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Structural parameters and molecular model of Shendong subbituminous coal

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ABSTRACT

Coal has a highly complex chemical structure, similar to polymers, coal is a macromolecular structure composed of a large number of "similar compounds", which is called the basic structural unit. Understanding coal structure is the basis of its transformation and utilization. Shendong (SD) coal was analyzed by FTIR, XRD, XPS, and NMR. The results show that SD coal normalized structure formula is $C_{100}H_{68.5}O_{35.7}N_{1.2}S_{0.2}$ and the average number of aromatic rings is 1.98. $-CH_2-$ content accounts for about 82% in aliphatic C—H region, and the ratio of ether bond C—O, aromatic ether C—O and C═O is about 2:1:11 in oxygen-containing functional group region. The d_{002}, L_C, L_a and N_C of SD coal microcrystalline structure parameters are 0.1832 nm, 1.4688 nm, 2.0852 nm and 9.017, respectively. Aromatic carbon and aliphatic carbon ratios of SD coal are 55.67% and 29.97%, aromatic cluster size and average methylene chain length are 0.224 and 1.817. Based on these structural parameters, molecular model of SD coal was constructed with ^{13}C SSNMR experimental spectra as a reference. The model was constructed with an atom composition of $C_{214}H_{214}O_{49}N_2S$.

1. Introduction

China is relatively rich in coal resources and subbituminous coal accounts for about 40% of the total coal [1]. Shendong coalfield (SD), a kind of subbituminous coal, is one of the eight largest coalfields in the world, with the advantages of convenient mining and excellent quality [2]. Understanding SD coal structure is the basis of its transformation and utilization.

It is well-known that coal has a highly complex chemical structure, similar to polymers, coal is a macromolecular structure composed of a large number of "similar compounds" known as basic structural unit [3,4]. Due to the complexity and diversity of coal, its molecular structure has not been fully understood [5]. The methods to study coal structure are mainly chemical and physical methods. The chemical method is complicated, time-consuming and low sensitivity, which is gradually replaced by physical method [6]. The earliest structural models were based on conventional analyses such as proximate analysis and ultimate analysis [7]. With the development of a series of advanced analytical techniques such as Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and solid-state nuclear magnetic resonance spectroscopy (SSNMR), more than 125 coal molecular models have been proposed [8,9]. Wang *et al.* [10] investigated the Inner Mongolia lignite structure by using XRD, ^{13}C NMR, TEM and XPS techniques and constructed its molecular model, the molecule formula is $C_{166}H_{130}O_{49}$. Lin *et al.* [11] investigated Indonesian brown structure by using ^{13}C NMR, FTIR, XPS and XRD, the results indicated that the ratio of bridge carbon/

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surrounding carbon is 0.0696 and the molecule formula for Indonesian brown coal is $C_{190}H_{170}O_{50}N_2$. Baysal *et al.* [12] investigated Turkish lignites by using XRD, ^{13}C NMR, FTIR and XPS, the results shown that the XRD aromaticity of the coals ranged between 0.642 and 0.777. Okolo *et al.* [13] investigated South African bituminous coal by using XRD, FTIR, ^{13}C NMR and TEM, the results shown that the aromaticity of the samples determined by ^{13}C NMR ranged from 0.74 to 0.87. Zhang *et al.* [14] investigated Xishan bituminous coal by using ultimate analysis, TEM, LD-TOF MS, ^{13}C NMR and XPS analytical techniques, the proposed molecule model consists of 62 individual molecules. To our knowledge, there are few models of subbituminous coal and no molecular model of SD coal.

Revealing the structural characteristics of coal is the basis of realizing efficient and clean utilization of SD coal, and it is also a key subject problem to be solved urgently in developing coal chemistry theory and coal directional conversion technology. In this paper, SD coal was characterized by conventional analyses, FTIR, XRD, XPS, magic angle spinning ^1H SSNMR(^1H MAS SSNMR)and cross polarization and magic angle spinning ^{13}C SSNMR(^{13}C CP/MAS SSNMR) techniques. Through peak fitting analysis and formula calculation, a series of structural parameters and components of SD coal were obtained. Two different NMR analysis methods, peak fitting and without peak fitting, are compared. The molecular model of SD coal was constructed mainly based on the experimental spectrum of ^{13}C SSNMR experimental spectra as a reference. The purpose of this paper is to obtain structural information of SD coal. In principle, it can provide support for the structure of SD coal, various processing and utilization ways, and provide theoretical basis for the research of high value-added products in coal.

2. Experimental

2.1. Coal sample

SD subbituminous coal was obtained from Shendong coalfield (Yulin, Shannxi, China). Evenly select large and small pieces of SD coal for crushing on jaw crusher (EP-1, China), further crushed on planetary ball mill (PM-2L, China) and then passed through 80-mesh standard sieve. The grinding process adopted the method of small amount, short grinding and multiple times, and the grinding time did not exceed 2 min each time. In this process, no coal samples were lost and all selected coal samples are completely ground. Subsequently, SD coal sample was vacuum-dried at 110 °C for 4 h and placed in a brown bottle.

2.2. Conventional analyses

Proximate analysis of SD coal was conducted using an automatic industrial analyzer (SDTGA5000a, China) in terms of GB/T 212—2008 (proximate analysis of coal). Ultimate analysis of SD coal was obtained by means of an elemental analyzer (Vario MACRO cube, Germany) in terms of GB/T 476—2001 (ultimate analysis of coal). Proximate and ultimate analysis can provide the overall characteristic of SD coal, which is considered to be important parameters in coal model construction.

Molar fraction of elements in SD coal is determined by Eq. (1).

$$X_i = \frac{i_{\mathrm{daf}} \Big/ M_i}{C_{\mathrm{daf}} \Big/ 12 + H_{\mathrm{daf}} \Big/ 1 + O_{\mathrm{daf}} \Big/ 16 + N_{\mathrm{daf}} \Big/ 14 + S_{\mathrm{daf}} \Big/ 32} \tag{1}$$

where i = C, H, O, N, S; X_i is molar fraction of C, H, O, N and S; M_i is relative atomic mass of C, H, O, N and S.

The ratio of the oxygen-containing functional group (Z_j, j = —O—, –C═O, –OH and –COOH) was calculated by Attar equations (Eqs. (2)–(7)).

$$u = (100X_{\mathrm{O}}/X_{\mathrm{C}})^2 \cdot (1/M) \tag{2}$$

$$M = \sum X_i \cdot M_i \tag{3}$$

$$Z_{\mathrm{—O—}} = 17.83u^{-0.6483} \tag{4}$$

$$Z_{\mathrm{—C=O}} = 2.8138u^{-0.4334} \tag{5}$$

$$Z_{\mathrm{—OH}} = 2.083u^{-0.6043} \tag{6}$$

$$Z_{\mathrm{—COOH}} = 0.1835 + 0.0185u - 0.000119u^2 \tag{7}$$

The structural parameters such as aromaticity (f_a), ring condensation degree (u) and average number of aromatic rings (R) were calculated by van Krevelen equation (Eqs. (8) and (9)).

$$f_{\mathrm{a}} = \frac{\left(100 - V_{\mathrm{daf}}\right) \times 1200}{1240C_{\mathrm{daf}}} \tag{8}$$

$$u = 2\left(\frac{R-1}{C}\right) = 2 - f_{\mathrm{a}} - \frac{H}{C} \tag{9}$$

2.3. FTIR analysis

FTIR spectrum of SD coal in the range of 4000–400 cm^{-1} was recorded by Fourier transform infrared spectrometer (Vertex 7.0, Bruker, Germany) with a total of 32 scans at a spectral resolution of 4 cm^{-1}. The sample was prepared by KBr pellet method and dried under infrared lamp to remove the adsorbed moisture on the surface of SD coal.

