ABSTRACT: Petroleum cokes with different chemical structures and oxygen-containing functional groups were obtained from two kinds of naphthenic- and paraffin-base crude oils by simulating an in situ combustion (ISC) process with the same reaction atmosphere and different reaction temperatures. $^{13}$C wide-cavity solid-state nuclear magnetic resonance ($^{13}$C NMR) spectroscopy was used to identify and investigate the oxygen-containing functional groups of petroleum cokes obtained under different compositions and reaction temperatures. This study demonstrated that with the increase of coking temperature, the content of alkyl side chain and active oxygen-containing functional groups in naphthenic-base crude coke decreased obviously, while the content of aromatic carbon increased. The $^{13}$C NMR analysis of the two kinds of petroleum cokes obtained at 500 °C further revealed that the paraffin-base petroleum coke retained a high content of oxygen- and nitrogen-rich functional groups, while the naphthenic-base petroleum coke had a lower amount of carbonyl groups and oxygen-containing functional groups.

1. INTRODUCTION

In situ combustion (ISC) is a quite promising, green, and economical thermal enhanced oil recovery (EOR) technique in which energy is generated by a combustion front that is propagated along the reservoir, and it is suitable for the development of unconventional heavy crude oil reservoirs. $^{2-4}$

ISC mainly refers to injecting air or any gas containing oxygen into the reservoir and igniting the oil reservoir under high temperature, using petroleum coke deposited by oxidation cracking of crude oil as fuel to maintain the combustion front, where the combined action of heat and flue gas would induce an oil displacement and enhanced oil recovery, facilitating the movement of the oil flow toward the production well along with in situ-generated heat energy, CO$_2$ mixed with injected N$_2$, evaporation of light oil fractions, etc. $^{5,6}$ In the combustion zone, coke is an important intermediate fuel and is the main energy source for thermal cracking and for maintaining stable combustion in the process of in situ combustion, and the stable combustion of coke is required for the stable advancement of the ISC leading edge, formation of which is one of the key factors that determine the economy, feasibility, and applicability of the ISC project. $^{7,8}$ Therefore, regulating coke formation and controlling the reaction is key for the success of ISC projects. Coke is formed during the combustion stage both in the low-temperature oxidation (LTO) and the high-temperature oxidation (HTO) reactions. $^{9}$ The LTO reaction is significant because of its lower reaction temperature region than 380 °C from the combustion front; it has been considered as one of the main mechanisms for controlling fuel supply in the process of in situ combustion and has received much attention over the years. $^{7,10-15}$ In addition, the HTO reaction of coke is also considered to be the main stage of significant oxygen consumption, which also provides the main source of heat generation in oil displacement and facilitates the production of carbon monoxide, carbon dioxide, and water. $^{3,16}$ Thus, it is equally necessary to gain insights into the preparation and characterization of coke which is stimulated by HTO. It is known that the macromolecular structure and the activity of various organic functional groups of coke formed in crude oil at different oxidation temperatures determine the different reactions in the conversion process. $^{17}$

The oxygen in coke is mainly present in the form of a carboxyl group, hydroxyl group, carbonyl group, and active ether bond or non-active ether bond, which are typically determined by $^{13}$C wide-cavity solid-state NMR. $^{18,19}$ As a nondestructive method for the determination of carbon atoms, $^{13}$C solid-state NMR with a high resolution can perfectly analyze the
distribution state of carbon atoms, providing a possibility for a study on the state of oxygen connected to the carbon atoms, and this method can be applied to the characterization of coke to obtain more information, which is of great significance.

