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# Chemical-structural properties of the coke produced by low temperature oxidation reactions during crude oil in-situ combustion



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#### HIGHLIGHTS

• A novel experimental method was proposed to prepare the crude oil LTO coke.

- The coke properties were studied using EDS, FTIR, Raman, XRD and HRTEM.
- Coke properties were analyzed to study the changes in the coke amount and reactivity.

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## ABSTRACT

Chemical-structural properties of the coke produced by crude oil low temperature oxidation (LTO) reactions during in-situ combustion are still highly lacking due to the difficulty in coked sand characterization. This study proposed an experimental methodology to prepare the useful LTO coke with the chemical-structural properties studied using a combination of Energy-dispersive X-ray spectroscopy, attenuated total reflection Fourier transform infrared spectroscopy, Raman spectroscopy, X-ray diffraction (XRD) and high resolution transmission electron microscopy (HRTEM) techniques. The XRD and the HRTEM analyses showed the LTO coke mainly consisted of highly disorder amorphous structures with limited amount of poorly order 'onion-like' structures. The LTO coke was found to contain numerous oxygen functionalities and highly-substituted aromatic rings. The concentration of the carbonyl showed no significant decline with the LTO temperature increasing to 310 °C. Nevertheless, the carbon structure with sp<sup>3</sup>-rich characteristics was found to selectively consumed by O<sub>2</sub> to reduce the amount of coke deposition, and enriched the aromatic layer systems as inferred by Raman and FTIR analyses. There was a good agreement between the amount of the 'onion-like' structures viewed from HRTEM and the changes in the ether bridging groups. Additionally, the changes in the coke chemical-structural properties agreed with the measured coke reactivity by Thermogravimetric analyses.

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## 1. Introduction

In-situ combustion (ISC) is an enhanced oil recovery technique used to exploit unconventional heavy crude oil resources [1,2]. The released reaction energy that is directly generated by burning of

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the solid residue at the combustion front to heat the reservoir [1]. The combustion gas, produced steam and hot water then jointly drive the heated oil towards the production wells [3]. The solid coke residue on the sand grain surface is the main fuel consumed in the oil reservoir. The coke oxidation reactivity is regarded as an important diagnostic parameter in the laboratory to judge whether a crude oil reservoir is suitable for ISC recovery [4,5].

In ISC, the coke is identified as substance that is insoluble in toluene after all the saturate, aromatic, resin and asphaltene (SARA) fractions in the crude oil have dissolved [6]. Coke has been found to be main product of two kinds of reactions, low temperature oxidation (LTO) and pyrolysis of crude oil at the

Abbreviations: ISC, in-situ combustion; LTO, low temperature oxidation; SARA, saturate, aromatic, resin and asphaltene; EDS, Energy-dispersive X-ray spectroscopy; MRS, microscopic Raman spectroscopy; ATR-FTIR, attenuated total reflection Fourier transform infrared spectroscopy; XRD, X-ray diffraction; HRTEM, high resolution transmission electron microscopy; TGA, thermogravimetry analysis.

reservoir conditions [7]. LTO reactions were significant in reservoirs due to air channeling into zones with temperatures lower than 300 °C from the combustion front [7,8]. The LTO reactions are gas-liquid heterogeneous reactions where the oxygen permeates into the porous medium and then diffuses to liquid oil interfaces. The high specific area of the porous medium facilitates the heterogeneous LTO reactions on the micro-level thick oil films, which are coated on the oil-wet sand surface as shown in Fig. 1. Indeed, the crude oil property and reaction conditions during ISC coke formation are significantly different from the coal and biomass chars. The surface chemistry and structural property differences among the coke, coal chars and biomass char are still significant open questions due to dramatically different formation processes [9,10]. However, comparably little attention has been paid to the chemical-structural properties of the coke during ISC.

