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Performance of CuO_x–neutral Al_2O_3 sorbents on mercury removal from simulated coal combustion flue gas

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ABSTRACT

Copper based sorbents are used to control mercury emissions in coal-fired flue gas. CuO_x impregnated on neutral Al_2O_3 (CuO_x–Al_2O_3) sorbents were found to enhance catalytic oxidation of elemental mercury in the presence of hydrogen chloride (HCl). The Hg^0 oxidation rates increased along with the increasing HCl concentration and temperature. The mercury oxidation rates were over 65% in the presence of 50 ppm HCl and the mercury adsorption amounts were over 75% in the early stage of the mercury removal process. CuO_x–Al_2O_3 sorbents demonstrated good mercury removal capacity. The effect of HCl is due to the formation of active chlorine. CuO_x–Al_2O_3 sorbents also have excellent sulfur resistance in the presence of HCl. A mixture of CuO_x–Al_2O_3 and activated carbon can remove more than 90% Hg^0 with a lower mercury removal cost for industrial applications. The characterizations of the CuO_x–Al_2O_3 sorbents were measured suggesting CuO_x species work as catalysts via the redox shift between Cu^{2+} and Cu^+. The mercury oxidation mechanism of the sorbents is proposed to follow the Mars–Maessen mechanism.

1. Introduction

Mercury is widely distributed in the environment causing global air pollution due to its persistence and long-range mobility [1,2]. In 2005, global mercury emissions from fossil fuels (primarily coal) combustion accounted for 45% of total anthropogenic mercury emissions with power plants being the main source of mercury emissions from fossil fuels combustion in most countries [3]. Therefore, mercury emission controls are urgently needed for coal-fired power plants worldwide. In December 2012, the U.S. Environmental Protection Agency (EPA) finalized a set of adjustments to the Mercury and Air Toxics Standards (MATS) to restrict mercury emissions from power plants [4]. The UN Minamata Convention on Mercury was signed worldwide in 2013 to restrict mercury emissions [5]. Mercury emission control technologies are needed to meet the stringent environmental limits.

Mercury exists in coal-fired flue gases as: elemental (Hg^0), oxidized (Hg^{2+}) and particulate-bound (Hg^P) mercury [6]. During coal combustion, mercury is released as Hg^0 to the flue gas and some Hg^0 converts to Hg^{2+} as the flue gas temperature drops. Since chlorine is present in coal, Hg^{2+} may also exist as $HgCl_2$ in the coal-fired flue gas. The proportion of Hg^{2+} and Hg^P is determined by a variety of factors including the flue gas component [7,8], the chlorine content in the coal [9,10], the flue gas temperature [11], the existing air pollution control devices (APCD) in the power plants [12–14], etc. Hg^{2+} and Hg^P can be removed from the flue gas by existing APCDs, such as wet flue gas desulfurization (WFGD) and electrostatic precipitator (ESP). However, Hg^0 is difficult to remove by the existing APCDs. It has been suggested to convert Hg^0 to Hg^{2+} or Hg^P to capture more Hg^0.

Mercury oxidation sorbents are investigated here to improve the mercury capture process. $CuCl_2$ modified non-carbon sorbents have been shown to be promising mercury sorbents [15,16]. Copper, a transition metal, may have special catalytic effects for mercury oxidation due to its ability to store/release oxygen via the redox shift between Cu^{2+} and Cu^+ [17]. This study investigates the mercury removal capacities of cupric oxide impregnated neutral alumina in different flue gas components at low temperatures (140–300 °C). The possible catalytic oxidation mechanisms are discussed.

2. Experimental

2.1. Sorbent preparation

Neutral alumina was demonstrated to be a good carrier of modified mercury sorbents in our previous study [15]. In the current investigation, neutral alumina was selected as mercury oxidizer carrier to evaluate catalytic oxidation by CuO_x. The particle sizes of neutral Al_2O_3 are 100–200 mesh (74–149 μm). The precursor of CuO_x was copper nitrate tri-hydrate (99%, Aladdin) with deionized water used for the sorbent preparation. CuO_x modified neutral alumina was prepared by wet impregnation method. $Cu(NO_3)_2 \cdot 3H_2O$ was dissolved in deionized water at different concentrations (5–15 wt.%) at room temperature. During impregnation, 5 g of the carrier was submerged into 30 ml $Cu(NO_3)_2$ solution in a plugged conical flask, magnetically stirred

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for 3 h and left to stand for another 3 h. After impregnation, the prepared sorbents were filtered and dried at 80 °C for 12 h, and then calcined in a N_2 atmosphere at 500 °C for 2 h. The weight percentage of the impregnated Cu was determined by ICP-AES from the Cu remaining in the rinsed water after filtering. The Cu loading on the sorbents impregnated by 15 wt.%, 10 wt.% and 5 wt.% solution was 3.5%, 1.5% and 1%, respectively, and the sorbents were written as Cu(3.5)–Al_2O_3, Cu(1.5)–Al_2O_3 and Cu(1)–Al_2O_3. As sorbents with higher copper loading may bring negative effects to the environment, Cu(1.5)–Al_2O_3 and Cu(1)–Al_2O_3 are the main research objects and Cu(3.5)–Al_2O_3 is only discussed in the characterization analysis.

