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Copper slag as a catalyst for mercury oxidation in coal combustion flue gas

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ABSTRACT

Copper slag is a byproduct of the pyrometallurgical smelting of copper concentrate. It was used in this study to catalyze elemental mercury (Hg^0) oxidation in simulated coal combustion flue gas. The copper slag exhibited excellent catalytic performance in Hg^0 oxidation at temperatures between 200 °C and 300 °C. At the most optimal temperature of 250 °C, a Hg^0 oxidation efficiency of 93.8% was achieved under simulated coal combustion flue gas with both a high Hg^0 concentration and a high gas hourly space velocity of 128,000 h^{-1} . Hydrogen chloride (HCl) was the flue gas component responsible for Hg^0 oxidation over the copper slag. The transition metal oxides, including iron oxides and copper oxide in the copper slag, exhibited significant catalytic activities in the surface-mediated oxidation of Hg^0 in the presence of HCl. It is proposed that the Hg^0 oxidation over the copper slag followed the Langmuir-Hinshelwood mechanism whereby reactive chlorine species that originated from HCl reacted with the physically adsorbed Hg^0 to form oxidized mercury. This study demonstrated the possibility of reusing copper slag as a catalyst for Hg^0 oxidation and revealed the mechanisms involved in the process and the key factors in the performance. This knowledge has fundamental importance in simultaneously reducing industrial waste and controlling mercury emissions from coal-fired power plants.

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1. Introduction

Copper slag is an oxide-rich byproduct of the pyrometallurgical smelting of copper concentrate (Huanosta-Gutiérrez et al., 2012). Approximately 2.2–3.0 tons of copper slag are generated during the production of a ton of copper metal (Ambily et al., 2015). In 2003, the production of copper slag was estimated to be more than 24.6 million tons (Gorai et al., 2003). Due to the increasing global demand for copper, more and more copper slag is being produced every year and many landfill sites are needed for its disposal. More importantly, copper slag contains heavy metals that are environmental hazards (Alter, 2005). To avoid these environmental challenges related to the disposal of copper slag, researchers are increasingly interested in alternative uses for copper slag, including its use as a raw material for other processes such as cement and concrete production. Several environmental friendly technologies have demonstrated technical and economic feasibility (Al-Jabri et al., 2009; Mithun and Narasimhan, 2016). Like copper slag, another waste product, coal combustion fly ash, has recently been

diverted from landfills (Ahmaruzzaman, 2010) and reused as a raw material in concrete (Ding et al., 2012). Because even a negligible increase in carbon content would substantially lower the concrete's performance (Li et al., 2016), fly ash with a low carbon content is more desirable, and the introduction of extra carbon into fly ash is unwelcome. For example, coal-fired power plants are generally unwilling to adopt the activated carbon injection (ACI) method to capture mercury (Hg), even though this method achieves the maximum achievable mercury control technology (Pavlish et al., 2003), because ACI increases the carbon content of fly ash and limits its usability and marketability. As stated above, both coal combustion fly ash and copper slag can be reused as concrete raw material. Therefore, the introduction of copper slag into coal combustion fly ash does not inhibit its reuse as a raw material in concrete. In fact, copper slag can produce fine aggregates and thus contribute to high-performance concrete with excellent strength and durability properties (Al-Jabri et al., 2009).

Of the three different mercury species in coal combustion flue gas, i.e., elemental mercury (Hg^0), oxidized mercury (Hg^{2+}), and particulate-bound mercury (Hg^p), Hg^0 is easily to be emitted into the atmosphere (Wang et al., 2010; Galbreath et al., 2005). In contrast, Hg^{2+} , which is less volatile and more soluble, can be easily

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adsorbed on a particulate surface to form Hg^{p} and/or absorbed by wet flue gas desulfurization (WFGD) solutions (Li et al., 2012; Liu and Wang, 2014). If copper slag can facilitate Hg^{0} oxidation to Hg^{2+} , it can be used as an alternative to activated carbons. The injection of copper slag upstream of particulate matter control devices (PMCDs) can not only overcome many of the disadvantages associated with ACI, it could also solve the problems of the disposal of copper slag. Copper oxide (CuO) always exists in copper slag, and a small amount of CuO can lead to an enormous increase in Hg^{0} oxidation by hydrogen chloride (HCl) (Ghorishi et al., 2005; Schwaemmle et al., 2012; Yamaguchi et al., 2008). The positive effect of CuO on Hg^{0} oxidation probably occurs because CuO can accelerate the transformation of HCl to chlorine (Cl_2) via the Deacon mechanism (Over and Schomacker, 2013), which greatly enhances Hg^{0} oxidation. Like CuO, ferric oxide (Fe_2O_3) in the copper slag is also able to facilitate Hg^{0} oxidation (Presto and Granite, 2006), as shown by the oxidation rate of more than 90% Hg^{0} achieved over model fly ash containing Fe_2O_3 . In comparison, only 10% conversion of Hg^{0} to Hg^{2+} was observed when Fe_2O_3 was removed from model fly ash (Ghorishi et al., 2005). Similar to Fe_2O_3 , one study found a positive correlation between the magnetite (Fe_3O_4) content in coal combustion fly ash and improved Hg^{0} oxidation performance at 180 °C (Dunham et al., 2003). Although most of the iron in copper slag exists in the form of fayalite (Fe_2SiO_4), the iron oxide content of copper slag is generally higher than the conventional coal fly ashes (Alp et al., 2008). The weight percentage of iron in copper slag is generally greater than 40% (Alter, 2005). Compared to coal fly ashes, copper slag with a higher percentage of iron oxides could be more favorable to Hg^{0} oxidation. Several other transition metal elements exist in copper slag in the form of oxides such as manganese dioxide (MnO_2), chromium trioxide (CrO_3), and molybdenum trioxide (MoO_3) (Gorai et al., 2003). Studies have demonstrated that all of these metal oxides are efficient catalysts for Hg^{0} oxidation (Presto and Granite, 2006; Granite et al., 2000; Li et al., 2010; Kamata et al., 2009; Ji et al., 2008). Accordingly, it is very reasonable to hypothesize that the transformation of Hg^{0} to Hg^{2+} could be catalyzed by copper slag and that the injection of copper slag as an alternative to activated carbon could not only achieve mercury control, it could also reduce the amount of copper slag waste in landfill.