The coke kinetics is very important in the ISC reservoir simulation, which is necessary parameter in the reservoir simulation. Fundamental analyses of the coke chemical-structural properties are highly required to understand the different coke oxidation behaviors. Zhang [11] experimentally verified that the oxidation rate at 350 °C of the two kinds of coked sand samples were at least two orders of magnitude different, with those produced by LTO reactions being more reactive. Dabbous et al. [8] described that the coke properties were altered by the oil LTO reactions with changes in the hydrogen content, color and odor, compared with those by pyrolysis reactions. Cinar et al. [4] acquired highresolution X-ray photoelectron spectroscopy C 1s spectra of the two coked sand samples. The results showed that the coke derived from the LTO reactions had more carboxyl and hydroxyl groups. However, little is known about the crystalline or amorphous structure of the LTO coke. Furthermore, the evolution of the LTO coke chemical-structural properties with the increasing LTO temperature is unclear although the effect of LTO temperature on the amount of the coke formation has been reported [12]. More new knowledge of the coke characteristic helps us effectively take advantage of the previous knowledge about the relationships between the chemical-structural characteristics and the oxidation kinetics to evaluate the reasonability of the experimental kinetics data, and even to predict the oxidation reactivity qualitatively and quantitatively.

An important technique challenge is to artificially simulate coke formation similar to ISC and then to acquire useful coke samples for chemical-structural characterization. To the best of



Fig. 1. Schematic representation of the heterogeneous LTO reactions during ISC.

the knowledge, the chemical-structural property analyses for the LTO coke are very lacking due to the difficulty in characterization of the coked sand. Xu et al. [12] produced the coked sand from the oil sand under reservoir reaction conditions. The scanning electron microscopy image of the coked sand showed the coke coated on the sand surface with the other in pores and in pore bridges [12]. Since the coke distributed heterogeneously with very low concentration and the major material in the coked sand is the sandstone or the glass bead, FITR could not directly characterize such coke without regard to the effects on the irregular morphology and the sand composition [4]. Zhang [11] also showed the quality of the IR spectrum was bad with the significant baseline shift and weak effective signals for the coked sand. Furthermore, reasonable amount of coke cannot be collected from the coked sand to be characterized without any property destruction. Therefore, the coke in the coked sand have been demonstrated as inefficient experimental samples for many advanced characterization techniques. More attention should be paid to solve this problem.

In the present study, an experimental apparatus was constructed to physically simulate the coke formation with crude oil ISC conditions. Micron-level thick crude oil films were coated on single-crystal silicon wafers by a spin coater to simulate the oil films on the sand surfaces in the oil sand. The thin oil films kept great gas-liquid interfaces for LTO reactions to produce the coke. The experimental methodology for the sample preparation was similar to previous studies of nucleation, growth and arrangement characteristics of solid products on reactant surfaces during gassolid reactions [13,14]. The simplification focused on the product properties solely affected by the heterogeneous reactions. What should be pointed out was that such coke formation technique provided an opportunity to characterize the coke deposited on the uniform Si substrates with various analytical methods, instead of the irregular coked sand. The present study combined the Energy-dispersive X-ray spectroscopy (EDS), attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR), Raman spectroscopy, X-ray diffraction (XRD) and high resolution transmission electron microscopy (HRTEM) techniques to analyze the coke chemical-structural properties. In addition, Thermogravimetric analysis (TGA) was used to determine the amount and the oxidation reactivity of the coke produced at different LTO temperatures. The coke chemical and structural properties were detailed analyzed to study the evolution of the coke amount and its oxidation behavior.

## 2. Material and methods

## 2.1. Crude oil films preparations

The crude oil used in the study from the Xinjiang reservoir had a density of 0.94 g·cm<sup>-3</sup> at 20 °C and a viscosity of 2339 mPa·s at 50 °C. The SARA fractions were measured as described elsewhere [12]. Polished single-crystal Si  $\langle 100 \rangle$  wafers of 5 mm diameter by 1 mm thick were employed as the inert substrates for the samples. A high-speed spin coater was used to spread the thin crude oil films on the Si wafers as illustrated in Fig. 2. About 8 µm thick oil films could be achieved at a speed of 6500 rpm for 150 s. The as obtained samples were used as the samples for the LTO reactions.

