



## Full Length Article

# Characterization of coal char surface behavior after a heterogeneous oxidative treatment



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## ABSTRACT

Two typical types of bituminous coal (JN and SH) were employed for thorough devolatilization, then the samples were functionalized by O<sub>2</sub> at 1073 K to different conversion ratios (JN: 0.21, 0.34, 0.40, 0.53 and 0.63; SH: 0.15, 0.22, 0.32, 0.42 and 0.52) before the surface oxygen containing complexes C(O) were qualitatively and semi-quantitatively characterized by Fourier transform infrared spectroscopy (FT-IR) and temperature programmed desorption (TPD). A deconvolution method was applied to analyze the C(O) adsorption in the spectral region of 1800–1000 cm<sup>-1</sup> in the FT-IR spectra, and the results indicated that the type and thermal stability of these functional groups were as follows: carboxylic (1250 K) < phenol (1350 K) < ether/anhydride (1550 K) < lactone/quinone (1650 K). The TPD results demonstrated that more active sites were generated on the particle surface after the oxidative treatment under O<sub>2</sub> atmosphere, especially the samples with low conversion degree (J2, S2, and S3), coal type and conversion ratio had small effects on the ratios of metastable stable complexes to stable complexes C<sub>wea</sub>(O)/C<sub>str</sub>(O) under the experimental conditions. The oxidized char samples were significantly more reactive than the raw char, and per unit mass of each oxidized sample could reduce more NO than raw char during the temperature programmed reduction (TPR) process, and phenol, ether and anhydride were the main reactants participated in the NO reduction reaction under high-temperature condition (1173–1600 K).

## 1. Introduction

Coal is a pervasive carbonaceous solid fuel with significant applications, such as combustion or gasification for energy production, absorbents for gaseous or solid pollutants, and catalysts and/or catalyst support for homogeneous or heterogeneous reactions. The properties of carbonaceous materials expressed during a reaction are mostly determined by the particle surface chemical species, particularly the surface oxygen-containing complexes [1].

Pershing et al. [2] and Harding et al. [3] hold the view that the volatile burning time is approximately 10 ms and the char reaction period is approximately 300 ms. Because of the obvious difference of reaction time, the complex oxidation process of coal can be divided into two parts: a. homogeneous oxidation of volatiles; and b. heterogeneous reactions between the char and the oxygen reactants, which, as stated above, the reactions between the char and the oxygen reactants are the main part of the whole reaction period. During the combustion and gasification process of carbon materials, the formation and desorption reactions of surface oxygen-containing complex species occur simultaneously [4,5], this process consists of two steps [6–8]: a. oxygen atoms

combined with char surface active sites, forming the surface oxygen containing complexes; b. The decomposition of C(O) occurs with the variation of the thermal or chemical condition. Thus, the amount, structure, and distribution of the functional groups on the particle surface have great effects on coal char reactivity.

Oxygen-containing complexes and active sites on the char the particle surface are important participants in char heterogeneous oxidation and reduction reactions. Moreover, oxygen-containing functional groups are the most important intermediate reactants and have a great effect on coal char reactivity with gaseous reactants (such as O<sub>2</sub>, NO, CO<sub>2</sub> and H<sub>2</sub>O). Char reaction process can be represented as a carbonaceous material reaction mechanism proposed by Campbell et al. [6]. Moreover, the reaction between char and NO is a typical heterogeneous reaction, tightly associated with low NO<sub>x</sub> emission technology. During the coal combustion process, dissociation of NO molecules leads to the generation of C(N) and C(O) complexes, which are formed by the preferential combination of nitrogen and oxygen atoms with carbonaceous material surface vacant active sites [9,10]. Orikasa et al. [11], Arenillas et al. [12] and Pevida et al. [10] who worked on the migration path of fuel nitrogen emission by employing synthetic coal chars to

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**Table 1**  
Ultimate and Proximate analyses of the materials.

Sample	Ultimate analysis (wt% dry and ash free)					Proximate analysis (wt% as received)			
	C	H	N	S	O <sup>a</sup>	Moisture	Volatiles	C <sub>fixed</sub>	Ash
JN-char	89.27	0.36	1.25	1.45	7.67	1.43	1.58	59.29	37.7
SH-char	97.92	0.44	1.20	0.37	0.07	0.98	3.69	90.28	5.05

<sup>a</sup> Calculated by difference.

monitor the generation mechanism of CO, CO<sub>2</sub>, HCN, and N<sub>2</sub> during the oxidation and reduction experiments.

Actually, it is widely accepted that apparent enhancement in the reducing reactivity of coal char is observed in the presence of O<sub>2</sub> [13–16]. This positive effect of O<sub>2</sub> resulted from the variation in the chemical structure of the particle surface. Oxygen-containing complexes, which are formed after oxidizing treatment on the particle surface, and their behaviors determined the chemisorption of NO at relatively low-temperature region and influenced the reduction reaction between NO and char at the high-temperature region [16]. Suzuki [15] conveyed that an enhancement in the NO consumption rate resulted from the generation of new surface active sites upon the decomposition of C(O) and that these sites were more reactive than the active sites on the original char the particle surface. Therefore, clarifying the characteristics of surface oxygen-containing complexes on coal char surface (such as specific chemical structure, decomposition temperature, and gas products), are of great importance for the investigation of coal char combustion with low NO<sub>x</sub> combustion.

