



Full Length Article

Investigation of demineralized coal char surface behaviour and reducing characteristics after partial oxidative treatment under an O₂ atmosphere

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ABSTRACT

Shenhua (SH) demineralized char was employed to determine the relationship between the char conversion ratio and the surface behavior of particles. The amount, distribution and thermal stability of C(O) generated during the combustion process were clarified by temperature-programmed desorption (TPD) and Fourier transform infrared spectroscopy (FTIR). CO₂ was the primary gaseous product released during the TPD process of each partially oxidized sample. Based on the TPD and FTIR deconvolution results, the decomposition temperature of each functional group could be determined as follows: phenol (1000 K) < carboxyl (1150 K) < ether/anhydride (1400 K) < quinone (1600 K) < lactone (1650 K). Partial oxidative treatment promoted the generation of C(O) on the particle surface, with the maximum amount of C(O) existing on the surface of samples with an intermediate conversion ratio (0.33–0.47). Due to the increase in C(O), the reducibility of the partially oxidized sample was also enhanced. The demineralized chars collected in the intermediate stage (0.33–0.47) expressed the strongest reducibility, and the maximum NO was consumed by per unit mass of these samples. Phenol, carboxyl, anhydride and ether were the main forms of C(O) and were involved in the rapid and successive consumption of NO as major reactants, leading to an apparent reduction of the NO released during the char combustion process.

1. Introduction

Abundant reserves of fossil fuel resources, especially coal, are found around the world. Coal is widely utilized for direct combustion, gasification, liquefaction, and other processes. To date, approximately 50% of the power generation worldwide is still coal electricity [1]. However, because the utilization of coal-based fuels leads to serious environmental problems (e.g., greenhouse effects, acid rain, photochemical smog), the removal of gaseous pollutants from downstream gases in the combustion process has become a subject of widespread concern. CO₂ and NO_x are two of the main gaseous products in the exhaust gases of various combustion processes. And they are considered the main contributors to the environmental issues mentioned above. Ultra-clean coal (UCC) is a coal-based solid fuel with an extremely trace ash content produced by extraction of organic matters or acid soaking treatment [2], and it has the potential for direct combustion in a gas turbine combined cycle (GTCC) or a direct carbon fuel cell (DCFC) with a net power generation efficiency greater than 48% [3]. Compared to direct coal combustion, the utilization of UCC in a GTCC could reduce the

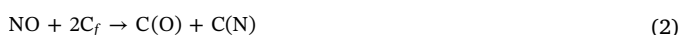
emission of gaseous pollutants and CO₂ [4–6]. Because the CO₂ emissions (captured and sequestered) and generation of by-products (mainly slag and soot) during combustion process are limited in the GTCC and DCFC system, some inferior fuels with high ash contents will become acceptable for comprehensive utilization [7]. In all cases, the demineralization treatment will lead to a significant enhancement of the calorific value, an apparent reduction of fly ash and gaseous pollutant emissions, and an obvious reduction of the costs of burner maintenance and operation.

Additionally, NO is the main component of the NO_x found in the exhaust gas during the coal-based fuel (coal or demineralized coal) combustion process, especially under high-temperature conditions [8]. The catalytic decomposition of NO into N₂ during the combustion process is an ideal way to reduce NO_x emissions, and the carbon content of coal-based fuels has proven to be an effective reactant and catalyst for NO reduction [9,10]. Research into the characteristics of nitrogen evolution during the coal char combustion process has already been widely carried out [11–14]. In the two primary paths of NO generation during coal-based fuel combustion, the NO is derived partly from the

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conversion of elemental nitrogen in the volatile materials and partly from the gasification of elemental nitrogen in the char. Meanwhile, Pershing et al. [11] and Harding et al. [12] demonstrated that devolatilization occurs immediately when pulverized coal particles are sprayed into the combustor, and they found that the reaction rate of volatile matter was generally higher than that of char (approximate 10 ms for volatile and 300 ms for char). The reactivity of char with oxidizing agents is lower than that of volatile materials, so the heterogeneous reaction dominates the coal combustion process. In addition, the NO released during the char combustion process represents approximately 35% of the total amount of NO emitted during the coal combustion process [13]. Thus, the surface behavior and reaction characteristics of coal char should be investigated systematically. Melek et al. [14] reported that the demineralizing treatment of coal-based fuel had no appreciable influence on the NO_x emission levels during the combustion process.

Due to the attachment of oxygen atoms to vacant surface active sites (C_f), a large amount of C(O) is generated on the surface of the char particles during the combustion process [15]. Based on the research by Fan et al. [15,16] and Wang et al. [17], it can be concluded that the C(O) on the surface of the char particles is a vital participant and an intermediate reactant in the heterogeneous reactions between coal char and O₂ or NO. Meanwhile, the appearance of oxygen has an obvious and favourable effect on the NO reduction process [15,16], and the primary properties (amount, distribution and thermal stability) of C(O) have significant effects on the reducibility of coal char to NO. Stanmore et al. [18] investigated the surface chemical behavior of char obtained under different reaction atmospheres and reported that the generation and decomposition of C(O) occurred simultaneously under high-temperature conditions. Rodriguez et al. [19] and Yang et al. [20] investigated the mechanism of reaction between carbonaceous materials and NO under combustion conditions and revealed that the main reaction pathways could be summarized as (1) – (6). The mechanism illustrated that C(O) generally reacted with NO indirectly and that the gaseous product CO and new active sites (C_f) generated by C(O) decomposition are commonly involved in NO consumption.



