

Molecular structure of coal macerals and thermal response behavior of their chemical bonds obtained by structural characterizations and molecular dynamics simulations

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Nomenclature

Symbols

A	Ash content (%)
M	Moisture content (%)
V	Volatile content (%)
FC	Fixed carbon content (%)
f_{α}	Percentage of total sp^2 hybridized carbon (%)
f_{α}^C	Percentage of aromatic carbon linked to carbonyl or carboxyl groups (%)
f_{α}^H	Percentage of protonated aromatic carbon (%)
f_{α}^P	Percentage of aromatic carbon linked to oxygen atoms (%)
f_{α}^S	Percentage of alkylated aromatic carbon (%)
f_{α}^B	Percentage of aromatic bridgehead carbon (%)
f_{α}^N	Percentage of non-protonated aromatic carbon (%)
f_{α}'	Percentage of total aromatic carbon (%)
f_{al}^*	Percentage of methyl carbon in aliphatic hydrocarbons (%)
f_{al}^H	Percentage of methylene, quaternary, or hypomethyl carbon (%)
f_{al}^O	Percentage of aliphatic carbon attached to the oxygen atom (%)
f_{al}	Percentage of total sp^3 hybridized carbon (%)
X_{BP}	Ratio of bridge carbon to peripheral carbon (-)
A^*	Area of the peak (-)
DOA	Degree of aromatization (-)
DOB	Degree of branching of aliphatic side-chains (-)
DOC	Degree of condensation (-)
C	Maturation of coal (-)
P	Generation potential of hydrocarbons (-)
$^{Ali}CH_3$	Aliphatic methyl
$^{Ar}CH_3$	Aromatic methyl
CH_2	Methylene
CH	Methyne
QC	Quaternary carbon
OCH_3	Methoxy
$O-AliC$	Oxy-Aliphatic carbons
$P-ArC$	Protonated aromatic carbon
$Bri-ArC$	Bridgehead aromatic carbon
$Bra-ArC$	Branched aromatic carbon
$O-ArC$	Oxy-Aromatic carbons
$Cx C$	Carboxyl carbon
$Cn C$	Carbonyl carbon
4H	Ortho disubstituted aromatic hydrocarbons
3H	Ortho trisubstituted aromatic hydrocarbons

^2H	Ortho tetrasubstituted aromatic hydrocarbons
*C-O	C-O in phenol, alcohol, ether, phenoxy, and ester
$^{\text{Ali}}\text{CH}$	Aliphatic methyne
$^{\text{A}}\text{CH}_3\&\text{CH}_2$	Asymmetric deformation of methyl and methylene
$^{\text{Ar}}\text{C}=\text{C}$	Aromatic C=C
$^{\text{C}}\text{C}=\text{O}$	Conjugate C=O
$^{\text{A-Ali}}\text{CH}_2$	Asymmetric aliphatic methylene
$^{\text{A-Ali}}\text{CH}_3$	Asymmetric aliphatic methyl
$^{\text{Alc}}\text{OH}$	Alcoholic hydroxyl
$^{\text{I}}\text{O}$	Inorganic oxygen
$^{\text{A}}\text{O}$	Adsorbed oxygen
$^{\text{PD}}\text{N}$	Pyridine nitrogen
$^{\text{PO}}\text{N}$	Pyrrole nitrogen
$^{\text{Q}}\text{N}$	Quaternary nitrogen
$^{\text{O}}\text{N}$	Nitrogen oxides
$^{\text{A}}\text{S}$	Alkyl sulfide
$^{\text{T}}\text{S}$	Thiophene sulfide
$^{\text{S}}\text{S}$	Sulfoxide sulfide
M_r	Relative molecular mass (-)
N	Average number of aromatic rings (-)
δ	Relative error (%)
σ	Standard error (%)
BDE	Bond dissociation energy (kcal/mol)

Abbreviations

^{13}C -NMR	^{13}C nuclear magnetic resonance spectroscopy
FTIR	Fourier transform infrared spectroscopy
XPS	X-ray photoelectron spectroscopy
MD	Molecular dynamics
DFT	Density functional theory
ReaxFF	Reactive force field
IC-R	Raw coals of the imported coking coal
NC-R	Raw coals of the native gas coal
IC-I	Inertinite enrichments from imported coking coal
NC-I	Inertinite enrichments from native gas coal
IC-V	Vitrinite enrichments from imported coking coal
NC-V	Vitrinite enrichments from native gas coal
ad	Air dry basis
t	Total
I	Inertinite
V	Vitrinite
L	Liptinite

M	Mineral
CP-MAS	Cross-polarization magic angle spinning
2D	Two-dimensional
3D	Three-dimensional
XRD	X-ray diffraction

Abstract

应该采用一两句话从煤结构认识，应该谈到或给出 很少被开展的煤岩微观结构认识 的重要性。

Revealing the intrinsic properties of coals at the micro-level holds significance in sustainable coal chemical production.

概括性给出主要的研究方法及全部的研究内容。

This study compares the molecular structure characteristics and bond-breaking response discrepancies of macerals from coking coal and gas coal through multiple structural characterizations and molecular dynamics calculations.

The results indicate that although vitrinite has stronger thermal reactivity than inertinite due to its higher aliphatic content, macerals of coking coal with higher metaplastic quality and gas coal with more pyrolysis gas have the maximum values in *P* (generation potential of hydrocarbons) and *DOB* (degree of branching of aliphatic side-chains) index, respectively. After obtaining the structural parameters, the molecular formulas ($C_{212}H_{127}O_{13}N_3$, $C_{191}H_{139}O_{10}N_3$, $C_{172}H_{113}O_{19}N_3$, and $C_{134}H_{103}O_{12}N_3$) of vitrinite and inertinite from two coals have been derived by prioritizing heteroatom configuration and controlling aromaticity. Meanwhile, the ratio of the longest bonds is approximately 2-5 times higher in vitrinite, and the C/H-O bonds are broken later or more dispersed during pyrolysis compared to inertinite. Furthermore, the thermal response of heteroatom bonds in macerals from gas coal is almost twice that of coking coal, both vitrinite and inertinite of coking coal have N-H cleavage to produce active hydrogen in the late stage of bond dissociation, while gas coal lacks this feature.

最后应该有一句话概括出本研究的价值，即 对精准高效利用煤资源以及针对煤炭清洁利用技术等方面的意义或价值。

Keywords: Coal macerals; Chemical structure; Molecular modelling; Molecular dynamics; Pyrolysis behavior

1. Introduction

Despite the fossil fuel-dominated energy market contributing to the broader integration of coal resources and chemicals [1], global decarbonization policies put forward a challenge to the sustainability of related products [2]. Exercising precise control over the composition of coal undeniably proves effective in enhancing its utilization [3], contributing momentarily to the coal industry to address issues of resource wastage and empirical operations [4]. However, attaining this level of control requires a deeper understanding of the individual physicochemical properties of coal-based feedstocks.

Fortunately, the successful separation of vitrinite and inertinite has facilitated research into the classification and utilization of coal in low-temperature pyrolysis reactions, which is the theoretical basis of the coal chemical process [5]. Extensive efforts have been made to essentially confirm that vitrinite has thermotropic activity in coal gasification and liquefaction through the behavior of volatile organic compounds generation during pyrolysis [6][7]. For another valuable process, cokemaking [8], it is also found that vitrinite is more advantageous than inertinite in terms of swelling and mobility by dilatometer and rheometer [9][10]. While relationships between coal compositions and their characteristics are being established, the above methods fall short of elucidating the micro-discrepancies between different coals and their macerals. For instance, the thermally active vitrinite from coking coal exhibits a maximum expansion capacity 7 times greater than that of gas coal [11]. Consequently, growing interest has been focused on the chemical structure of macerals in anticipation of revealing the source of the intrinsic properties in raw coals.

With the assistance of ^{13}C nuclear magnetic resonance (^{13}C -NMR) spectroscopy [12], Fourier transform infrared (FTIR) spectroscopy [13], and X-ray photoelectron spectroscopy (XPS) [14], coal and its macerals have been fundamentally recognized as composed of aromatic carbons complemented by aliphatic carbons and heteroatomic functional groups [15][16]. It is noteworthy that vitrinite has more aliphatic structures than inertinite and its content decreases as the coal matures

[17], which seems to make it possible to evaluate the activity indicators of coals including thermal adhesion [18], gas generation [19], and hydrocarbon production by determining the content of carbon structures [20]. Nevertheless, since the coal-based molecules also contain heteroatoms that have a strong impact on the pyrolysis reactions [21][22], it is hardly convincing to predict the reaction behavior from this single perspective. To further access the chemical mechanisms in the reaction stage, a comprehensive insight into the molecular reactivity of macerals is indispensable.

Nowadays, molecular dynamics (MD) and density functional theory (DFT) calculations are regarded as effective ways to capture the microscopic physicochemical properties of coal [23][24], revealing mechanisms that are not limited to catalytic pyrolysis [25], surface modification [26], and off-gas sequestration [27]. Remarkably, the reasonableness of molecular models for coal feedstocks should be thoroughly considered before employing calculation tools [28]. However, innumerable computational physicochemical studies still rely on decades-old coal molecular models for relevant property analyses [29][30][31]. As the diversity of coal structures increases with the growth of coal types and the decline of their qualities [32], a substantial deviation between calculated and actual results becomes inevitable [33]. Crucially, there is a scarcity of molecular models for coal macerals [17], and structures that align with experimental results must be developed for efficient calculations under the microscale [34].

Simultaneously, the present calculations on thermal properties with the carbon-based molecular are mainly implemented in the reactive force field (ReaxFF) [35], a popular methodology that is suitable for statistical analysis of structural fragments. Numerous researchers have analyzed the production features of pyrolysis gas and tar to deduce the cracking reaction behavior of coal [36][37]. Nevertheless, a disadvantage is that the simulated temperatures for calculations differ significantly from the actual reaction temperatures and the representation of the performance differences is still at the product level [28][38][39]. Although the reorganization of broken chemical bonds is potentially important in influencing the pyrolysis reaction paths [40], the differences in the transformation of

various bond types have scarcely been systematically explored, even less to establish their connection with the specific attributes of raw coals. Accordingly, based on obtaining the molecular structure of coal macerals, probing their microscopic properties with the help of a low-cost ordinary force field at settable temperature can be regarded as a convenient and effective way to access their pyrolysis mechanism.

