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Modes of Occurrence of Chromium and Their Thermal Stability in Low-Rank Coal Pyrolysis

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Abstract: Chromium (Cr) and the emission of its compounds into the environment have caused long-term environmental contamination. In this study, the modes of occurrence of Cr in low-rank coal and their thermal stability in pyrolysis were investigated by sequential chemical extraction (SCE), single-component samples (SCS) pyrolysis, and thermochemical equilibrium simulation. The results showed that organic matter, aluminosilicate, and carbonate were the dominant modes of occurrence of Cr in low-rank coal. The modes of occurrence and chlorine (Cl) content affected the volatilization of Cr in coal. The characteristic release temperature range of Cr bounded to aluminosilicate was >600 °C and 400–600 °C for Cr bounded to a disulfide. Cr bounded to organic matter almost released completely before 600 °C. Cl enhanced the volatility of Cr and reduced its release temperature in Cr bounded to aluminosilicate. The simulation showed the content of gas products was very low, mainly chlorides. While the content of solid products, sulfides, and oxides, was much higher than gas products, showing their high thermal stability. The sulfides and oxides in chars were closely related to the carbonate and aluminosilicate bound form of Cr. The results of the equilibrium simulation were consistent with the experimental results.

Keywords: toxic trace elements; low-rank coal; modes of occurrence; single-component samples pyrolysis; release behavior; thermochemical equilibrium simulation

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1. Introduction

Coal was one of the most important energies in the world, especially in China. It played an important role in the development of social and economic development. However, a large amount of toxic trace elements (TTEs) emissions to the environment caused serious atmosphere, soil, water pollution, and human health issues during coal processing [1–3]. Furthermore, as one of the common TTEs in coal, chromium (Cr) had been listed as hazardous air pollutants (HAPs) and had drawn special attention. Cr and its compounds were very easy to pollute water and soil. It could combine with hemoglobin through the red blood cell membrane. They would cause genetic defects and carcinogenesis and do great harm to humans [4]. Consequently, paying attention to the emission of Cr and other TTEs during coal combustion was of great significance for the development of clean coal technology and environmental protection.

Pyrolysis is an important initial step or intermediate process in coal combustion, gasification, and liquefaction [5]. In recent years, pyrolysis was considered as an effective and promising way for coal upgrading and removing TTEs before combustion. Hence, the pyrolysis technology had attracted increasing attention [6,7]. However, only a few pieces of literature had studied the release behavior of TTEs in coal during the pyrolysis process. For example, Guo et al. [8–10] investigated the effects of temperature, pyrolysis rate, atmosphere, and residence time on the volatility of TTEs in bituminous coal, and the modes of occurrence of elements were studied by the sequential chemical extraction (SCE). The author found that the volatility of TTEs increased with the rise of pyrolysis temperature and residence time, decreased at advanced pressure, and rapid pyrolysis rate. The H_2 atmosphere was favorable for the evaporation of TTEs. The modes of occurrence might be a crucial factor for TTEs during pyrolysis. Khare et al. [11] reported the thermal behavior of trace elements at various temperatures in high sulfur coals and found that Cr showed variable affinity at different temperatures due to its interaction with carbon, sulfur, and chlorine. Wei et al. [12] studied the volatilization of TTEs during oxidative pyrolysis and modes of occurrence through SCE in anthracite coal. The results showed that the volatility of TTEs exhibited a close correlation with the modes of occurrence. Therefore, it was necessary to investigate the modes of occurrence of TTEs in coal besides the influence conditions of the pyrolysis process.

Many scholars had conducted researches on the release and transfer behaviors of TTEs in the coal combustion process. The release behavior of Cr and other TTEs during the coal combustion process had been extensively investigated [13–17]. For example, Zhang et al. [18] investigated the release behavior of Cr and other TTEs from coal in the initial stage of the combustion process. The author concluded that the volatility of elements mainly depended on the modes of occurrence of elements. A study by Wang [19] indicated that the volatilization of heavy metals was dependent on their thermochemical properties of themselves. Wang [20] studied the release and transformation of as during the co-combustion of coal and biomass as well as the effects of mineral elements in biomass on its volatilization. The results showed that the mineral elements inhibited the volatilization of arsenic when Na, K, Mg, Ca, Al, Fe, and Si were added to coal. This indicated that modes of occurrence of as in coal had an important influence on its release. According to this literature, the volatility or transfer behaviors of TTEs during coal combustion were not only dependent on their thermochemical property but also their modes of occurrence. Therefore, it was highly important to understand the modes of occurrence of TTEs in coal before coal combustion, gasification, and other coal processing.

The modes of occurrence of Cr and other TTEs in coal had been studied extensively by many scholars [21–25]. As the direct characterization method, XAFS and SEM-EDX were applied in researching modes of occurrence of TTEs. As the indirect method, statistical analysis, float-and-sink tests, and SCE were applied in investigating modes of occurrence of TTEs. However, indirect methods had been used commonly due to the extremely low content of TTEs in coal and the limitations of direct characterization methods [26]. The method of statistical analysis and float-and-sink tests were the physical method to study the modes of occurrence by obtaining the relationship between elements and organic matter and inorganic minerals. It lacks precision and theoretical depth. In addition, pyrolysis, as a thermochemical process, could also identify the modes of occurrence of TTEs in coal. Luo et al. [24,27] identified modes of occurrence of Hg in coal through temperature-programmed pyrolysis. Guo et al. [28,29] identified modes of occurrence of Hg in bituminous coal by combing temperature-programmed pyrolysis with the online atomic fluorescence spectrometry method. Thus, the temperature-programmed pyrolysis identified modes of occurrence of TTEs mainly based on the relationship between the decomposition temperature of specific inorganic minerals or organic matter with the release temperature range of TTEs. However, due to the diversity of modes of occurrence of TTEs in coal, the release temperature range of TTEs was too large. The peaks formed by the release of TTEs were broad and might overlap. Hence, it made it difficult to identify the specific forms and investigate their thermal ability. Besides, few authors studied the volatility characteristics or release behavior of TTEs in low-rank coal during the pyrolysis process [30,31]. Low-rank coal owned high volatile matter, reactivity, and low ash than high-rank coal, which made a suitable material for coal chemistry. Therefore, it was extremely necessary to study the modes of occurrence and their release behavior of TTEs during the pyrolysis process for low-rank coal.

