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$CaFe_2O_4$ oxygen carrier characterization during the partial oxidation of coal in the chemical looping gasification application

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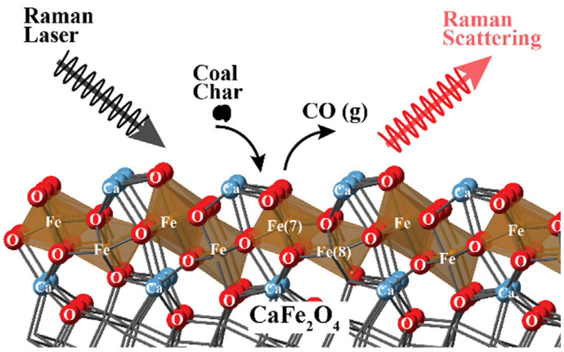
HIGHLIGHTS

- Coal CLG with Ca ferrite evaluated using DFT/Raman spectroscopy/XRD.
- Oxygen ion diffusion-controlled regime occurred at the Fe octahedral sites.
- Ca functions to control O^{2-} movement and rate of carbon oxidation in coal char.
- Removal of O^{2-} from Fe—O—Ca occurs only during deep reduction of $CaFe_2O_4$.

GRAPHICAL ABSTRACT



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ABSTRACT

The calcium ferrite ($CaFe_2O_4$) oxygen carrier characterization during chemical looping coal gasification was conducted using X-ray diffraction and Raman spectroscopic analysis. Density functional theory (DFT) analysis and experimental data were used to elucidate the mechanism for the selective oxidation of coal char. The Raman spectroscopic analyses indicated that the initial reduction of $CaFe_2O_4$ were at the $Fe_{(8)}O_6$ and $Fe_{(7)}O_6$ octahedral sites which are related to the morphological changes at the [4 0 0] and [2 1 2] crystal planes. After the initial reduction, the Raman spectroscopic data indicated the remaining oxygen from Fe-O sites containing Ca (e.g. Fe—O—Ca) participated in the reduction reaction. Deep reduction of the $CaFe_2O_4$ led to the removal of oxygen from the Fe—O—Ca bonds, indicated by the decrease in Raman intensities of the corresponding species, and the appearance of the CaO and Fe^0. The oxygen ion diffusion controlling regime was due to the oxygen transfer occurring at the Fe octahedral sites. These results indicated calcium functions to control both the movement of oxygen ions through the solid and the rate of carbon oxidation in coal char leading to the selective oxidation to produce CO, the desirable product of the chemical looping gasification application.

1. Introduction

Technologies such as chemical looping methane reforming [1,2] and chemical looping coal gasification [3–6] to produce H_2 and CO from fossil fuels were conceptualized from chemical looping combustion (CLC) processes of methane [3,7] and coal. Researchers have sought to gasify solid fuels through the chemical looping gasification (CLG) process using various materials such as calcium oxides and sulfates [8,9], nickel-based ferrites [10], iron oxide supports [11], and perovskites [12]. The biggest challenge in the chemical looping

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gasification (CLG) process is the selection of an oxygen carrier which would react with the fuel to produce syngas but does not combust with the syngas, so the reaction may be controlled at the syngas production step [13]. Most metal oxides react with syngas, and it is difficult to control the reaction at the syngas stage. We have reported unique oxygen carriers, Ca-ferrite and Ba ferrite [1,2], which are favorable for CLG application. The group II ferrites react with coal directly via solid-solid interaction to produce H_2 and CO [5], but they do not react with syngas.

The selective oxygen transfer from the oxygen carrier to coal for the partial oxidation of coal without combusting the coal is the fundamental concept of CLG. The solid-solid interaction and oxygen transfer between coal char and $CaFe_2O_4$ have been investigated using thermogravimetric analysis (TGA) which focused on the reaction kinetics and the carbon conversion at different temperatures [4]. It was found the reaction of the solid chars with the metal ferrite occur via direct solids contact at elevated temperature, and the controlled oxygen release from the oxygen carrier is responsible for selective formation of CO. In general, the solid-solid reaction is considered slow, but the reaction of coal char with Ca ferrite proceed at higher rates similar to the coal-gaseous oxygen reactions.

With the development of CL technology, researchers have made the effort to select candidate oxygen carriers by elucidating the crystal structures and relevant performances using first principle theoretical calculation approaches [14,15]. In addition, the theoretical evaluations of chemical reduction and oxygen vacancy formation energies in various metal oxide oxygen carriers have also been investigated [16,17]. These computational approaches have also shown a relationship between electronic properties of the oxygen carrier and the reactivity in the chemical looping process [18]. However, the details of the specific interactions between coal char and the reactive oxygen in the $CaFe_2O_4$ crystal plane have not been reported in the literature. A correlation between experimental analysis (X-ray diffraction and Raman Spectroscopy) during coal char reduction and the density functional theory analysis of the $CaFe_2O_4$ material is also not reported. Even though the CLG of coal with Ca and Ba ferrites have been reported [4,5], spectroscopic experiments coupled with the theoretical molecular modeling have not been conducted to explore the specific structure of group II ferrites selectively oxidize coal char to produce CO. It is important to understand the specific oxygen sites of Ca ferrite that contribute to the overall solid fuel conversion in CLG. This knowledge of the reduction pathway is crucial to the understanding and modeling of reduction kinetics for complex metal oxides. These results are an excellent measure to the supplement of engineering development for oxygen carriers in CLG technology. The understanding of the relevant chemical structures that participate in the CLG coal reaction is important in developing novel materials for the process.