This study aimed to elucidate the reasons for the differences in low-temperature pyrolytic reactivity of coals by gaining a comprehensive understanding of the structuring differences between vitrinite and inertinite from various coal grades, and by obtaining the chemical-thermal reactive bonding mechanisms of macerals at the molecular level. The chemical structures of vitrinite and inertinite were initially characterized using the elemental analyzer, ^{13}C -NMR, FTIR, and XPS. Moreover, the molecular structure was refined by ChemDraw and MestReNova software depending on the semi-quantitative results. Eventually, the molecules were further optimized and subjected to molecular dynamics calculations via Materials Studio software to reveal the bond-change response behavior of coals before and after heating.

2. Materials and methods

2.1 Materials

Raw materials of the imported coking coal (IC-R) and native gas coal (NC-R) were subjected to purify the inertinite (IC-I, NC-I) and vitrinite (IC-V, NC-V) enrichments. The fundamental properties of all samples are displayed in **Table 1** [41]. It should be noted that there is a substantial increase in the purity of both vitrinite and inertinite in the enrichments of the two different coal-rank feedstocks, all samples are conspicuously different in a range of physicochemical properties, which have been verified in our previous studies [11][41].

Table 1. Analysis of fundamental properties of coal and its maceral enrichment.

Coal sample	Proximate analysis (%)				Ultimate analysis (%)					Petrographic analysis (%)			
	A_{ad}	M_{ad}	V_{ad}	FC_{ad}	C_{ad}	H_{ad}	O_{ad}	N_{ad}	$S_{t, ad}$	I	V	L	M
IC-R	7.87	1.62	19.29	71.22	81.11	4.93	2.55	1.50	0.42	21.39	67.89	3.82	6.90

IC-I	8.23	1.23	15.46	75.08	79.83	3.79	5.28	1.17	0.47	64.62	26.24	2.02	7.12
IC-V	5.52	1.76	23.68	69.04	81.27	4.56	4.95	1.48	0.46	16.86	76.82	4.29	2.03
NC-R	7.78	1.31	39.56	51.35	77.10	5.17	6.46	1.70	0.48	22.01	69.45	2.50	6.04
NC-I	8.47	1.12	21.16	69.25	74.85	3.93	9.78	1.29	0.56	72.00	19.04	2.74	6.22
NC-V	5.45	2.04	33.87	58.64	78.66	4.46	7.33	1.51	0.55	8.02	82.76	5.05	4.17

A: ash; M: moisture; V: volatile; FC: fixed carbon; ad: air dry basis; t: total; I: inertinite; V: vitrinite; L: liptinite; M: mineral

2.2 Structural parameter determination

2.2.1 Solid-state Carbon-13 nuclear magnetic resonance (¹³C-NMR) spectroscopy analysis

The solid-state ¹³C-NMR spectrometer (Bruker-600M, Switzerland) was used for the identification of carbon skeleton in all feedstocks. The determination was performed using 200 mg of sample ground to less than 0.075 mm in an agate mortar, in cross-polarization magic angle spinning (CP-MAS) mode [42], with a rotation speed of 5 kHz, a contact time of 2 ms and a recycle delay time of 3 s [43]. PeakFit software (SeaSolve, America) was availed to fit the spectra to the split peaks, and then the individual carbon-related characteristic structure indexes were analysed semi-quantitatively by the correlation parameters, which were calculated as shown in **Eq. (1)-(13)** [12][34].

$$f_{\alpha} = \frac{A_{100-220}^*}{A_{0-220}^*} \quad (1)$$

$$f_{\alpha}^C = \frac{A_{165-220}^*}{A_{0-220}^*} \quad (2)$$

$$f_{\alpha}^H = \frac{A_{100-129}^*}{A_{0-220}^*} \quad (3)$$

$$f_{\alpha}^P = \frac{A_{148-165}^*}{A_{0-220}^*} \quad (4)$$

$$f_{\alpha}^S = \frac{A_{137-148}^*}{A_{0-220}^*} \quad (5)$$

$$f_{\alpha}^B = \frac{A_{129-137}^*}{A_{0-220}^*} \quad (6)$$

$$f_{\alpha}^N = f_{\alpha}^P + f_{\alpha}^S + f_{\alpha}^B \quad (7)$$

$$f'_{\alpha} = f_{\alpha}^H + f_{\alpha}^N \quad (8)$$

$$f_{al}^* = \frac{A_{0-22}^*}{A_{0-220}^*} \quad (9)$$

$$f_{al}^H = \frac{A_{22-50}^*}{A_{0-220}^*} \quad (10)$$

$$f_{al}^O = \frac{A_{50-90}^*}{A_{0-220}^*} \quad (11)$$

$$f_{al} = f_{al}^* + f_{al}^H + f_{al}^O \quad (12)$$

$$X_{BP} = \frac{f_{\alpha}^B}{f_{\alpha}^H + f_{\alpha}^P + f_{\alpha}^S} \quad (13)$$

where, f_{α} is the percentage of total sp^2 hybridized carbon (%); f_{α}^C is the percentage of aromatic carbon linked to carbonyl or carboxyl groups (%); f_{α}^H is the percentage of protonated aromatic carbon (%); f_{α}^P is the percentage of aromatic carbon linked to oxygen atoms (%); f_{α}^S is the percentage of alkylated aromatic carbon (%); f_{α}^B is the percentage of aromatic bridgehead carbon (%); f_{α}^N is the percentage of non-protonated aromatic carbon (%); f_{α}' is the percentage of total aromatic carbon (%); f_{al}^* is the percentage of methyl carbon in aliphatic hydrocarbons (%); f_{al}^H is the percentage of methylene, quaternary, or hypomethyl carbon (%); f_{al}^O is the percentage of aliphatic carbon attached to the oxygen atom (%); f_{al} is the percentage of total sp^3 hybridized carbon (%); X_{BP} is the ratio of bridge carbon to peripheral carbon (-); A^* is the area of the peak in the corresponding range of chemical shift (-).

2.2.2 Fourier transform infrared (FTIR) spectroscopy analysis

The FTIR spectrometer (Nicolet™ iS50, America) was applied to analyze the types of functional groups. Each sample was blended well with KBr at a mass ratio of 1:100 in an agate mortar [38], and the mixed powder was held in a special mold at a pressure of 20 MPa for 1 min. The wavenumber range of 400-4000 $1/cm$ was scanned 32 times with a resolution of 4 $1/cm$ to obtain the FTIR spectra [44]. The peak-differentiation-imitating was carried out in PeakFit software, and the specific structural indexes were calculated by **Eq. (14)-(18)** [13][38][42][44].

$$DOA = \frac{A_{700-900}^*}{A_{2800-3000}^*} \quad (14)$$

$$DOB = \frac{A_{2915-2940}^*}{A_{2950-2975}^*} \quad (15)$$

$$DOC = \frac{A_{700-900}^*}{A_{1600}^*} \quad (16)$$

$$C = \frac{A_{1650-1800}^*}{A_{1650-1800}^* + A_{1600}^*} \quad (17)$$

$$P = \frac{A_{2800-3000}^*}{A_{2800-3000}^* + A_{1600}^*} \quad (18)$$

where, *DOA* is the degree of aromatization (-); *DOB* is the degree of branching of aliphatic side-chains (-); *DOC* is the degree of condensation (-); *C* is the maturation of coal (-); *P* is the generation potential of hydrocarbons (-); *A** is the area of the peak in the corresponding range of wavenumber (-).

2.2.3 X-ray photoelectron spectroscopy (XPS) analysis

The XPS instrumentation (Escalab™ 250Xi, America) was employed for evaluating the presence of heteroatoms O, N, S, and the major element C in all samples. The conventional Al *Kα* (*hν*=1486.6 eV) monochromator was operated for the analysis at 200 W [45]. The binding energy position was calibrated in Advantage software (Thermo Scientific, America) with the C1s peak (284.8 eV) and then split-peak fitting was executed using Peakfit software.

2.3 Molecular construction and optimization

2.3.1 Establishment of two-dimensional (2D) molecular models

The chemical fragments of different coal-based feedstocks can be available at the obtained structural parameters, and the entire configuration can be assembled by ChemDraw software (PerkinElmer, America) [46]. Thereafter, MestReNova software (Mestrelab Research, Spain) was implemented to forecast the ¹³C-NMR spectra of the constructed molecular models [47]. By comparing it with the measured spectra, the process was repeated until the calculated data were in good agreement with the experimental results to obtain the 2D molecular models.

2.3.2 Energy minimization of three-dimensional (3D) molecular models

The Forcite module within Materials Studio software (Accelrys, America) was harnessed to spatialize the 2D structure of coal macerals. Geometry optimization, as the initial step of effective evaluation, was set to fine quality. Parameters such as energy, force, and max iteration were individually defined as 0.001 kcal/mol, 0.5 kcal/(mol·Å), and 50000, respectively [48]. Dreiding forcefield and QEq charges were invoked to execute these computations under atom-based conditions accounting for both electrostatic and van der Waals interactions [39].

The minimum potential energy conformations for maceral molecules were ascertained via Anneal workflow [49], which involved specifying 10 annealing cycles, an initial temperature of 300 K, a mid-cycle temperature of 600 K, 5 heating ramps per cycle, and 10000 dynamic steps per ramp [40]. The NVT ensemble was coupled with random initial velocities and Nose thermostat [43]. All other parameters were consistent with the regime stipulated for preliminary geometry optimization.

2.4 Molecular dynamics (MD) simulation

The Forcite module was employed to execute the Dynamics task on the lowest energy configuration of individual macerals, thereby capturing the movement of chemical bonds in each sample just prior to undergoing a reaction. Since the present research was on bituminous coals utilized in coking, the kinetic temperature was set to 600 K to reveal the differences in the thermal reaction behavior of different coals and their macerals, based on the softening onset temperature of the coal near this temperature [11]. All remaining computational conditions were the same as the operating rules used during Anneal.

3. Results and discussion

3.1 Chemical structure variations of coal macerals

Carbon is the basic molecular skeleton of coal and is given preferential treatment in this section. The ¹³C-NMR carbon spectra of all samples and their peak-differentiation-imitating are exhibited in **Fig. 1**. Corresponding chemical shift intervals of aliphatic, aromatic, and carbonyl carbons are

distinguishable [17][39], approximately in 0-90 ppm, 90-160 ppm, and 160-240 ppm.

