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Characterization of sulfur products on CaO at high temperatures for air and oxy-combustion

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ABSTRACT

Oxy-coal combustion is a novel technology that seeks to reduce carbon dioxide emissions from electricity generating units, but the unique combustion environment could potentially affect the manner in which the flue gas and fly ash interact. Of particular interest is the ability of fly ash to reduce SO_x emissions, a source of concern in implementing oxy-coal technology. This study seeks to examine the way SO_x interacts with calcium oxide, an important fly ash metal oxide, under a variety of flue gas conditions and temperatures. Using DRIFTS and XRD, the major products under the various reaction conditions were analyzed. The dominant sulfur containing product was found to be calcium sulfate. However, a secondary calcium carbonate product was formed under certain oxy-fuel conditions. Additionally, EDX was employed to examine the temperature dependence for sulfur retention.

1. Introduction

Rising atmospheric levels of carbon dioxide (CO_2), which are currently approaching 400 ppm, are a cause for concern (Dlugokenchy and Tans, nd). As of 2012 one of the main emitters of CO_2 in the United States are power plants burning fossil fuels, accounting for nearly 38% of the total CO_2 emitted or roughly 2.0 billion tons of CO_2 (U.S. Environmental Protection Agency, 2016). One way power plants can lower their CO_2 emissions is by incorporating carbon capture and sequestration (CCS) technologies. One such CCS technology that has shown promise as being both scalable and economically feasible is oxy-fuel combustion (Stanger et al., 2015; Wall et al., 2009; Wall, 2007). It operates by combusting the fuel in a mixture of oxygen (O_2) and carbon dioxide resulting in a relatively pure CO_2 stream after combustion that can then be treated and prepared for storage. The mixture is made by mixing recycled flue gas with O_2 separated from air to reach a desired O_2/CO_2 ratio. In addition to lowering CO_2 emissions, oxy-combustion has shown promise in lowering nitrogen oxide (NO_x) emissions while the final sulfur oxide (SO_x) emissions on a mass of S to coal basis have been shown to either be lowered or remain unaffected (Croiset et al., 2000; Croiset and Thambimuthu, 2001; Kiga et al., 1997; Klostermann, 2008; Liu et al., 2005; McCauley et al., 2009; Wall et al., 2009; Woycenko et al., 1995; Zhuang and Pavlish, 2012). Of the pollutants present in coal combustion, SO_x species are particularly important. Due to the presence of a possibly untreated recycled flue gas stream and the decreased flue gas volume from the exclusion of N_2, sulfur dioxide (SO_2) concentrations within the flue gas will increase dramatically. The rise in SO_2 concentrations leads to a corresponding increase in sulfur trioxide (SO_3) in the flue gas (Croiset et al., 2000; Croiset and Thambimuthu, 2001). This increase is one of the main challenges facing oxy-coal combustion as SO_3 is a precursor to sulfuric acid (H_2SO_4), which would form when flue gas temperature drops below 500 °C and potentially corrode equipment increasing operating costs (Francis, 1952; Hardman and Stacy, 1998). While much research has gone into examining homogeneous SO_x reactions during oxy-combustion, research is still lacking in heterogeneous reactions that occur between SO_x species and the coal fly ash, which can play an important role limiting SO_x emissions (Cheng et al., 2003; Davis and Fiedler, 1982; Sheng et al., 2000; Spörl et al., 2013; Sturgeon et al., 2009; Yu et al., 2011).

Fly ash is a solid mixture of the non-volatile components of coal that remain after the combustion reaction. It primarily consists of a variety of metal oxides, whose individual weight percentages can vary greatly depending on the source and type of coal being utilized. Silica (SiO_2), alumina (Al_2O_3), and iron oxide (Fe_2O_3) are generally the most abundant with weight percentages of 37–60%, 17–30% and 5–29% respectively (Hower et al., 1996; Stanton et al., 2002; Stimpson et al., 2013; Yu et al., 2011). However, fly ash is comprised of many other oxides to lesser degrees, most notably calcium oxide (CaO) at 1–40 wt%, magnesium oxide at 0–10 wt%, sodium oxide (Na_2O) at 0–6 wt% and potassium oxide (K_2O) at 0–4 wt% respectively (Ahmaruzzaman, 2010; Hower et al., 1996; Stanton et al., 2002; Stimpson et al., 2013). These various