2.4. XRD analysis

XRD spectrum of SD coal was measured by X-ray diffractometer (Rigaku D/max-2400X, Japan) using Cu K_α radiation (λ = 0.15418 nm). The X-ray generator voltage and current were held at 40 kV and 150 mA, respectively. The X-ray intensities were measured in the range of 5°–90° with a step size of 0.01 (°)·s^{-1}.

The interlayer distance (d_{002}) is calculated by Bragg equation, Eq. (10).

$$d_{001} = \frac{\lambda}{2\sin\theta_{002}} \tag{10}$$

The average crystallite stack height (L_C) and crystallite diameter (L_a) are calculated by Scherrer equation, Eqs. (11) and (12). The layer numbers (N_C) is calculated by Eq. (13).

$$L_{\mathrm{C}} = \frac{K_1\lambda}{\beta_{002}\cos\theta_{002}} \tag{11}$$

$$L_{\mathrm{a}} = \frac{K_2\lambda}{\beta_{100}\cos\theta_{100}} \tag{12}$$

$$N_C = \frac{L_C}{d_{002}} + 1 \quad (13)$$

The aromaticity (f_a) can be calculated by Eq. (14).

$$f_a = \frac{C_A}{C} = \frac{A_{002}}{A_{002} + A_\gamma} \quad (14)$$

where A_{002} and A_γ are the areas of 002 and γ bands, respectively.

2.5. XPS analysis

XPS spectrum of SD coal was obtained by an electron spectrometer (ESCALab220i-XL, USA) using 300 W Al-Kα X-ray source. The binding energies were calibrated by C 1s at 284.8 eV and the distribution of elements were analyzed by peak fitting method.

2.6. ^{13}C CP/MAS SSNMR analysis

Solid-state ^{13}C NMR was performed at Hefei Institutes of Physical Science, Chinese Academy of Sciences, Hefei, China, using a superconducting nuclear magnetic resonance spectrometer (Bruker AVANCE III 600, Switzerland). ^{13}C CP/MAS SSNMR spectrum of SD coal was recorded at 150.9 MHz resonance frequency using a 4 mm MAS probe with 14 kHz spinning rate. A contact time of 2 ms and a recycle delay of 5 s were used to completely polarize all carbons in SD coal.

2.7. ^{1}H MAS SSNMR analysis

^{1}H MAS SSNMR test of SD coal was simultaneous with the ^{13}C CP/MAS SSNMR. ^{1}H MAS SSNMR spectrum of SD coal was recorded at 600.1 MHz resonance frequency using a 4 mm MAS probe with 14 kHz spinning rate. A π/2 pulse length of 2.57 μs and a recycle delay of 5 s were used for ^{1}H MAS NMR experiment. The chemical shifts of ^{13}C and ^{1}H were externally referenced to tetramethylsilane.

3. Results and Discussion

3.1. Conventional analyses results

Table 1 shows conventional analyses of SD coal. As can be seen from Table 1, SD coal contains 51.18% (mass) fixed carbon, 36.87% (mass) volatile content and 6.10% (mass) ash content. The element contents of C, H, N, S and O in SD coal are 64.49% (mass), 3.68% (mass), 0.90% (mass), 0.23% (mass) and 30.70% (mass), respectively, which is considered as an important parameter for the construction of coal molecular model [15].

Table 2 shows molar fractions of elements in SD coal. SD coal normalized structure formula is $C_{100}H_{68.5}O_{35.7}N_{1.2}S_{0.2}$.

Attar proposed the calculation equations of oxygen-containing functional groups in coal [16]. Table 3 shows contents of oxygen-containing functional groups in SD coal, the ratio of the oxygen-containing functional group —O—:C═O:—OH:—COOH is about 7:3:1:4.

Table 2
Molar fractions of elements in SD coal

X_C	X_H	X_O	X_N	X_S	H/C	O/C	N/C	S/C
0.487	0.333	0.174	0.006	0.001	0.685	0.357	0.012	0.002

Table 3
Contents of oxygen-containing functional groups in SD coal (%)

$X_{—O—}$	$X_{C═O}$	$X_{—OH}$	$X_{—COOH}$	X_{other}
29.92	13.68	4.35	17.70	34.35

Table 4
Structural parameters of SD coal

f_a	u	R
0.947	0.368	1.988

Table 4 shows structural parameters of SD coal calculated by van Krevelen equation [17]. As can be seen from Table 4, aromaticity (f_a) and ring condensation degree (u) of SD coal is 0.947 and 0.368, respectively. The average number of aromatic rings (R) is an important parameter to calculate aromatic cluster size, and R value of SD coal is 1.988.

3.2. FTIR results

Infrared analysis has the advantages of strong characteristics, wide application, quick detection and easy operation, and can provide information of various functional groups and structural parameters in coal [18]. There are overlapping peaks and weak peaks in FTIR spectrum, which can be solved by peak fitting [19]. Fig. 1 shows FTIR spectrum of SD coal. The spectrum is divided into 4 regions, namely aromatic C—H substitution region

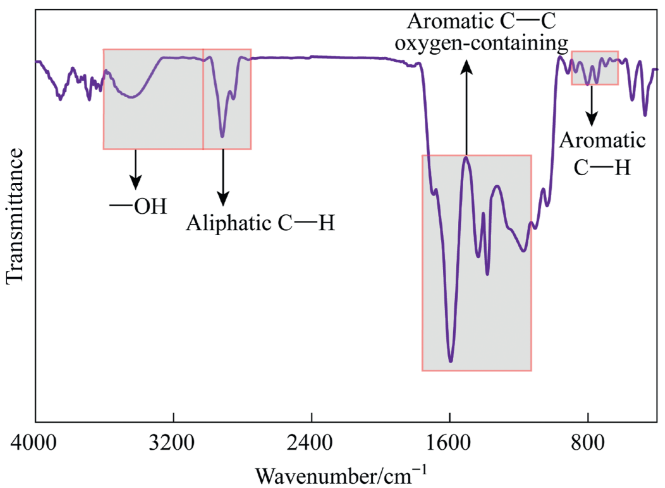


Fig. 1. FTIR spectrum of SD coal.

Table 1
Conventional analyses of SD coal (% (mass))

Proximate analysis (ad)				Ultimate analysis (daf)				
M	A	V	FC	C	H	N	S	O*
5.85	6.10	36.87	51.18	64.49	3.68	0.90	0.23	30.70

Note: daf, dry and ash-free basis; ad, air-dried basis; *, by difference.

(900–720 cm^{-1}), aromatic C–C and oxygen-containing functional groups region (1800–1120 cm^{-1}), aliphatic C–H region (3000–2800 cm^{-1}) and –OH region (3700–3000 cm^{-1}) [20].

Peak fitting was performed for each region. Fig. 2 shows curve fit diagrams of FTIR. The correlation constants (R^2) between experimental spectrum and fitting curves in 4 regions are all greater than 0.99. The 4 regions were fitted with 6, 4, 6 and 3 Gaussian peaks, respectively, and the specific results are shown in Table 5.

It can be seen that –OH in SD coal is mainly self-associated OH group (HO···OH), which is consistent with the inherent moisture content of SD coal determined by proximate analysis. In aliphatic C–H region, $-CH_2-$ content accounts for about 82%. In oxygen-containing functional groups region, the ratio of ether bond C–O, aromatic ether C–O and C=O is about 2:1:11. In aromatic C–H substitution region, the ratio of monosubstituted, bisubstituted and trisubstituted aromatic ring is about 2:3:1. The peak area in Table 5 was used to calculate the structural parameters of SD coal [21], and the specific results are shown in Table 6.

3.3. XRD results

Fig. 3 shows XRD and its curve fit spectrum of SD coal. The experimental curve was smoothed and background corrected. Then the smooth curve was fitted with 4 Gaussian peaks. Typically, 002 peak and 100 peak are located near 25° and 44°, respectively. The 002 peak is related to the spacing of aromatic layers and is used to determine d_{002} (interlayer distance) and L_c (average crystallite stack height). The 100 peak is related to the size of the aromatic layers and is used to determine L_a (crystallite diameter) [22]. The γ peak to the left of 002 peak is related to the aliphatic carbon and is used to calculate f_a (aromaticity) [12]. The microcrystalline structure parameters of SD coal are shown in Table 7.