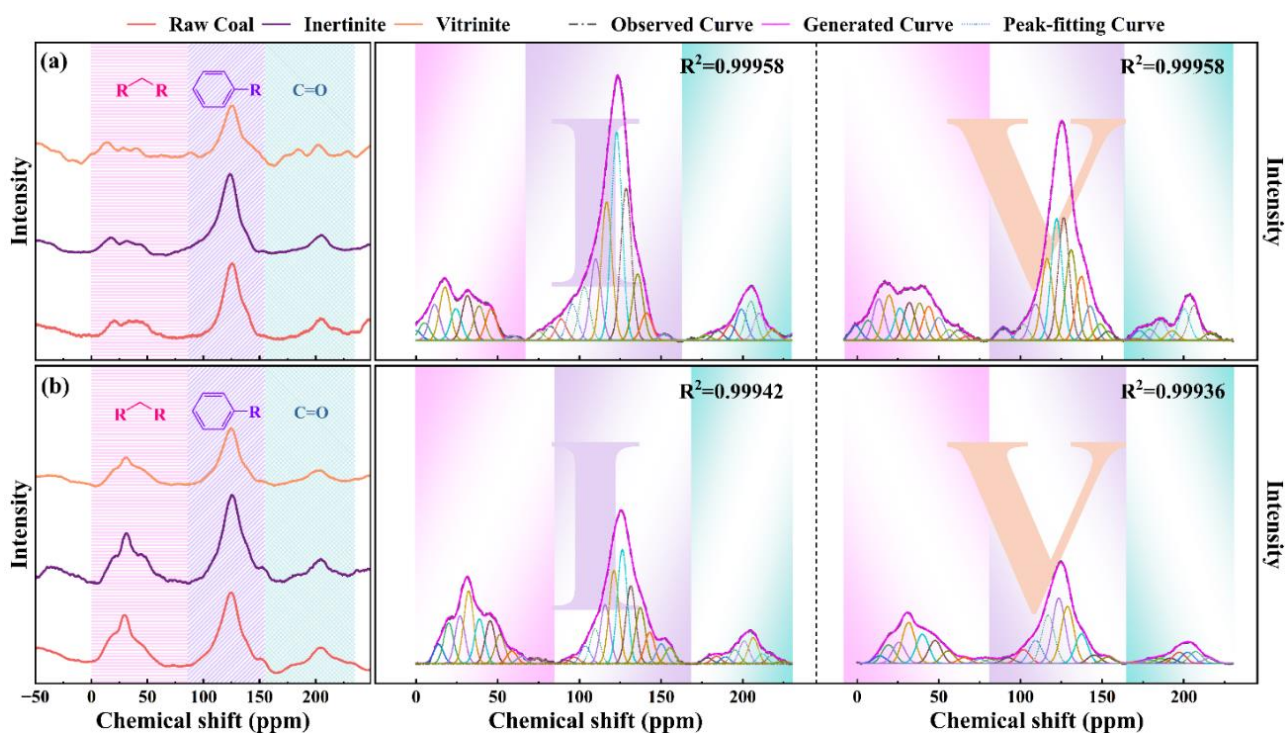


Fig. 1. Analysis of ^{13}C -NMR spectra and peak fitting results of different macerals: (a) IC; (b) NC.

Upon integrating the distinctive structural peak assignments and semi-quantitative analysis findings outlined in **Table 2**, it becomes evident that the aromatic carbon distribution stands out prominently, boasting the largest peak area within the three specified regions. Notably, the peak intensity of macerals within the aromatic carbon region is consistently higher in IC compared to NC, irrespective of maceral species. Additionally, inertinite exhibits a stronger aromatic carbon peak than vitrinite, a characteristic unrelated to the coal types.

Table 2. Carbon type assignment and area percentage for each coal-based sample.

Type	Assignment	IC-I		IC-V		NC-I		NC-V	
		Chemical Shift (ppm)	Area percent (%)	Chemical Shift (ppm)	Area percent (%)	Chemical Shift (ppm)	Area percent (%)	Chemical Shift (ppm)	Area percent (%)
Aliphatic	AliCH_3	0.07		-0.84					
		5.10	5.11	6.72	7.31	13.84	2.03	13.83	1.57
		11.35		13.28					
	ArCH_3	17.75	4.37	19.64	4.32	20.00	4.26	19.31	3.88

	CH ₂	24.39 31.54	6.28	26.30 32.03	6.70	26.94 32.25	12.61	25.61 31.59	12.91
	CH	38.74	2.82	38.34	3.56	38.83	4.68	40.04	6.06
	^Q C	46.07	2.61	43.83 50.04	5.44	45.42	4.49	47.80	4.78
	^O CH ₃	58.57	0.39	56.35	1.01	51.43 58.73	4.38	55.74	2.62
	^O -AliC	75.07 82.27 88.87	3.62	61.86 67.89 89.56	2.65	64.45 74.31	1.34	65.66 75.29 82.59	3.09
Aromatic						91.91 96.93 103.71		92.50 101.85	
	^P -ArC	95.73 103.07 109.98 116.71 122.85	42.44	101.51 109.25 116.33 122.19 126.52	36.31	109.61 115.78 121.21 126.31	34.43	109.28 116.94 123.51	32.46
	^{Bri} -ArC	128.59 135.69	17.92	131.04 137.36	14.84	131.49 137.34	14.02	128.85	11.82
	^{Bra} -ArC	141.12	2.25	142.72 148.83	4.87	143.09	3.28	137.47 145.16	7.94
	^O -ArC	152.26	0.48	153.64	0.86	150.21 155.49	3.74	153.80	1.39
	^{Cx} C	177.32 184.82	1.23	169.46 172.88 179.18 186.02	4.11	178.62 183.92 189.31	2.08	171.39 178.95 185.79	2.11
	^{Cn} C	192.44 199.18 204.96 210.06 218.40 229.97	10.50	192.91 200.26 206.30 216.16	8.02	195.24 200.92 206.44 212.05 217.88 224.23	8.66	191.75 197.22 202.32 207.26 215.62	9.37

^{Ali}CH₃: Aliphatic methyl; ^{Ar}CH₃: Aromatic methyl; CH₂: Methylene; CH: Methyne; ^QC: quaternary carbon; ^OCH₃: Methoxy; ^O-AliC: Oxy-Aliphatic carbons; ^P-ArC: Protonated aromatic carbon; ^{Bri}-ArC: Bridgehead aromatic carbon; ^{Bra}-ArC: Branched aromatic carbon; ^O-ArC: Oxy-Aromatic Carbons; ^{Cx}C: Carboxyl carbon; ^{Cn}C: Carbonyl carbon.

As presented in **Table 3**, calculations of structural parameters focused on aromatic and aliphatic carbon, which are the predominant carbon forms in coal. It is concluded from the data that the f_{al} value representing the content of aliphatic structure in all samples follows the pattern of NC-V > NC-I > IC-V > IC-I, which is just the opposite of the f'_a values representing the aromatic content. Furthermore, the deviation in the two carbon structural contents of NC-I and NC-V from gas coal is

much narrower than those of IC-I and IC-V from coking coal. Therefore, inertinite and vitrinite are typically abundant in aromatic and aliphatic structures, and the difference in carbon structure magnitude between two macerals from the same raw coal also increases as the coal rank grows.

Table 3. ^{13}C -NMR featured parameters of each coal-based sample.

Sample	$f_{\alpha}(\%)$	$f_{\alpha}^{\text{C}}(\%)$	$f_{\alpha}^{\text{H}}(\%)$	$f_{\alpha}^{\text{P}}(\%)$	$f_{\alpha}^{\text{S}}(\%)$	$f_{\alpha}^{\text{B}}(\%)$	$f_{\alpha}^{\text{N}}(\%)$	$f_{\alpha}'(\%)$	$f_{\alpha\text{I}}^*(\%)$	$f_{\alpha\text{I}}^{\text{H}}(\%)$	$f_{\alpha\text{I}}^{\text{O}}(\%)$	$f_{\alpha\text{I}}(\%)$	$X_{\text{BP}}(-)$
IC-I	74.80	11.73	42.44	0.48	2.25	17.92	20.64	63.08	9.48	11.71	4.01	25.20	0.3968
IC-V	69.01	12.13	36.31	0.86	4.87	14.84	20.57	56.88	11.63	15.70	3.67	30.99	0.3529
NC-I	66.21	10.74	34.43	3.74	3.28	14.02	21.04	55.47	6.29	21.78	5.72	33.79	0.3382
NC-V	65.09	11.48	32.46	1.40	7.94	11.82	21.15	53.61	5.45	23.74	5.71	34.91	0.2828

Moreover, the X_{BP} values indicated the degree of development and maturity of coal aromatic units as IC-I> IC-V> NC-I> NC-V. This suggests that the aromatic units of inertinite are larger than those of vitrinite, and the maturity of macerals from IC is consistently stronger than that from NC. Noticeably, we have derived the average number of stacked aromatic layers of the target samples by X-ray diffraction (XRD) technique in the preceding work [41]. The maturity order of each sample determined in this manner was IC-I> NC-I> IC-V> NC-V, which is a certain discrepancy with the effects in this work. Combining the two results can indicate the unlikeness of the carbon structure between IC-V and NC-I is tiny. Nonetheless, we do not believe the exact parameters obtained by the two measures are equivalent: the results from XRD chiefly consider the dimensional information during the stacking process of 3D layers, while those from ^{13}C -NMR mainly prevail over the breadth and spreading degree of the carbon skeleton. Accordingly, determining the coal macerals aromatization is only reasonable by synthesizing the assorted characterization results.

Probing the nature differences of functional groups endowed in various macerals is instructive for analyzing their thermal reactivity degree. As shown in **Fig. 2**, four main infrared bands displaying miscellaneous structural types have been identified, including the aromatic absorption band of 700-

900 1/cm, oxygenated functional group absorption band of 1000-1800 1/cm, aliphatic absorption band of 2800-3000 1/cm, and hydroxyl absorption band of 3000-3600 1/cm, through FTIR profiles [43][44]. It is particularly from **Fig. 2** that the wavenumber reflecting information about oxygen-containing functional groups has the widest range.