Thus, a single-component samples (SCS) pyrolysis method was proposed at present. The components containing single modes of occurrence of TTEs, called SCS, were prepared by SCE. It was able to accurately investigate the thermal stability of components containing single modes of occurrence of elements by the SCS pyrolysis. The advantage of SCE was able to identify and quantify the modes of occurrence of TTEs in coal by extracting a certain form of elements into selective acid or alkaline solutions through a chemical method. Therefore, modes of occurrence of TTEs in coal could be identified, quantified and their thermal stability could also be investigated more accurately by coupling SCE with SCS pyrolysis.

In the present study, two Chinese low-rank coal from Xinjiang province named NMH coal; Inner Mongolia named GL coal, and SCS were pyrolyzed in a fixed-bed reactor. The final temperature was 400–800 °C with an interval of 100 °C at atmosphere pressure. The heating rate was 5 °C/min and the residence time was 60 min at the final temperature. Modes of occurrence and preparation of SCS of Cr were carried out by SCE. The release behavior of Cr in raw coal and SCS was investigated during pyrolysis. Thermochemical equilibrium simulation software FactSage 7.3 was used to simulate the migration and transformation of Cr in two low-rank coal pyrolysis.

2. Materials and Methods

2.1. Materials

Two Chinese low-rank coal samples were used in the present study, named NMH coal (Xinjiang province) and GL coal (Inner Mongolia) separately. The two raw materials were crushed and milled to get the particle size less than 2 mm. All samples were heated to 80 °C and maintained at this temperature for 12 h in a vacuum-dried oven to remove the moisture. All coal samples were divided into two parts by division. One part was used for experiments, and the other part was split as the stored samples. The representative samples of raw coals were taken as proximate, ultimate, and XRF analyses. Results of proximate and ultimate analyses of raw coal samples are shown in Table 1. NMH and GL coal owned high volatile matter, showing its low-rank characteristic, and low ash content. Total sulfur content in GL was obviously higher than NMH coal. Results of XRF are shown in Table 2. SiO_2 was the main ash composition, followed by Al_2O_3, Fe_2O_3, CaO, and SO_3 in NMH and GL coal.

Table 1. Analysis of samples.

Sample	Cr_d (μg/g)	Cl_d (μg/g)	Proximate Analysis (wt%)				Ultimate Analysis (wt%)				
			M_{ad}	A_d	V_{daf}	FC_{daf}	C_{daf}	H_{daf}	O_{daf}	N_{daf}	$S_{t,daf}$
NMH	5.22	60	9.16	9.95	52.76	47.24	77.41	6.60	13.23	2.16	0.60
GL	14.56	910	10.13	12.13	38.49	61.51	76.72	5.07	15.39	0.81	2.01

M: moisture; A: ash; V: volatile; FC: fix carbon; S_t: total sulfur; ad: air-dry basis; d: dry basis; daf: dry and ash-free; O: by difference.

Table 2. Ash composition in coal.

Sample	SiO_2	Al_2O_3	Fe_2O_3	CaO	Na_2O	MgO	K_2O	SO_3
NMH	39.35	16.64	5.88	23.30	2.95	1.23	0.38	8.83
GL	32.57	14.03	10.11	17.00	0.57	6.43	0.42	17.84

2.2. Materials Analysis

Moisture, ash, volatile matter, and fixed carbon were determined according to the Chinese Standard Method GB/T 212-2008. The content of carbon, hydrogen, nitrogen, and sulfur were determined using a vario MACRO cube. XRF (XRF-1800) was employed to measure the concentrations of major element oxides in the coal ash sample.

Mineralogical characteristics of NMH and GL raw coal were determined using XRD analysis. Low-temperature ash of coal samples was obtained by burning samples at 250 °C in a muffle furnace for 60 h prior to XRD analysis. Two raw coals were analyzed using a Japanese Rigaku D/max-2500PC X-ray diffractometer (Rigaku Corporation, Tokyo, Japan) with a Cu tube. The XRD pattern was recorded over a 2θ range of 5–70° with a step size of 0.02°, the scanning speed was 2°/min. The accelerating voltage and the tube current of the X-ray diffractometer were 40 kV and 150 mA, respectively. The XRD results of NMH and GL raw coal are shown in Figure 1. In NMH coal, kaolinite, quartz, anhydrite, and calcite had been identified, while kaolinite, quartz, anhydrite, calcite, pyrite had been identified in GL coal.