In this study, the naphthenic-base crude oil from Xinjiang oilfield (date of sampling: October 2018, viscosity at 50 °C: 1440 mPa·s⁻¹, composition and fraction are provided in Table 1) was used as the raw material to prepare different petroleum cokes under the same reaction atmosphere at different reaction temperatures. Then, the high-temperature coke was compared with the Changqing paraffin-base crude oil (date of sampling: October 2018, viscosity at 50 °C: 383 mPa·s⁻¹, composition and fraction are provided in Table 1) high-temperature coke. The differences in oxygen-containing functional groups of as-prepared petroleum cokes were further evaluated by ¹³C solid-state NMR; the distribution range of carbon atoms, the structural state of oxygen linked to carbon atoms, and the type of oxygen-containing functional group were studied in detail. Meanwhile, the effects of oxidation reaction temperature and crude oil structure types on the occurrence model and distribution pattern of oxygen-containing functional groups in the obtained coke were further investigated.

2. EXPERIMENTAL SECTION

2.1. Analysis of Crude Oil. A certain amount of crude oil was dissolved in n-hexane and centrifuged at a high speed for a few minutes; then, 20 μL of the supernatant was collected for further use. Its alkane component types and molecular weight distribution were analyzed by gas chromatography-mass spectroscopy (GC-MS) and high-performance liquid chromatography-mass spectroscopy (HPLC-MS) instruments successively.

2.2. Preparation, Separation, and Purification of Coke. The petroleum coke was prepared by simulation of the ISC oxidation process in a kettle reactor. Thirty grams of crude oil was placed at the bottom of the reactor, and then a gas mixture containing 5% O₂, 79% N₂, and 16% CO₂ was introduced into the reactor at the rate of 50−100 mL min⁻¹. The internal pressure of the reactor was set at 0.1 MPa with continuous stirring. The heating rate of the coking reaction was 3 K min⁻¹, and the heating was discontinued at 350 and 500 °C keeping for 40 min. When the reaction mixture was cooled to room temperature, solid samples were obtained.

Five grams of each of the above-collected samples were ground and crushed and then refluxed with 100 mL of hexane. When the solution was cooled to room temperature, solid−liquid separation was carried out and the separated solids were thermally extracted using hexane three times. The solid samples of petroleum coke were extracted with 100 mL of chloroform at 25 °C for 5 h; this process was repeated three

| oil sample | saturated | aromatic | resins | asphaltenes |
|------------|-----------|----------|--------|-------------|
| Xinjiang oil | 51.88  | 13.54 | 32.67 | 1.91 |
| Changqing oil | 65.10 | 11.55 | 21.23 | 2.13 |

Figure 1. GC total ion flow and HPLC-MS molecular weight distribution of alkane components in the two crude oils ((a, c) naphthenic-base crude oil and (b, d) paraffin-base crude oil).
times. The separated solids were then extracted with 100 mL of trichloroethylene for 5 h, and the operation was also repeated three times. Finally, the petroleum coke was obtained by centrifugation and vacuum drying at 60 °C.

2.3. Characterization. A 13C solid-state NMR carbon spectroscopy (Avance III 400 MHz, Bruker Technologies Ltd.) instrument was used to measure the characteristics of the purified petroleum coke. Fourier transform infrared (FTIR) spectra were analyzed using Fourier transform infrared spectrometer (VERTEX 70, Bruker Technologies Ltd.).

3. RESULTS AND DISCUSSION

3.1. Elements of Alkane Carbon Type of Crude Oil and Petroleum Coke. Crude oil can be divided into two main types, naphthenic-base and paraffin-base, the former contains a large number of naphthenic and aromatic hydrocarbons, and the latter is mainly composed of straight and branched aliphatic chains in the form of alkylbenzenes.