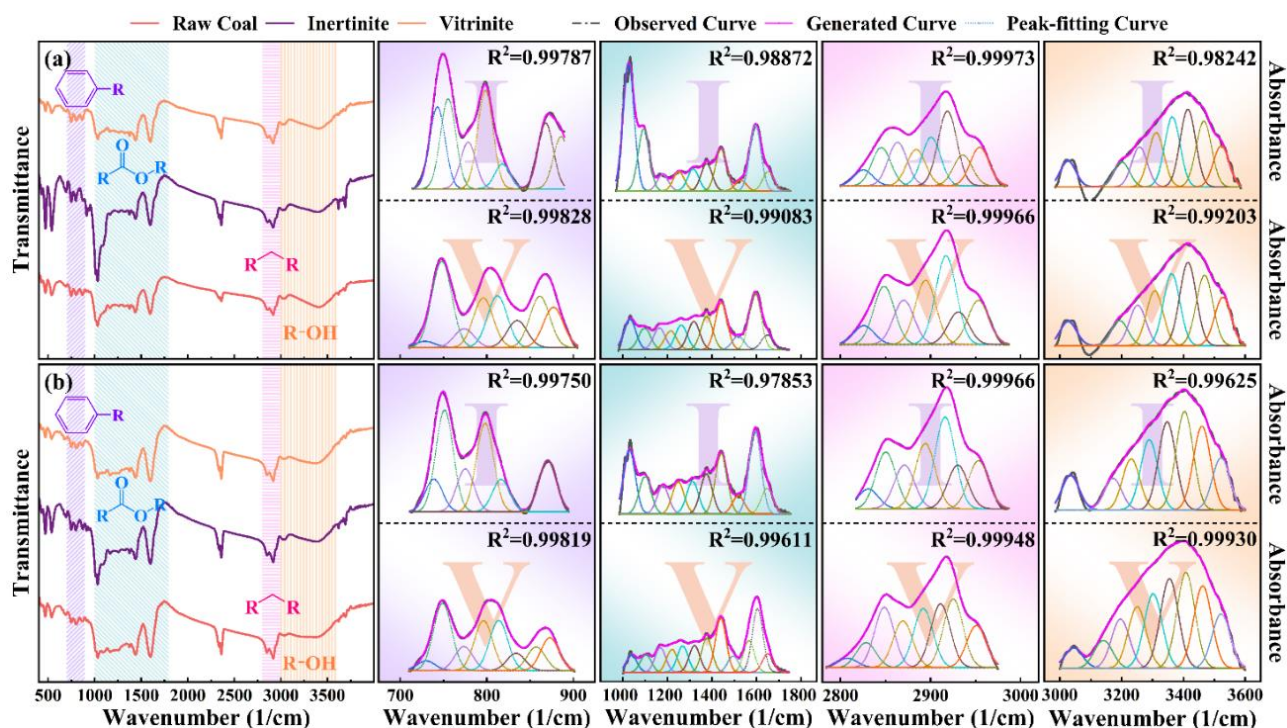


Fig. 2. Analysis of FTIR spectra and peak fitting results of different macerals: (a) IC; (b) NC.

Table 4 presents quantitative results of the relevant structures, which highlights the presence of numerous oxygen structures in coal. According to the ash content, it in inertinite is higher than that in vitrinite, and macerals from IC had much greater ash content than those from NC. The oxygen-containing functional group absorption bands reveal a pronounced presence of C-O, with a comparatively lower occurrence of C=O. Compared to inertinite, the corresponding content of these two oxygen structures obtained from the experimental data is larger in vitrinite, whereas the gap between the two is only about 1%. The main reason for this result is the ultra-high percentage of ash in inertinite, which significantly interferes with FTIR detection of the coal matrix structure. The

finding serves as a reminder of the deficiencies that need to be circumvented in future related work.

Table 4. Functional group assignment and area percentage for each coal-based sample.

Type	Assignment	IC-I		IC-V		NC-I		NC-V	
		Wave number (1/cm)	Area percent (%)	Wave number (1/cm)	Area percent (%)	Wave number (1/cm)	Area percent (%)	Wave number (1/cm)	Area percent (%)
Aromatic	⁴ H	742.95	2.85	728.69	2.15	738.92	2.36	730.01	1.64
		755.34		747.99		751.18		748.98	
		778.44		773.80		775.21		773.49	
	³ H	798.44	1.61	795.91	2.49	797.95	1.60	796.18	1.91
		818.12		812.26		816.52		813.78	
				835.17				833.88	
	² H	868.02	2.03	861.29	1.77	870.37	0.68	857.10	0.92
		885.90		877.03				872.92	
	Ash	1025.89	22.51	1032.32	6.58	1030.08	10.83	1040.07	3.14
Oxygen functional group	*C-O	1094.11	17.28	1097.61	18.60	1099.93	16.45	1103.48	16.58
		1178.98		1163.84		1179.55		1168.17	
		1251.21		1214.52		1248.49		1220.61	
				1262.13				1267.96	
	^{Ali} CH	1315.46	3.89	1318.47	6.08	1312.35	5.50	1321.45	4.86
	^{Ali} CH ₃	1375.85	4.86	1376.15	7.13	1374.68	6.75	1377.05	6.18
	^A CH ₃ &CH ₂	1440.80	7.45	1441.20	10.14	1441.78	10.22	1439.30	12.73
								1494.41	
	^{Ar} C=C	1528.52	13.55	1517.20	15.06	1518.55	17.15	1565.50	17.27
		1594.53		1593.02		1593.40		1604.42	
	^C C=O	1652.36	3.44	1647.91	3.17	1646.89	4.29	1649.98	3.36
Aliphatic	^{A-Ali} CH ₂	2825.43	2.35	2826.09	2.34	2830.91	1.78	2828.50	2.49
		2845.37		2848.37		2850.31		2848.61	
		2863.36							
	^{A-Ali} CH ₃	2884.03	0.88	2870.22	1.35	2870.99	1.01	2869.22	1.23
		CH		2894.47		2894.18		2891.96	
	^A CH ₂	2918.76	2.54	2917.11	3.69	2916.08	3.14	2911.13	3.48
		2935.77		2930.91		2930.22		2925.19	
	^A CH ₃	2954.51	0.93	2953.02	1.34	2953.13	1.11	2950.87	1.10
	OH-N	3026.71	0.83	3027.45	0.94	3034.79	0.55	3044.80	0.79
Hydroxyl	^{Alc} OH	3199.98	2.07	3193.08	2.54	3172.09	2.62	3140.94	2.99
		3257.71		3251.93		3230.83		3196.35	
								3250.41	
	OH-O	3311.84	3.93	3307.35	4.89	3289.16	5.02	3301.83	8.76
		3363.88		3361.72		3347.29		3354.83	
	OH-OH	3414.43	4.53	3414.90	5.92	3403.67	5.77	3408.20	6.91
		3465.98		3468.39		3460.04		3462.41	
	OH-II	3522.26	1.30	3527.64	1.87	3521.61	1.65	3521.98	2.11

⁴H: Ortho disubstituted aromatic hydrocarbons; ³H: Ortho trisubstituted aromatic hydrocarbons; ²H: Ortho tetrasubstituted aromatic hydrocarbons; *C-O: C-O in phenol, alcohol, ether, phenoxy, and ester; ^{Ali}CH: Aliphatic methyne; ^ACH₃&CH₂: Asymmetric deformation of methyl and methylene; ^{Ar}C=C: Aromatic C=C; ^CC=O: Conjugate C=O; ^{A-Ali}CH₂: Asymmetric aliphatic methylene; ^{A-Ali}CH₃: Asymmetric aliphatic methyl; ^{Alc}OH: Alcoholic hydroxyl.

The FTIR characteristic parameters of coal macerals are shown in **Table 5**. Both *DOA* and *DOC* reflected the aromaticity and condensation degree of the carbon structure have the sequential relationship of IC-I> IC-V> NC-I> NC-V, which is consistent with the developmental pattern of X_{BP} . Furthermore, the maturity index of *C* is in final agreement with the previous XRD observations. There is an interesting result that IC-V and NC-V have the largest *P*-value (characterizing the generation potential of hydrocarbons) and *DOB*-value (characterizing the degree of branching of aliphatic side-chains), respectively. Followed by the fact that both macerals from IC have larger *P*-values than NC, but smaller *DOB*-values than NC. This had to be linked to the findings of previous work: coking coals (IC) have better swelling capacity, while gas coals (NC) have stronger weight loss properties, with IC-V and NC-V having the strongest of the former and latter properties[11]. Considering the current analysis of various structural parameters, it can be shown that vitrinite has more aliphatic and branched-chain structures, explaining the reason for stronger reactivity and product transformation ability. A more significant observation is that the differences in the thermally active vitrinite of diverse coal species can be judged by *P* and *DOB*, where caking is more closely related to the former and gas production capacity is more relevant to the later.

Table 5. FTIR characteristic parameters of each coal-based sample.

Sample	<i>DOA</i> (-)	<i>DOB</i> (-)	<i>DOC</i> (-)	<i>P</i> (-)	<i>C</i> (-)
IC-I	0.8255	2.7406	0.4792	0.3673	0.2027
IC-V	0.6008	2.7490	0.4257	0.4147	0.1737
NC-I	0.5417	2.8215	0.2702	0.3328	0.1999
NC-V	0.4542	3.1509	0.2588	0.3630	0.1629

Determination of the form in which each element exists is advantageous for accurately constructing the molecular structure. As illustrated in **Fig. 3**, the element C and the heteroatoms O, N, and S are detected, and the binding energies of these four elements are generally separated into

280-290 eV, 520-540 eV, 395-405 eV, and 160-170 eV [40]. From the flatness of the experimental curves and the values of the fitting coefficients, the refinement is good for C1s and O1s, N1s and S2p demonstrate slightly less effectiveness in peak splitting because of their low content and resultant low signal-to-noise ratios.

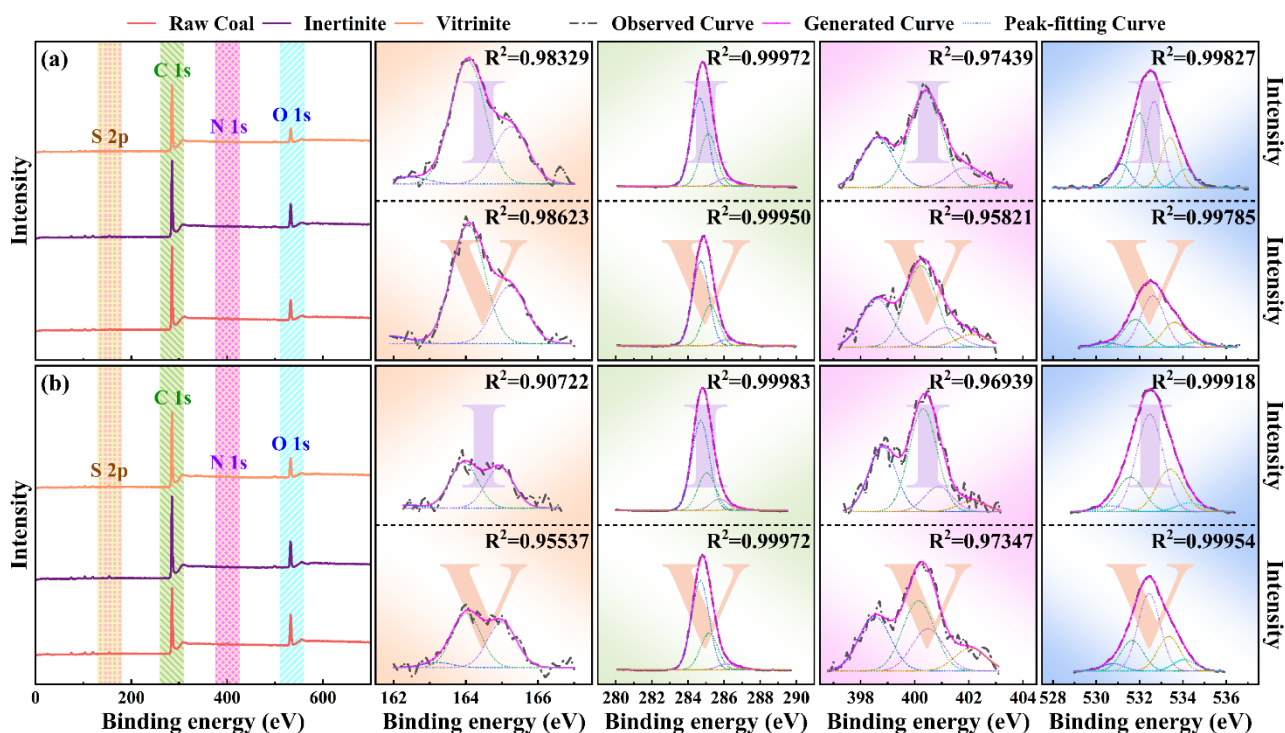


Fig. 3. Analysis of XPS spectra and peak fitting results of different macerals: (a) IC; (b) NC.

