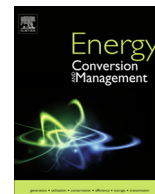




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Effect of potassium-doping and oxygen concentration on soot oxidation in O₂/CO₂ atmosphere: A kinetics study by thermogravimetric analysis

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ABSTRACT

In oxy-fuel combustion, switching from nitrogen to carbon dioxide atmosphere with higher oxygen concentration will affect the oxidation rate of soot, and it was observed in our recent study on soot emission from biomass pyrolysis that potassium (K) crystals are embedded in soot and its precursor clusters. In this study, the effects of K-doping (KCl and K₂SO₄) and O₂ concentration on soot oxidation in O₂/CO₂ atmosphere are studied using thermogravimetric analysis (TGA), and the extent of catalysis is compared with that in O₂/N₂ atmosphere. The delays on start, peak and end temperatures of soot oxidation are observed in O₂/CO₂ atmosphere. However, increase in O₂ concentration which promotes oxidation significantly reduces the delay. All the K-doping cases results in accelerated soot oxidation rate, but catalytic role of the K-doping in O₂/CO₂ is significantly lower than that in O₂/N₂ because the CO₂-enriched environment inhibits the performance of potassium as oxygen carrier. The accelerating degree from K-doping is also affected by the potassium type, doping mass and oxygen concentration. KCl acts as a better, more efficient doping agent than K₂SO₄ with the increase in doping mass. The catalytic effect of K₂SO₄ will not change and even decrease at 375 μmol(K)/g(soot) for K₂SO₄ while the catalytic role of KCl keeps increasing even at 600 μmol(K)/g(soot) for KCl. In O₂ concentration range of 5–30%, the accelerating degree from K-doping presents the minimum value around 15%. This phenomenon strongly approves the hypothesis that potassium as the oxygen carrier and accelerating the oxygen transportation, because in the cases of without K-doping and at a high O₂ concentration there is no additional active site for more O₂ adsorption thus inducing the slow accelerating degree. The kinetic analysis indicates the first order reaction for soot oxidation and also a good compensation relation between apparent activation energy *E* and logarithmic frequency factor *A*. *E* is generally reduced with the atmosphere changing from O₂/N₂ to O₂/CO₂, with K-doping, and with O₂ concentration decreasing. This study is beneficial to demonstrate the mechanism of how potassium doping and oxygen concentration affect soot oxidation rate in oxy-fuel combustion environment.

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1. Introduction

The awareness of the increase in greenhouse gas emission in large stationary sources has resulted in the development of new technologies that can accommodate capture and sequestration of carbon dioxide [1]. Oxy-fuel combustion has generated significant interest since it was proposed as a competitive carbon capture technology for new built and retrofitted coal-fired power plants, considering the advantages of a relatively moderate efficiency

penalty and the lowest retrofit capital expenditure [2]. The concept of oxy-fuel combustion is removal of nitrogen from the oxidizer and then utilize flue gas recycle (mainly carbon dioxide and moisture) in its replacement for combustion process in oxygen [3]. The coal combustion process in oxy-fuel combustion is expected to be different with that in normal air combustion from the aspects of combustion chemistry, mass transfer, and radiation heat transfer. CO₂ has a larger specific molar heat than N₂, and the coal may be gasified by the CO₂, thus the use of CO₂ instead of N₂ causes a reduction in the propagation speed, stability of the flame and increase in the unburned carbon content. These problems can be overcome by increasing oxygen concentration in oxy-fuel

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combustion [4–6]. In the past decade, quite a lot of investigations have been made to probe into different challenges associated with oxy-fuel combustion. Recent studies have shown the flame radiation heat transfer under oxy-fuel conditions were strongly promoted, due to the higher levels of CO₂ and H₂O, as well as in-flame soot compared to air combustion conditions [7,8].

Soot formation in solid fuel combustion is regarded as a result of secondary pyrolysis of volatile matter especially tar based on polycyclic aromatic hydrocarbons hypothesis, inception, surface growth and surface oxidation [9]. Soot is one of the fine particle pollutants but also important to combustion facilities because of its strong radiation heat transfer effect, that the near-burner coal flame temperature could be lowered by several hundred degree due to the radiation heat transfer to surrounding wall by soot [10–12]. After soot is formed in the flame region of reducing atmosphere at high temperatures, soot oxidation will occur in oxidative post-flame region under a relatively lower temperature as a result of attack by molecular oxygen, O₂, and the OH radical [13]. The reaction kinetics of soot oxidation is important to the removal efficiency of soot in combustion facilities, and a number of studies have been performed on soot or carbon oxidation by experimental measure and modeling methods. The effects from oxygen partial pressure, temperature, particle size, catalysis and other gas species have been investigated [14–18]. De Soete [19], Marsh and Kuo [20] proposed the reaction scheme of soot oxidation involving free carbon sites, chemisorbed localized molecular and atom oxygen, chemisorbed mobile molecular oxygen, and chemisorbed mobile atoms of oxygen. It indicated that the chemical absorption controls the total process with the reaction order around 1.0. Stanmore et al. [21] has reviewed the oxidation of soot from the aspects of experiments, mechanisms and models. Most of previous studies are under air combustion conditions, but recent preliminary studies on soot formation indicated a trend toward a larger soot cloud size and lower soot cloud temperature when replacing N₂ with CO₂. On the other hand, soot oxidation kinetics should be also changed in oxy-fuel combustion, because O₂ concentration in oxy-fuel combustion is usually increased up to 30–40% and the high concentration of CO₂ in oxy-fuel combustion also might enhance the interaction reaction between carbon and CO₂ [5,22,23]. However, the studies on soot oxidation under oxy-fuel combustion conditions are limited.

