INTRODUCTION

With the rapid development of economy, the demand for oil resources has increased. However, available global oil reserves can last only for <50 years.\(^1\) It is necessary to explore unconventional alternative energy resources to ensure reliable and safe energy supply. China is rich in oil shale resources. Reasonable utilization of oil shale can significantly resolve the issues ailing energy supply. Oil shale ash, such as coal, is a solid fuel having significant combustible organic matter in it.\(^2,3\) Pyrolysis is the most important thermal conversion method for oil shale and involves the important steps of combustion and gasification. A large number of solid, liquid, and gas products can be obtained from pyrolysis. Carbon monoxide (CO) is one of the main combustible gases obtained during pyrolysis of fossil fuels.\(^4\) The complex structure of oil shale plays an important role during pyrolysis and gas precipitation. Therefore, it is very important to study the composition of oil shale and the mechanism of CO reaction during pyrolysis, which could help realize efficient and clean utilization of oil shale.

In recent years, many scholars have used a variety of technical means to explore the structure of oil shale as comprehensively as possible. Hillier et al\(^5\) analyzed the pyrolysis products (light gas, tar, and tar) of Colorado Green River shale using \(^{13}\)C nuclear magnetic resonance spectroscopy (NMR) and Fourier-transform infrared spectroscopy (FTIR) techniques. The thermogravimetric-Fourier-transform infrared spectroscopy (TG-FTIR) was used to pyrolyze samples and study their kinetics at four different heating rates. Meanwhile, the peak fitting method was used to study the carbon monoxide (CO) produced during the pyrolysis process. The results indicated that the oil shale was mainly composed of aromatic, aliphatic, hydroxyl, and oxygen-containing functional groups, among which the aliphatic group was the most abundant. The pyrolysis process of oil shale was divided into four stages, whereas the pyrolysis weight loss and volatilization were concentrated in the second stage. When the number of peaks was 4, the fitting results were the best, which indicated that the precipitation of CO gas was affected by the four different types of reactions and was mainly the result of oxygen group and its side chain fracture.
Atomic ratio

Porada et al. found that the formation curve of CO can be divided into 3-5 regions, representing different functional groups. Wang et al. analyzed the chemical composition of oil shale using $^{13}$C NMR and FTIR. The results of $^{13}$C NMR showed that the oil shale was mainly composed of aliphatic carbon, whereas the FTIR analysis showed that methylene was mostly in the form of long straight chains in aliphatic hydrocarbons. Fourier-transform infrared (FTIR) spectrum and X-ray photoelectron spectroscopy (XPS) measurements were conducted on soft and hard coals with metamorphism varying from bituminous coal to anthracite. Liu et al. analyzed coal and coal-bearing shale samples using atomic force microscopy (AFM), attempting to gain clearer insights into the nanopore characteristics and surface roughness.

The thermogravimetric analyzer (TG) is usually used to monitor the change in the quality of oil shale pyrolysis in real time, whereas the light gas produced during pyrolysis is detected using FTIR. The combination of the two methods (TG-FTIR) can provide a better understanding of the pyrolysis process. Kaljuvee et al. used TG-FTIR to study the pyrolysis characteristics of different oil shale samples. According to different absorbances in the infrared spectrum, different gases, produced in pyrolysis, were distinguished. Chen et al. found that the variation in volatile absorbance during pyrolysis was consistent with the loss in weight as determined from the thermogravimetric curve and that the output of light gas increased with the increase in temperature. The mechanism of the formation of gas can be analyzed by fitting the release curve of pyrolytic gas. Porada et al. found that the formation curve of CO can be divided into 3-5 peaks during pyrolysis. Giroux et al. studied the relationship between oxygen-containing functional groups and CO during coal pyrolysis, and reported that the temperature of CO was higher (400-900°C), which was affected by three reactions.

According to the weight loss of oil shale, the activation energy and frequency factor of the reaction can be obtained, and the factors influencing the pyrolysis can be summarized. Based upon this information, the reaction mechanism of pyrolysis can be revealed. The Flynn-Wall-Ozawa (FWO) method is usually used to calculate the activation energy, which assumes that the activation energy of pyrolysis is the same at the same conversion rate at different heating rates. This employs that the reaction rate at a certain conversion rate is only a function of temperature. This method can produce theoretical results without knowing the reaction mechanism, whereas the obtained data are more accurate. According to the weight loss of oil sands, Hao et al. calculated the conversion-related kinetic parameters at different heating rates and reported that the activation energy values lied within the range of 93.74-215.99 kJ/mol. Scaccia et al. studied the non-isothermal kinetics of coal using iso-conversion method and found that the apparent activation energy remained almost constant when the conversion rate was within the range of 5%-40%, indicating that the process consisted of an elementary reaction. With the increase in conversion rate, the pyrolysis process of coal goes through multi-step reaction.