Table 6 shows the categorization of elemental states in four macerals. Interestingly, O1s analysis detected adsorbed oxygen in addition to inorganic oxygen which was confirmed partially with the dictation of ash from FTIR, presumably owing to a lack of demineralization of the raw coal before sorting and poor sealing of the storage environment. The C-O structure is the predominant form of O1s in all samples, with more occurrence in NC-I and NC-V. Besides both C=O and COO- structures are more abundant in two inertinites. Low nitrogen presence with the maximum and minimum forms represented by pyrroles and nitrogen oxides. IC group samples exhibit more N1s structural arrangements in vitrinite, and this pattern is also conspicuous in NC group samples, except for pyrrole

and pyridine. The trace form of S2p has three conformations, of which the alkyl group is negligible and the most common sulfur form is thiophene, which is slightly more abundant in vitrinite than inertinite and is centrally enriched in IC group.

Table 6. Element valence assignment and area percentage for each coal-based sample.

Type	Assignment	IC-I		IC-V		NC-I		NC-V	
		Binding energy (eV)	Area percent (%)	Binding energy (eV)	Area percent a (%)	Binding energy (eV)	Area percent (%)	Binding energy (eV)	Area percent (%)
C1s	C-C, C-H	284.65	41.16	284.71	49.19	284.70	44.25	284.69	48.65
	C-O	285.13	24.67	285.24	23.57	285.05	18.61	285.18	20.06
	C=O	286.06	3.69	286.16	3.60	285.75	5.66	286.13	3.15
	COO-	287.08	0.66	287.20	0.43	286.78	1.06	286.90	0.81
O1s	¹ O	531.17	2.65	530.47	0.80	530.84	0.89	530.76	1.17
	C=O	531.99	8.32	531.81	5.26	531.67	5.30	531.66	4.90
	C-O	532.67	9.68	532.61	9.77	532.48	14.90	532.44	12.32
	COO-	533.41	5.60	533.62	4.71	533.31	6.50	533.35	5.51
	^A O	534.11	2.06	534.65	0.92	534.13	1.35	534.07	1.83
N1s	^{PD} N	398.63	0.33	398.59	0.38	398.60	0.41	398.53	0.40
	^P O	400.42	0.63	400.23	0.65	400.29	0.66	400.15	0.51
	^Q N	401.85	0.13	401.11	0.15	400.93	0.16	400.49	0.31
	^O N	402.94	0.03	402.11	0.10	402.33	0.07	402.06	0.17
S2p	^A S	162.46	0.01	161.96	0.02	162.07	0.01	163.22	0.01
	^T S	164.05	0.26	164.06	0.30	163.85	0.09	164.02	0.11
	^S S	165.25	0.12	165.22	0.15	165.01	0.08	164.99	0.09

¹O: Inorganic oxygen; ^AO: Adsorbed oxygen; ^{PD}N: Pyridine nitrogen; ^PO: Pyrrole nitrogen; ^QN: Quaternary nitrogen; ^ON: Nitrogen oxides; ^AS: Alkyl sulfide; ^TS: Thiophene sulfide; ^SS: Sulfoxide sulfide.

3.2 Molecular construction characteristics of coal macerals

Having clarified the dissimilarities in chemical structures among all macerals, the ultimate and rational molecular model is derived by meticulous configuration of their cumulative elements, continuously adjusting the configuration. In the conventional approach to coal-based molecular modelling, it is customary to assume the relative molecular mass (M_r) initially and allocate various atoms and their specific forms in elemental proportions [34][47]. Consequently, if the initial model

is deemed unreasonable, the time-consuming multi-process work may need to be repeated by incrementing or decrementing the relative molecular weight and cycling through the process. To streamline discussions and reduce costs, it is both desirable and necessary to construct the molecule by excluding the trace element sulphur [39]. In such circumstances, once the minimum value of nitrogen (ranked second trace element) is determined, the overall molecular weight and the abundance of other configurations can be precisely controlled by adjusting the element ratio.

Therefore, in conjunction with the specific results obtained in XPS regarding N1s, structures containing two pyridines and one pyrrole are introduced into inertinite and vitrinite. Taking aromatic ring as a breakthrough and six representative architectures (A, B, C, D, E, F) as shown in **Table 7** are selected [34][45]. The number of individual constructs is adjusted by the mathematical relationship of **Eq. (19)-(20)** [50]:

$$\frac{2(N-1)}{6+2(N-1)} = X_{BP} \quad (19)$$

$$\frac{3+A+2B+3C+3D+4E+5F}{3+A+B+C+D+E+F} = N \quad (20)$$

where, N is the average number of aromatic rings (-).

The final configuration of each aromatic ring can also be obtained in **Table 7**. Paramountly, the total of aromatic carbons needs to be scaled up by the f_a value and the aromaticity of the nitrogen ring are to be considered. Meanwhile, the relative molecular mass after nitrogen fixation, the oxygen-containing group is roughly determined according to the ratios of C=O, C-O, and COO- obtained from ultimate analysis and XPS, and the specific distribution after repeated adjustments is shown in **Table 8**.

Table 7. Aromatic carbon configurations and their corresponding quantities.

Aromatic types	Numbers
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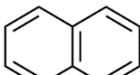
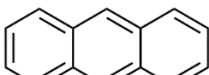
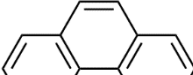
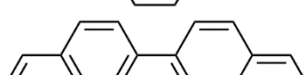
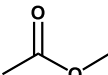
	IC-I	IC-V	NC-I	NC-V
	2	2	2	2
	1	1	1	1
	$A_{IC-I}=1$	$A_{IC-V}=1$	$A_{NC-I}=1$	$A_{NC-V}=1$
	$B_{IC-I}=1$	$B_{IC-V}=2$	$B_{NC-I}=1$	$B_{NC-V}=1$
	$C_{IC-I}=2$	$C_{IC-V}=2$	$C_{NC-I}=3$	$C_{NC-V}=2$
	$D_{IC-I}=1$	$D_{IC-V}=1$	$D_{NC-I}=2$	$D_{NC-V}=2$
	$E_{IC-I}=3$	$E_{IC-V}=3$	$E_{NC-I}=3$	$E_{NC-V}=1$
	$F_{IC-I}=3$	$F_{IC-V}=1$	$F_{NC-I}=0$	$F_{NC-V}=0$

Table 8. Oxygen-containing functional groups configurations and their corresponding quantities.

Aromatic types	Numbers			
	IC-I	IC-V	NC-I	NC-V
	4	3	4	2
	5	5	11	6
	2	1	2	2

Upon completion of the above process, all the budgeted carbon atom remainders are derived from aliphatic carbon, including ring, chain, and bridge carbons. After further complementing them, the actual parameters of each sample are matched with the calculation parameters of the model to the

greatest extent. As shown in **Fig.4**, the molecular optimal solution models of inertinite and vitrinite from IC and NC obtained in this work are as follows: (1) IC-I: $C_{212}H_{127}O_{13}N_3$, $M_r=2921$; (2) IC-V: $C_{191}H_{139}O_{10}N_3$, $M_r=2633$; (3) NC-I: $C_{172}H_{113}O_{19}N_3$, $M_r=2523$; (4) NC-V: $C_{134}H_{103}O_{12}N_3$, $M_r=1945$. The relevant quantitative relationships fundamentally satisfy the conventional view that the molecular weight of bituminous coal is around 2000-3000 [34][45][47]. At the level of coal and maceral types, it is incontrovertible that advanced maturity clusters with more aryl rings are endowed in IC and inertinite, respectively.