The difference in alkyl carbon structures between naphthenic-base and paraffin-base crude oils led to the difference in coking rate and oxygen-containing functional groups. Two different types of crude oils from Xinjiang oil (naphthenic-base) and Changqing oil (paraffin-base) were used as samples for coke in the simulated ISC process. Their composition changes in the two oil samples were investigated through the SARA fractionation process as shown in Table 1. The SARA method adopted is improved and established based on “SY/T 5119-2016 analysis of soluble organic matter in rocks and group composition of crude oil.” Reagents and materials: n-hexane (analytically pure); dichloromethane (analytically pure); methanol (analytically pure); silica (200–300 mesh); glass column (diameter 80 mm, length 1500 mm); glass bottles; distilled water, etc. The steps are as follows: (1) Take 2000 g of silica, soak in hydrochloric acid for 24 h, wash with distilled water until neutral, dry and activate in an oven at 140 °C, and use after cooling. (2) Take 200 g of crude oil, add 10 times of n-hexane (2000 mL), fully mix, and then allow the reaction mixture to stand. After the asphaltene are completely precipitated, filter and volatilize the solvent to get the dry asphaltene and weigh. The filtrate is recovered and evaporated to get deasphalting oil. (3) Take the treated silica and put it into a column by the wet method. Weigh 30 g of the oil sample according to the ratio of a silica/oil sample of about 60/1, add 1 time of n-hexane to dilute, and then load the sample.

According to the results of liquid chromatography, judge the time for changing the solvent. First, wash with n-hexane until the alkane components are washed away, then wash the aromatic components with dichloromethane, and finally wash the non-hydrocarbon components with methanol. (4) Distill the obtained eluent to remove the solvent, volatilize the n-hexane solution to obtain the alkane component, volatilize the dichloromethane solution to obtain the aromatic component, and volatilize the methanol solution to obtain the non-hydrocarbon component. The SARA fractions (wt %) of Xinjiang oil were 51.88, 13.54, 32.67, and 1.91, while the SARA fractions (wt %) of Changqing oil were 65.10, 11.55, 21.23, and 2.13. The two types of crude oils were similar in the aspects of aromatic and asphaltene contents, while their saturation degrees and resin contents varied greatly. These differences may lead to the formation of different structures of coke during oxygenation.

The molecular weight distribution and alkyl carbon types of the crude oils were analyzed by LC-MS and GC-MS. According to the GC-MS spectra in Figure 1a,b, it can be inferred that the alkane fraction of Xinjiang crude oil was mainly composed of various types of substances with a cyclic alkane structure (Figure 1a), while the alkane fraction of Changqing oilfield crude oil was mainly composed of straight alkyl chains and their branched isomers (Figure 1b). There were significant differences in the structural composition between the two types of crude oils. From the HPLC-MS study, it can be concluded that the average molecular weight of Xinjiang crude oil was 600, and that of its Changqing counterpart was 617, and they both had a molecular weight distribution of the primary substance in the range of 250–1050 (Figure 1c,d).

The hydrogen, carbon, and oxygen contents of the petroleum coke which was prepared from naphthenic-base crude oil at 500 and 350 °C were further measured. The hydrogen (7.238%) and oxygen (6.875%) contents of the petroleum coke using naphthenic-base crude oil prepared at 350 °C were significantly higher than those prepared at 500 °C (hydrogen: 3.280%, oxygen: 2.749%), while the carbon content is lower than that of petroleum coke prepared at 500 °C, thus indicating that the carbon-to-hydrogen ratio increased and the oxygen-to-carbon ratio decreased as the reaction temperature increased. The phenomenon also suggests that the cracking dehydrogenation reaction was
intensified, while the reactive oxygen functional group may have undergone thermal decomposition or converted to a stable oxygen-containing functional group, resulting in a lower oxygen content. The elemental content of petroleum coke obtained from paraffin-base crude oil prepared at 500 °C was 91.023, 3.084, and 2.985% for carbon, hydrogen, and oxygen, respectively.

By comparing the elemental content of petroleum coke obtained from the crude oils of different origins, it can be inferred that the cracking dehydrogenation reaction of crude oil and the thermal decomposition reaction of reactive oxygen functional groups were highly dependent on the reaction temperature.