3.4. XPS results

Fig. 4 shows XPS spectrum of SD coal. The XPS spectrum shows that there are obvious C (1s) and O (1s) peaks at the binding energies of 280–290 eV and 527–537 eV, respectively. Weak peaks of N (1s) and S (2p) exist at the binding energies of 395–405 eV and 155–178 eV, respectively. XPS can determine the chemical composition of coal surface layer in nm scale [23]. The surface element content of SD coal was determined by peak area ratio. It was found that the surface element content of C, O, N and S were 64.699%, 33.944%, 0.748% and 0.610%, respectively, which is similar to the overall percentage determined by ultimate analysis. The small difference is due to the fact that XPS cannot detect H [24].

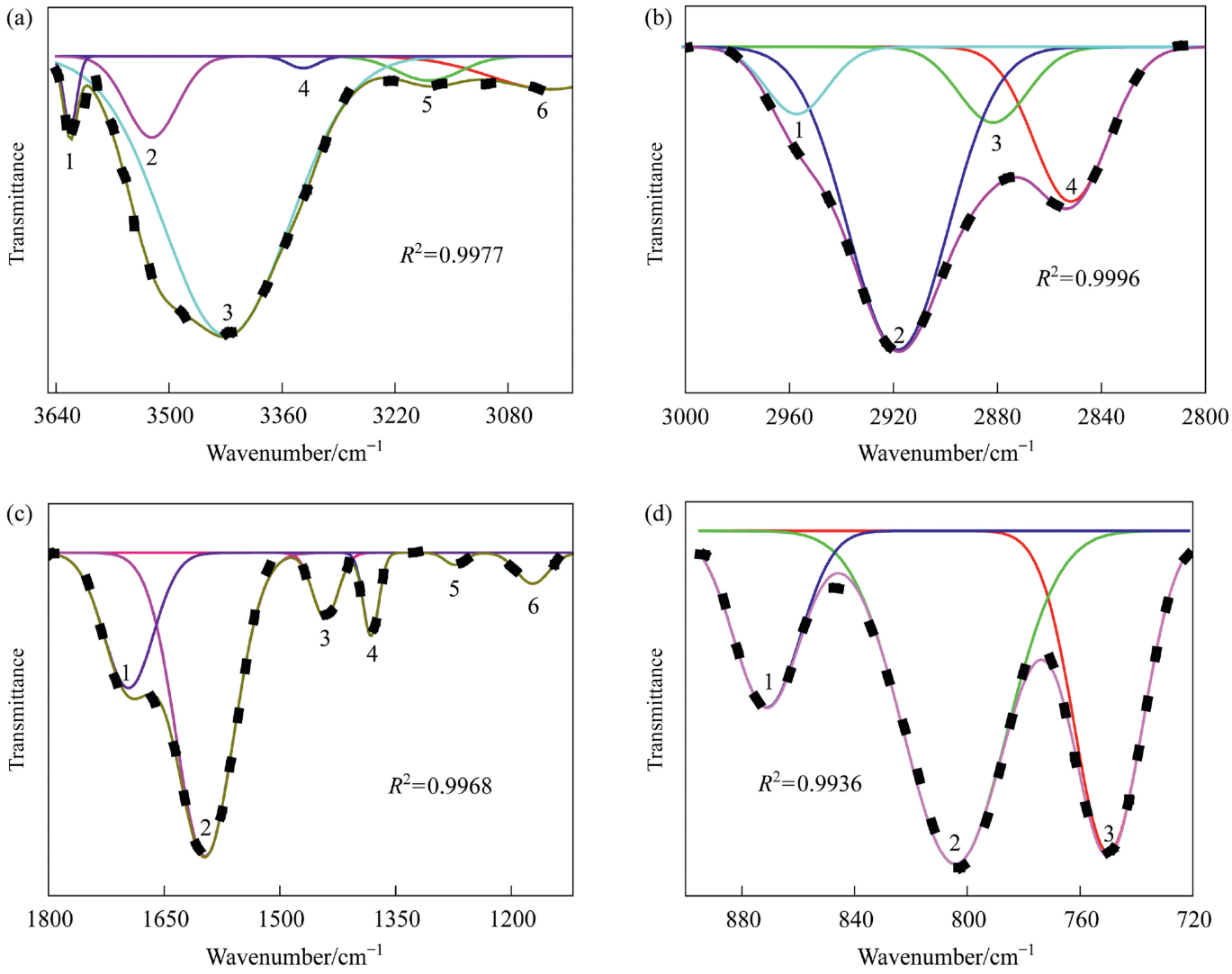


Fig. 2. Curve fit diagrams of FTIR: (a) 3700–3000 cm^{-1}; (b) 3000–2800 cm^{-1}; (c) 1800–1120 cm^{-1}; (d) 900–720 cm^{-1}.

Table 5
Peak fitting results of FTIR

Regions/cm^{-1}	Wavenumber/cm^{-1}	Peak assignment	Area	Area/%
3700–3000	3622.26	Free –OH	0.101	2.06
	3521.32	OH···π	0.459	9.35
	3428.64	HO···OH	3.859	78.58
	3333.76	OH···ether oxygen	0.039	0.80
	3178.33	Cyclic –OH	0.171	3.48
	3027.05	HO···N	0.282	5.73
3000–2800	2957.21	Asymmetric—CH_3	0.244	8.10
	2918.21	Asymmetric—CH_2—	1.782	59.18
	2881.72	Symmetric—CH_3	0.306	10.17
	2851.76	Symmetric—CH_2—	0.679	22.55
1800–1120	1696.06	C=O	4.458	23.69
	1597.01	Aromatic C=C	11.569	61.52
	1441.04	Aliphatic CH_2 and CH_3	1.104	5.87
	1381.84	—CH_3 attached to benzene ring	0.857	4.56
	1272.89	Aromatic ether C–O	0.164	0.87
	1172.14	Ether bond C–O	0.662	3.50
900–720	871.15	Trisubstituted aromatic ring	0.198	16.95
	804.26	Bisubstituted aromatic ring	0.583	50.92
	749.90	Monosubstituted aromatic ring	0.371	32.13

Table 6
Structural parameters of SD coal

Parameter	Definition	Value	Meaning and note
H_{ar}/H_{al}	$R = A_{720-900}/A_{2800-3000}$	0.383	Aromaticity index
H_{ar}/H	$f_{ar}^{H} = A_{720-900}/(A_{720-900}+A_{2800-3000})$	0.277	The ratio of H_{ar} to H assumed that only H_{ar} and H_{al} are present in coal
Organic maturity index	$C = A_{1700}/(A_{1700}+A_{1600})$	0.278	Represent the maturity of coal
Aromatic ring condensing index	$D = A_{720-900}/A_{1600}$	0.099	An index of the degree of aromatic ring condensation the lower C and D values, the more mature the coal
C_{ar}/C	$f_{ar}^{C} = 1 - \frac{C_{al}}{C} = 1 - \frac{H_{al}}{H} \times \frac{H}{C} \Big/ \frac{H_{al}}{C_{al}}$	0.725	The ratio of Car to C, $H_{al}/C_{al} = 1.8$ assumed that only C_{ar} and C_{al} are present in coal
CH_3/CH_2 ratio	$CH_3/CH_2=(A_{2957}+A_{2881})/(A_{2918}+A_{2851})$	0.223	Represent the length of aliphatic chain the higher CH_3/CH_2 value, the shorter aliphatic chain

Note: $H=H_{al}+H_{ar}$, C_{al}, H_{al} (2800–3000 cm^{-1}) is aliphatic hydrogen, H_{ar} (720–900 cm^{-1}) is aromatic hydrogen, ; $C=C_{al}+C_{ar}$, C_{al} is aliphatic carbon, C_{ar} is aromatic carbon.