Previous studies focused on the relationship between pyrolytic CO and temperature of oil shale. However, only a handful studies have focused on the type of CO release reaction and the changes in functional groups of oil shale. In this paper, FTIR and $^{13}$C NMR were used to analyze the structural characteristics of oil shale samples, whereas the weight loss of oil shale samples during pyrolysis was studied using TG-FTIR at four different heating rates. Furthermore, the kinetic parameters of the pyrolysis of samples were calculated and discussed based on TG data. The precipitation kinetics of light gas release curve was calculated using peak splitting and fitting method. The reaction mechanism of pyrolytic gas was explored based upon the changes in functional groups.

## 2 | EXPERIMENTAL

### 2.1 | Sample preparation

In this paper, oil shale was obtained from the Wangqing area of Jilin province, China. The oil shale was crushed and ground to <0.2 mm size according to the International Standard ISO 18283:2006. After drying to a constant weight in a drying oven at 40°C for 24 hours, industrial analysis, elemental analysis, and aluminum retort experiments were carried out on the oil shale samples. The calculation of atomic ratio, and the oil content are listed in Tables 1 and 2, respectively.

### 2.2 | Methodology

#### 2.2.1 | FTIR experiments

The structural characteristics of samples were determined using Spectrum Two Portable FTIR, which was procured from PerkinElmer Inc, USA. During the experiment, 1 mg of the sample and 100 mg of dried potassium bromide were...
mixed and ground in agate mortar in the ratio of 1:100. The samples were kept under 10 MPa pressure for 3 minutes to be pressed into a transparent sheet. All the spectral information was collected within the range of 8300-350 cm\(^{-1}\). The spectral resolution was 0.5 cm\(^{-1}\), and the cumulative number of scans was 16.

2.2.2 | Solid carbon NMR (\(^{13}\)C NMR)

The \(^{13}\)C NMR experiments were carried out using Bruker AVANCE III-400 MHz superconducting NMR instrument, which was procured from Brook Company in Switzerland. At the same time, cross-polarized (CP), magic angle rotation (MAS) and rotating sideband total suppression (TOSS) were used to characterize the structure of carbon skeleton of the sample. The solid-state double-resonance probe with ZrO\(_2\) rotor 4 mm with Kel-F was selected for the experiments. The rotational speed was set to 5000 Hz, whereas the resonance frequency was 100 MHz. Additionally, the cross-polarization contact time was 2 mseconds, and the cycle delay time was 6 seconds. Last but not the least, the number of data points collected was 9000. All \(^{13}\)C (CP/MAS) chemical shifts were based on the resonance states of C\(_{10}\)H\(_{16}\) internal standard (\(\delta_{CH2} = 38.5\)).

2.2.3 | TG-FTIR experiments

The TG-FTIR analysis of the oil shale sample was carried out on TGA/DSC 1 thermogravimetric analyzer and NICOLETis10 FTIR, which were procured from Mettler-Toledo Company of Switzerland and Nicolet Company of USA, respectively. Before the experiment, high purity (99.999%) nitrogen was used to sweep the system for 30 minutes to remove any impurity gases present in the reaction system. The flow rate was set to be 50 mL/min. The crucible with 10 mg of the sample was placed in the online TG-FTIR for pyrolysis. The temperature was increased from room temperature to 50°C, where it was maintained for 3 minutes. The heating rates were successively changed through values of 10, 20, 40, and 80°C/min. The system was operated under positive pressure until the temperature increased to 900°C. The TG analyzer and FTIR were connected through a tube, whose inner diameter was 2 mm and length was 1 m. In order to reduce the possibility of gas condensation inside the tube, the temperature of gas pool and tube was maintained at 180°C.