The $CaFe_2O_4$, shown in Fig. 1, crystallizes in the orthorhombic Pnma structure consists of distorted FeO_6 octahedral sharing edges and corners with eight-coordinated calcium atoms. The unique properties of the Ca—Fe—O structure may help facilitate the partial oxidation of solid fuels to produce CO in chemical looping gasification (CLG). The present study aims to address the research gaps and to provide a better understanding of the solid-solid reaction mechanism. In-situ Raman spectroscopy, density functional modeling, and X-ray diffraction studies were conducted to understand the detailed structure of $CaFe_2O_4$ and which atomic structures participate in the reaction with coal char. The results of these studies are reported in this paper.

2. Experimental section

2.1. Preparation and characterization of the sorbents

Calcium ferrite was prepared through direct decomposition of calcium and iron nitrate precursors. Nitrate precursors were combined in stoichiometric ratios for the formation of $CaFe_2O_4$ phases after calcination [19,20]. Mixtures of calcium hexahydrate (GHS Chemicals) and Iron (III) nitrate (non-hydrate, Fisher Scientific) were ground with a mortar and pestle into a homogeneously distributed mixture. The mixture was then calcined to 500 °C at 4 °C/min and held isothermally for 6 h. The calcined mixture was then ground and subjected to a 1000 °C calcination at a ramp rate 4 °C/min and held isothermally for 6 h. The phase of the metal oxide was verified using X-ray diffraction [4]. The $CaFe_2O_4$ samples were then separated through sonic sieving to obtain 43–53 μm particles for testing. BET surface area of the metal oxide ranged from 0.2 to 1.5 m^2/g.

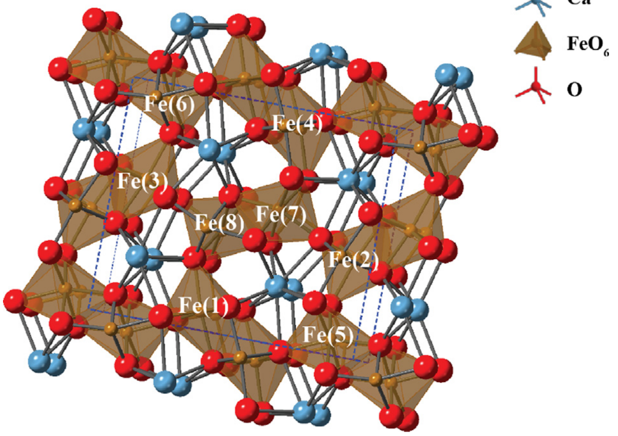

Fig. 1. Elementary cell of $CaFe_2O_4$ [27].

2.1.1. Coal and coal chars

Wyodak (DECS-24) coal sample was obtained from the Penn State Coal Sample Bank. Bulk coal samples were crushed, ground in a ball mill, and blended to homogenize. Chars were produced by pyrolysis of the ground coal samples in a quartz tube furnace at a ramp rate of 200 °C/min, under Argon flow at 100 sccm, to 950 °C and held isothermal for 30 min. Pyrolyzed char samples were then separated through sonic sieving into the size range between 43 and 53 μm. Analysis of the coal and char samples in accordance with ASTM D7582-15, has been reported previously [4]. Pyrolyzing the coal samples to 950 °C removed the volatile content producing coal chars with predominant carbon contents ranging from 68 to 83%, with insignificant amounts of hydrogen, nitrogen, sulfur, oxygen, and the balance ash.

The reduction of the $CaFe_2O_4$ and gasification of the coal char was performed in a thermogravimetric analyser (TGA, TA Instruments model Discovery) equipped with an online mass spectrometer (MS, Pfeiffer Vacuum Omnistar GSD-320). The samples for the $CaFe_2O_4$-coal char reactions were prepared by physical mixing of 24 mg of $CaFe_2O_4$ with 6 mg of Wyodak coal char. This ratio was chosen based on the equivalent molar quantities of available carbon in the char and the available transferable oxygen in the lattice of the metal ferrite for gasification. For a typical test, 30 mg of $CaFe_2O_4$-coal char was placed into a 100 μl platinum crucible. Samples were equilibrated at 50C for 45 min at 200 ml/min flow of UHP argon to ensure an inert oxygen free atmosphere at the initiation of the experiment. Gas flows of UHP argon were 20 ml/min for the balance chamber and 45 ml/min for the sample gas delivery port. Samples were then heated at 200 °C/min and held at 850 °C for 30, 90, 180, or 240 min. The samples were then rapidly cooled under Argon flow after the desired reaction time and collected for post Raman and XRD analysis.

2.2. Equipment and methods

2.2.1. Raman spectroscopy

The Raman equipment was a Horiba LabRAM HR Evolution Raman

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