Table 7
Microcrystalline structure parameters of SD coal

Positions/(°)			Microcrystalline structure parameters/Å					
γ	002	100	d_{002}	L_c	L_a	N_c	L_a/L_c	f_a
20.124	24.889	44.136	1.832	14.688	20.852	9.017	1.419	0.748

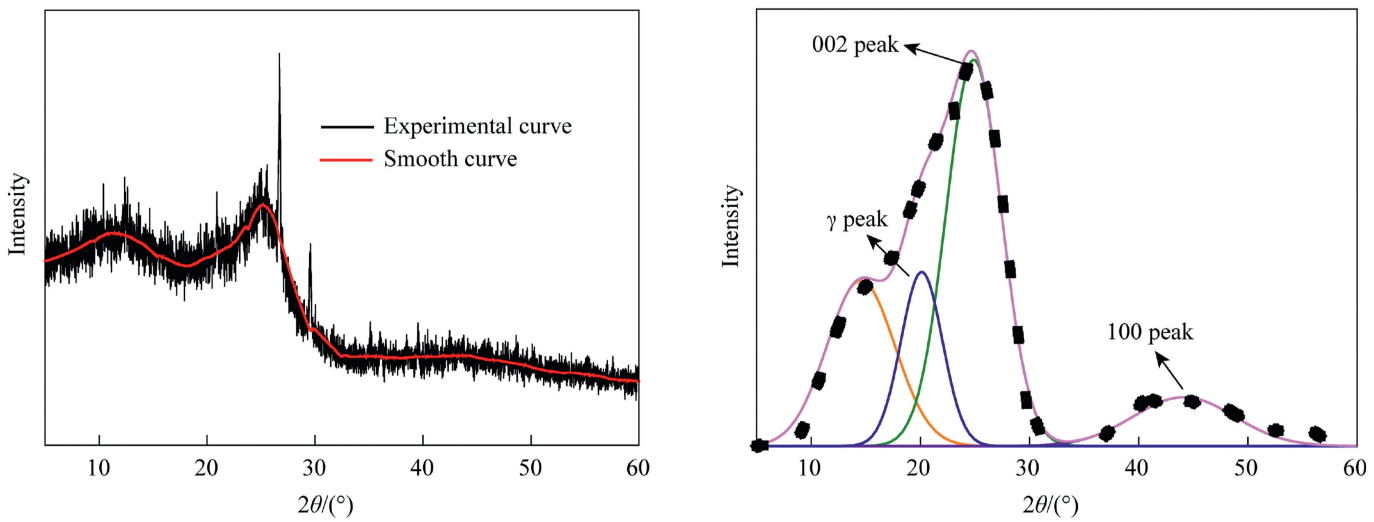


Fig. 3. XRD and its curve fit spectrum.

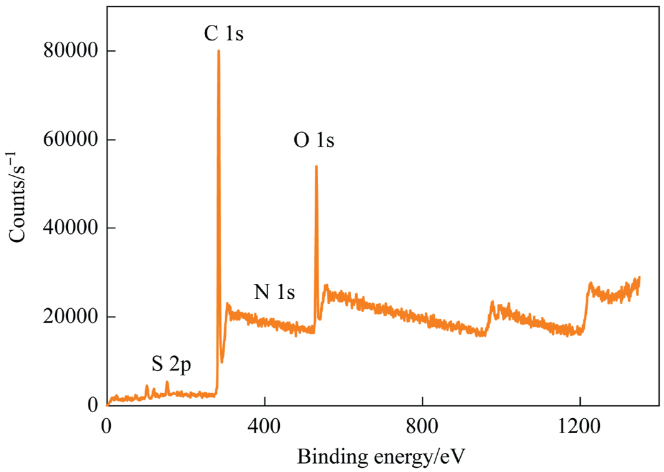


Fig. 4. XPS spectrum of SD coal.

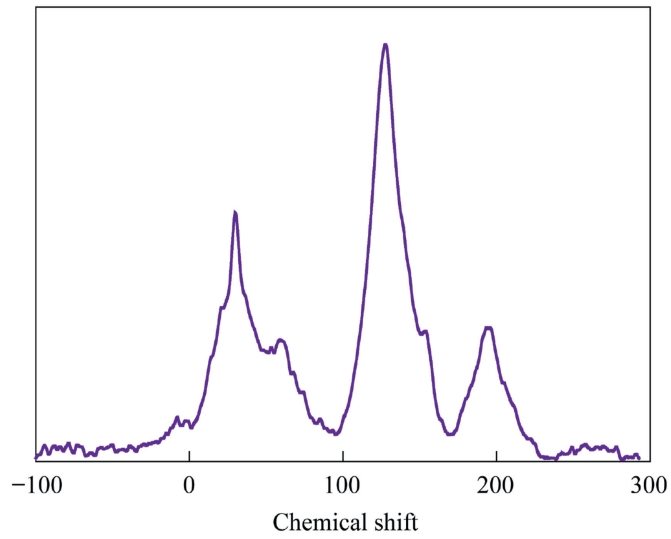


Fig. 6. ^{13}C CP/MAS SSNMR spectrum of SD coal.

Fig. 5 (a)–(d) show peak fitting spectra of C (1s), O (1s), N (1s) and S (2p). The 4 regions were fitted with 3, 5, 5 and 5 Gaussian peaks, respectively [14,25], and the specific results are shown in Table 8. It can be seen from Table 8 that the oxygen structure of SD coal is mainly C–O and COO—, and the content is about 66.02%. The nitrogen in SD coal is mainly pyridine and pyrrole, and the content is about 81.01%. Organic sulfur is mainly sulfoxide and thiophene.