2.2.4 | Kinetic model

The activation energy and the frequency factor of the pyrolysis reaction can be calculated from the reaction kinetics. Based on TG-FTIR results, the kinetic parameters of Wangqing oil shale were calculated and discussed based upon the first-order reaction kinetic model.\(^{20}\)

According to the basic principle of the kinetics of thermal analysis, the reaction rate equation can be expressed using Equations (1) and (2).

\[
\frac{da}{dt} = kf(a) \quad (1)
\]

\[
k = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) \quad (2)
\]

where \(a\) is the pyrolysis conversion (%), \(t\) is the pyrolysis time (seconds), \(k\) is the Arrhenius constant, \(E\) is the reaction activation energy (kJ/mol), \(A\) is the frequency factor (s\(^{-1}\)), \(R\) is gas constant (\(R = 8.314\) kJ/mol K), \(T\) is the absolute temperature of the sample (K), and \(\beta\) is the heating rate (K/s).

The chemical conversion was calculated using Equation (3).

\[
a = \frac{m_0 - m}{m_0 - m_\infty} \quad (3)
\]

where \(m_0\) is the initial mass of the sample at the beginning of pyrolysis, \(m\) is the mass of the sample at any time during pyrolysis, and \(m_\infty\) is the mass of the sample at the end of pyrolysis.

Based upon Equations (1) and (2), the nonisothermal kinetic equations can be written as Equation (4).

\[
\frac{da}{dt} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right)f(a) \quad (4)
\]

Flynn-Ozawa-Wall method

The kinetics of oil shale pyrolysis\(^{24}\) was calculated using Flynn-Ozawa-Wall (FWO) method. The right- and left-hand sides of Equation (4) were integrated with the limits of 0 – \(a\) and 0 – \(T\), respectively.

\[
\int_0^a \frac{da}{f(a)} = \int_0^T \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) \quad (5)
\]

\[
G(a) = \int_0^T \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) dT \quad (6)
\]
When $T = \beta$ and $u = \frac{E}{RT}$, Equation (7) is obtained.

$$dT = -\frac{E}{R\beta}du \quad (7)$$

From Equations (6) and (7), Equation (8) is obtained.

$$G(\alpha) = \int_0^T \frac{A}{\beta} \exp \left( -\frac{E}{RT} \right) dT = \frac{AE}{R\beta} \int_0^\infty u^{-\frac{E}{u^2}}du = \frac{AE}{R\beta} p(u) \quad (8)$$

According to the Doyle approximation, Equation (9) is obtained.

$$\log P(u) = -2.315 - 0.4567 \frac{E}{RT} \quad (9)$$

According to Equations (7) and (8), the Ozawa equation is obtained, which is given as Equation (10).

$$\log \beta = \log \frac{AE}{RG(\alpha)} - 2.315 - 0.4567 \frac{E}{RT} \quad (10)$$

When the conversion $\alpha$ is constant, $G(\alpha)$ is also a constant value independent of temperature, whereas the relationship between $\log \beta$ and $\frac{1}{T}$ turns out to be linear. According to the slope, the reaction's activation energy ($E$) can be obtained under different conversion rates.

**Coats-Redfern method**

The Coats-Redfern (C-R) method is used to calculate the kinetic parameters for gas precipitation. Considering $f(\alpha) = (1 - \alpha)^n$, integrating Equation (4) and then, taking the natural logarithm of both sides of resulting equation yields Equation (11).

$$\ln \left[ -\ln \left( \frac{1 - \alpha}{T^2} \right) \right] = \ln \left[ \frac{AR}{\beta E} \left( 1 - \frac{2RT}{E} \right) \right] - \frac{E}{RT} \quad (11)$$

Equation (11) is the C-R integral. In terms of most $E$ values and general reaction temperature ranges, $\frac{E}{RT} >> 1$, whereas $1 - \frac{2RT}{E} \approx 1$. Therefore, the first term on the right-hand side of Equation (4) is usually a constant. When $n = 1$, $\ln \left[ -\ln \left( \frac{1 - \alpha}{T^2} \right) \right]$ and $\frac{1}{T}$ are linearly related to each other. The activation energy $E$ and the frequency factor $A$ can be obtained from the slope and the intercept of the straight line, respectively.