#### 2.2. Experimental apparatus

A schematic diagram of the experimental apparatus used for the coke formation is shown in Fig. 3. The reactor consisted of upper and lower parts with the experimental samples fixed between the parts. The upper and lower parts were composed of 2520



Fig. 2. Schematic illustration of the experimental samples prepared by the spin coater.

stainless-steel tubes with 2520 stainless-steel powders sintering inside as the porous medium. The powders were sintered at 1400 °C in vacuum environment to cement the powders and the reactor internal faces to achieve the surface touch between them. The porous medium of the upper part was used as a gas distributor to efficiently preheat the injected air and stabilize the flow. The sintered powder effect on gas flow and temperature has also been verified by CFD simulation. According to the reactor design, the injected air can quickly reach the set LTO reaction temperature and uniformly permeate through the upper porous medium. As in ISC, the oxygen diffused to the oil surface and finally participated in the LTO reactions to produce the coke on the Si substrates. The coke products were used in chemical-structural characterization and Thermogravimetric analysis.

#### 2.3. Experimental procedures

The experiments started with the crude oil film preparation. followed by the sample transference to the reactor. After all the connections and sensors were hooked up, the reactor was checked for leaks by pressurizing to the experimental pressure of 5.0 MPa with the air. The experimental pressure was used to simulate Xinjiang Reservoir pressure. The air was then injected into the reactor at a rate of 50 mL/min controlled by a Brooks SLA5850S mass flow meter and the furnace started to work. The air flowed to the oil film surface and finally participated in the LTO reactions with the crude oil to produce the coke on the Si substrate. During the LTO reactions, the furnace firstly provided a ramped temperature heating rate of 3 °C/min and then kept the reactor at the desired LTO temperature for 5 h. 5 h reaction time have been demonstrated to achieve great coke formation [12]. Once the required reaction time was reached, the heating was stopped and the reactor was immediately cooled to ambient temperature. The produced samples were collected in centrifuge tubes and soaked in toluene for 10 h at 60 °C. The toluene dissolved the SARA fractions but retained the coke residues on the substrates. The filtrate was then removed after soaking and the samples were vacuum dried for 10 h to remove the residual toluene. Finally, the coke samples were preserved in a vacuum container for further characterization.

A series of samples were produced at 225 °C, 250 °C, 280 °C and 310 °C in air as the LTO coke, as well as produced at 450 °C in N<sub>2</sub> as the pyrolysis coke. The previous study [12,15] found the critical temperature for coke formation in LTO runs was about 200 °C. Furthermore, temperatures higher than 310 °C would result in distinct coke consumption with the oxygen and lead to little coke deposition [12,15]. Therefore, the temperatures for the LTO runs were set between 225 °C and 310 °C.



#### 2.4. Sample characterization

ISM-7001F SEM-EDS instrument was used to analyze the element compositions in the coke samples. The ATR-FTIR spectra of the coke samples were acquired using a PerkinElmer Spotlight 400 FTIR spectrometer at a spectral resolution of  $2 \text{ cm}^{-1}$  for frequencies of 4000–650 cm<sup>-1</sup> with 32 scans per wavelength. 50 nm Au films were deposited on the Si wafers by ion sputtering for the samples to be used for the ATR-FTIR characterization. The Au films help suppress interference by the Si wafers of the infrared rays to improve the ATR-FTIR signal-noise ratio. Raman spectra between 800 and 1800 cm<sup>-1</sup> Raman shift were recorded with a resolution of  $1.0 \text{ cm}^{-1}$  using a LabRAM HR800 spectrometer with a 325 nm ultraviolet laser as the incident excitation light source. The 325 nm ultraviolet laser was used to reduce the great fluorescence background for the coke samples. The original laser power of 34.1 mW was reduced to 10% to inhibit the coke degradation by the laser irradiation. The crystal structure of the coke sample deposited on the Si wafers was analyzed using the grazing incidence XRD method using CuK $\alpha$  radiation with a 2° glancing angle on a Rigaku D/max-2500/PC system. TG experiments were performed using TA/TGA Q500 with the precision of 0.1 µg. As to the HRTEM characterization, the thin specimens were firstly prepared by embedding scraped coke powder samples into epoxy resins. Once the resins had hardened, the resin was sliced into thin sample with average thicknesses of 70 nm with a Leca EM FC7 ultra microtome. The HRTEM images were eventually taken using a 200 kV JEOL JEM 2010F with a nominal resolution of 0.23 nm.