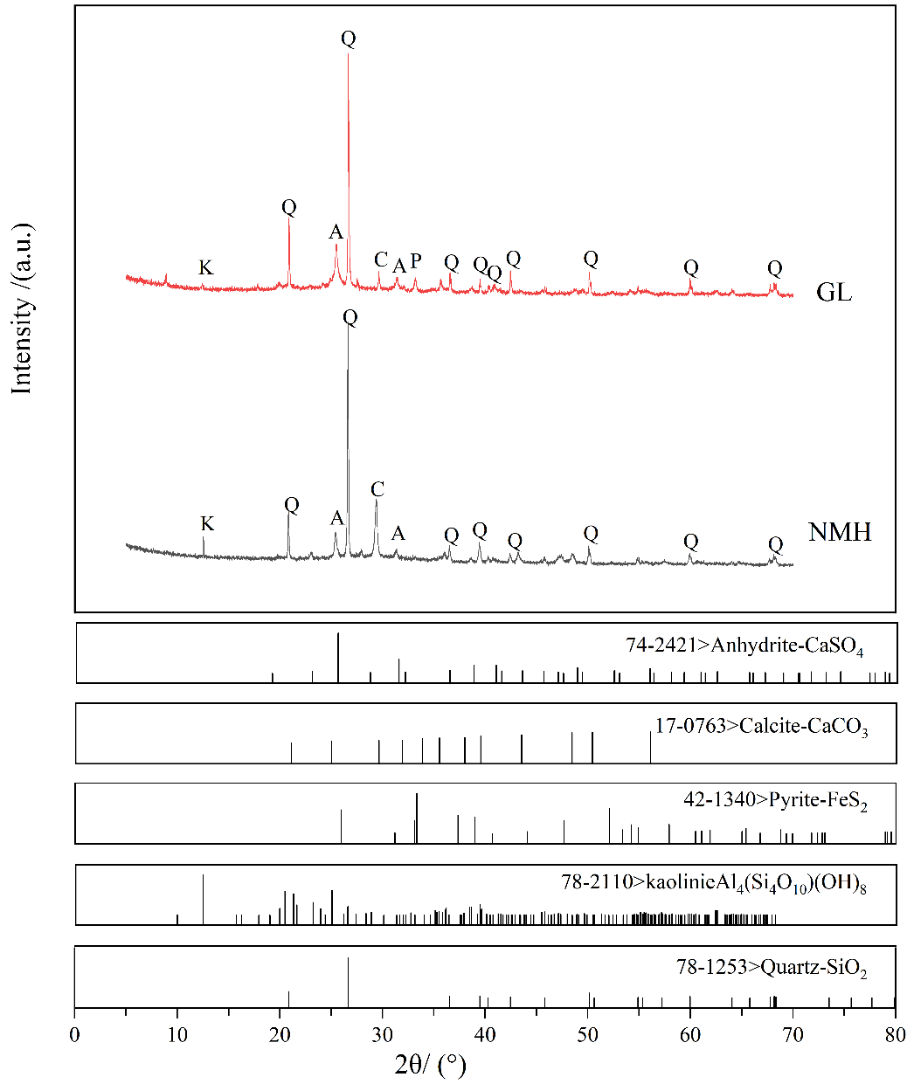

Figure 1. XRD patterns of low-temperature ash of NMH and GL. Q: quartz; A: anhydrite; K: kaolinite; P: pyrite; C: calcite.

2.3. SEM-EDX Analysis

The physical structure of the surface of NMH and GL coal were characterized by scanning electron microscopy (SEM)-energy dispersive X-ray spectrometer (EDX) (SU8020 Series). The results are shown in Figure 2. It found that pyrite, anhydrite, and aluminosilicate were easy to be identified in coal, but calcite was hard to be identified in GL coal.

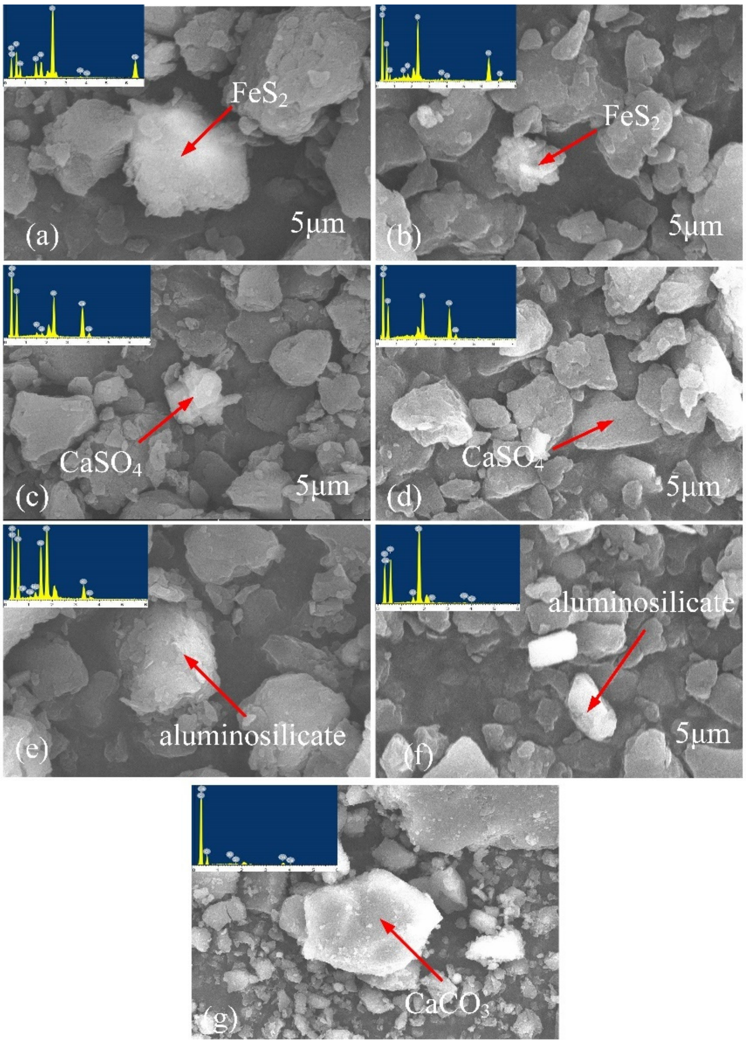

Figure 2. SEM-EDX images of minerals in NMH (**a**,**c**,**e**,**g**) and GL (**b**,**d**,**f**) coal.

2.4. Concentration Analysis of Cr and Cl

Samples were crushed and then ground to pass through a 74 μm mesh for Cr and Cl analysis. The guaranteed reagents for 100 mg sample digestion were 6 mL HNO_3, 3 mL H_2O_2, and 3 mL HF. The microwave digestion procedures are presented in Table 3. After the digestion by microwave digestion system, Cr concentration in samples was determined by using ICP-MS (NexlON300X). ICP-MS has good reproducibility and a low detection limit for the determination of trace elements [32]. Cl concentration in samples was determined using the ST-1 high-temperature hydrolysis chlorine analyzer according to the Chinese Standard Method GB/T 3558-2014. Prior to ICP-MS analysis, the samples were digested using the microwave digester (CEM MARS 5). The water used in the microwave digestion process was ultrapure water produced by the Milli-Q™ A10 system to reduce the background value. All data of elements content were the average value through three measurements.

Table 3. The running program of microwave digester.

Stage	Power (W)	Ramp (min)	Temperature (°C)	Hold (min)
1	1600	8	120	4
2	1600	8	160	5
3	1600	5	185	25
4	Cooldown			

2.5. SCE

In this study, the above four guaranteed reagents in Section 2.4 were used to successively extract minerals and organic matter from raw coals. Specific extraction conditions and procedures are shown in Table 4 according to other scholars [33,34]. Through the experiment, Cr associated with different parts of the coal could be removed. Then, the extracts were measured by ICP-MS to investigate the modes of occurrence.

Table 4. Sequential chemical extraction procedures.

Step	Reagent	Time/h	Temperature/°C	Occurrence Modes
1	5 mol/L HCl	6	60	Bound to carbonate
2	40% HF	6	60	Bound to aluminosilicate
3	5 mol/L HNO_3	6	45	Bound to disulfide
4	30% H_2O_2	6	85	Bound to organic matter

The modes of occurrence of Cr in coal could be divided into four categories: Cr bounded to carbonates (including monosulfide, sulfate, phosphate, and oxide, the same below), Cr bounded to aluminosilicate, Cr bounded to disulfide and Cr bounded to organic matter. To investigate the thermal stability of various occurrence modes of Cr, NMH, and GL raw coal were extracted by $HCl/HNO_3/H_2O_2$, $HCl/HF/H_2O_2$, $HCl/HF/HNO_3$ in three different order. Therefore, three SCS containing a single occurrence mode of Cr were obtained, which were recorded as $HCl/HNO_3/H_2O_2$-NMH (GL), $HCl/HF/H_2O_2$-NMH (GL), $HCl/HF/HNO_3$-NMH (GL), respectively. The three samples represented Cr bounded to aluminosilicate, Cr bounded to disulfide and Cr bounded to organic matter, separately. It was a pity that the sample of Cr bounded to carbonates could not be obtained by this method due to the addition of HCl.