## 3 | RESULTS AND DISCUSSION

### 3.1 | FTIR analysis

The FTIR spectrum of Wangqing oil shale is shown in Figure 1. Due to large number of functional groups and various types of samples, there is a certain degree of superposition and overlapping in this region. According to some previous studies, each group has its specific absorption peak in the infrared absorption spectrum. The spectrum of 4000-400 cm$^{-1}$ is divided into four regions, which are represented by the aromatic vibration region (900-700 cm$^{-1}$), the oxygen-containing functional group vibration region (1800-1000 cm$^{-1}$), the aliphatic vibration region (3000-2800 cm$^{-1}$), and the hydroxyl vibration region (3600-3100 cm$^{-1}$). The spectrum in each interval was fitted using Origin 9 software to determine the types of functional groups present in oil shale. Additionally, the spectral parameters were adjusted to satisfy the condition of $R^2 > 0.999$ for the fitting degree. The fitting results are shown in Figure 2. The location and attribution of different functional groups in each section are presented in Tables 3-6.

Within the wavelength range of 900-700 cm$^{-1}$, the absorption peaks of all kinds of aromatic C-H flexural vibrations outside the plane are observed. Based upon this observation, the properties of the substituents on benzene rings can be analyzed. The fitting results of the peaks in this region are shown in Figure 2A. There are five peaks in this region, representing three different groups. The absorption peak at 714.81 cm$^{-1}$ represents (CH$_3$)$_n$, where $n \geq 4$, and accounts for only 3.65%. The absorption peaks at 731.56 and 763.07 cm$^{-1}$ are substituted by benzene ring with only four hydrogen atoms on the benzene ring and accounted for 60.29%. The absorption peaks of 785.64 and 801.11 cm$^{-1}$ were substituted by benzene ring with only three hydrogen atoms on the benzene ring and accounted for 36.06%. It can be seen that the substituents of benzene ring in Wangqing oil shale are mainly di-substituted and trisubstituted.

Within the wavelength range of 1800-1000 cm$^{-1}$, the absorption peaks of various oxygen-containing functional groups in oil shale are observed. According to these peaks, the C-O, O = C-O (carboxyl), C-OH (alcohols, phenols, etc.)
and ethers), C = O (carbonyl groups), or O-C-O groups can be analyzed. The fitting results of the peaks in this region are shown in Figure 2B. There are eight peaks in this region, which represent seven different oxygen-containing groups. The absorption peak at 1022.07 cm⁻¹ belongs to alkyl ether and accounted for 40.84%. The absorption peak at 1104.08 cm⁻¹ belongs to hydroxyl alcohol and accounted for 0.89%. The absorption peaks at 785.64 and 801.11 cm⁻¹ belong to phenolic hydroxyl groups and accounted for 36.99%. The stretching vibration peak at 1720.20 cm⁻¹ belongs to carboxyl group and accounted for only 0.99%. The results show that alkyl ether and hydroxyl groups are the main oxygen-containing groups in the Wangqing oil shale. This result is in good agreement with the results reported in a previous work.28

Within the wavelength range of 3600-3000 cm⁻¹, the only major absorption peak observed was of hydroxyl group. This group plays a significant role in the reaction. The determination of functional groups in the absorption region of this spectrum is easily affected by moisture in oil shale or the absorption of air moisture by potassium bromide during sample preparation. Therefore, it is necessary to prepare the sample extremely carefully, so that the error could be reduced as much as possible. The peak-to-peak fit results in this region are shown in Figure 2C. The results show a total of five peaks in this region, which represent four different hydroxyl groups. The absorption peaks at 3298.57 cm⁻¹ belong to OH-O bond and accounted for 50.74%. The absorption peaks at 3411.39 and 3468.17 cm⁻¹ belong to OH-OH bond and accounted for 38.86%. The results also show that the hydrogen bond terminal of CH₃, ring CH₂, and high-strength CH can be analyzed.29 The fitting results of the peaks in this region are shown in Figure 2C. There are five peaks in this region, which represent four different groups. The absorption peaks at 2822.17, 2853.54, and 2928.97 cm⁻¹ belong to -CH₂- stretching vibration and accounted for 30.03%. The absorption peak at 2891.70 cm⁻¹ represented C-H stretching vibration and accounted for 20.66%. The absorption peaks at 2962.47 and 2980.67 cm⁻¹ belonged to -CH₂- reverse-stretching vibration and accounted for 49.42%. It can be seen that the aliphatic group in Wangqing oil shale mainly consists of methylene. However, it is not completely long branched chain and also has a short branched chain structure.