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oxides can play an important role in the reactions that take place between the gas phase SO_x and the coal fly ash. The sulfur retention in coal fly ash has been shown to strongly correlate with the alkali and alkaline earth metal oxide composition, with increased weight percentages leading to greater retention (Belo et al., 2014; Cheng et al., 2003; Davis and Fiedler, 1982; Raask, 1982; Sheng et al., 2000; Spörl et al., 2013; Sturgeon et al., 2009; Yu et al., 2011). While the actual fly ash composition is not dependent on the combustion environment (air or oxy) in which it is formed, oxy-combustion studies exhibit greater sulfur capture than air-combustion (Croiset and Thambimuthu, 2001; White et al., 2010; Yu et al., 2011). To a lesser degree the Fe_2O_3 may play an important role in retention as it can oxidize SO_2 to SO_3, which may facilitate increase in sulfur retention on the alkaline oxides (Marier and Dibbs, 1974). While it seems clear that oxy-combustion enhances sulfur capture on the coal fly ash, there is still a lack of understanding of how the reaction changes at high temperatures under different gas environments. Many existing studies concerning the characterization of surface sulfur species on CaO are from experiments operated under more controlled conditions, such as lower temperatures, in inert/air environments, or low pressures (Allen and Hayhurst, 1996a, 1996b; Baltrusaitis et al., 2007; Goodman et al., 2001; Goodsel et al., 1972; Ishihara et al., 1992; Low et al., 1971; Martin et al., 1987; Rodriguez et al., 2000a; Rodriguez et al., 2000b; Rodriguez et al., 2001).

The current mechanism presented in the literature suggests that the SO_2 reacts with CaO through Reactions (1) and (2a)–(2c) (Allen and Hayhurst, 1996a, 1996b; Martin et al., 1987).

$$CaO + SO_2 + 1/2O_2 \rightleftarrows CaSO_4 \tag{1}$$

$$CaO + SO_2 \rightleftarrows CaSO_3 \tag{2a}$$

$$4CaSO_3 \rightleftarrows 3CaSO_4 + CaS \tag{2b}$$

$$2CaSO_3 + SO_2 \rightleftarrows 2CaSO_4 + 1/2S_2 \tag{2c}$$

Thermodynamic calculations predict that calcium sulfate ($CaSO_4$) will be the dominant product as calcium sulfite ($CaSO_3$) is unstable at temperatures above 727 °C. This temperature dependence is confirmed via Fourier transform infrared (FTIR) spectroscopy, where higher temperatures led to the conversion of the sulfite to the more stable sulfate on CaO (Goodsel et al., 1972; Ingraham and Marier, 1971; Low et al., 1971). While calcium sulfide (CaS) is shown as a possible intermediate in Reaction (2b), it has also been shown to be oxidized at 800 °C in favor of either the sulfate or the oxide (Song et al., 2007). The sulfide and sulfite become more pronounced in oxygen free conditions, such as N_2, He, or Ar, where multiple sulfur products can be observed (Allen and Hayhurst, 1996a, 1996b; Munoz-Guillena et al., 1994). Thermogravimetric analysis into the oxidation of CaS by Song et al. reported significant sulfide remaining after 2 h of exposure to 5 vol% O_2 at 950 °C (Song et al., 2007). After experiments where CaO exposed to SO_2 in He, Martin et al. concluded that Reaction (2b) is unimportant as they do not identify any sulfide in their FTIR-PAS (photoacoustic spectroscopy) spectra even at 900 °C, while also proposing that Reaction (2c) could occur with the resulting sulfur gas being oxidized or reacting with fresh CaO (Martin et al., 1987). Along with the crystalline products, it is important to understand the manner in which the adsorbing sulfur species binds to the surface. Martin et al. observed that SO_2 binds through a surface oxygen in a monodentate structure (Martin et al., 1987). Density functional theory (DFT) calculations for sulfur adsorption on CaO (100) surface likewise predict that a monodentate structure is the most energetically favorable where the sulfur binds to a surface oxygen site (Galloway et al., 2015; Sasmaz and Wilcox, 2008). In fact, DFT calculations predicted that this orientation is energetically favorable for NO_x, SO_x, and CO_2 on a variety of alkaline metals, not just CaO (Karlsen et al., 2003; Rodriguez et al., 2001). Once adsorbed, surface sulfur species could polymerize creating a S_xO_y structure on the surface, particularly on calcium carbonate ($CaCO_3$), where thiosulfate (S_2O_3) species were observed (Martin et al., 1987). It is likely that the air atmosphere allows for an oxidation reaction to readily occur at the temperatures being used despite the relatively short times the samples are exposed suggesting why no sulfide is generally observed.