Fourier transform infrared spectroscopy (FTIR) was further carried out to characterize the chemical bonds of petroleum cokes at 350 and 500 °C as shown in Figure 2. Some characteristic peaks emerged at about 3400 cm⁻¹ for the two samples, which can be attributed to intermolecular hydrogen bonding or association peak of π−π conjugation; it can be observed obviously that the intensity of paraffin-base petroleum coke at about 732 cm⁻¹ is significantly higher than that of naphthenic-base petroleum coke at 500 °C, thus revealing the existence of (CH₂)n−. It can be inferred that n = 2 in naphthenic-base petroleum coke, while n is greater than 4 in paraffin-base petroleum coke. Other peaks emerged at about 2925.5, 2875.95, 1370.29, 3040.72, 1940.09, and 1596.35 cm⁻¹, which corresponded to the C−H stretching vibration, symmetrical deformation vibration peak of CH₃, stretching vibration peak of 〓C−H, strong stretching vibration peak in C〓C〓C propadiene, and stretching vibration peak of the benzene ring skeleton, respectively. By comparing the infrared spectra of petroleum cokes at 350 and 500 °C, we found that their infrared spectra were similar, which indicated that the surface structure of coke at different temperatures was similar but only the abundance of functional groups was different. The biggest difference was the peak of the alkyl crown group at 2925.5 and 2857.95 cm⁻¹, which decreased obviously with the increase in carbonization temperature. This shows that the alkyl content of petroleum cokes at 350 °C is much higher than that at 500 °C. Comparing the infrared spectra of two different types of alkane carbon crude oils for the preparation of petroleum coke, it can be established that the coke prepared from naphthenic-base crude oil is basically similar to that prepared using paraffin-base crude oil and that the infrared spectra structure of petroleum coke is basically similar under the same gas atmosphere and the same temperature. This can further prove that the alkane type of crude oil is not a key factor in determining the structure of coke produced, and similar coke reactions have been carried out at high temperatures. However, there are significant differences in coke yield mentioned above, which may be related to the differences in the SARA fraction.

3.2. Analysis of 13C NMR Spectra and Carbon Functional Groups. Carbon is the most fundamental element in organic compounds, whose structure of the molecular skeleton can be obtained by fractional peak analysis. This method was widely used in the determination of the molecular structure of organic compounds, reaction mechanisms, isomer discrimination, macromolecules, and other research. This method has become an indispensable analytical tool in chemistry and other related fields.

1H NMR chemical shifts usually have a narrow range of δ = 0−15 ppm, whereas 13C NMR chemical shifts can range from 0 to 300 ppm, resulting in a higher resolution of 13C spectra than for 1H NMR.24 Besides, 13C NMR spectra can give characteristic absorption peaks of similar functional groups; thus, the information on the molecular skeleton structure can be deduced. A saturated hydrocarbon carbon atom, olefin carbon atom, alkyne carbon atom, and carbonyl carbon atom have different chemical shift δ values due to the different shielding effects of carbon atoms in compounds in a different environment. This can provide more evidence on the state of hybrid orbitals, the induced and conjugated effects of substituent groups, and the stereoscopic structure of molecules to determine which are the main factors affecting the chemical shifts of carbon atoms.

The carbonyl group does not have a corresponding signal in the 1H NMR spectrum but does have a corresponding characteristic absorption peak in the 13C NMR spectrum. The π bond of C=O in carbonyl compounds is easy to polarize so that the density of the electron cloud on the carbonyl carbon atom becomes smaller, and the chemical shift value tends to be lower than that of olefin, which is generally in the range of 160−220 ppm. Petroleum coke carbon spectra were resolved by splitting the peaks using Peak-Fit software.28