Within the wavelength range of 3000-2800 cm⁻¹, the only major absorption peak observed was of hydroxyl group. This group plays a significant role in the reaction. The determination of functional groups in the absorption region of this spectrum is easily affected by moisture in oil shale or the absorption of air moisture by potassium bromide during sample preparation. Therefore, it is necessary to prepare the sample extremely carefully, so that the error could be reduced as much as possible. The peak-to-peak fit results in this region are shown in Figure 2C. The results show a total of five peaks in this region, which represent four different hydroxyl groups. The absorption peaks at 3298.57 cm⁻¹ belong to OH-N bond and cyclic hydroxyl bond, respectively, and accounted for only 2.52% and 7.88%, respectively. The absorption peak at 3298.57 cm⁻¹ belongs to OH-OH bond and accounted for 50.74%. The absorption peaks at 3411.39 and 3468.17 cm⁻¹ belong to OH-OH bond and accounted for 38.86%. The results also show that the hydrogen bond

**Table 3** Functional group bands of the Fourier-transform infrared spectroscopy spectra for 900-700 cm⁻¹ of WQ oil shale

| Peak no | Position, cm⁻¹ | Assignment | Area percentage, % |
|---------|----------------|------------|--------------------|
| 1 | 714.81 | (CH₃)ₙ, where n ≥ 4 | 3.65 |
| 2 | 731.56 | 4H | 18.60 |
| 3 | 763.07 | 4H | 41.69 |
| 4 | 785.64 | 3H | 28.86 |
| 5 | 801.11 | 3H | 7.20 |
WANG et Al. in Wangqing oil shale is mainly composed of OH‐O bond and OH‐OH bond. Similar results have been reported in a previous work.30

3.2 | 13C NMR analysis

The solid‐state 13C NMR spectrum can provide more details about the structure of carbon skeleton of Wangqing oil shale. Figure 3 shows the 13C-NMR spectrum of the sample. It can be seen that there are three main forms of carbon structure in the oil shale. These three forms are the aliphatic carbon (0‐90 ppm), aromatic carbon (90‐165 ppm), and carbonyl carbon (165‐220 ppm). Table 7 presents the chemical shifts of different carbon-bearing functional groups in Wangqing oil shale. According to the results presented in Table 7 and those reported in some previous studies,31,32 the 13C-NMR spectral curves of the samples were fitted to determine the relative proportions of different types of carbons in Wangqing oil shale. The fitting results are shown in Figure 4. Table 8 lists the parameters characterizing the structure of carbon skeleton of the oil shale.

Table 8 shows that aliphatic carbon accounts for 64.61 and is the largest component of the structure of carbon skeleton. The aliphatic groups in the samples mainly include chained alkanes and chained alkane substituents (long and short chains). The main function of chain alkanes is to connect the aromatic ring or make free macromolecules cross-link with each other. The data given in Table 7 show that, in the fatty carbon of organic matter of Wangqing oil shale sample, the content of methylene, methylene carbon, and aromatic ring within the range of 16‐36 ppm is higher, while the resonance signal within the range of 50‐90 ppm is weak. For example, the contents of all kinds of fatty alcohols and ethers are the lowest. The average length of the methylene chain (Cn) and degree of branching of alkane chain (BI) were used to characterize the aliphatic chain length and branching chain in oil shale. The degree of branching of alkane chain was low, which indicated that the structure of oil shale was dominated by alkanes and had less branching. This is consistent with the results obtained from FTIR analysis.

Aromatic carbon is another important component of the macromolecular structure of Wangqing oil shale, which is mainly formed by the linkage of aliphatic group and ether bridge, and contains four different types. These types are protonated aromatic carbon ($f^H_a$), bridged aromatic carbon ($f^B_a$), branched aromatic carbon ($f^S_a$), and oxygen-bonded...
The protonated aromatic carbon within the range of 100-129 ppm and the aromatic carbon in bridgehead within the range of 129-137 ppm are the most abundant. The ratio of bridged carbon to peri-cyclic carbon (Xb) and the aromatic ring substitution (δ) was used to characterize the degree of condensation of aromatic structure in oil shale. The ratio of aromatic carbon was not connected to hydrogen. The content of fatty carbon (64.61%) in the sample was higher than that of the aromatic carbon (31.12%), which means that 65 fatty carbon and 31 aromatic carbon were present per 100 carbon atoms, thus indicating that Wangqing oil shale has strong oil generating capability and higher volatile content.