Raman and ATR analyses were repeated with at least 3 sets of coke samples at each LTO temperature. Actually, Raman scanning was again repeated at different locations in each coke sample due to the micrometer size of light spot. Boxplot was used to visualize the statistical distribution of Raman and ATR data. Student's T-tests were also used to help statically evaluate the difference between two data sets.

Furthermore, all the characterization methods except for HRTEM did not need any complicated sample preparations. The samples can be reused in some characterization methods if in the right order, such as ATR-FTIR and then EDS. This study showed such coke formation and characterization technique was easy, quick and controlled.

## 3. Results

#### 3.1. Surface morphology

The 3-dimension surface morphology of the coke samples deposited on the Si substrate was imaged with a Talysurf 5P-120 topographer, as shown in Fig. 4. The surface was enough uniform with less than 300 nm roughness for GIXRD, ATR and Raman characterization. The raised points on the coke film were introduced from the impurities in the crude oil such as carbonates, since EDS showed that the compositions in these raised points included Mg, Al, K, Ca and Fe. No significant evidence showed that the limited number of the impurities affected the coke characterization in this study.

#### 3.2. Coke amount and coke oxidation reactivity

The coke oxidation reactivity was determined by isothermal TGA at 300 °C. The temperature increased to 300 °C in N<sub>2</sub> and kept isothermal for 300 min in Air. By burning out the coke, the amount of coke deposited on the substrate was measured through the mass loss. Furthermore, the mass error caused by thermal buoyancy was found during TGA. To eliminated the error, blank TG experiments



Fig. 4. Surface morphology of the coke deposited on Si substrate.

were performed with the same experimental operation conditions with the nonreactive Si wafer to acquire the thermal buoyancy correcting curve. The experimental results were eventually corrected to obtain the coke burn-off with the TG reaction time. Fig. 5 shows the TG burn-off curves of the LTO coke produced at different temperatures. Compared to the average final burn-off of 42.5% for the 225 °C, 250 °C LTO coke, the final burn-off of the 310 °C LTO coke decreased greatly to only 26.7%. The 310 °C LTO coke showed a significantly lower reactivity than other LTO coke samples. The change in the reactivity is mostly related to a change in the coke chemical-structural properties, which will be focused on.

Fig. 6 shows the measured amount of the coke deposited on the Si substrate with the increasing LTO temperature in the present study and those from the previous study by traditional method [12]. The coke amount was expressed as the coke mass per gram of the initial reactant, crude oil. The results between the present study and the previous study were similar. The consistent results verified that the new method can successfully simulate the LTO reactions as in oil sand. Both the results showed the coke amount decreased slowly with the LTO temperature increasing from 225 °C to 280 °C, while it decreased significantly to about half of the peak coke amount at 310 °C LTO temperature. These similar results



Fig. 5. Changes in the coke burn-off curves with the LTO temperature.



Fig. 6. Changes in the LTO coke amount with the LTO temperature.

suggested the coke samples were partially consumed with the oxygen with the release of gas products but not the solid residue, leading to the mass loss of the residual coke [12,15]. To investigate the coke amount and the coke reactivity change, the chemical-structural property changes with the LTO temperature were then studied.

## 3.3. Chemical-structural studies

## 3.3.1. EDS and ATR-FTIR studies

Fig. 7 shows the IR spectra for the coke samples produced from the LTO reactions at different LTO temperatures from 225 °C to 310 °C and produced from the crude oil pyrolysis reactions at 450 °C. The prominent IR bands were analyzed following the previous studies [16–18].

To investigate the chemical functionality characteristics in the LTO coke, the IR spectra of the LTO coke were compared with that of the pyrolysis coke. The aromatic C–H stretch at 3050 cm<sup>-1</sup> showed the coke aromatic nature. This band intensity for the pyrolysis coke was significantly greater than that for the LTO coke.



Fig. 7. IR analysis of the pyrolysis coke (450  $^\circ\text{C},\,N_2)$  and the LTO coke (225–310  $^\circ\text{C},$  Air).