Aiming to rationalize the behaviors of C(O) on the surface of carbonaceous materials, Du et al. [17] reported the existence of metastable complexes C<sub>wea</sub>(O) and stable complexes C<sub>str</sub>(O) on the surface of oxidized coal char. The main difference between the two complexes is thermal stability: C<sub>wea</sub>(O) is very reactive and the desorption of CO or CO<sub>2</sub> occurred rapidly in low-temperature range (773–1173 K), whereas the desorption of C<sub>str</sub>(O) is instead started in the high-temperature range (1173–1773 K). Thus, decomposition temperature is the basis for the classification of C<sub>wea</sub>(O) (773–1173 K) and C<sub>str</sub>(O) (1173–1773 K). The concept of C<sub>wea</sub>(O) and C<sub>str</sub>(O) has also been postulated by Chen et al. [18], who obtained the TPD spectra of bituminous and lignite coal char in the temperature range of 273 K to 1923 K to determine the two type of surface complexes. Many researches were carried out to identify the specific chemical structure of C(O) [19–21], and the specific chemical structure of C(O) formed under O<sub>2</sub> atmosphere were mainly carboxylic, lactone, phenol, carbonyl, anhydride, ether and quinone. However, the experimental temperature region of previous researches was generally less 1273 K [22–27], only a few investigations about the amount, distribution and chemical structure of C<sub>str</sub>(O) were carried out, and the nature of C<sub>str</sub>(O) is a necessary factor for understanding the reaction characteristics of coal char under high-temperature condition.

To investigate the properties of the surface oxygen complex, a variety of techniques were employed to characterize the functional groups on the surface of the carbonaceous material. TPD/TPR [28–33] and FT-IR [34–38] are the most commonly used methods for surface chemical structure investigation. The application of the TPD method is ubiquitous because it can furnish a comprehensive quantitative analysis of the surface oxygen complexes [39] and active sites while monitoring the concentrations of CO and CO<sub>2</sub> in the evolved gases. It is generally true that TPD spectra obtained with activated carbonaceous materials express overlapping CO and CO<sub>2</sub> peaks that demand deconvolution before performing surface composition analysis. FT-IR is extensively used in the qualitative analysis of the surface property and the semi-quantitative analysis of the functional groups [40,41]. The FT-IR spectrum consists of composite peaks from various functionalities, and each band may contain contributions from multifarious functional groups. Because of the difference in thermal stability and the dissimilarity in the IR assignments among the oxygen

complexes, it is feasible to establish some general regulations of the C<sub>str</sub>(O) generation and decomposition.

To date, few researchers have pursued studies on the effect of amount and structure of oxygen-containing complexes on coal char reducing reactivity with NO under high-temperature condition. In the present research, JN and SH char samples were pre-oxidized to different conversion degree by O<sub>2</sub> at moderate temperature (1073 K) to avoid the decomposition of stable complexes on the char surface. Subsequently, The properties of C<sub>str</sub>(O) were investigated with the application of FT-IR, TPD and TPR methods.

## 2. Experimental

### 2.1. Char samples preparation

The pulverized coal samples were sieved to the particle sizes of uniform distribution in the range of 100–125 μm. A pyrolysis process was performed in a horizontal quartz fixed-bed reactor under inert atmosphere (Ar) for 30 min at 1137 K. The char samples were tested by the particle size analysis, and the results showed that the char the particle size distribution was still in the range of 100–125 μm. Approximate and ultimate analysis results of the char samples are summarized in Table 1. In an attempt to investigate the effect of conversion ratio on the surface chemical structure of coal char, the materials were oxidized in the reaction atmosphere (concentration of O<sub>2</sub> is 30%, balanced with 70% Ar) for 30, 45, 60, 75 and 90 s in the fixed-bed device at 1073 K. The sample number and conversion ratio of each sample are shown in Table 2.

Based on the ultimate analysis of each JN and SH sample and the measurement of CO and CO<sub>2</sub> released amount during the pre-oxidative process, the variation of carbon content in each sample could be calculated, thus the conversion ratio of JN and SH pre-oxidative samples could be determined.

### 2.2. FT-IR test

FT-IR spectra of each sample recorded using a Nicolet 5700 spectrometer in the 400–4000 cm<sup>-1</sup> wavenumber range. 64 scans were taken per sample at a resolution of 4 cm<sup>-1</sup>. To prepare the pellets, each of the samples was ground to powder in an agate mortar and then mixed with KBr at a ratio of 1:400. Then, fully grinding and uniformly blending of char and KBr could lead to spectra of high quality via optimization of the signal-to-noise ratios [41]. A hydraulic machine was used to press the mixture of KBr and chars to 5 mm in radius at 10 MPa

**Table 2**  
Conversion ratio of JN and SH samples.

Samples	Reaction time and Conversion ratio <sup>a</sup>					
	0 s	30 s	45 s	60 s	75 s	90 s
J1–J6	0	0.21	0.34	0.40	0.53	0.63
S1–S6	0	0.15	0.22	0.32	0.42	0.52

<sup>a</sup> Calculated by the variation of the elemental content (dry and ash free) of each char sample. J1 and S1 are JN raw char and SH raw char, respectively.

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