensities of splitting peaks of the pair was 1:2, separated in energy by 1.2 eV. The components at 168 (±0.5) eV and 168.5 (±0.5) eV have $2p_{3/2}$ and $2p_{1/2}$ peaks with fwhm of 1.5 (±0.5) eV, whereas the other peaks have fwhm of 1.1 (±0.1) eV.

2.4. XRD

XRD analyses of five oil shale kerogens were performed on a Shimadzu XRD MAXima-7000, which was equipped with a Cu tube and a monochromator. The source was a Cu Kα radiation that operated at 40 kV and 40 mA. Scan range was from 2 to 90° (2θ), and scanning speed was 4° per minute.