The weak aryl C-H stretch showed the loss of the aromatic hydrogens and suggested the LTO reactions increased the extent of the aromatic substitutions. This result was consistent with the decrease in the aromatic C-H out-of-plane wags in the 911-700 cm<sup>-1</sup> regions for the LTO coke. The number of adjacent aryl hydrogens on benzene rings provided the information about the degree of aromatic substitution patterns. The prominent peak at 911 cm<sup>-1</sup> due to the lone aromatic C-H wags for the LTO coke represented tri-substitutions on the benzene rings and even more [17,19]. Since the LTO coke showed characteristic bands within 1850–1650 cm<sup>-1</sup> (attributed to the carbonyl groups) and 1300–  $1000 \text{ cm}^{-1}$  regions (attributed to the overlapping of C–O–C and C-O groups), it appeared that the oxygen functionalities in the LTO coke resulted in the increase in the aromatic substitutions and the decrease in the aromatic hydrogen. Furthermore, the three prominent peaks at 1845, 1775 and 1720 cm<sup>-1</sup> showed the existence of carbonyl groups in various oxygen functionalities, including acid anhydride groups (1845 and 1775 cm<sup>-1</sup>), lactone and alkyl esters and carboxylic acid (1775 cm<sup>-1</sup>), alkyl aldehyde and ketone and phenolic esters (1720 cm<sup>-1</sup>) as well as those highly conjugated with the benzene rings (below  $1700 \text{ cm}^{-1}$ ). The detailed exact IR wavenumbers of these oxygen functionalities were dependent on whether the C=O groups were adjacent with the other polar atom and whether the C=O groups were in conjunction with the benzene rings. Meanwhile, the broad band around 1300–1000 cm<sup>-1</sup> also showed the existence of alkyl and aryl ethers, alcoholic and phenolic components in the LTO coke. Compared to the pyrolysis coke, however, these bands due to oxygen functionalities were almost absent.

For better quantitation, the IR finger-print region between  $2000 \text{ cm}^{-1}$  and  $650 \text{ cm}^{-1}$  was curve-fitted to get the relative absorbance intensity proportions of the aryl C–H wags and the C=O stretching vibrations for the two kinds of coke samples. The curve-fitting method followed the previous study [19]. The proportions were expressed as the ratio of the corresponding band areas and the total area of the finger-print region. The curve-fitting analysis in Fig. 8 showed the proportion of the aryl C–H wags increased from ca. 24.6% for the pyrolysis coke to ca. around 3.35–6.27% for the LTO coke. Nevertheless, the proportions of the C=O stretch for the LTO coke were around 31.7–37.7%, while the proportion dropped significantly to 8.03% for the pyrolysis coke. The quantifications agreed with the visual observation. The numerous produced oxygen functionalities and the highly-substituted aromatic rings in the LTO coke implied that the oxygens substituted most



**Fig. 8.** Comparison of C=O stretches and aromatic C-H wags between the LTO coke and the pyrolysis coke.

aryl hydrogens and they were also added in the aliphatic groups in the polycyclic aromatic hydrocarbons during the LTO reactions.

To investigate the variations in functional groups with the increasing LTO temperature, all the IR spectra for the LTO coke at different LTO temperatures were compared. The peak of the band within 1300–1000 cm<sup>-1</sup> due to C–O and C–O–C stretching vibrations shifted from 1202 cm<sup>-1</sup> for the 225 °C LTO coke up to a higher wavenumber, 1263 cm<sup>-1</sup> for the 310 °C LTO coke. Fig. 9 quantitatively shows the relative absorbance intensity of the O-C and C-O-C stretching vibrations decreased from ca. 35.5% for 225 °C LTO coke to ca. 25.1% for 310 °C LTO coke with 1% significance level. The result indicated the concentration of O-C and C-O-C groups in the LTO coke reduced with the LTO temperature. Some active C-O and C-O-C groups were subjected to break down by the oxygen [20] or convert to the other more stable oxygenated groups, such as carbonyl groups, by intramolecular reactions with the increasing LTO temperature [21]. The C=O stretching intensity within  $1850-1650 \text{ cm}^{-1}$  did not show a significant decline with the increasing LTO temperature, as showed in Fig. 8. Additionally, the previous carbonaceous material pyrolysis study in Argon environments [16] showed the C–O–C stretching in cellulose dramatically decreased with the temperature and then disappeared from the spectra at around 350 °C, but the peak of more thermally stable carbonyl groups did not change until 300 °C. Therefore, the low chemical and thermal stability of C-O and C-O-C led to their reduced concentrations at the high LTO temperature. EDS experiments were also performed to evaluate the evolution of the oxygen/carbon atom ratio for the same coke samples used in the ATR-FTIR characterization. Fig. 10a shows a typical EDS spectrum for the LTO coke sample (including the Si substrate and the Au film) and Fig. 10b shows the change in oxygen/carbon ratio with the LTO temperature. It was interesting to note the oxygencarbon elementary ratios kept almost constant (evaluated by ttest) with the mass loss of coke deposition from 250 °C to 310 °C. The constant oxygen-carbon elementary ratios were believed to be due to the balance of the production and the consumption rate of the oxygen functionalities in air during the LTO reactions, similar to the char gasification process [22]. The previous char gasification study indicated oxygen functionalities even increased with burn off [22].