2.6. TG Analysis

To investigate the release behavior of Cr during the pyrolysis process, pyrolysis behaviors of NMH and GL coal in TGA at 10 °C/min from room to 900 °C and atmospheric pressure were studied by utilizing TG and DTG plots. The TGA was carried out using a Mettler-Toledo TGA/DSC 1 thermogravimetric analyzer. Nitrogen was used as the carrier gas (at 50 mL/min) to ensure an oxygen-free environment.

2.7. Pyrolysis

Pyrolysis experiments of NMH and GL raw coal, as well as SCS, were conducted in a fixed-bed reactor as schematically illustrated in Figure 3. Approximately 20 g of coal samples were weighed and placed into a quartz crucible. Highly pure nitrogen (99.999%) was introduced to the quartz crucible, and the reaction zone was closed. Then, it was heated from ambient temperature to final temperature of 400–800 °C with an interval of 100 °C. The heating rate was 5 °C/min and the residence time was 60 min. Nitrogen gas was introduced into the reactor at a flow rate of 50 mL/min to sweep the volatile products out of the reactor. Subsequently, char samples were obtained from pyrolysis at the different pyrolysis temperatures of 400, 500, 600, 700, and 800 °C. Char samples were weighed and stored hermetically after the quartz crucible cooled to ambient temperature.

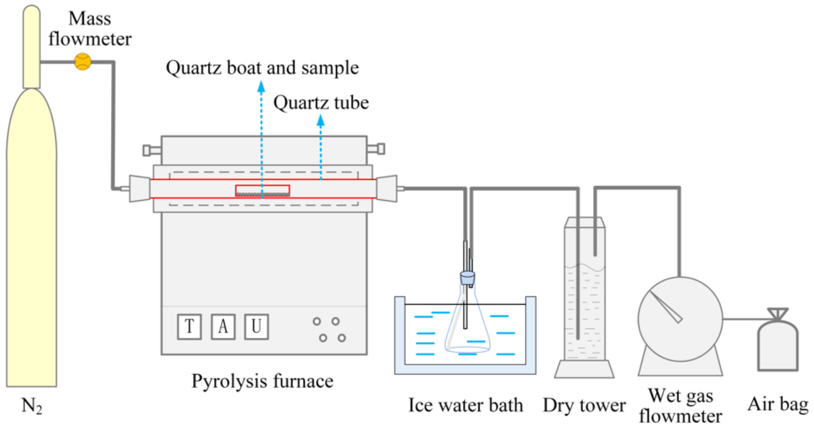

Figure 3. Schematic diagram of tube furnace pyrolysis device.

2.8. Release Ratio and Extraction Ratio of Cr

The release ratio of Cr was used to evaluate the release extent of the Cr during coal pyrolysis and was defined as:

$$Rr = (C_{rawcoal} - C_{char})/C_{rawcoal} * 100\% \tag{1}$$

where Rr was the release ratio of Cr, $C_{rawcoal}$ was the content of Cr in raw coal, C_{char} was the content of Cr in char. The content of Cr in coal or char was obtained by the concentration of Cr measured multiplied by the mass of raw coal or char.

To evaluate the extraction ability of different extraction processes for Cr and organic/inorganic matter, the concept of extraction ratio was introduced, which was defined as:

$$Er = C_{extracts}/C_{rawcoal} * 100\% \tag{2}$$

where Er was the extraction ratio of the Cr or minerals, $C_{extracts}$ was the content of Cr or minerals in the extracts, $C_{rawcoal}$ was the content of Cr or minerals in raw coal.

2.9. Thermochemical Equilibrium Simulation

The Equilib module of FactSage thermochemical calculation software was able to use Gibbs free energy minimum principle to calculate mineral phase in the equilibrium state. In this paper, FactSage 7.3 was used to simulate the migration and transformation of Cr during NMH and GL coal pyrolysis. Before calculation, two databases of FactPS and FToxide under Datasearch were selected firstly. In the calculation, it was assumed that a 100 g coal sample was used, and content of C, H, O, N, S, Cr, Cl, and the major components of coal ash was used to represent the coal. The N_2 value was 500 g, the pressure was 1 atm, the simulated temperature was 300–900 °C and the temperature interval was 100 °C. The specific input value of elements and oxides in coal is shown in Table 5.

Table 5. Initial input value for calculation.

Element	Mass/g		Ash Composition	Mass/g	
	NMH	GL		NMH	GL
C	77.41	76.72	SiO_2	3.92	3.95
H	6.60	5.07	Al_2O_3	1.66	1.70
O	13.23	15.39	CaO	2.32	2.06
N	2.16	0.81	SO_3	0.88	2.16
S	0.60	2.01	MgO	0.12	0.78
Cr	5.22E-4	1.46E-3	K_2O	0.04	0.05
Cl	6.00E-3	9.10E-2	Na_2O	0.29	0.07
			Fe_2O_3	0.59	1.23

3. Results and Discussion

3.1. Modes of Occurrence of Cr

The results of the extraction ratio of minerals and organic matter in NMH and GL raw coals are presented in Figure 4a. 37.7% and 42.9% carbonate in two coals were extracted with 5 mol/L HCl respectively. 59.3% and 52.7% aluminosilicate were extracted with 40% HF separately. 2.8% and 3.9% disulfide were extracted with 5 mol/L HNO_3 respectively. The remaining 0.2% and 0.5% of minerals remained in raw coals. It could be concluded that most of the residues in raw coal extracted by HCl/HF/HNO_3 were the organic matter. Therefore, the main inorganic minerals in the two coals were aluminosilicate and carbonate, accounting for 97% and 95.6%, respectively. They were consistent with the results of XRD and XRF (Figure 1 and Table 2).