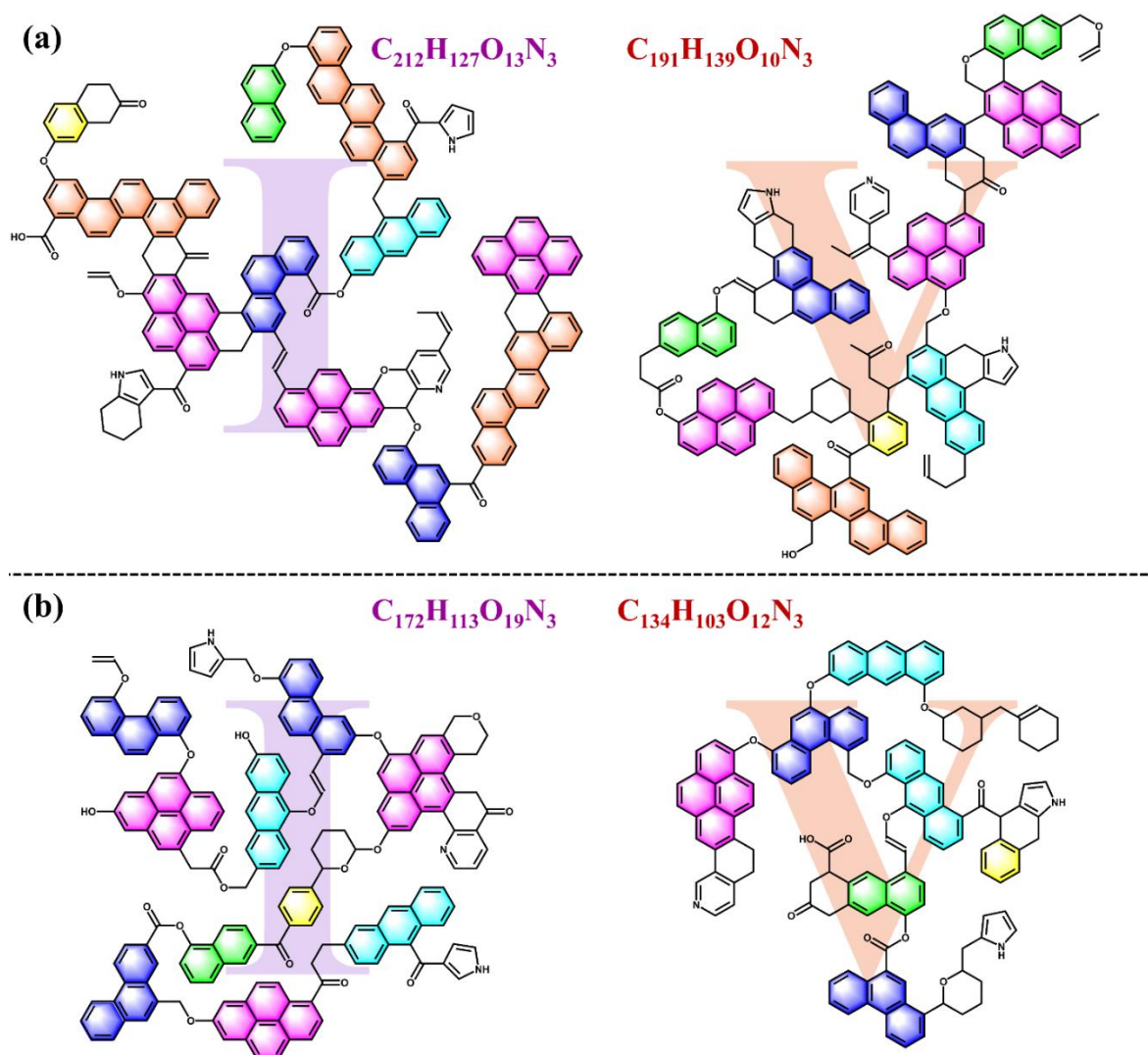


Fig. 4. Plane model of macerals from two kinds of coal: (a) IC; (b) NC.

It is compulsory to confirm the plausibility of the constructed molecular models. Multi-scale

validation outcomes comprising spectral characterization, element, and aromatic parameters are available in **Fig. 5** to illustrate the gap between the actual structure and the calculated molecules. To start with, from the ^{13}C -NMR curves, the carbon skeleton configurations of the four samples are well matched to the real situation, except for the calculated molecules which may have microscopic deletions in the carbonyl region. Secondly, in terms of the primary physicochemical properties, although the element ratios of the constructed molecules are higher than the actual values, especially in the O/C ratio, the difference between the H/C and N/C ratio is below 0.8% in both instances. Finally, with the caveat that the *N*-value overlap is supremely excellent for the individual samples due to the emphasis on their maturity discrepancies at the molecular construction stage. In summary, there is a remarkably high degree of reliability in the molecular modelling of these four coal-based samples constructed.

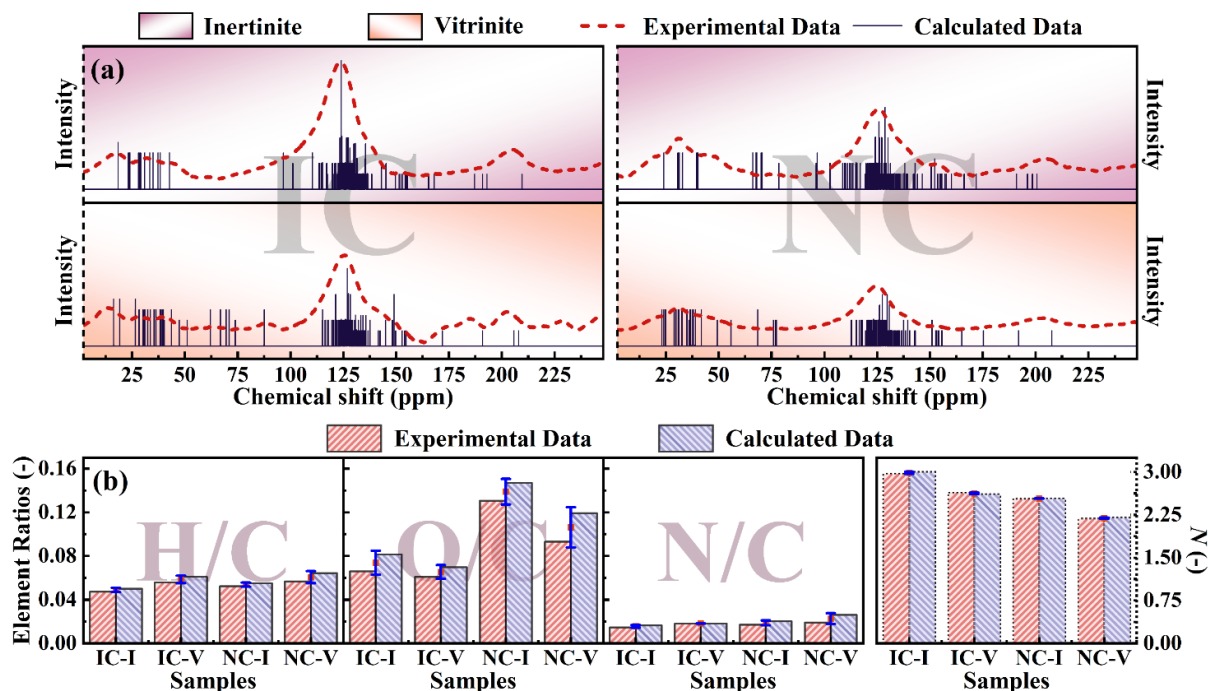


Fig. 5. Comparison of results between each calculated parameter of the constructed molecular model and its corresponding experimental detected parameter: (a) ^{13}C -NMR spectroscopy; (b) element ratio and average number of aromatic rings (*N*).

Moreover, we compared the disparities between a variety of experimental coals and calculated molecules, as shown in **Table 9**. It is evident from the relative error (δ) of the element ratio that none of the constructed molecules can consider all the element contents in line with the actual situation. Studies that use a combination of simulation and experiment often face the challenge of the molecular characteristics of coal being quite different from those of raw coal. For instance, the maximum δ of H/C, O/C, and N/C in these works reach 102.86% [40], -69.46% [37], and 826.81% [37], respectively. In contrast, the molecules we constructed have little difference in element content, with N/C from NC-V having the largest δ -value of 36.01%. The standard error (σ) reveals the fluctuation of the control of each element. Taking Guizhou coal as an example [40], the σ of its nitrogen content is tiny at 3.95%, but its hydrogen element is large at 73.36%. All of our models have σ -values less than 10%, proving that we have a stable operation for element allocation and reducing the occurrence of losing sight of the other. Accordingly, with the existing state of research as a reference, our work is representative.

Table 9. Comparison of elemental ratio errors between coals used for experiments and their molecules used to calculate properties in reported works

Coal sample	References	δ (%)			σ (%)
		H/C	O/C	N/C	
Yongcheng coal	[23]	36.46	8.65	15.81	11.79
Daliuta coal	[30]	62.98	-43.07	-60.34	54.52
Yangquan coal	[31]	7.50	5.92	-22.46	13.76
Shangwan coal	[32]	8.51	-0.06	64.39	28.58
Qinxin coal	[32]	24.90	5.55	27.72	9.85
Yonghong coal	[32]	0.70	5.66	11.32	4.34
Yilan coal	[33]	-0.51	-6.43	-51.93	22.97
Meihuajing coal	[37]	12.67	-69.46	826.81	404.54
Shanxi coal	[40]	102.86	0.37	-38.59	59.66
Chongqing coal	[40]	19.92	0.96	-30.35	20.73
Guizhou coal	[40]	73.36	20.87	3.95	29.55
Gansu coal	[40]	36.48	6.90	-26.83	25.86

IC-I	This work	5.89	23.50	12.60	7.26
IC-V	This work	8.85	14.51	0.58	5.72
NC-I	This work	5.01	12.62	18.02	5.34
NC-V	This work	13.77	28.02	36.01	9.20

δ : Relative error; σ : Standard error

For obtaining more stable maceral stereochemistry molecules and utilizing them for slave calculations, geometry optimization and annealing of them are indispensable. The evolution of the molecular morphology in the three stages is shown in **Fig. 6**. An impressive bond-twisting and layer-curling occurred in the initial molecular structure of each maceral after two consecutive steps. Further calculations revealed that distinct types of energy regulation are the main contributors to the above phenomenon. In **Table 10**, the expansion and contraction of the bond length allows the bending and twisting of the bond and dihedral angle, as reflected in the iterative changes in angle and torsion of valence energy. Alternatively, the total molecular energy of all macerals decreases with the bond of valence energy and van der Waals of non-bond energy diminishing dramatically in the overall process, which leads to a significant enhancement of the molecular stability.

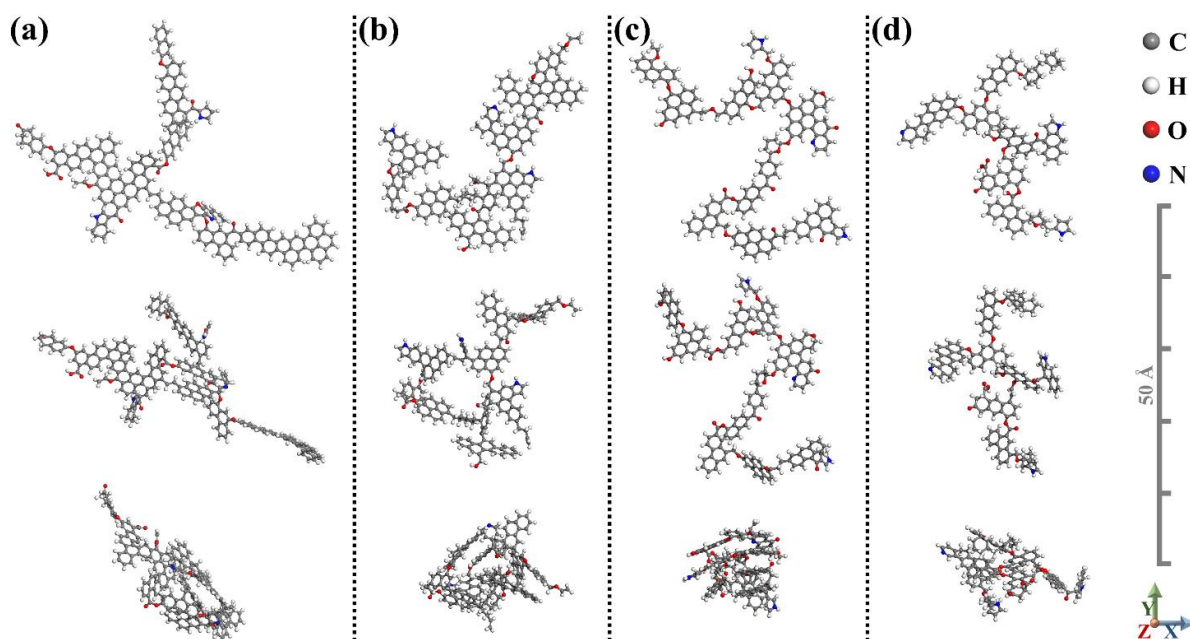


Fig. 6. From top to bottom are the initial, geometrically optimized, and finally annealed 3D

morphologies of all macerals at the same scale: (a) IC-I; (b) IC-V; (c) NC-I; (d) NC-V.