As can be seen from Figures 4 and 7, there are four types of oxygen-carbon structure in Wangqing oil shale. These four types are oxygen-grafted methyl methylene and methylene carbon (50-75 ppm), intracyclic oxygen grafting fat carbon (75-90 ppm), carboxylic carbon (164-188 ppm), and carbonyl carbon (188-220 ppm). The 13C NMR and FTIR results showed good consistency with regard to the content of oxygen-containing functional groups. However, the contents of C-O and C-OH were higher, followed by C-O, O-C-O, or O = C-O. Most of the C-O and C-OH groups were bound to aliphatic carbon (such as, alkyl ether).

### 3.3 Pyrolysis and kinetic analysis

Wangqing oil shale was heated from 50°C to 900°C at four different heating rates. The TG and DTG curves of pyrolysis are shown in Figure 5. It is generally accepted that, during pyrolysis, some unstable semicoke intermediates and small molecular-weight gaseous products are produced due to the pyrolysis of polymer compounds in oil shale. When the temperature increases, these unstable intermediates will continue to undergo chemical reactions and produce intermediate transition products. After a series of chemical reactions, such as dehydrogenation and condensation of aromatic structures,

| Chemical shift | Major assignment                      | Characters | Mole percent |
|----------------|---------------------------------------|------------|-------------|
| 14~16          | Terminal methyl carbon                 | fa          | 5.59        |
| 16~22          | Methyl carbon on aromatic ring         | fa          | 25.07       |
| 22~36          | Methylene and methine carbon in aliphatic carbon | fa          | 25.80       |
| 36~50          | Carbon alpha bonded to aromatic ring, quaternary carbon | fa          | 5.73        |
| 50~55          | Methoxy carbon                         | fa          | 2.14        |
| 55~75          | o-substituted aliphatic carbon         | fa          | 0.10        |
| 75~90          | o-bonded carbon in aliphatic carbon    | fa          | 0.17        |
| 100~129        | Protonated aromatic carbon             | fa          | 9.88        |
| 129~137        | Bridgehead aromatic carbon             | fa          | 15.06       |
| 137~148        | Alkyl substituted aromatic carbon      | fa          | 2.80        |
| 148~164        | o-substituted aromatic carbon in phenols and ethers | fa          | 3.38        |
| 164~188        | Carbon in COOH(R)                      | fa          | 4.26        |
| 188~220        | Carbon in carbonyl group               | fa          | 0.02        |
TABLE 8 Carbon structural parameters of the oil shale sample

| Structural parameters | Symbol | Definition                                      | Value  |
|-----------------------|--------|------------------------------------------------|--------|
| Aliphaticity          | $f_{al}$ | $f_{al} = f_{al}^1 + f_{al}^2 + f_{al}^3 + f_{al}^4$ | 64.61  |
| Aromaticity           | $f_a$  | $f_a = f_a^H + f_a^B + f_a^S + f_a^O$             | 31.12  |
| Ratio of carbonyl carbon | $f_C$ | $f_C = f_C^1 + f_C^2$                              | 4.27   |
| Ratio of oxygen content | $f_O$ | $f_O = f_O^1 + f_O^2 + f_O^3 + f_O^4$             | 10.06  |
| Average methylene chain length | $C_n$ | $C_n = f_{al}^{2g}f_{al}^s$                       | 9.21   |
| Alkyl chain branching degree | $BI$  | $BI = (f_a^1 + f_a^4)/f_{al}$                      | 8.87   |
| Molar fraction of aromatic bridgehead carbon | $X_B$ | $X_B = f_B^1/f_a$                                 | 0.48   |
| Substitutive degree of aromatic ring | $\delta$ | $\delta = (f_a^2 + f_a^3)/f_a$                  | 0.20   |

these intermediates will eventually be converted to oil shale semicoke.33

Figure 5 shows the loss in mass at each stage. It can be seen that the TG curves at different heating rates are very similar to each other. The TG curves of each sample have four distinct descending stages, indicating that the pyrolysis of oil shale occurs in four steps. Furthermore, the whole pyrolysis process has good morphological characteristics. When the temperature is <400°C, the TG curve drops smoothly, and the weight loss of the sample becomes very small. In this stage, the mass loss is mainly due to the evaporation of water, the release of a small amount of adsorbed gas, and the decomposition of some organic matter having low bond energy. The decomposition and rearrangement of pyrolytic bitumen molecules, associated with the release of volatile substances in oil shale, are also accompanied by the pyrolysis of certain minerals, which represents the transition stage of pyrolysis.22