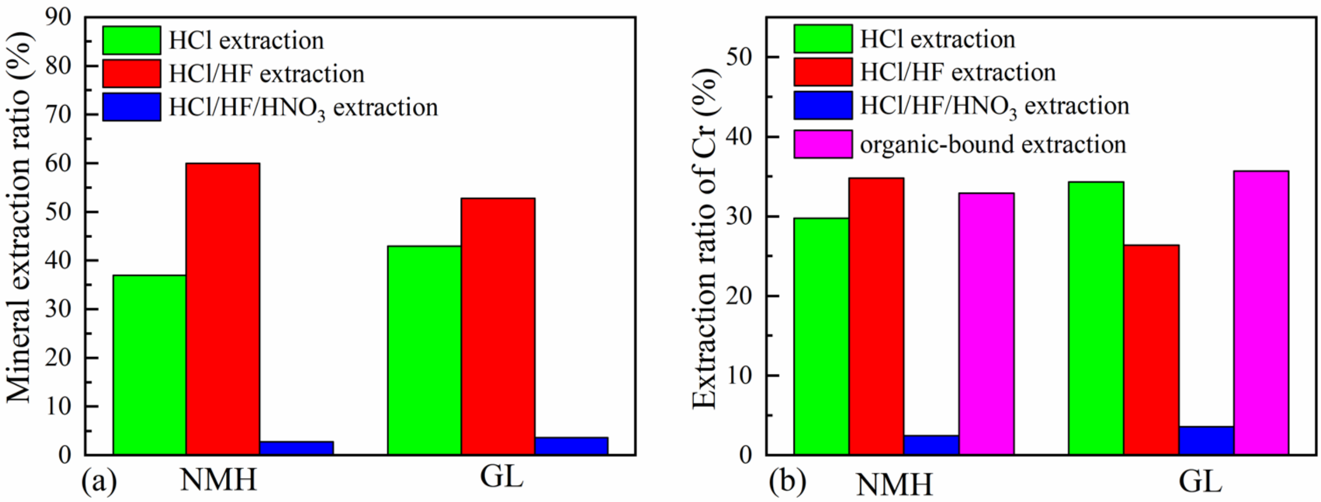

Figure 4. Extraction ratio of minerals and organic matter (**a**) and Cr (**b**) in NMH and GL coal.

The results of the extraction ratio of Cr in two coals are presented in Figure 4b. the relationship of Cr content in NMH coal among the various modes of occurrence in order was Cr bounded to aluminosilicate (34.8%) > Cr bounded to organic matter (32.9%) > Cr bounded to carbonate (29.8%) > Cr bounded to disulfide (2.5%). For GL coal, the order was Cr bounded to organic matter (35.7%) > Cr bounded to carbonate (34.3%) > Cr bounded to aluminosilicate (26.4%) > Cr bounded to disulfide (3.6%). Therefore, organic matter, aluminosilicate, carbonate were the main modes of occurrence of Cr in the coal, only a small part of Cr occurred in disulfide. This result was similar to the results of other reports on low-rank coal [35–37]. However, the major modes of occurrence of Cr in high-rank coal (bituminous and anthracite coal) were aluminosilicate minerals [8,38].

3.2. Pyrolysis Experiment

3.2.1. Pyrolysis in Thermogravimetric Analyzer

To investigate the release behavior of Cr, the pyrolysis behavior of two coals was studied by TGA. In Figure 5a, the maximum mass loss of NMH and GL raw coal was about 60 wt% and 40 wt%, respectively. The mass loss of NMH coal was always higher than GL coal in the whole process of thermal decomposition. It was mainly depending on their different volatiles and ash content (Table 1). The higher the volatile matter was, the more unstable side chains and oxygen-containing functional groups were in coal, and the easier to decompose at high temperatures. The first stage was from the beginning to around 200 °C, where only water and a few peripheral mobile phases from the macromolecular structure decomposed. The second stage was from 200 to about 600 °C, where a large mass loss of NMH and GL coal, approximately 33 wt% and 20 wt%, was produced. The maximum decomposition peak of the two coals was shown at around 450 °C at the same time, corresponding to the sharp decrease in the TG plot. This phenomenon was caused by a large amount of volatiles produced in a narrow temperature range. As low-rank coal, there were a higher number of oxygen-containing functional groups contained in it, which could decompose quickly at moderate temperature. This could cause the release of TTEs bound to organic matter. The third stage was from 600 to 900 °C. The remaining macromolecular structures in coal were mainly dense polycyclic aromatic compounds in the immobile phase. Then they were further decomposed at a relatively lower rate and produced about 16 wt% (NMH) and 12 wt% (GL) volatile matter. At high temperatures, some minerals would decompose or transform, leading to the release of TTEs associated with these minerals.

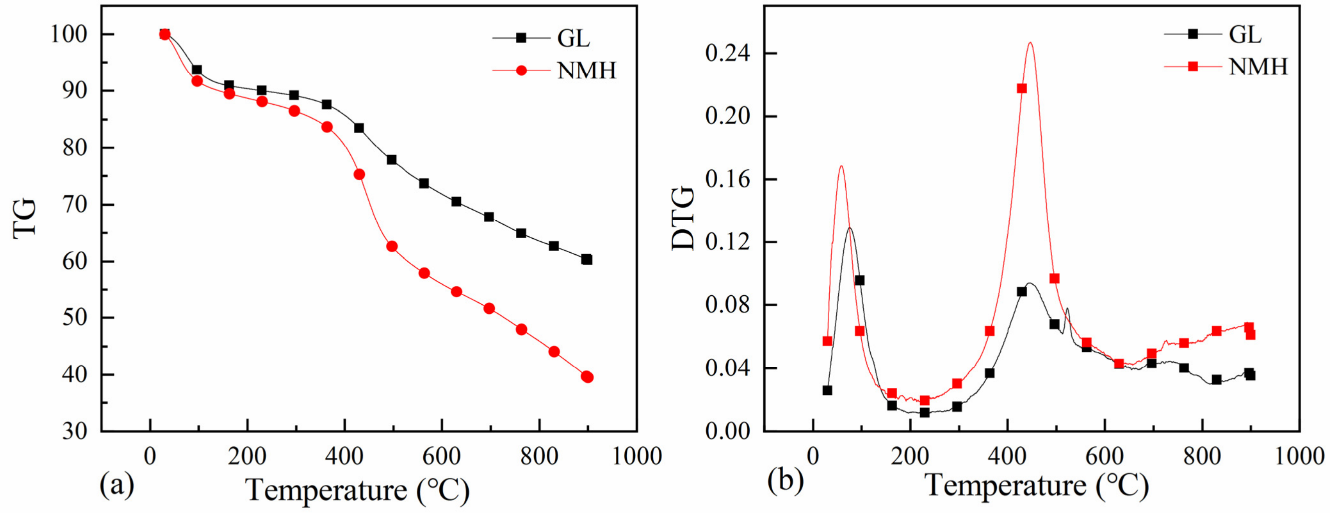

Figure 5. Pyrolysis behavior NMH and GL raw coal in TG (**a**) and DTG (**b**).