Fig. 9 indicated the CH deformation intensity within about  $1312-1460 \text{ cm}^{-1}$  has no significant decrease with the increasing LTO temperature. The comparison showed the methylene or methyl groups were more stable than C–O and C–O–C groups.



Fig. 9. Changes in the relative absorption intensities of the vibrations with the LTO temperature (boxplot).



Fig. 10a. EDS spectrum of the LTO coke.



Fig. 10b. Changes in oxygen/carbon atom ratios with the LTO temperature.

#### 3.3.2. Raman studies

Fig. 11 shows a typical Raman spectrum collected from a coke sample. The Raman spectrum is significantly different from those for highly order carbonaceous materials, showing more bordered G (graphitic) and D (defect) bands, much overlap between the two bands and non-negligible shoulders on the outside. The wide D band width indicated the highly disorder aromatic layer structure in the LTO coke, far away from the graphite crystals. Much structural information is hidden in the overlap and shoulder regions such as amorphous and sp<sup>3</sup>-rich structures [23]. Therefore,



Fig. 11. A typical example of a Raman spectrum derived from the LTO coke with deconvolution into eleven bands.

all the Raman spectra were curve-fitted with eleven Gaussian bands using Origin software for quantification, which is slightly different from previous studies [23–25]. After the first ten band deconvolutions, another weak peak was used at about 1760 cm<sup>-1</sup> to represent the considerable carbonyl groups in the present study. Fig. 11 also shows a typical example of the curve-fitted Raman spectra derived from the coke samples. The structural assignments have been discussed in detail elsewhere [23,25]. The deconvolution method has been successfully applied to highly disordered char structure evolution, for example, during pyrolysis [23], oxidation [24,26] or gasification [25] .The S an S<sub>L</sub> bands mainly represented the sp<sup>3</sup>-rich structures, such as the aromatic (aliphatic) ether C-O-C bridging groups. In Li et al.'s study [23], the S and S<sub>L</sub> bands were considered as a brief measure of cross-linking density and substitutional groups. Fig. 12a shows the relative Raman intensity  $I_{(S_t+S)}/I_D$  decreased with the temperature increasing from 225 °C to 280 °C with a 5% significance level. The FTIR analyses showed a similar decreasing concentration of O-C and C-O-C groups. Both the Raman and FTIR results implied that some active ether C-O-C bridging groups eliminated, or less formation of the ether C-O-C bridging groups at the higher LTO temperature, which were believed to be due to their low stability at the higher LTO temperature. A consistent HRTEM analyses will be provided more information later to make them more clear.

The D band was assigned to the poly-aromatic carbon structures with sp<sup>2</sup> characteristics. The increasing relative intensity  $I_D/I_G$  with the increasing LTO temperature in Fig. 12b showed that the relative enrichment of poly-aromatic structures. This was due to the reduced concentration of the sp<sup>3</sup>-rich structures and thermal and chemical stability of the sp<sup>2</sup> poly-aromatic carbon within the LTO temperature range. The changes of D bands and S<sub>L</sub> and S bands were very similar to the Keown et al.'s study [24] about the evolution of the biomass char structure during oxidation. They also indicated the reactions between char and O<sub>2</sub> led to relative enrichments of the aromatic ring structures represented by the D band.