Table 10. Energy distribution of maceral molecules in three states.

Samples	State	Total energy (kcal/mol)	Valence energy (kcal/mol)				Non-bond energy (kcal/mol)		
			Bond	Angle	Torsion	Inversion	Hydrogen bond	van der Waals	Electrostatic
IC-I	Raw	9698.00	3871.50	52.92	143.00	3.87	0.00	5623.98	2.74
	GeomOpt	927.47	107.18	94.71	166.02	3.53	0.00	529.90	26.13
	Anneal	857.96	106.51	95.00	168.23	3.30	0.00	463.93	21.00
IC-V	Raw	10186.49	3151.87	55.93	128.01	4.75	0.00	6880.86	-34.93
	GeomOpt	809.13	100.71	108.44	143.92	4.19	0.00	461.19	-9.31
	Anneal	691.97	99.88	95.07	122.83	1.66	-0.02	386.70	-14.15
NC-I	Raw	5711.90	3173.16	51.28	141.62	2.92	0.00	2392.56	-49.64
	GeomOpt	621.56	74.59	88.16	76.59	0.78	0.00	414.82	-33.39
	Anneal	504.94	72.95	93.27	89.10	1.81	0.00	292.56	-44.75
NC-V	Raw	4575.38	2245.23	43.67	97.95	3.12	0.00	2220.83	-35.41
	GeomOpt	451.73	57.10	71.17	65.15	0.88	0.00	304.94	-47.50
	Anneal	385.07	56.47	77.34	58.66	1.43	-3.95	251.81	-56.70

3.3 Thermal reaction mechanisms of chemical bonds in coal macerals

The establishment of inertinite and vitrinite molecules from different coal ranks signaled the possibility of understanding their reactivity from a more microscopic perspective. It should be specified that the single and double bond types of chemical bonding are not considered in this study. **Fig. 7** shows the top three occupied bond types in all samples are C-C, C-H, and C-O. Each bond type was artificially partitioned into intervals according to their bond length distribution characteristics for discussion. It is generally believed that the longer the bond length, the greater the likelihood of reaction [51]. No matter the longest bond or the shortest bond, their length in NC is always greater than that in IC, which is consistent with the stereotype that the reactivity of gas coal is stronger than that of coking coal. However, this relationship is unsettled among the maceral, and only the longest bond values of vitrinite in C-C bonds were found to be greater than that of the corresponding inertinite.

Further discussion of the interval occupancy for bond lengths revealed potential regularities in reactivity for macerals. Specifically, when considering the percentage of intervals with bond lengths >1.50 Å and >1.10 Å in C-C and C-H types, vitrinite was respectively about 3 and 2 times that of inertinite, which evinces that vitrinite has more highly reactive bonds than inertinite. While the regularity of bond length intervals in C-O was weaker compared to the first two bond types, meaningful results still emerged. Under the condition of intervals >1.40 Å, vitrinite had the largest proportion in IC, whereas inertinite dominated in NC. Synthesizing the results from the previous two bond types, both IC and NC demonstrate a trend of stronger reactivity in the predominant C and H atomic bonds of vitrinite. However, whether the asynchronous pattern of C-O bonds in these two coal types indicates that oxygen plays a leading role in causing differences in the thermal bonding behavior needs further investigation.

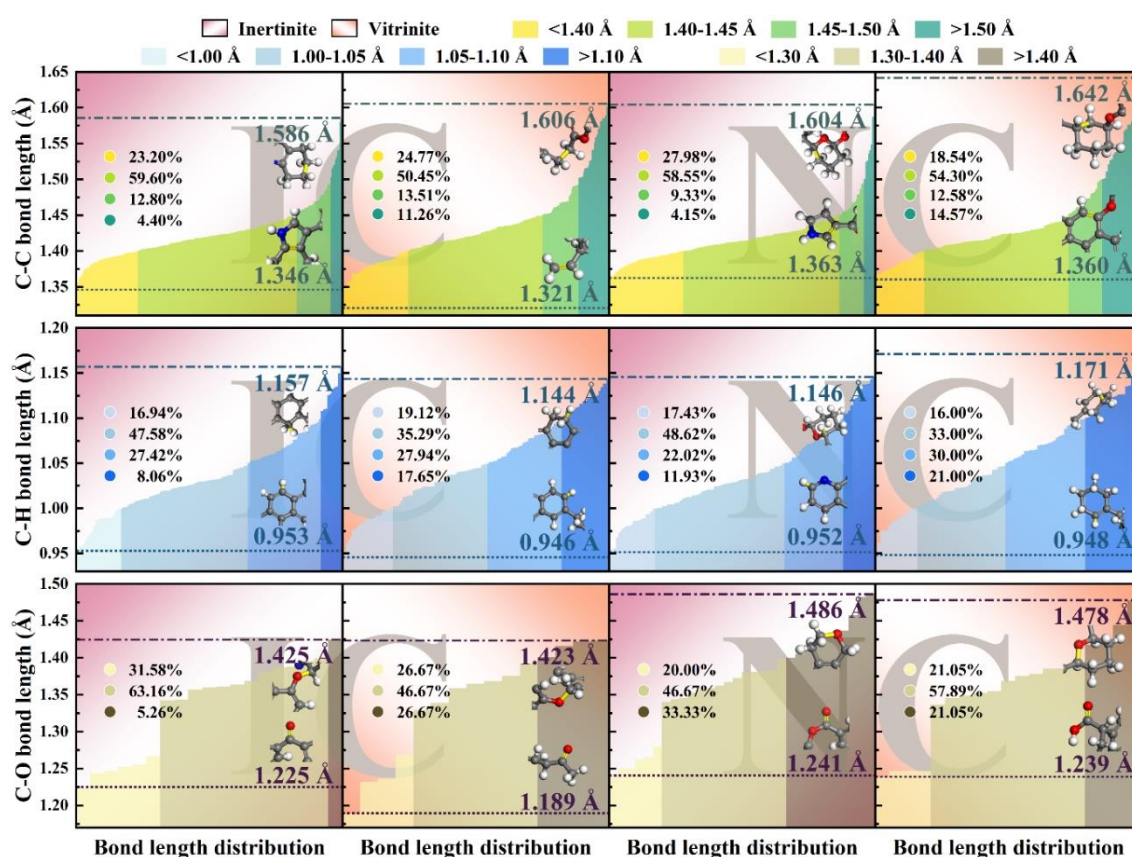


Fig. 7. Variations in the distribution of the C-C, C-H, and C-O bonds in different macerals.

The above bond length analysis of macerals at room temperature showed that vitrinite has a superior propensity to react than inertinite, but the manifestation of activity at elevated temperatures is still to be elucidated. To this end, we have counted the bond strain response of macerals treated with 600 K dynamics compared to the 300 K state, where the degree of variation of the bond length is >1 , as shown in **Fig. 8**. First, the bonds with the most dramatic altered in all macerals had a substantial similarity, except NC-I which were N-H bonds, and in the rest of the samples were C-H bonds. Afterward, in terms of the relative amount of chemical bond alterations, the C-C bonds had the maximum responsive occupancy of all bonds, followed by the C-H bonds, with the remaining C-O, C-N, N-H, and O-H bonds contributing weakly to the reaction.

Simultaneously, compared with vitrinite and inertinite belonging to gas coal of NC, macerals belonging to coking coal of IC had higher ratios of C-C and C-H bond stretching permutation. Nonetheless, the rates of change of all heteroatom-containing bonds were $10.35\pm0.85\%$ and $5.65\pm0.15\%$ in macerals of NC and IC, correspondingly. This nearly doubled data suggests that a considerable quantity of heteroatoms would be participating in the reaction during the softening stage of the gas coal. Noteworthy, C-O bonds were the main source of these reactive heteroatomic bonds, which led to the belief that the largest concentration of oxygen heteroatoms in coal strongly deteriorates the adhesion properties [52]. On the report of this conclusion, interpretations will be attempted to explain the mechanism of the coal bonding weakening by oxygen-containing bonds.

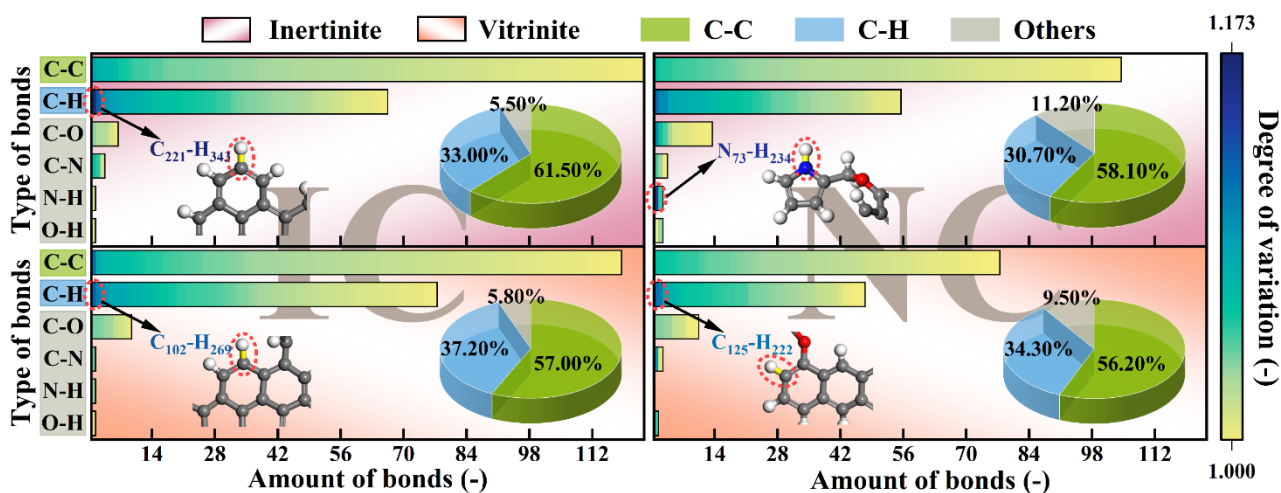


Fig. 8. Variations in the temperature response of each bond type in different macerals and their distribution patterns.