3.2.2. Pyrolysis in Fixed-Bed Reactor

To investigate the release behavior of Cr, the pyrolysis behavior of NMH and GL raw coal was studied by a fixed-bed reactor. The chars yield of coal during the pyrolysis process are shown in Table 6. With the increase in the pyrolysis final temperature, the chars yield of NMH and GL coal decreased gradually, from 70% at 400 °C to 51% at 800 °C, and from 78% at 400 °C to 61% at 800 °C, respectively. The reason why the char yields of GL coal were always higher than that of NMH coal was that the ash content of GL coal was higher than that of NMH coal, while the volatile matter of GL coal was lower than that of NMH coal.

Table 6. Char yields of NMH and GL raw coal in pyrolysis.

Char Yield/%	400 °C	500 °C	600 °C	700 °C	800 °C
NMH	73.06	64.33	59.24	56.45	55.72
GL	78.65	68.31	66.01	62.83	61.64

3.3. *Release Behavior of Cr in Raw Coal*

The release ratio and reaction rate (by fitting) of Cr during pyrolysis of NMH and GL coal are shown in Figure 6. The release ratio of Cr increased with the rising of temperature. Besides, the release ratio of Cr in GL coal was higher than that in NMH coal, from 3.87% to 25.24% (GL) and 3.98% to 8.53% (NMH), respectively, in 400–800 °C. The higher release ratio of Cr in GL coal was due to the more content of Cr bound to organic matter and less content of minerals associated form of Cr in GL coal. Besides, Cl was likely to be the reason for this phenomenon, which would be discussed in detail in Section 3.4.1. In Figure 6b, the reaction rate of Cr in NMH coal increased before 600 °C, then decreased between 600 to 700 °C, finally increased again after 800 °C, and changed little during the whole pyrolysis temperature range. However, the reaction rate of Cr in GL coal decreased slowly before 450 °C, then sharply increased between 450 to 650 °C, finally decreased rapidly after 650 °C.

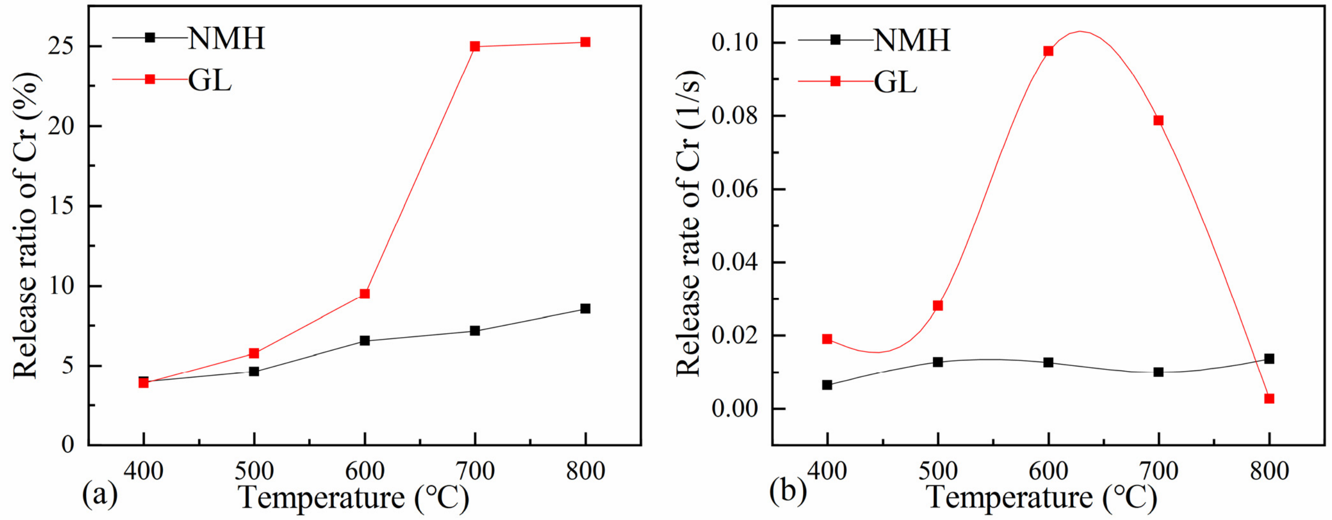

Figure 6. The release behavior (**a**) and reaction rate (**b**) of Cr at different final temperatures during pyrolysis.

As is shown in Figure 4, the Cr bounded to disulfide accounted for 3.6% of the Cr content in GL raw coal. During the entire pyrolysis process, the release ratio of Cr in GL coal was about 25.24%. It was assumed that the Cr bounded to disulfide was completely decomposed and released, the Cr bounded to disulfide accounted for 14.26% of the total Cr release from the raw coal. The release ratio of Cr in GL was 15.49% from 600 to 700 °C, which was consistent with the content of Cr bounded to a disulfide. Moreover, pyrite, as the main component of disulfide, began to decompose after 500 °C [12]. Therefore, it was concluded that the sharp increase in the release ratio and reaction rate of Cr in GL coal instead of Cr in NMH coal was mainly due to the decomposition of disulfide, considering the reaction rate at 600 °C.

3.4. Release Behavior of Cr in SCS

To investigate the effect of occurrence modes of Cr on its release behavior, the pyrolysis behavior of SCS obtained by SCE was studied in the fixed-bed reactor and shown in Figure 7. The release ratio of Cr was calculated based on Cr content in each SCS.

3.4.1. Release Behavior of Cr in $HCl/HNO_3/H_2O_2$-Sample Pyrolysis

Cr in $HCl/HNO_3/H_2O_2$-sample presented as the Cr bounded to aluminosilicate. As is shown in Figure 7a, the release ratio of Cr in $HCl/HNO_3/H_2O_2$-NMH increased from 2.35% to 9.86% with the increasement of pyrolysis temperature. It showed that Cr in $HCl/HNO_3/H_2O_2$-NMH was released after 600 °C. The release temperature was higher than that for Cr in $HCl/HF/H_2O_2$-NMH and $HCl/HF/HNO_3$-NMH coal. The high release temperature should be attributed to the higher thermal stability of Cr [11] and aluminosilicate in coal. The Cr bounded to aluminosilicate was difficult to dissociate and release in the middle and low-temperature regions. Even at high temperatures, a large part of the Cr existed in the solid residue together with aluminosilicate [8,12].