Recently, we sampled soot particles and its precursors from biomass pyrolysis in a drop tube furnace at 1000–1300 °C and analyzed the morphology and elemental composition by Scanning Transmission Electron Microscopy (STEM, TECNAI G2 F30 TWIN, FEI, United States). In Fig. 1, potassium (K) crystals were found to be embedded in soot precursor clusters, with the potassium crystals formed through the condensation of potassium vapor. This indicates potassium in biomass not only catalytically affects the soot formation in devolatilization and tar decomposition as widely reported [24–28], but also might play a catalytic role on soot oxidation at lower temperatures when potassium vapor condensed. The catalytic oxidation of soot has been widely studied in diesel engine to lower the ignition temperature and promote the burnout of diesel soot [29–31]. The metal oxides (CuO, MoO₃, F₂O₃, PbO, MnO₂, Co₃O₄, La₂O₃, V₂O₅, Ag₂O, etc.) [21] and some composite catalysts (Cu-V-K, Cu-Mn-K, Cu-Fe-K) have been tested and shown a significant catalysis on accelerating soot oxidation rate at low temperatures [31,32]. There are many studies on char combustion and gasification with loaded/doped alkali metals and alkaline earth metals [33–36] but the effect of potassium on soot oxidation is not yet fully explored. Considering the catalytic mechanism that metal atoms play in accelerating the transportation of O₂ and CO₂ on soot surfaces, it is reasonable to make the hypothesis that the catalytic acceleration degree of soot oxidation will be changed in oxy-fuel combustion in which there is a higher O₂ concentration

and enriched CO₂ concentration compared with air combustion [37].

Based on the hypothesis above, in this study, the effects of K-doping and O₂ concentration on model soot oxidation in O₂/CO₂ atmosphere are studied using thermogravimetric analysis (TGA), and the degree of influence of K-doping is compared with that in O₂/N₂ atmosphere. The effect of K-doping concentration and type (KCl, K₂SO₄) is also considered. The reaction order *n*, apparent activation energy *E* (kJ.mol⁻¹) and frequency factor *A* (s⁻¹) are further determined through a classical integral method for all the 29 cases in this work.

2. Material and methods

2.1. Material sample properties

The soot (PRINTEX U, Evonik Degussa, Germany) was used after 2 h drying at 105 °C in the cases without potassium doping. The major properties of soot used in TGA tests are shown in Table 1, with a low volatile content, no ash, large surface area, and nano-scale diameter. The morphology of the model soot used is shown in Fig. 2 analyzed by Transmission Electron Microscopy (TEM, HT7700, Hitachi, Japan), and the original particle size is in the scale of 20–30 nm.

2.2. TGA equipment and test method

Soot oxidation test was conducted by using a TGA apparatus (STA409PC, NETZSCH, Germany). The fuel sample was heated in an alumina crucible under a desired atmosphere in the furnace. The weight loss was recorded on-line by the data recording system as fully described in [38]. In each test, about 5 mg soot samples were heated from ambient temperature to 900 °C with a heating rate of 20 °C min⁻¹ and a total flow rate of 200 ml min⁻¹. The oxygen concentration of O₂/CO₂ atmosphere was changed in the range of 5–40%. The measurement accuracies of TGA for temperature and mass were 0.1 °C and 0.2 μg, respectively. Thermogravimetric (TG) curves were obtained by continually recording the mass loss with increasing temperature. Derivative thermogravimetric (DTG) curves were obtained by differentiating TG curves.

2.3. K-doping method

The doping method being able to distribute K on soot surface “tightly” is important for a good catalysis, thus the dipping method is adopted in this study [32]. The original soot samples are immersed into KCl or K₂SO₄ solutions with stirring for 12 h and then dried in an oven of 80 °C for 24 h. After that the dried K-doping samples are ground for TGA tests. We define the K-doping concentration as the mole amount of K per gram soot sample, μmol(K)/g(soot). Three K-doping concentrations are selected in this study: 150, 375, and 600 μmol(K)/g(soot).

2.4. Characteristic parameters and kinetics analysis method

Three characteristic temperatures have been identified including the starting temperature *T*_s, the ending temperature *T*_e, and the peak temperature *T*_p. The identification method is shown in Fig. 3 and has also been used in our previous works [39]. To evaluate the soot oxidation process more reasonably, the comprehensive oxidation index *S* was defined including the effects from *T*_s, *T*_e, maximum mass loss rate *w*_{max}, and average mass loss rate *w*_{mean} as: $S = (w_{\max} \times w_{\text{mean}}) / (T_s \times T_e)$.

The component of soot is simple and the differential curve of mass loss shows only one peak, therefore, Coats-Redfern integral

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