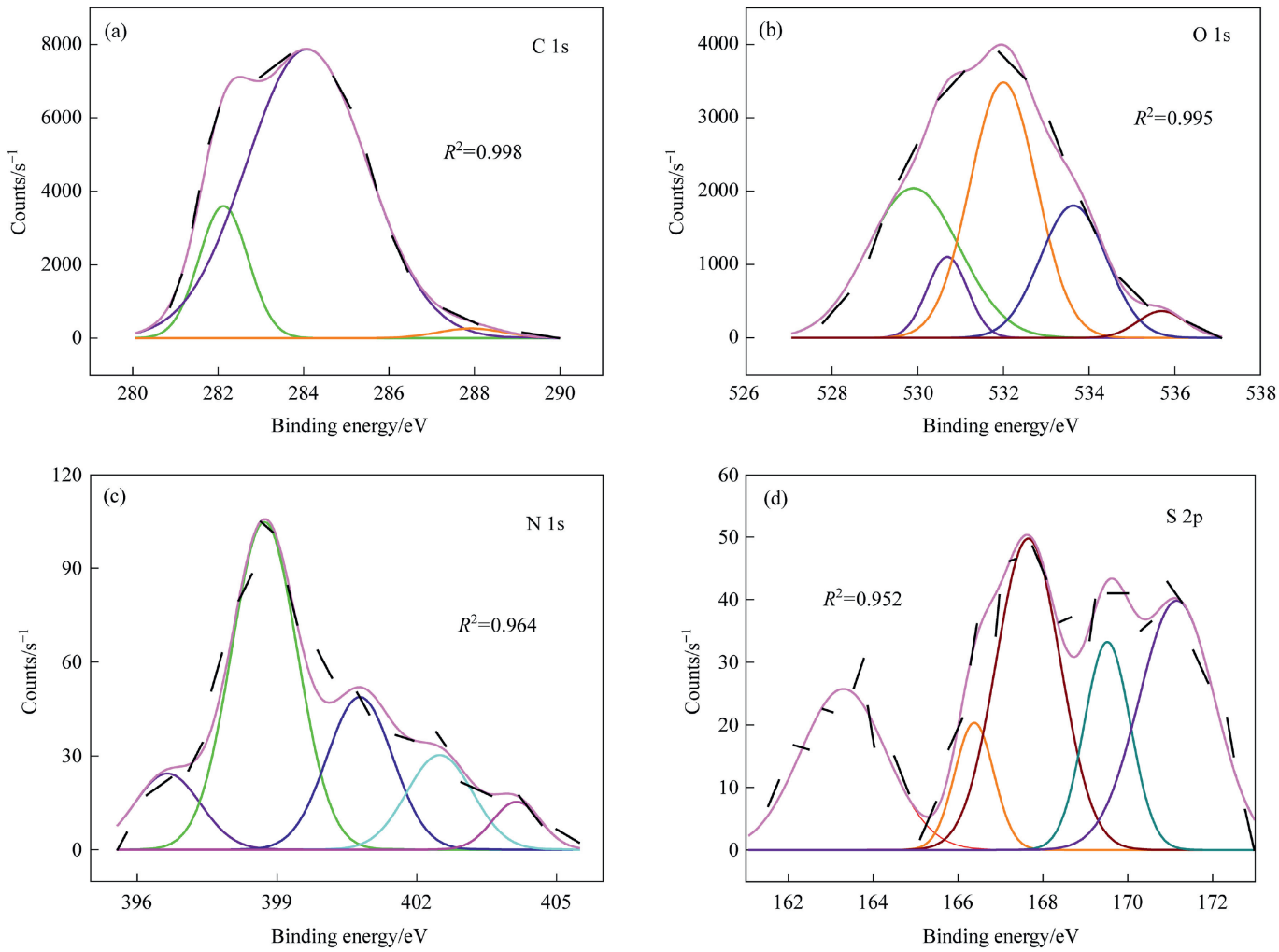


Fig. 5. Peak fitting spectra of (a) C (1s), (b) O (1s), (c) N (1s) and (d) S (2p).

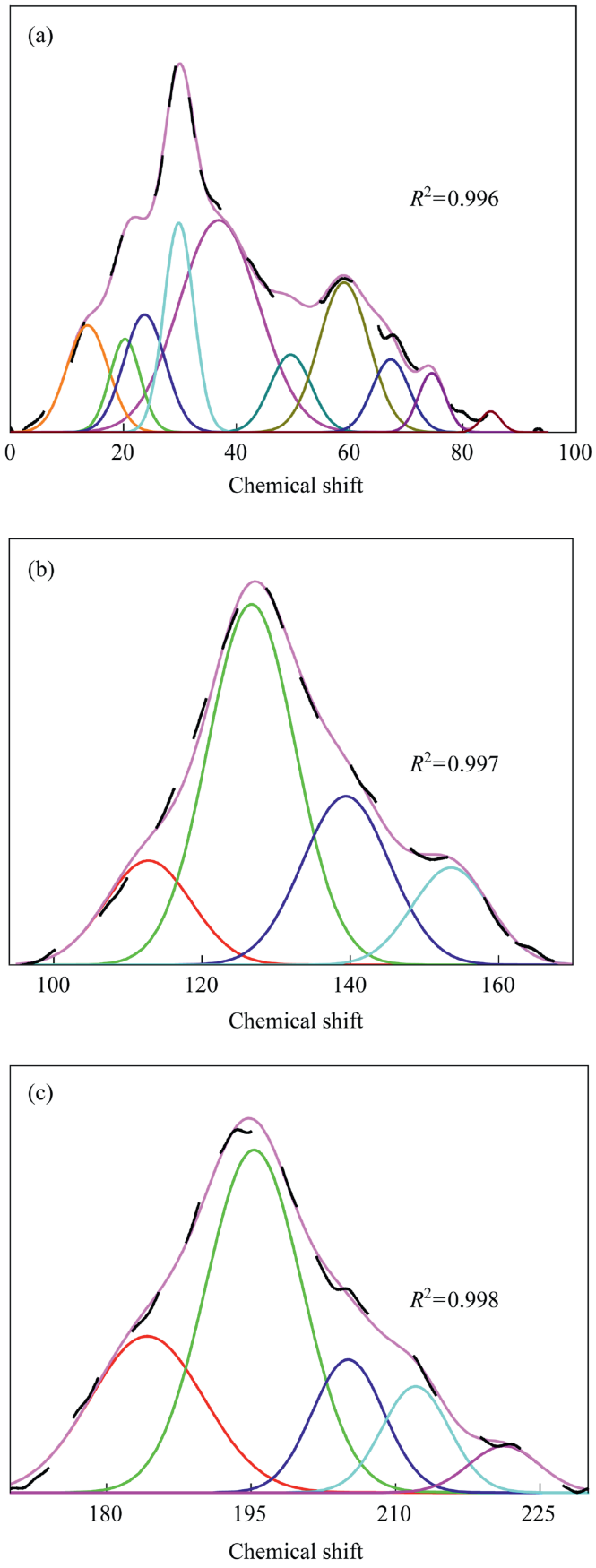


Fig. 7. Curve fit diagrams of ^{13}C NMR (a) 0–90; (b) 90–165; (c) 165–220.

Table 8
Peak fitting results of XPS

Element	Binding energy/eV	Form	Content/%
C	282.13	C–Si	15.48
	284.07	C–C, C–H	82.98
	287.92	C=O	1.54
O	529.90	Inorganic oxygen	31.08
	530.69	C=O	7.43
	532.00	C–O	38.67
	533.63	COO—	19.92
	535.69	Absorbance oxygen	2.90
N	396.64	Pyridine nitrogen	10.44
	398.73	Pyrrolic nitrogen	48.16
	400.77	Pyrrolic nitrogen	22.41
	402.49	Quaternary nitrogen	13.89
	404.14	Oxidized nitrogen	5.10
S	163.29	Pyrite and thiophenol	20.44
	166.38	Sulfoxide	7.44
	167.65	Thiophene	30.00
	169.51	Sulfonate	14.43
	171.15	Sulfate	27.68

3.5. ^{13}C CP/MAS SSNMR results

^{13}C NMR can provide information on the structure of carbon skeleton in coal [26]. Fig. 6 shows ^{13}C CP/MAS SSNMR spectrum of SD coal. There are 3 regions in the spectrum, namely aliphatic carbon region (0–90), aromatic carbon region (90–165) and carbonyl carbon region (165–220) [27]. Their contents are 32.91%, 52.98% and 14.11%, respectively. There are two analytical processing methods for ^{13}C NMR spectrum. One is the use of peak fitting and the other is without peak fitting. It is very important to have a unified and reliable analysis standard. So the differences between the two analysis methods are compared.

Fig. 7 shows peak fitting spectra of ^{13}C NMR. The 3 regions were fitted with 10, 4 and 5 Gaussian peaks, respectively [28]. R^2 are all greater than 0.99. At the same time, the ^{13}C NMR spectrum was analyzed without peak fitting [29]. The specific results are shown in Table 9.

The values in Table 9 were used to calculate the structural parameters of SD coal [28], and the specific results are shown in Table 10. As can be seen from Table 10, it was found that the parameters XBP and δ obtained by the two methods differ greatly. Only when there are overlapped peaks in the spectrum can the peak fitting be carried out and the smooth curve does not to require peak fitting. But when the local smooth curve is caused by different carbon types, there will be errors in peak fitting. The ^{13}C NMR spectrum analysis without peak fitting is more reliable and stable.

3.6. ^{1}H MAS SSNMR results

Fig. 8 shows ^{1}H MAS SSNMR and its curve fit spectrum of SD coal. Similar to ^{13}C NMR analysis, two analytical processing methods were used for ^{1}H NMR spectrum [30]. The specific results are shown in Table 11. As can be seen from Table 11, only 4 types of hydrogen can be obtained by peak fitting spectrum of ^{1}H NMR. Fig. 9 shows an example of ^{1}H MAS SSNMR peak fitting spectrum. As can be seen from Fig. 9, the ^{1}H NMR spectrum cannot be artificially divided into several peaks to analyze different types of H. Therefore, without peak fitting is preferred to analyze ^{1}H NMR spectrum.