Fig. 9(a) illustrates the bond-breaking patterns observed during pyrolysis across all coal-based samples. Notably, the delocalization of reactive hydrogen attached to a carbocyclic or heterocyclic ring was the predominant process. Subsequently, the rupture of C-C or C-N bonds within the ring initiated depolymerization, forming chain compounds. This process continued, causing further fragmentation of bonds along the carbon chain, ultimately producing small molecules. Finally, in the event of carbonyl or carboxyl double-bond rupture, the heteroatomic oxygen bond underwent breakage. As depicted in **Fig. 9(b)**, from the magnitude of the bond dissociation energy (BDE) of the simple hydrides, the values of BDE_{C-H} and BDE_{N-H} are close [53][54], but both are smaller than BDE_{O-H} [55]. This led to the realization that hydrogen is bound to the carbon and nitrogen atoms to a comparable degree, while it is most deeply bound to oxygen atoms, which explains to some extent why oxygen has a strong ability to seize hydrogen.

Based on the above calculations and their distinctive features, the various types of reactive bonds can be categorized into three groups: (1) C-H and N-H bonds are important sources of free hydrogen atoms, the former of which are more abundant in coal than the latter; (2) C-O and O-H bond breakage

can expose oxygen sites, but the latter can provide hydrogen atoms to some extent; (3) the remaining C-C and C-N bonds. After summarizing the post-reaction characteristics of all bonds, the order of their dissociation in vitrinite and inertinite was determined. As shown in **Fig. 9(b)**, four characteristic routes of the thermal softening reaction were obtained as *Route I* and *Route I'*, which are dominant and auxiliary hydrogen supply for the system after bond breaking. *Route II* and *Route II'*, which are rampant and mild hydrogen robbery.

The order of bond cleavage in IC-I and IC-V exhibited only slight differences in the O-H and N-H reaction sequences. However, the transmogrification of all oxygen-containing bonds was more centralized in IC-I, whereas the continuum reaction of C-O and O-H was interrupted by an auxiliary hydrogen supply from N-H bonds in IC-V. By contrast, the distinctions between NC-I and NC-V were more pronounced. Both N-H and C-H reacted in the pre-bond dissociation stage of NC-I, but only C-H appeared in NC-V. More eye-catching is that the C-O of NC-I was the first to react among the four samples, and the bond reaction pattern of NC-V was extremely similar to that of IC-I, only in the absence of N-H participation in the response. The evolutionary behavior of these four pathways in the dissociation of maceral bonds indicates that the reaction of oxygen-containing bonds in inertinite is more concentrated or forward compared to that in vitrinite. Therefore, it is presumed that a substantial amount of hydrogen in inertinite will be rapidly consumed during the bonding process, particularly in the case of NC-I from the gas coal.

Since the pyrolytic variability of macerals is already specified, it is convenient to explore distinctions in their parent raw coals. It is evident from **Fig. 9(b)** that at the late stage of bond dissociation in both coals, hydrogen complementation provided by *Route I'* is present only in vitrinite and inertinite from IC, whereas this property is absent in macerals from NC. It should not be

negligible that the maceral of NC is not beneficial for the retention of the adherent phase during the pyrolytic caking period, given that NC contains more oxygen than IC. In conclusion, the coal automatically undergoes a three-step reaction during the thermal adhesive stage as illustrated in **Fig. 9(c)**. The poorly caking coal, such as NC, intensifies the skimming of active hydrogen in *Step 2*, ultimately leading to the loss of hydrogen-containing phases from the system.

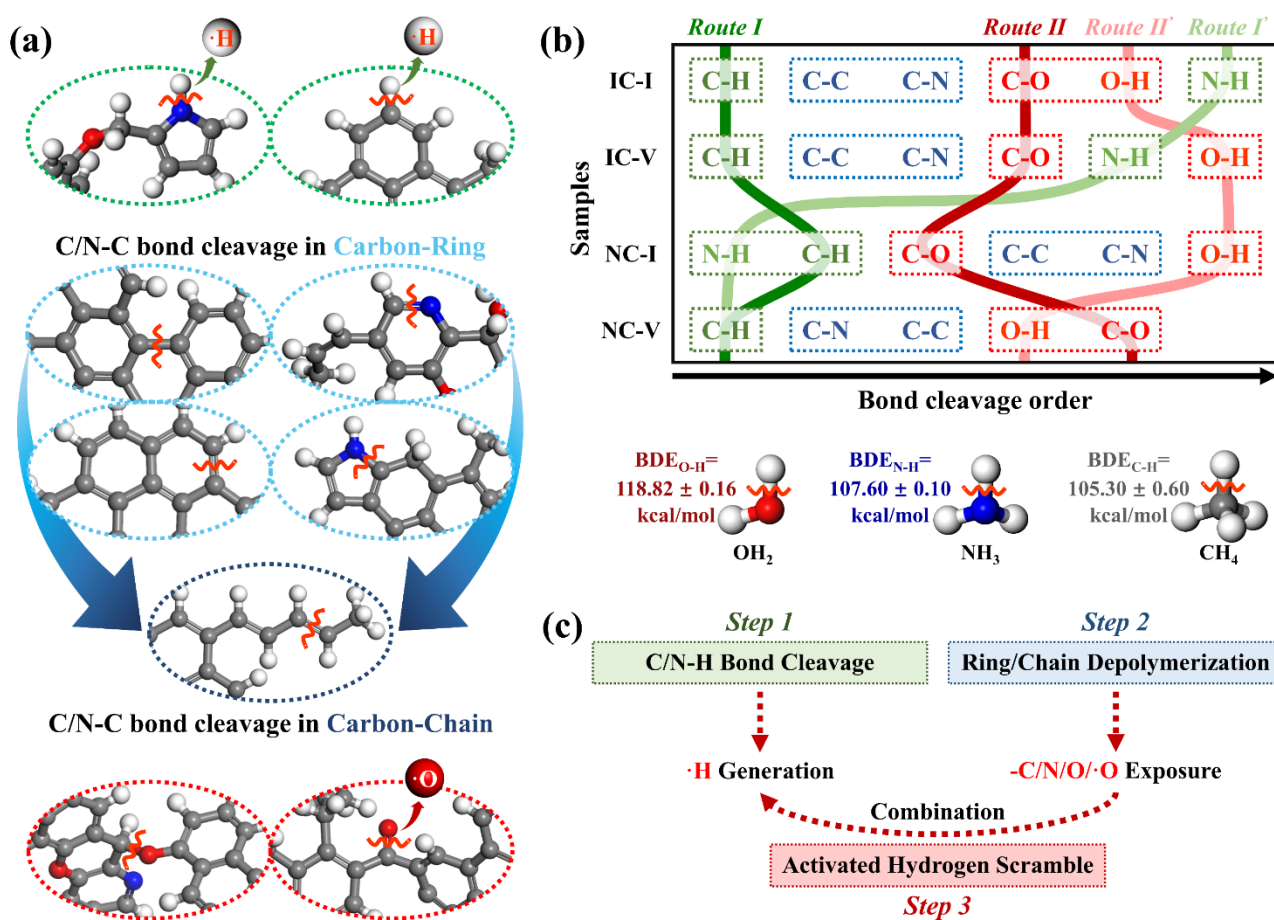


Fig. 9. Molecular reaction mechanisms of macerals during the heating process: (a) exposed forms of atoms; (b) bond cleavage order of different macerals; (c) interatomic bonding steps.

4. Conclusions

This work has effectively constructed the molecular structures of coal macerals based on systematically obtaining their structural properties and revealed the low-temperature pyrolysis properties of bituminous coal by investigating the length of the bonds and their thermal behaviors in

the molecules. The conclusions obtained are as follows:

(1) The greatest structural differences in macerals appear in the carbon skeleton and oxygen-containing functional groups but remain controlled by coal rank. Although inertinite has a higher proportion of aromatic carbon and a lower aliphatic structure than vitrinite, the macerals aromaticity of IC as coking coal is always greater than that of NC as gas coal.

(2) The generation potential of hydrocarbons (P) and degree of branching of aliphatic side-chains (DOB) are biased toward characterizing the pyrolytic soft caking and gas production properties of coal macerals, corresponding well with the results that vitrinite of coking and gas coals each have maxima in P and DOB .

(3) Determination of the trace element structure and the ratio of bridge carbon to peripheral carbon (X_{BP}) in coal maceral contributes to the efficient construction of maceral molecular models. Verification of macerals by spectra, elemental composition, and maturity can further enhance the accuracy and applicability of their constructed models.

(4) Coal undergoes three steps of hydrogen release, oxygen exposure, and oxygen seizure of hydrogen during the thermal bonding stage. Inertinite has more concentrated or preferred reactions for oxygen-containing bonds than vitrinite, coking coal has hydrogen complement in macerals due to the lag in the thermal response of the N-H bonds compared to gas coals.

The relevant ideas and methods of this work are significant for investigating the structural modeling and thermal response mechanisms of various carbon energy sources. However, there are still some limitations that need to be attended to as follows:

(1) The purity of vitrinite and inertinite has room for improvement to reduce the influence of impurity organic components and inorganic minerals on structural detection, thus further improving

the accuracy of the constructed molecular models.

(2) Variations in pyrolysis reactivity of different coals are recognized only from the lengths of chemical bonds and thermal change properties of macerals, and the pyrolysis product generation behaviors of molecules are not examined using other calculation methods.

5. Challenges and future directions

The success of the macerals characterization and calculations has facilitated the recognition of the differences in coal properties, and the subsequent intensive purification of all components and through co-pyrolysis experimental design are expected to further address the great challenge of unclear interactions between different coals and their macerals. Meanwhile, combining structural detection and computational chemistry to mutually verify various other physicochemical properties of the obtained molecules will also be an essential direction for us to achieve more accurate construction and application of coal-based molecules to solve practical problems.

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