As most of the previous studies investigating sulfur adsorption on CaO were done in air or an inert environment, it is important to consider the effect of other gases that the fly ash particles are likely to be exposed to. Since the application for these sulfur adsorption studies is in combustion flue gas, the effect of water is of the utmost importance as it can affect the surface composition. DFT calculations by de Leeuw et al. show that water will dissociatively adsorb to low-coordinated surfaces of CaO like (110) or (111) planes, but only physisorb onto the more stable and abundant (100) plane (de Leeuw et al., 2000; de Leeuw et al., 1995). Furthermore, they predict that the water will create a pair of hydroxyl groups on the surface with higher coverages of water creating a more and more stable surface, possibly due to the greater stability provided by adjacent hydroxyl pairs (Carrasco et al., 2008; de Leeuw et al., 1995). Their further simulations show that water adsorbed onto various $CaCO_3$ surfaces can cause surface reconstructions, but not dissociation of the water molecule (de Leeuw and Parker, 1997). This agrees with an attenuated total reflection (ATR)-FTIR study by Al-Hosney and Grassian, who observed a water film covering the $CaCO_3$ surface, which promoted the decomposition of the carbonic acid species that would otherwise cover the surface (Al-Hosney and Grassian, 2005). Their work also proposed multiple mechanisms for calcium sulfite formation from $CaCO_3$ depending on if the water and SO_2 react in an Eley-Rideal or Langmuir-Hinshelwood type mechanism. Several studies have shown how increasing the partial pressure of water can increase the conversion of limestone to $CaSO_4$, with increasing temperature having a similarly beneficial effect (Duan et al., 2013; Jiang et al., 2013). Baltrusaitis et al. reported similar results as x-ray photoelectron spectroscopy spectra showed significantly greater sulfite than sulfate on $CaCO_3$ samples when water is present (Baltrusaitis et al., 2007). The $CaCO_3$ formation, which becomes prevalent in oxy-combustion conditions, is itself dependent on water concentration as investigation of carbonation of lime ($Ca(OH)_2$) slurries by Van Balen (Van Balen, 2005) and Cizer et al. (Cizer et al., 2012) show a strong dependence on gas-phase water content in the formation of $CaCO_3$. While many of the experiments investigating the effect of water were done with $CaCO_3$ at ambient temperatures and not with CaO, they still illustrate the impact water plays in the sulfation reaction.

Examining the effect of sulfur and water on $CaCO_3$ and CaO under various inert and/or low-temperature conditions can aid in understanding the sulfation mechanism in oxy-combustion. The higher partial pressure of CO_2 in oxy-combustion allows for the carbonate to be stable at higher temperatures. $CaCO_3$ is stable up to ~900 °C in pure CO_2 atmosphere (de Diego et al., 2013; García-Labiano et al., 2011; Reid, 1970). If the starting CaO is converted to $CaCO_3$ during the experiment, it is proposed that the resulting reaction mechanism changes such that SO_2 would no longer adsorb to CaO, but to $CaCO_3$ as shown in Reactions (3) and (4) (de Diego et al., 2013; García-Labiano et al., 2011; Reid, 1970).

$$CaO + CO_2 \rightleftarrows CaCO_3 \tag{3}$$

$$CaCO_3 + SO_2 + 1/2O_2 \rightleftarrows CaSO_4 + CO_2 \tag{4}$$

At temperatures between 850–900 °C, the mechanism changes from the indirect sulfation of Reactions (3) and (1) to the direct sulfation mechanism of Reaction (4). However, there are likely some kinetic limitations as analysis of fly ash showed the presence of oxide, carbonate and sulfate of calcium indicating that all of the reactions above are important to sulfur capture (Vassilev and Vassileva, 1996). Additionally, Martin et al. proposed an additional reaction whereby the sulfation of