3.7. Aromaticity obtained from various analytical analyses

Aromaticity is an important parameter of coal structure [31], which is calculated by means of FTIR, XRD and NMR. The

Table 9
Type and distribution of carbon in SD coal

Shift	Assignment	Structure	Symbol	Content/%	
				Peak fitting	Without peak fitting
14–16	Aliphatic CH_3	R—CH_3	f_{al}^{M}	0.71	2.68
16–22	Aromatic CH_3	Ar—CH_3	f_{al}^{A}	3.05	1.72
22–50	Methyl carbon	CH_3,CH_2,CH,C	f_{al}^{H}	18.00	16.92
50–70	Methoxyl carbon	O—CH_3,O—CH_2,O—CH	f_{al}^{O}	7.35	8.08
75–90		R—O—R	$f_{al}^{O'}$	0.84	3.51
100–129	Aromatic protonized carbon	Ar—H	f_{ar}^{H}	26.77	7.55
129–137	Aromatic bridge carbon	Ar	f_{ar}^{A}	12.45	26.60
137–148	Aromatic branched carbon	Ar—C	f_{ar}^{C}	9.91	12.46
148–165	Oxy-aromatic carbon	Ar—O	f_{ar}^{O}	6.54	6.37
170–190	Carboxyl carbon	COOH	f_{ca}^{H}	4.05	10.13
190–220	Carbonyl carbon	C=O	f_{ca}^{O}	10.31	3.98

Table 10
Structural parameters of SD coal

Parameter	Symbol	Definition	Value	
			Peak fitting	Without peak fitting
Aromatic carbon ratio	f_{ar}	$f_{ar}^{H}+f_{ar}^{A}+f_{ar}^{C}+f_{ar}^{O}$	52.98%	55.67%
Aliphatic carbon ratio	f_{al}	$f_{al}^{M}+f_{al}^{A}+f_{al}^{H}+f_{al}^{O}$	32.91%	29.97%
Average methylene chain length	C_n	f_{al}^{H}/f_{ar}^{C}	1.358	1.817
Aromatic cluster size	XBP	$f_{ar}^{A}/(f_{ar}^{H}+f_{ar}^{A}+f_{ar}^{C}+f_{ar}^{O})$	0.502	0.224
Branching degree of alkyl chain	BI	S33-50/f_{al}	42.45%	29.83%
Substitutive degree of aromatic ring	δ	$(f_{ar}^{A}+f_{ar}^{C}+f_{ar}^{O})/f_{ar}$	85.73%	51.92%

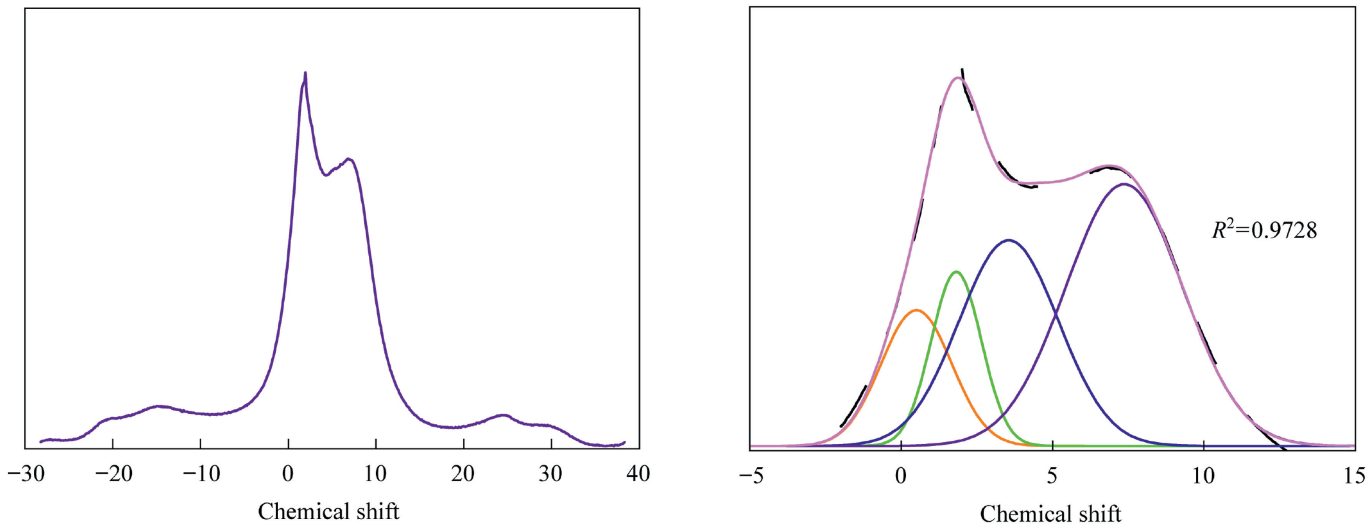


Fig. 8. ^{1}H MAS SSNMR and its curve fit spectrum.

Table 11
Type and distribution of hydrogen in SD coal

Hydrogen type	Shift	Structure	Symbol	Content/%	
				Peak fitting	Without peak fitting
Hydrogen on the γ position of an aromatic ring	0.5–1.0	RCH_3	H_γ	13.77	4.07
Hydrogen on the β position of an aromatic ring	1.0–2.0	$ArRCH_2R$	H_β	12.57	9.92
Hydrogen on the α position of an aromatic ring	2.0–4.0	$ArCH_2R$	H_α	29.53	18.07
Olefin hydrogen	5.0–6.0	HC=C	$H_{C=C}$	–	8.45
Aromatic hydrogen	6.8–9.0	H–Ar	H_{ar}	44.13	16.49
Carbonyl hydrogen	9.0–13	R—HC=O	$H_{C=O}$	–	12.22
Carboxyl hydrogen	13–15	RCOOH	H_{O-H}	–	1.75

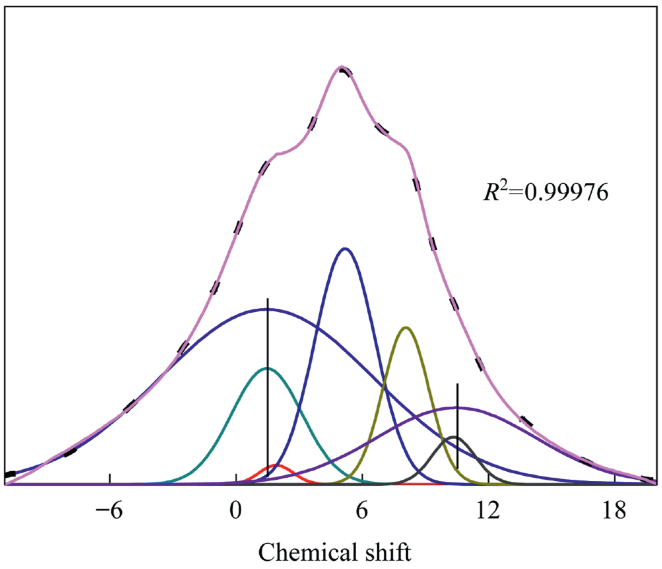


Fig. 9. An example of ^{1}H MAS SSNMR peak fitting spectrum.