3.3. Analysis of 13C NMR Spectra of Petroleum Coke of the Same Alkane Carbon Type Prepared at Different Temperatures. Xinjiang naphthenic-base crude oil was selected to prepare petroleum coke at 350 and 500 °C. The obtained petroleum coke was washed with n-heptane, chloro-
The signals \( \delta \) of chemical shifts \( \delta \) of various carbon types were analyzed in the NMR spectra. Peaks with chemical shifts \( \delta \) of 20.4, 29, and 37.8, which correspond to alkane secondary carbon, alkane tertiary carbon, and alkane quaternary carbon, respectively. The peaks with chemical shifts \( \delta \) of 100–155 ppm can be divided into five peaks with chemical shifts \( \delta \) of 111.9, 121, 128, 138.4, and 150.1 ppm, respectively. These peaks correspond to the carbon on the benzene ring skeleton, bridgehead carbon of aromatic hydrocarbons, carbon of the substituted aryl group, and carbon of aliphatic–aromatic ethers. Peaks with chemical shifts greater than 200 ppm can be split into triple peaks (chemical shifts \( \delta \) of 221.9, 228.5, and 239), which correspond to the carbon of the substituted aryl group, and carbon of the cycloalkanone carbonyl group, carbon of the carbon–sulfur double bond, and sp\(^2\) hybrid carbocation, respectively.

As shown in Figure 3b, the \(^{13}\)C NMR spectrum of petroleum coke obtained at the lower temperature of 350 °C with chemical shifts \( \delta \) ranging from 0 to 75 ppm can be divided into multiple peaks. The chemical shifts \( \delta \) of 14.7, 22.7, 30.6, 37.9, 44.2, 50.5, and 57.5 ppm were attributed to the carbon of aliphatic methyl, aromatic substituted methyl, methylene, aliphatic tertiary, amine, and aliphatic ether, respectively. By comparing the properties of petroleum coke prepared at two different temperatures, it was found that when the same sp\(^3\) hybridization was present, the coke generated at 350 °C had a higher proportion of aliphatic carbons. When the coking temperature was 500 °C, the hydroxy-carbon and fatty ether carbon–oxygen bonds present in the 350 °C coke would break to generate a more stable carbon–carbon bond coke. The peaks with chemical shifts \( \delta \) in the range of 100–175 ppm can be divided into seven peaks. Chemical shifts \( \delta \) of 111.5, 118.8, 124.1, 129.1, 135.1, 141.0, and 148.0 ppm were attributed to the skeletal carbon atoms of aromatic rings, aromatic heterocyclic carbon atoms, and carbon atoms of aromatic rings with a substituent, respectively. Peaks with chemical shifts greater than 175 ppm can be divided into five peaks of 194.4, 201.1, 207.4, 213.0, and 219.3, which were mainly attributed to ketone carbonyl carbon atoms of different structures, such as aromatic ketones and cycloalkyl ketones.

It can be concluded that with the increase in temperature, the peak area at 10–75 ppm decreases obviously, while the peak area in the range of 100–175 ppm increases obviously, thus indicating that as the temperature increases, the sp\(^3\) hybrid saturated aliphatic carbon content of the petroleum coke obtained at a high temperature decreases significantly. In contrast, the sp\(^2\) hybrid aromatic hydrocarbon carbon content increases. The carbon content of saturated aliphatic hydrocarbons in petroleum coke also decreases in the context of increased aromatic carbons atoms, which can be ascribed to the fact that dehydrogenation of saturated alkanes occurs at a certain temperature to generate cycloalkanes and olefins, as well as the dehydrogenation and condensation of cycloalkane into aromatic substances, thus increasing the content of unsaturated carbon of sp\(^2\) hybridization. On the other hand, the cleavage of the side chains of saturated alkanes continues in low-temperature coke as the coking temperature increases, mainly resulting in a significant increase in the aromatic peak area of the coke skeleton.

The oxygen-containing functional groups connected with a carbon atom in petroleum coke will disappear or transform into oxygen-containing functional groups of low activity with the increase of reaction temperature. The oxygen-containing functional groups in petroleum coke obtained at 350 °C mainly include alkyl–alkyl ether groups with chemical shifts \( \delta \) of 50–59 ppm, aliphatic–aromatic ether groups with chemical shifts \( \delta \) of 150 ppm, and a small number of carboxylate groups with chemical shifts \( \delta \) of 164 ppm. When the reaction temperature was increased to 500 °C, the three oxygen-containing functional groups in the resulting petroleum coke decreased significantly. However, the content of carbonyl ketone-type carbon with a chemical shift at 220 ppm increased substantially. It can be concluded that as the reaction temperature increased, the content of reactive oxygen-containing functional groups in petroleum coke decreased, while the content of nonreactive oxygen functional groups increased.