As is shown in Figure 7b, the release ratio of Cr in $HCl/HNO_3/H_2O_2$-GL increased from 1.37% to 61.56% with the increasement of pyrolysis temperature. Cr in $HCl/HNO_3/H_2O_2$-GL released after 500 °C. The release temperature of Cr in $HCl/HNO_3/H_2O_2$-GL was lower than that for Cr in $HCl/HNO_3/H_2O_2$-NMH and the release ratio of Cr in $HCl/HNO_3/H_2O_2$-GL was obviously higher than that for Cr in $HCl/HNO_3/H_2O_2$-NMH. The reason for this phenomenon was probably due to the high content of Cl in GL coal (Table 1). The Cl in coal reacted with H_2 produced by pyrolysis to produce reducing gas, such as HCl, and the reducing gas reacted with Cr bounded minerals to produce Cr chloride with a lower boiling point, enhancing the volatility of Cr and reducing the volatilization temperature of Cr [12,13]. Another reason might be attributed to the mineral eutectic occurring between SiO_2, Al_2O_3, and CaO [39], which could absorb and prevent the escape of elements. It was worth noting that the content of SiO_2, Al_2O_3, and CaO in NMH coal was higher than that in GL coal. Thus, this was also the reason why the volatilization ratio of Cr was higher in GL raw coal during the pyrolysis process.

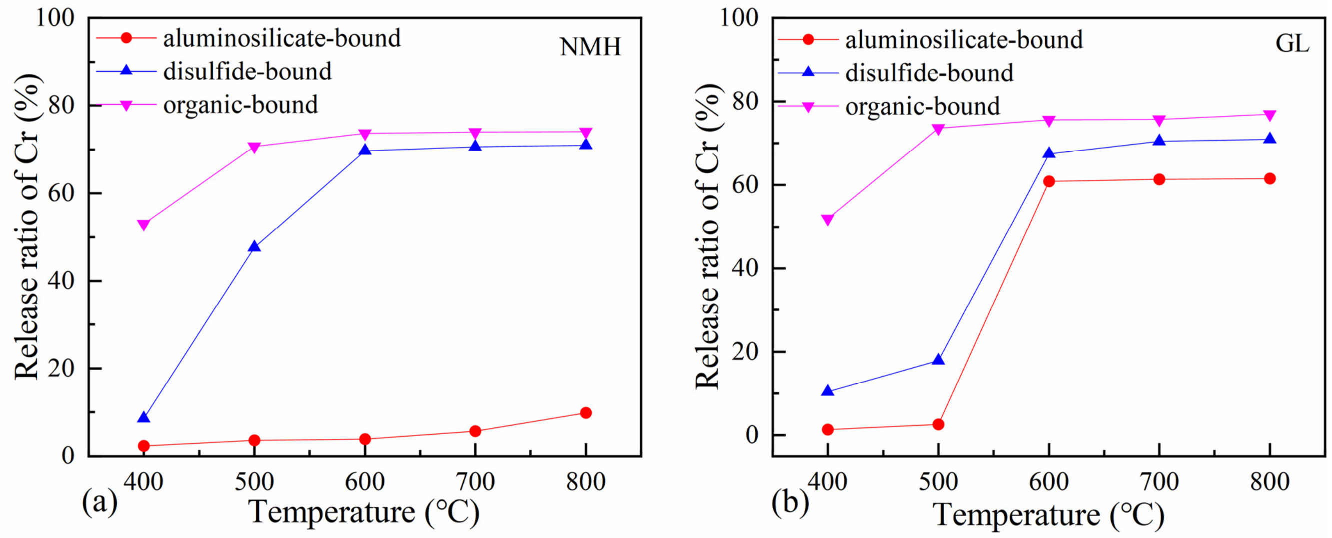

Figure 7. Release behavior of Cr in different SCS of NMH (**a**) and GL (**b**).

3.4.2. Release Behavior of Cr in HCl/HF/H_2O_2-Sample Pyrolysis

Cr in HCl/HF/H_2O_2-sample presented as the Cr bounded to disulfide (mainly pyrite). The release ratio of Cr in HCl/HF/H_2O_2-NMH and GL was 8.63–70.97% and 10.34–70.92% separately in the range of 400–800 °C. The release temperature range was 400 to 600 °C for Cr bounded to disulfide due to the decomposition temperature of pyrite being around 500 °C. During the thermal treatment process, FeS_2 was oxidized to form Fe_2O_3 and SO_2 between 490 °C and 690 °C [12]. Therefore, Cr bounded to disulfide dissociated and released at a temperature range of 400–600 °C accompanied by the decomposition of pyrite.

3.4.3. Release Behavior of Cr in HCl/HF/HNO_3-Sample Pyrolysis

Cr in HCl/HF/HNO_3-sample presented as the Cr bounded to organic matter. The release ratio of Cr in HCl/HF/HNO_3-NMH and GL was 53.06–74.01% and 51.98–76.93%, respectively, in the range of 400–800 °C. Cr bounded to organic matter was almost completely released within 600 °C. Based on the TGA results of NMH and GL coal (Figure 5), a large number of oxygen-containing functional groups decomposed at 200–600°C caused the release of TTEs bounded to organic matter. Cr bounded organic matter was usually covalently bonded with carboxyl (-COOH), hydroxyl (-OH), and imino (-NH) functional groups [12]. These organic functional groups had poor thermal stability and generally disappeared with the increase in pyrolysis temperature at low temperatures [5].

3.5. Thermochemical Equilibrium Simulation

To obtain a more insight study on the release and transfer behavior of Cr, Global chemical equilibrium calculations were performed utilizing the program FactSage 7.3. It calculated the conversion behavior of Cr at different temperatures during the pyrolysis process. Thermochemical calculation results of Cr in NMH and GL coal are shown in Figure 8. In Figure 8a,b, it indicated that gas products were chlorides (CrCl, $CrCl_2$, $CrCl_3$, $CrCl_4$, $CrCl_5$, $CrCl_6$), hydroxides (Cr(OH), $Cr(OH)_2$, $Cr(OH)_3$, $Cr(OH)_4$), Cr, CrS, and oxides (CrO, CrO_2, CrO_3), among which chlorides was the dominant product. The chlorides content of Cr in GL was higher than that of NMH in the simulation process due to the higher content of Cl in GL coal (Table 1). On the contrary, the content of solid products remaining in chars such as CrO, Cr_2O_3, CrS, and Cr_2S_3, was higher as shown in Figure 8c,d. This indicated that Cr had good thermal stability and was not easy to volatilize, and most of it remained in the char in the above forms (Figure 6). Besides, the calculation results showed that solid products were mainly sulfides and oxides of Cr. They were closely related to the dominant form in the mineral-associated form of Cr, carbonate, and the aluminosilicate-associated form (Figure 4b), in NMH and GL coal. The equilibrium calculation results mentioned above were consistent with the experimental results.