The main weightlessness occurred between the temperature range of 400-600°C. The results showed that the TG curve dropped sharply, whereas the DTG curve showed the maximum peak value. Additionally, the sample showed the highest weightlessness at all heating rates. The mass loss in this stage is due to the pyrolysis of bitumen in oil shale. The initial stage is the precipitation of volatile compounds, after which the long chain hydrocarbon compounds in the pyrolytic asphalt are cracked into small hydrocarbon molecules. It also includes the release of a large number of nonhydrocarbons, such as CO₂ and H₂O. In addition, the DTG curve of each sample has two peaks, indicating that the process is divided into two steps. Within the temperature range of second peak-peak value, new substances take part in the reaction. This means that the oil’s mother material first undergoes violent bridge breaking, condensation and cracking reactions, producing tar, and a mixture of tar and other products, such as gas, which result in the acceleration of the rate of reaction. The precipitation of gases increased significantly at this stage.34 The results for TG curve show that the samples at four heating rates will no longer lose weight when the temperature reaches 800°C. At this point, the pyrolysis process is over. The pyrolysis at this stage is mainly caused by the decomposition of carbonate minerals, such as calcite, dolomite, and iron ore.

Although the weight loss of samples at different heating rates is approximately the same, there is still a slight deviation between the curves, which is due to the effect of heating rate on pyrolysis. It can be seen from Figure 5 that, when the heating rate increases, the DTG curve of the whole pyrolysis reaction deviates slightly toward the high temperature side. This is due to the slow pyrolysis rate at the beginning of the process, and when the heating rate is low, all of the sample can be involved in the reaction. With the increase in temperature, the surface of the sample reacts completely, though the center of the sample does not have the opportunity of sufficient heating for pyrolysis. When the temperature increases too fast, the difference between the rates of heat transfer inside and outside the sample results in the sample being unevenly heated, due to which the sample cannot be completely pyrolyzed.35 This phenomenon is obvious in the third stage of pyrolysis. Therefore, the lower heating rate creates a better environment for complete pyrolysis of the sample, and that is why the mass loss rate is higher in this stage.

Figure 6 shows the relationship between ln $\beta$ and $1000/T$ and the distribution of activation energy with conversion using FWO method for four heating rates. The values of activation energy are presented in Table 9. According to the data, the activation energy of the sample is higher when the conversion rate is low, which may be due to the lower ignition point of the sample. It is necessary to provide sufficient heat for the subsequent reaction from initial temperature to ignition point. The average activation energy of the whole pyrolysis process is 254.13 kJ/mol.

3.4 Analysis of pyrolytic carbon monoxide

The structure of oil shale is complex, and a large number of gaseous products are produced during the pyrolysis. By combining the FTIR with TG techniques, gaseous products can be detected at the same time, which is helpful for further
understanding the pyrolysis mechanism of Wangqing oil shale. Considering the heating rate of 40°C/min as an example, Figure 7 shows the three-dimensional distribution curve of infrared spectrum of oil shale gas precipitation. According to the characteristic wave numbers of different gases in the spectrum, the absorption peak of CO is taken to be at 2090 cm⁻¹. The carbon monoxide emission curve is shown in Figure 8.

The structure of oil shale is complex, and a large number of gaseous products, such as CO, are produced during the pyrolysis. The formation of these pyrolytic products may be the result of several chemical reactions, and these reactions take place simultaneously within the same temperature range. Due to this reason, it is difficult to distinguish among these chemical reactions. Previous studies have shown that CO takes part in 3-5 reactions. For the gas release curve, each maximum value and each inflection point on the graph correspond to a separate reaction, and each reaction has its own specific kinetic parameters. Origin 9.0 software was used to simulate the formation of CO gas by introducing 3-3 reaction complex peaks by changing the peak position and amplitude. The effect of single component on the release of combustible gas was further studied. It is found that, when the number of CO peaks is 4, the curve fitting produces the best results. In fact, at this point, the fitting curve coincides with the original curve. The fitting results have further research value, and the processing results are shown in Figure 9. The contribution of each reaction type to the total amount of CH₄ and CO formed during pyrolysis can be expressed by the integration area of each peak (shown in Figure 9). Each peak represents a certain reaction type. The temperature ranges of different reactions are different. The activation energy of each peak is calculated based upon the C-R reaction model, as explained above.