### 3.4. Analysis of \(^{13}\)C NMR Spectra of Petroleum Coke with Different Alkane Carbon Types Prepared at the Same Reaction Temperature

Both cokes obtained at 500 °C were subjected to \(^{13}\)C NMR analysis. The spectrum of the naphthenic-base crude oil petroleum coke is shown in Figure 4a, and the NMR carbon spectrum of the paraflin-base crude oil petroleum coke is shown in Figure 4b.
The $^{13}$C NMR spectrum of petroleum coke prepared from paraffin-base crude oil showed that there were two distinct independent split peaks appearing between 10 and 75 ppm with chemical shifts $\delta$ of 20.7, 37.9, 47.9, and 57.5 ppm, which were attributed to alkane secondary and alkane quaternary carbons of sp$^3$ heteroatoms, respectively. The chemical shift $\delta$ of paraffin-base petroleum coke at 40–90 ppm indicated saturated alkane carbons with O and N heteroatoms. It also contained an amino-adjacent carbon and a fatty ether carbon, which were absent in naphthenic-base petroleum coke. Its peaks with chemical shifts $\delta$ between 100 and 150 ppm can be divided into four peaks ($\delta = 110.8, 120.8, 128.1,$ and 138.1), which are attributed to the carbon of the benzene ring skeleton, bridgehead aromatic hydrocarbon, and the substituted alkyl group on the aryl group and the missing carbon of the aliphatic–aromatic ether. The peaks with chemical shifts $\delta$ greater than 200 ppm can be split into triple peaks ($\delta = 200.1, 208.0,$ and 217.3), which are attributed to quinone carbonyl, aromatic ketone carbonyl, and alkyl-substituted aliphatic ketone carbonyl carbons, respectively. A comparison of the carbon spectra of the naphthenic- and paraffin-base coke prepared at 500 °C showed that the paraffin-base crude oil retained a high content of oxygen and nitrogen heteroatom functional groups in the three regions of the carbon spectrum. Combined with the molecular structure characteristics of naphthenic-base crude oil, a small number of aliphatic–aromatic ether functional groups (which may be formed due to the condensation of aromatic phenols with fatty alcohols at high temperatures) were present in naphthenic-base high-temperature petroleum coke. When the chemical shift was in the range of over 200 ppm, the chemical shift of naphthenic-base petroleum coke was higher than that of paraffin-base petroleum coke, and it mainly displayed different forms of carbonyl carbon functional groups at this position.

4. CONCLUSIONS
In this study, the $^{13}$C NMR spectra of petroleum cokes prepared at different coking temperatures with the same alkane carbon type crude oil were investigated. Meanwhile, the NMR carbon spectra and FTIR of petroleum coke prepared at the same coking temperature using different alkane carbon types were also investigated. With the increase in coking temperature, the high-field chemical shift peak area of carbon atoms decreased, and the carbon content of sp$^3$ hybridized saturated aliphatic hydrocarbons in naphthenic-base petroleum coke also decreased significantly, but the carbon content of sp$^2$ hybridized aromatic hydrocarbons increased. This phenomenon indicated that the increase of coking temperature was conducive to the cleavage of alkane side chains of coke molecules or dehydrogenation to ring aromatization. Also, with the increase in the reaction temperature, the content of active oxygen functional groups in naphthenic-base petroleum coke decreased, while the content of inactive oxygen functional groups increased. Comparing the petroleum coke prepared from two different alkane carbon type crude oils at the same temperature, it was further revealed that the paraffin-base petroleum coke retained more oxygen and nitrogen atom functional groups than the naphthenic-base petroleum coke, and the carbon atom structure of low-field chemical shift is also different. These findings also provide a possible basis for further studies on the properties and structures of cokes of different sources in the process of ISC.

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