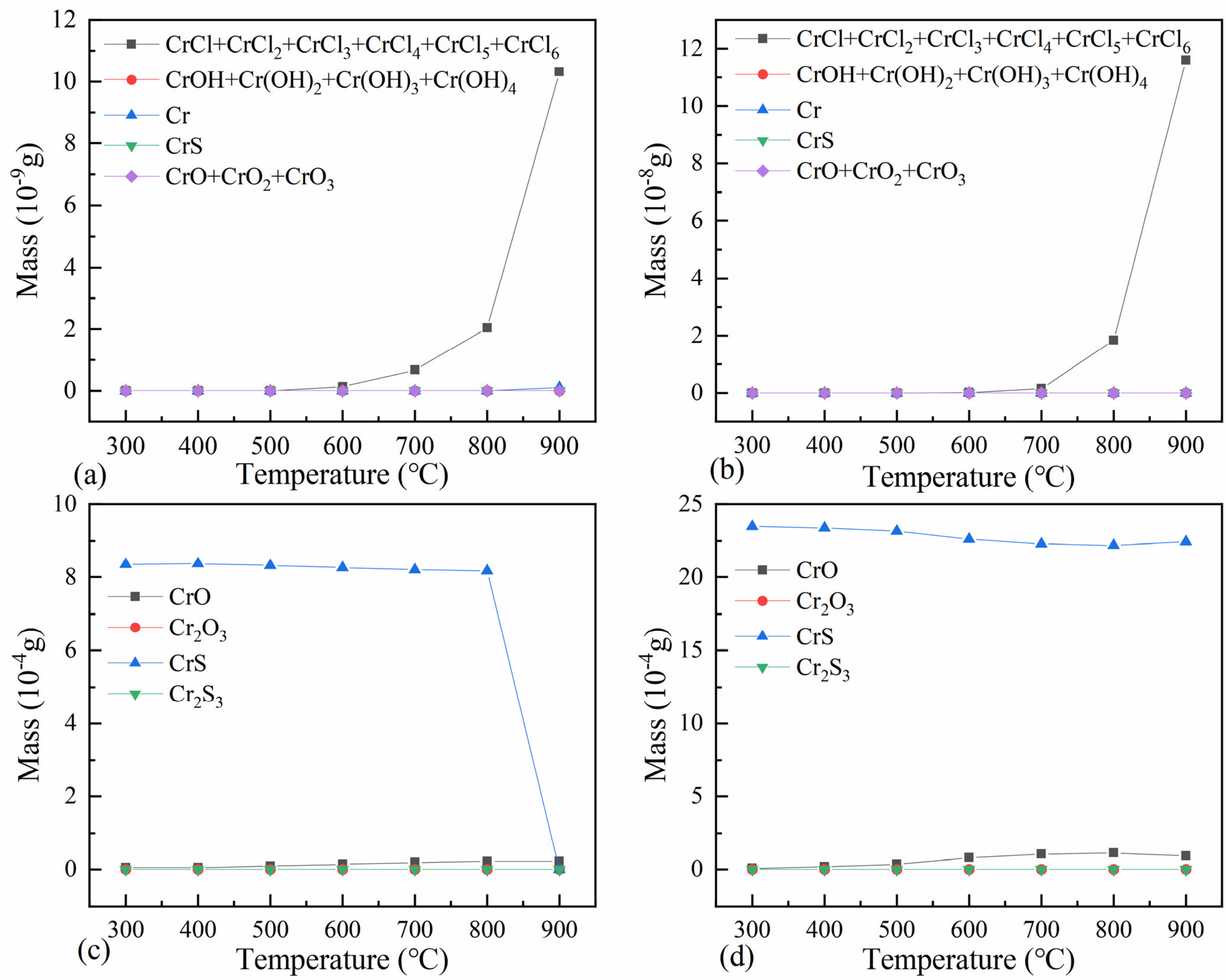

Figure 8. FactSage calculation results of Cr in NMH (**a**,**c**) and GL (**b**,**d**) coal.

4. Conclusions

The present study mainly focused on the modes of occurrence of Cr in two low-rank coals and their release and transfer behaviors in fixed-bed reactor pyrolysis. From the discussions, it could be concluded that:

(1) Sequential chemical extraction showed that the organic matter, aluminosilicate, carbonate (including monosulfide, sulfate, phosphate, and oxides) were the dominant modes of occurrence of Cr, share of which were 32.9%/35.7%, 34.8%/26.4%, and 29.8%/34.3%, separately, while Cr bounded to disulfide accounted for only a small part (about 3%) in two low-rank coals.

(2) Raw coal pyrolysis indicated that the release ratio of Cr increased with the rise of temperature. The release ratio of Cr in GL coal was higher than that in NMH coal in 400–800 °C, which was mainly attributed to the high content of Cr bound to organic matter and less content of the mineral associated form of Cr in GL coal. A rapid increase in the Cr release ratio in GL coal at 600 °C was due to the decomposition of disulfide.

(3) Single-component samples pyrolysis demonstrated that Cr bounded to organic matter was almost completely released within 600 °C. The release temperature range of Cr bounded to aluminosilicate and disulfide was shown to be >600 °C and 400–600 °C, respectively. At high pyrolysis temperature, Cl reacted with Cr bounded to minerals to form Cr chlorides with a lower boiling point, which enhanced the volatility of Cr and reduced the volatilization temperature of Cr.

(4) FactSage thermochemical simulation suggested that gas products were chlorides, hydroxides, Cr, CrS, and oxides, among which chlorides were the dominant product. The solid products were mainly CrO, Cr_2O_3, CrS, and Cr_2S_3, the content of which was much higher than that of gas products, showing their high thermal stability. The dominant form of Cr in chars were sulfides and oxides, which were closely related to the carbonate and aluminosilicate associated form of Cr, as the main form of Cr in raw coals. The results of the equilibrium calculation were consistent with the experimental results.

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