## 3.3.3. XRD and HRTEM studies

No characteristic peaks of coke materials were observed in the XRD profiles  $(10^{\circ} < 2\theta < 110^{\circ})$  of the coke samples from the LTO reactions at all the four LTO temperatures. Thus, the results showed that coke samples from the LTO reactions have less than 5% order structure.

The HRTEM analyses revealed that the LTO coke mainly consisted of highly disorder amorphous structures without any observable aromatic fringes. However, poorly order 'onion-like' structures can be found in some coke samples, as shown in Fig. 13. The 'onion-like' structure was not totally amorphous with distinguishable fringes. Short and tortuous aromatic fringes tended to stack in concentric circles, and overlapped with each other. The order was far away from the graphite aromatic fringes. It is noteworthy that the relative amount of 'onion-like' structures was limited, compared to the amorphous carbon structures. This observation agreed with non-detected peaks in XRD profiles and wide D band widths in Raman spectra.

The outer diameters of the spherical nanostructures were between 20 and 65 nm with an average diameter of about 35 nm. The diffraction pattern shown in Fig. 13d shows an intense diffused ring without any identifiable reciprocal lattices. The diffused ring inferred that the fringe separation distance differs significantly as a result of the highly curved fringes. A HRTEM image analysis algorithm was also compiled using MATLAB to extract the aromatic fringes and obtain the fringe length. The algorithm has been described in detail elsewhere and had successfully applied in a previous study on soot nanostructures [27,28]. The image analysis algorithm is described in the Supplementary materials. The analyses showed that the arithmetic mean fringe length was 1.261 nm with a great amount of the fringes in less than 1.0 nm length. The average size of the fringes corresponded to  $3 \times 3$  poly-aromatic layer with the molecular weight ranging from 300 to 349 amu based on Okolo et al.'s grouping method [18].

The 'onion-like' structures were very easily viewed in the 225 °C and 250 °C LTO coke samples, especially in the 250 °C LTO coke. For these two LTO cokes, the spherical nanostructures existed in groups and some of the nanostructures were interpenetrated and overlapped with each other, as shown in Fig. 13a-b. The 'onionlike' structures were formed by "local re-bonding" [29]. During the LTO reactions, the molecule oxygen can be easily capable of dehydrogenation and cross-linking reactions with the polycyclic aromatic carbon [30]. The cross-linking reactions were considered to begin with special oxygen-containing functional groups [21]. In the previous study [30], the cross-linking was assumed to be due to an ether bonding in polycyclic hydrocarbons. Similarly, the FTIR analyses in this study also showed a great amount of oxygenated groups existed in the LTO coke, including carbonyl and ether groups, especially when the LTO temperature was less than 250 °C. The structures were also reported in the investigation of



Fig. 12. Raman band ratios as a function of the LTO temperature (boxplot).



(e) high magnifications for 280°C LTO coke

coke

Fig. 13. TEM images of the coke samples with 'onion-like' structures inside.

self-assembling mesophase in pitch systems [31]. According to the previous study, the oxygenated substitutional groups such as carbonyl groups increased the molecular polarity, resulting in the increasing tendency for self-assembly compared to such groups with the same molecule weight with less oxygen [31,32]. Therefore, the LTO reaction at a proper temperature benefited the formation of the poorly order 'onion-like' structures due to the oxygen bonding and oxygen functionality polarity effects.

However, the 'onion-like' structures became scattered and existed in very limited amount when the LTO temperature exceeded 280 °C, resulting in the high searching difficulty. In addition, Fig. 13e showed the invisible fringes in the spherical nanostructures of the 280 °C coke samples even though the main element was carbon detected by EDS. The HRTEM experiments were repeated with at least three sets of coke samples, but the same behavior was observed to exclude the possible reason caused by heterogeneous coke samples. The Raman analyses showed the cross-linking density decreased with LTO temperature increasing to 310 °C, reflected by the decreasing Raman intensity of S and S<sub>L</sub> bands. In addition, the FTIR analysis suggested the concentration of C–O and C–O–C groups reduced with the LTO temperature,