In this study, copper slag was used to catalyze Hg^{0} oxidation in coal combustion flue gas for the first time. The mechanisms involved in Hg^{0} oxidation over copper slag were systematically investigated. The goal was to evaluate the technical feasibility of

using copper slag as a catalyst for Hg^{0} oxidation that can be injected upstream of the PMCDs. The improved understanding of the role of different copper slag constituents on Hg^{0} oxidation would maximize Hg^{0} oxidation and help coal-fired power plants reduce their overall mercury emissions.

2. Experimental section

2.1. Material and characterizations

Copper slag samples were provided by a metallurgical copper company located in Henan Province, China. Before the Hg^{0} oxidation experiment, the copper slag samples were dried, ground, and sieved through 100 meshes. Surface area analysis by N_2 adsorption was conducted on a micropore analyzer (Micromeritics ASAP 2020). The chemical compositions of the copper slag samples were examined using an inductively coupled plasma-optical emission spectrometer (ICP-OES). The corresponding metal oxides composition was calculated according to the elemental composition directly obtained from the ICP-OES. Before the ICP-OES test, 0.1 g copper slag was first dissolved into the mixture solution consisting of 10 ml nitric acid, 10 ml hydrofluoric acid and 2 ml perchloric acid. After heating, steaming and drying, the solid sample was then dissolved in the solution containing 5 ml nitric acid and 5 ml hydrochloric acid, and was finally transferred to a 50 ml volumetric flask for the ICP-OES analysis. It should be noted that for some element such as chlorine, their contents were identified by X-ray Fluorescence analysis. X-ray diffractometer (XRD) analysis was conducted on a SIMENS D500Bruker to identify the crystalline phase composition of the copper slag samples. The XRD analysis was performed at 40 kV, 40 mA using Cu $K\alpha$ radiation ($\lambda = 0.15406$ nm) in the range of 10° to 80° (2θ) with a step size of $0.02^\circ/\text{s}$.

2.2. Hg^{0} oxidation experiments

A bench-scale experimental system was built to evaluate the catalytic activities of the copper slag in Hg^{0} oxidation, the design of which was similar to that used in a previous study (Li et al., 2013). The schematic diagram is presented in Fig. 1. Different flue gas components were obtained from cylinders, except for water vapor and Hg^{0} . Mass flow controllers were used to precisely control the total gas flow rate to be 1000 mL min^{-1} for each test. A heated water bubbler was used to provide water vapor when

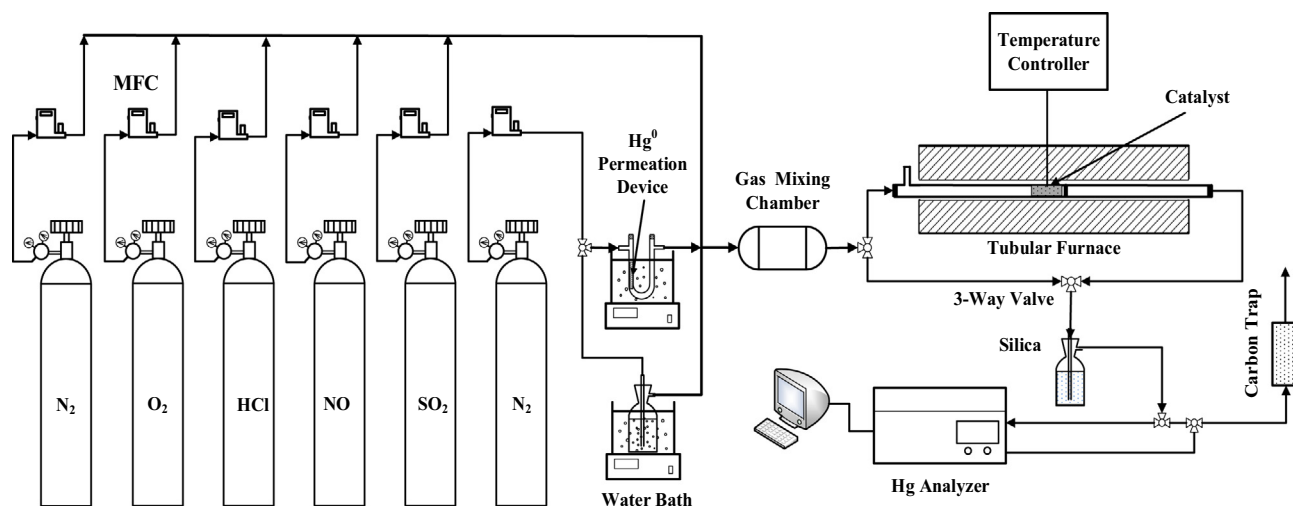


Fig. 1. Schematic diagram of the experimental system.

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