It is found from the data that the activation energy of chemical reaction should be within the range of 40-400 kJ/mol, and only when the activation energy is higher than 100 kJ/mol, the system should be heated. According to the activation energy of the reaction, it is considered that all the four fitting peaks have the characteristics of chemical reactions. Therefore, the formation of pyrolytic carbon monoxide in the pyrolysis process of oil shale macromolecules is composed of four different reaction types. According to the results of ¹³C NMR and FTIR, the formation of CO is
due to the fracture of different oxygen-containing groups and the cleavage of side chains in oil shale, such as aryl methyl ether, diaryl ether, and heterocyclic oxygen-containing structure. Different functional groups require different energies for their dissociations, which results in different temperature ranges for the release of CO.

The first stage reaction mainly occurred at 67-400°C and had the peak value of 221°C. The activation energy of Reaction Type I is 109.56 kJ/mol, and its contribution to total carbon monoxide production, is 12.13%. According to the vibration intensity of different functional groups, the thermal stability can be determined. The aldehyde group is one of the most active functional groups. Therefore, the main reaction in this stage is the formation of some CO at lower temperature through the fracture of weak aldehyde group. The stage also includes the production of hydrogen radical, which plays an important role in the subsequent pyrolysis process.

The second stage reaction mainly occurred at 210-505°C and had the peak value of 341°C. The activation energy of Reaction Type II is 168.41 kJ/mol, and its contribution to total amount of carbon monoxide, is 17.63%. The reaction at this stage is mainly attributed to the decomposition of carbonyl groups in the oil shale, which is consistent with the results obtained from 13C NMR and FTIR analyses. In addition, the methoxy group in the sample can promote the production of CO in this range of temperature.

The third stage reaction mainly occurred at 513-682°C and had the peak value of 584°C. The activation energy of Reaction Type III is 212.75 kJ/mol, and the contribution to total carbon monoxide production, is only 9.05%. The amount of CO generated at this stage is the lowest. When the fracture of the bond bridge plays a leading role in the cross-linking reaction, the evaporation of the fraction will lead to the release of tar during the pyrolysis process. Some of the coagulable products remain in the pores of oil shale. When the production of tar stops, the decomposition of these oxygen-containing structures leads to a rapid release of CO at about 600°C.

The fourth stage reaction mainly occurred at 604-900°C and had the peak value of 787°C. The activation energy of Reaction Type IV is 280.51 kJ/mol, and its contribution to total amount of carbon monoxide, is 61.19%. The FTIR analysis shows that hydroxyl groups and ether are the main causes of high temperature CO release during the pyrolysis of Wangqing oil shale. The reaction of high bond energy hydroxyl groups, such as methyl, and methylene with phenolic oxygen generates part of the CO. The condensation reaction between the ether group and the phenolic hydroxyl group in residual carbon chain also produces part of the CO. Furthermore, CO can be released from the residual oxygen in new carbon chain at high temperature. In addition, the decomposition of heterocyclic oxygen-containing structures at high temperatures (>700°C) also contributes to the release of CO at this stage.
4 | CONCLUSIONS

In this paper, the structure of functional groups of Wangqing oil shale was analyzed using FTIR and $^{13}$C NMR analyses. The pyrolysis was carried out using TG–FTIR, and the kinetics parameters were determined. The carbon monoxide gas produced in the pyrolysis process was studied using peak fitting. The following conclusions were drawn.

1. The FTIR spectra of Wangqing oil shale were divided into four parts. The substituents of benzene ring are mainly di-substituted and trisubstituted. Oxygen is mainly in the form of alkyl ether and hydroxyl group. The majority of aliphatic groups contain methylene. Hydrogen bond is mainly composed of OHO bond and OOH bond.

2. The results of $^{13}$C-NMR and FTIR spectra show good consistency. There are three main forms of carbon structures in the oil shale, in which the content of aliphatic group is the highest, followed by the aromatic carbon, thus indicating that Wangqing oil shale has strong oil generating capability and high volatile content.

3. The TG-FTIR analysis shows that the pyrolysis process of oil shale can be divided into four stages. The main weight loss occurs between 400 and 600°C, which coincides with the main precipitation section of the gas. Furthermore, smaller the heating rate of pyrolysis, greater is the weight loss of the sample. Additionally, lower the conversion rate, higher is the activation energy.

4. The formation of carbon monoxide during pyrolysis is a combination of four different types of reactions. The four reactions were related to the fracture of functional groups, such as aldehyde group, carbonyl group, hydroxyl group, oxygen-containing structure, and ether bond in the oil shale structure. The fourth stage reaction contributed the most to total CO generation, whereas the third stage contributed the least.

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