indicated by the decreasing IR stretching vibration of C–O and C–O–C groups. In addition, the formation of stable C–C bonds by the intermolecular reaction were very limited during the LTO reactions, compared to the pyrolysis reaction at the higher temperature [21]. Therefore, there was a good agreement between the amount of the 'onion-like' structures viewed from HRTEM and the changes in the ether bridging groups, as showed in the FTIR and Raman studies. The low thermal and chemical stability of C–O and C–O–C groups at the higher LTO temperature were believed to fail to effectively bond the aromatic carbons and weaken the "local re-bonding" strength. Therefore, the 'onion-like' structures were a good marker to show the degree of oxidative cross-linking for the LTO coke.

## 4. Discussions

The effects of the coke chemical-structural properties on the amount of the coke deposition and the coke oxidation reactivity were further discussed. The LTO coke was found to contain great amount of oxygen-containing groups with highly substituted aromatic rings. The oxygen/carbon atom ratio was as high as 0.20 in average for the LTO coke. The high oxygen functionality concentration in the LTO coke accounted for the higher reactivity than the pyrolysis coke, reported in the literature [11].

The present study and the previous study [12] both showed the net coke formation decreased significantly from 280 °C LTO temperature. In fact, the previous pressurized differential scanning calorimetry (PDSC) experiments [12] also concluded that some active structures in the produced coke were partially oxidized during the LTO reactions from the evidence of the net released reaction heat. Combining the evidences provided by FTIR, Raman and HRTEM results in this study, the sp<sup>3</sup>-rich structures, especially such as C-O and C-O-C groups, were found to be selectively reacted with O<sub>2</sub> with the increasing LTO temperature. The preferential removal of the active sp<sup>3</sup>-rich groups enriched the layer ring systems, then lowered the coke reactivity. The TGA results in Fig. 5 validated that the 310 °C LTO coke showed a much lower reactivity than the others, especially at the low burn-off period. The reactivity results agreed with the occurrence of the selective oxidation at the high LTO temperature.

Overall, all the characterization methods used in this study have provided a comprehensive understanding the changes in the coke amount, the coke reactivity and the chemical-structural properties with the LTO temperature and checked the result consistency. The potential work was to investigate the effect of crude oil compositions on the coke chemical-structural property, especially the LTO coke. The effect of crude oil on the LTO coke characteristics was still unclear. Such coke formation and characterization technique is potential to help understand more fundamental mechanisms during the coke formation and oxidation processes in the future.

## 5. Conclusion

The study presents a novel methodological insight into the coke formation from crude oil LTO reactions with the coke chemicalstructural properties studied using a combination of EDS, ATR-FTIR, MRS, XRD and HRTEM techniques. Such coke formation and characterization technique was demonstrated as an easy, quick and controlled method for fundamental studies.

Compared to the pyrolysis coke, the LTO coke contained numerous oxygen functionalities and the highly-substituted aromatic rings. The concentration of the carbonyl functionalities remained constant below 310 °C. Nevertheless, the decreasing IR stretching vibration of C-O and C-O-C groups showed the concentration of C–O and C–O–C groups reduced significantly with the increasing LTO temperature. In addition, the decreasing Raman intensity of S and S<sub>L</sub> bands also suggested that the aromatic ether crosslinking density decreased with the LTO temperature increasing from 225 °C to 280 °C. The selective oxidation of the sp<sup>3</sup> carbon structures reduced the amount of LTO coke deposition, and gave rise to the polyaromatic structures in the LTO coke, as known from the increasing Raman intensity of D bands. TGA showed the coke reactivity of the 310 °C LTO coke decreased greatly, which was consistent with these changes in the coke chemical groups and the structures.

The HRTEM and XRD analyses revealed that the LTO coke mainly consisted of highly disorder amorphous structures with limited amount of poorly order 'onion-like' structures with an average diameter of 35 nm. HRTEM image analyses showed the spherical 'onion-like' nanostructures were composed of short (ca. 1.261 nm) and tortuous fringes with various spacing in a partially ordered circular concentric stack. There was a good agreement between the amount of the 'onion-like' structures viewed from HRTEM and the changes in the ether bridging groups, as showed in the FTIR and Raman studies.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.fuel.2017.06.026.

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