Based on the reaction mechanism summarized above, it can be assumed that the structural characteristics and behavior of C(O) have significant effects on their reducibility. The thermal stability and decomposition characteristics of C(O) can generally be attributed to their specific chemical structure. Both Figueiredo et al. [21] and Wang et al. [22] investigated the chemical structure of the C(O) generated during the oxidation process of carbonaceous materials and reported that the chemical structures of C(O) were primarily phenol, carboxyl, ether, anhydride, quinone and lactone. Due to the differences in the chemical structure of C(O), the thermal stability and primary decomposition temperature range of each type C(O) is different. When the reaction temperature is fixed, the complexes with lower desorption temperatures below the reaction temperature will become unstable and participate in the reaction rapidly. Additionally, phenol, ether, and quinone are the precursors of CO, whereas carboxyl, anhydride and lactone are the precursors of CO₂ [23]. Wan et al. [24] conveyed that demineralization treatment had a negative effect on the formation C(O) on particle surface during oxidizing process, without the catalytic effect of metal salts, the total amount of C(O) existed on the surface of demineralized chars

was apparently less than that of raw chars. The determination of surface chemical structure is conducive to the development of high-efficiency/performance catalysts or additive agents for the comprehensive and efficient utilization of UCC in a GTCC or DCFC system with low pollutant emissions. However, few researchers have clarified the surface chemical behavior of C(O) on the surface of demineralized char obtained from oxidizing reactions or identified the relationship between a demineralized char surface chemical structure and the NO reducing characteristics of char. In an attempt to determine the decomposition characteristics of the complexes generated after oxidative treatment and to clarify the NO reducing reactivity of each partially oxidized sample, FTIR and TPD/temperature programmed reduction (TPR) were employed in this research. The decomposition temperature of each type of C(O) was clarified by the deconvolution of the FTIR and TPD results; the total amount of C(O) and the specific amounts of each complex were clarified by the TPD results; and the reducibility of each demineralized char sample with different conversion ratios was determined by TPR.

2. Experimental

2.1. Sample preparation

Pulverized raw SH coal was crushed and sieved to a uniform distribution in the range of 100–125 μm, and the parent SH coal sample was dried at 378 K for 24 h. Compared with the extraction of organic matter, acid soaking treatment was easier to achieve in the lab [2]. Thus, to prepare a demineralized sample, the dried SH coal sample was added to a reagent-grade aqueous solution of HCl (approximately 30%) and stirred for 4 h. After ultra-pure water filtration, the sample was added to a reagent-grade aqueous solution of HF (approximate 30%) and stirred for 4 h. After ultra-pure water filtration, the sample was added to a reagent-grade aqueous solution of HCl (approximately 30%) and stirred for 3 h. The demineralization treatment was carried out at room temperature, and the sample that was collected after ultra-pure water filtration was dried at 378 K for 24 h. The thorough devolatilization treatment was conducted in a fixed-bed device under an inert (Ar) atmosphere for 30 min at 1173 K [25], the argon gas flow rate was 1 L/min. After the devolatilization and demineralization treatment, the particle size of the char still remained in the original range (100–125 μm). Approximate and ultimate analysis results for the investigated samples are shown in Table 1.

To clarify the effect that the degree of conversion had on the demineralized char surface behaviour, the demineralized char was oxidized to a specific conversion ratio in the fixed-bed reactor at 1073 K under a 30% O₂ atmosphere (balanced with 70% Ar) by changing the residence time of the sample in the reaction zone (t = 60, 80, 100, 120, 180, 240 and 300 s), the flow rate of reaction gas was 1L/min. Prior to the partial oxidative treatment, the demineralized SH char was dried adequately at 378 K for 24 h. Merely trace amounts of volatiles, ash and moisture content remained in the particles, and the total amount of fixed carbon was more than 97% of the demineralized char particles. Therefore, almost all the mass loss of the demineralized chars during the oxidative reaction could be attributed to the consumption and gasification of fixed carbon, so the conversion ratio could be calculated by the variation in the sample weight before and after the oxidative treatment. The specific conversion ratio of each sample is calculated through Eq. (7), and the values are summarized in Table 2.

$$X_c = \frac{m_0 - m_t}{m_0} \times 100\% \quad (7)$$

where X_c is the conversion ratio (%) of each char sample; m₀ represents the initial mass (mg) of the demineralized char sample; m_t is the mass (mg) of the demineralized char sample after t seconds reaction.

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