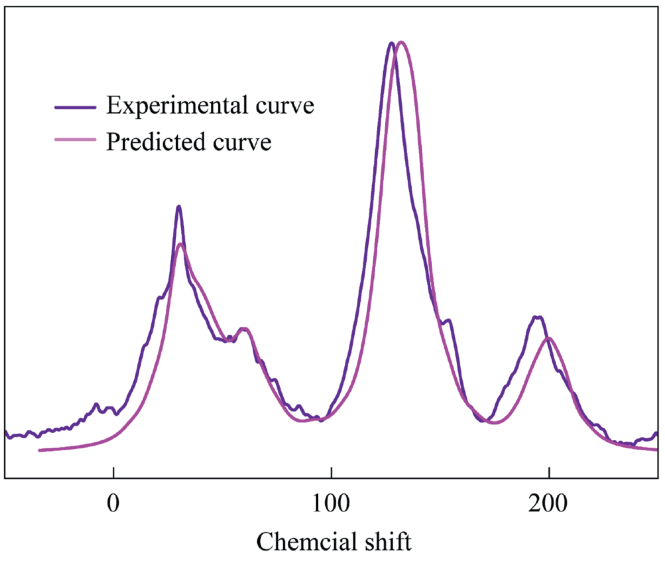


Fig. 11. Experimental and predicted ^{13}C NMR spectrum.

aromaticity value obtained by conventional analyses is calculated by the Van Krevelen empirical formula. When the aromaticity value is calculated by FTIR, it is assumed that only aromatic hydrogen and aliphatic hydrogen exist and only aromatic carbon and aliphatic carbon exist in coal. When the aromaticity value is calculated by XRD, only aliphatic carbon and aromatic carbon are considered and is related to the microcrystalline structure of coal. ^{13}C NMR is the best tool for determining aromaticity because it can give total aromatic groups and distinguish oxygenated and aliphatic groups in the carbon matrix.

3.8. Molecular model of SD coal

3.8.1. Aromatic skeleton structure

Aromatic structure is the skeleton structure of coal [32]. The XBP value is an important parameter of aromatic cluster size [11], and the XBP value of SD coal is 0.224. The XBP values of benzene, naphthalene, anthracene and pyrene are 0, 0.2, 0.286 and 0.375, respectively. It has been reported that when the carbon content is 70% to 80%, the average number of aromatic rings is 2 [33]. The average aromatic ring number of SD coal is 1.988. Therefore, single-ring and double-ring structures are the main aromatic skeletons of SD coal molecular model. It has been reported that the molecular weight of coal model is usually around 3000 [10]. Table 12 shows the types and quantities of aromatic structures in SD coal molecular model.

3.8.2. Incorporation of aliphatic carbons

The aromatic carbon ratio of SD coal is 55.67%, there are about 120 aromatic carbons in the model, so the total number of carbons in the model is about 210. The aliphatic carbon ratio of SD coal is 29.97%, so the total number of aliphatic carbons in the model is about 60, and the remaining 30 are carbonyl carbons. The types and contents of aliphatic carbons were added from the aspects of CH_3/CH_2 ratio,

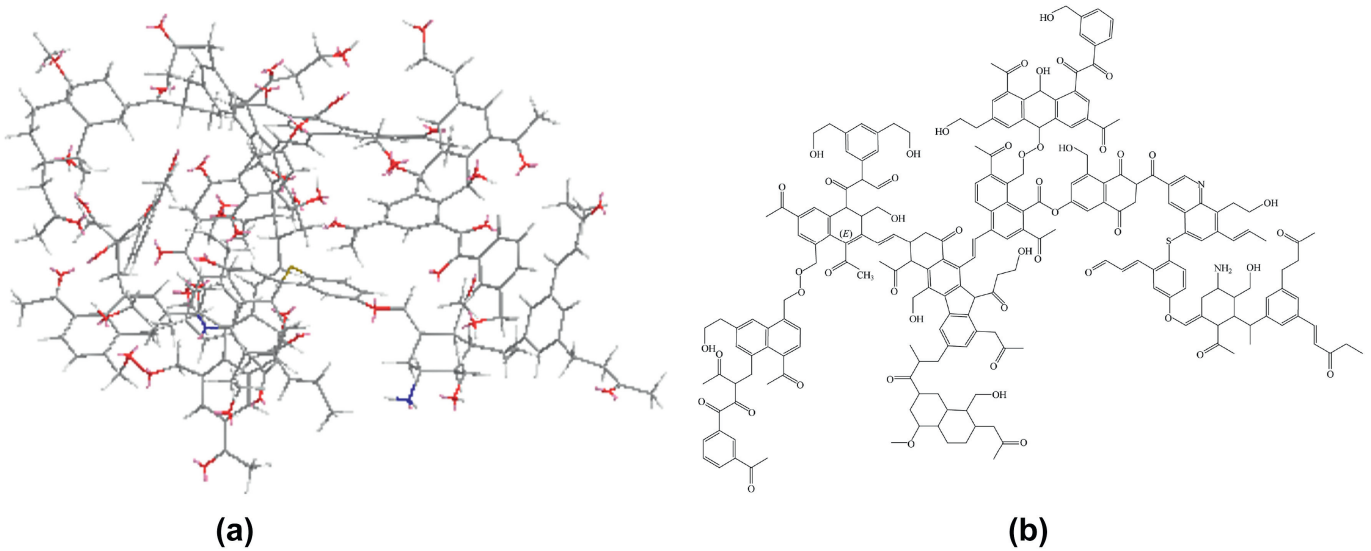
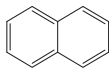
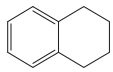
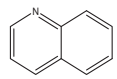
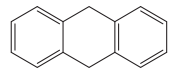


Fig. 10. SD coal molecular model: (a) 3D optimized structure; (b) 2D structure.

Table 12
Types and quantities of aromatic structures

Aromatic structures					
Quantity	6	2	3	1	1

average methylene chain length, branching degree of alkyl chain, substitutive degree of aromatic ring and f_{al}^{M}, f_{al}^{A}, f_{al}^{H}, f_{al}^{O}, $f_{al}^{O'}$, f_{ar}^{C} contents.

3.8.3. Addition of heteroatoms

Nitrogen, sulfur and oxygen are also important components of coal. SD coal normalized structure formula is $C_{100}H_{68.5}O_{35.7}N_{1.2}S_{0.2}$. So when the total number of carbon atoms is about 210, the number of oxygen atoms is about 70, the number of nitrogen atoms is about 2, and the number of sulfur atoms is about 1. Nitrogen and sulfur exist mainly in the form of pyridine and thioether. The types and contents of oxygen were added from the aspects of —O—:C═O:—OH:—COOH, ether bond C—O:aromatic ether C—O:C═O and f_{al}^{O}, $f_{al}^{O'}$, f_{ar}^{O}, f_{ca}^{H}, f_{ca}^{O} contents. Fig. 10 shows the SD coal molecular model and the model was constructed with an atom composition of $C_{214}H_{214}O_{49}N_2S$.

3.8.4. Predicted NMR spectrum of SD coal molecular model

The ^{13}C NMR spectrum of SD coal molecular model was predicted by ChemDraw software. Fig. 11 shows the experimental and predicted ^{13}C NMR spectrum of SD coal.

4. Conclusions

As one of the eight coal fields in the world, SD coal is a subbituminous coal, accounting for about 40% of the total coal. SD coal has the advantages of convenient mining and excellent quality. Understanding the structure of SD coal is the basis of its transformation and utilization. This paper mainly studies the structural parameters and molecular model of SD subbituminous coal. (1) SD coal was analyzed by FTIR, XRD, XPS and NMR, and it was pointed out for the first time that without peak fitting of NMR spectrum is more accurate. (2) ^{13}C NMR is the best method to determine aromaticity. (3) SD coal molecular model was constructed with ^{13}C NMR experimental spectra as a reference, and the chemical formula for the model was $C_{214}H_{214}O_{49}N_2S$. It provides a reference for the structural study of subbituminous coal.

CRediT Authorship Contribution Statement

Xiaoping Su: Writing — review & editing, Writing — original draft, Visualization, Software, Data curation, Conceptualization. Ning Li: Writing — original draft, Project administration, Data curation, Conceptualization. Longjian Li: Writing — review & editing, Supervision, Methodology, Formal analysis. Reyila Tuerhong: Visualization, Resources, Methodology, Funding acquisition, Formal analysis. Yongchong Yu: Writing — review & editing, Visualization, Software, Project administration, Funding acquisition, Data curation. Ping Zhang: Writing — review & editing, Supervision, Resources, Project administration, Investigation, Data curation. Qiong Su: Writing — review & editing, Supervision, Methodology, Funding acquisition, Conceptualization. Tao Shen: Supervision, Software, Project administration, Investigation, Funding acquisition, Formal analysis. Ming Sun: Writing — review & editing, Project administration, Formal analysis, Conceptualization. Xiaoxun Ma: Writing — review & editing, Methodology, Conceptualization.

Declaration of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

[1] X.X. Miao, M.G. Qian, Research on green mining of coal resources in China: current status and future prospects, *J. Min. Saf. Eng.* 26 (1) (2009) 1–14.
[2] W. Zhu, Mechanism and control of roof fall and support failure incidents occurring near longwall recovery roadways, *J. South. Afr. Inst. Min. Metall.* 117 (11) (2017) 1063–1072.
[3] L. Li, H.J. Fan, H.Q. Hu, Distribution of hydroxyl group in coal structure: a theoretical investigation, *Fuel* 189 (2017) 195–202.
[4] K. Bratek, W. Bratek, I. Gerus-Piasecka, S. Jasieńko, P. Wilk, Properties and structure of different rank anthracites, *Fuel* 81 (1) (2002) 97–108.
[5] M.W. Haenel, Recent progress in coal structure research, *Fuel* 71 (11) (1992) 1211–1223.
[6] S. Li, D.Z. Tang, H. Xu, Z. Yang, Advanced characterization of physical properties of coals with different coal structures by nuclear magnetic resonance and X-ray computed tomography, *Comput. Geosci.* 48 (2012) 220–227.
[7] H.A.G. Chermin, D.W. Vankrevelen, A mathematical model of coal pyrolysis, *Fuel* 36 (1957) 85–104.
[8] J.P. Mathews, A.L. Chaffee, The molecular representations of coal—A review, *Fuel* 96 (2012) 1–14.
[9] K.J. Li, R. Khanna, J.L. Zhang, M. Barati, Z.J. Liu, T. Xu, T.J. Yang, V. Sahajwalla, Comprehensive investigation of various structural features of bituminous coals using advanced analytical techniques, *Energy Fuels* 29 (11) (2015) 7178–7189.
[10] J. Wang, Y.Q. He, H. Li, J.D. Yu, W.N. Xie, H. Wei, The molecular structure of Inner Mongolia lignite utilizing XRD, solid state ^{13}C NMR, HRTEM and XPS techniques, *Fuel* 203 (2017) 764–773.
[11] H.L. Lin, K.J. Li, X.W. Zhang, H.X. Wang, Structure characterization and model construction of Indonesian brown coal, *Energy Fuels* 30 (5) (2016) 3809–3814.
[12] M. Baysal, A. Yürüm, B. Yıldız, Y. Yürüm, Structure of some western Anatolia coals investigated by FTIR, Raman, ^{13}C solid state NMR spectroscopy and X-ray diffraction, *Int. J. Coal Geol.* 163 (2016) 166–176.
[13] G.N. Okolo, H.W.J.P. Neomagus, R.C. Everson, M.J. Roberts, J.R. Bunt, R. Sakurovs, J.P. Mathews, Chemical–structural properties of South African bituminous coals: insights from wide angle XRD–carbon fraction analysis, ATR–FTIR, solid state ^{13}C NMR, and HRTEM techniques, *Fuel* 158 (2015) 779–792.
[14] Z.Q. Zhang, Q.N. Kang, S. Wei, T. Yun, G.C. Yan, K.F. Yan, Large scale molecular model construction of Xishan bituminous coal, *Energy Fuel.* 31 (2) (2017) 1310–1317.
[15] R. Gupta, Advanced coal characterization: a review, *Energy Fuel.* 21 (2) (2007) 451–460.
[16] A. Attar, W.H. Corcoran, Sulfur compounds in coal, *Ind. Eng. Chem. Prod. Res. Dev.* 16 (1977) 168–170.
[17] D.W. van Krevelen, Development of coal research—a review, *Fuel* 61 (9) (1982) 786–790.
[18] S.Q. Wang, Y.G. Tang, H.H. Schobert, Y.N. Guo, Y.F. Su, FTIR and ^{13}C NMR investigation of coal component of Late Permian coals from Southern China, *Energy Fuel.* 25 (12) (2011) 5672–5677.
[19] X. Cui, X.L. Li, Y.M. Li, S. Li, Evolution mechanism of oxygen functional groups during pyrolysis of Datong coal, *J. Therm. Anal. Calorim.* 129 (2) (2017) 1169–1180.

[20] D. Wu, G.J. Liu, R.Y. Sun, X. Fan, Investigation of structural characteristics of thermally metamorphosed coal by FTIR spectroscopy and X-ray diffraction, *Energy Fuel.* 27 (10) (2013) 5823–5830.
[21] M.A. Ahmed, M.J. Blesa, R. Juan, R.E. Vandenberghe, Characterisation of an Egyptian coal by Mossbauer and FT-IR spectroscopy, *Fuel* 82 (14) (2003) 1825–1829.
[22] L. Lu, V. Sahajwalla, C. Kong, D. Harris, Quantitative X-ray diffraction analysis and its application to various coals, *Carbon* 39 (12) (2001) 1821–1833.
[23] D.L. Perry, A. Grint, Application of XPS to coal characterization, *Fuel* 62 (9) (1983) 1024–1033.
[24] D.C. Frost, W.R. Leeder, R.L. Tapping, B. Wallbank, An XPS study of the oxidation of pyrite and pyrites in coal, *Fuel* 56 (3) (1977) 277–280.
[25] Z.Q. Zhang, Q.N. Kang, S. Wei, T. Yun, G.C. Yan, K.F. Yan, Molecular model of Xishan bituminous coal surface and its wetting properties, *Energy Fuels* 31 (9) (2017) 9094–9100.
[26] S.Q. Wang, Y.G. Tang, H. Chen, P.H. Liu, Y.M. Sha, Chemical structural transformations of different coal components at the similar coal rank by HRTEM *in situ* heating, *Fuel* 218 (2018) 140–147.
[27] M.S. Solum, R.J. Pugmire, D.M. Grant, Carbon-13 solid-state NMR of Argonne-premium coals, *Energy Fuel.* 3 (1989) 187–193.
[28] M.S. Solum, R.J. Pugmire, D.M. Grant, Carbon-13 solid-state NMR of Argonne-premium coals, *Energy Fuel.* 3 (2) (1989) 187–193.
[29] B.O. Erdenetsogt, I. Lee, S.K. Lee, Y.J. Ko, D. Bat-Erdene, Solid-state C-13 CP/MAS NMR study of baganuur coal, Mongolia: oxygen-loss during coalification from lignite to subbituminous rank, *Int. J. Coal Geol.* 82 (1–2) (2010) 37–44.
[30] Z.H. Sun, W.H. Zhang, Chemical composition and structure characterization of distillation residues of middle-temperature coal tar, *Chin. J. Chem. Eng.* 25 (6) (2017) 815–820.
[31] A.O. Odeh, Comparative study of the aromaticity of the coal structure during the char formation process under both conventional and advanced analytical techniques, *Energy Fuel.* 29 (4) (2015) 2676–2684.
[32] H. Takagi, T. Isoda, K. Kusakabe, S. Morooka, Relationship between pyrolysis reactivity and aromatic structure of coal, *Energy Fuels* 14 (3) (2000) 646–653.
[33] Z.K. Li, X.Y. Wei, H.L. Yan, Z.M. Zong, Insight into the structural features of Zhaotong lignite using multiple techniques, *Fuel* 153 (2015) 176–182.