2.2. Apparatus

The experimental setup for the tests of the mercury catalytic oxidation performances is similar to our previous research [15]. The reactor system is composed of four parts, i.e. Hg generation (PSA Cavkit 10.534 Mercury Generator), simulated flue gas mixing, fixed-bed reactor and tail gas treatment. The fixed-bed reactor is made of a 40 mm (inside diameter) quartz tube heated in a temperature-controlled furnace. For each experiment, Hg^0 carried by N_2 and the simulated flue gas was first heated to the experimental temperature in the pre-heating zone of the fixed-bed reactor, and then passed through the sorbent bed supported by a sintered quartz disc. The mercury concentration in the tests was monitored by an online cold vapor atomic absorption spectroscopic mercury analyzer (Thermo Fisher CEMS), which allows a continuous measurement of both the Hg^0 and Hg^{2+} concentrations. Teflon and quartz were used in the gas sampling lines to ensure accurate measurement. The Hg^P absorbed by the sorbents was analyzed by Lumex RA-915M (Russia) after each experiment. The experimental error range was found to be ±10% by repetitive experiments.

2.3. Mercury removal measurement

The mercury removal capacities of CuO_x–Al_2O_3 sorbents were measured in the fixed-bed reactor. During each test, the Hg^0 stream was switched on only after the reaction conditions attained. The experiments normally lasted 1 h and the reaction temperature was normally 140 °C. The inlet Hg^0 concentration was set at 20 μg/Nm^3 and the total flow rate was controlled at 2 L/min. 0.5 g of the prepared sorbent was well mixed with 5 g pre-washed quartz sand. The bed height of sorbent/sand mixture was about 6 mm (the residence time was 0.2 s). The simulated coal-combustion flue gas components are shown in Table 1.

The total Hg^0 oxidation rate and adsorption rate are defined as:

$$\text{Total oxidation rate } \eta_{oxi} = \frac{\sum_0^t c^t_{Hg^{2+}}}{c_0 \cdot t} \tag{1}$$

$$\text{Total adsorption rate } \eta_{ads} = \frac{m^t_{Hg^P}}{c_0 \cdot t \cdot v} \tag{2}$$

The Hg^0 removal rate is defined as:

$$\text{Total removal rate } \eta = \frac{\sum_0^t \left(c_0 - c^t_{Hg^0}\right)}{c_0 \cdot t} \tag{3}$$

Table 1
Simulated coal-combustion flue gas components.

Simulated flue gas	Gas composition (vol.%)						
	O_2	CO_2	H_2O	HCl	SO_2	NO	N_2
Basic flue gas	6	12	5.12				Balance
Complete flue gas	6	12	5.12	0.002–0.01	0.05	0.03	Balance

where c_0 is the inlet Hg^0 concentration, $c^t_{Hg^0}$ and $c^t_{Hg^{2+}}$ are the outlet Hg^0 and Hg^{2+} concentrations during the reaction, $m^t_{Hg^P}$ is the mercury mass adsorbed by the sorbents and v is the flow rate.

2.4. Characterization of the sorbents

The sorbent properties were characterized in various ways. The surface area and pore size of the sorbents were measured on an automatic nitrogen adsorption analyzer (Micrometritics ASAP2010). The surface area was measured using the Brunauer–Emmett–Teller (BET) method while the pore volume and pore size were measured using the Barrett–Joyner–Halenda (BJH) method. X-ray diffraction (XRD) was used to determine the crystals species in the sorbents using a diffractometer (Bruker D8, German) with Cu Kα radiation. X-ray photoelectron spectroscopy (XPS, 250Xi ESCA) was used to analyze the copper valence on the surface of the sorbents. The C1s line at 284.8 eV was taken as the reference for the binding energy calibration. Hydrogen temperature-programmed reduction (H_2-TPR) measurements were conducted on a CHEMISORB 2720 chemisorption analyzer by increasing the temperature from 60 to 700 °C at a heating rate of 10 °C/min.

3. Results and discussion

3.1. Mercury speciation in simulated coal-fired flue gas

As shown in Fig. 1, the overall mercury oxidation rates for 1 h were higher than 65% for both of the sorbents, but the mercury adsorption amounts were relatively low. The oxidation rates were increased with the increasing copper loading. Since the contact time of sorbents and flue gas in coal-fired power plants are always less than 1 min [18], the tests within 5 min were conducted to study the initial adsorption amounts of the sorbents in coal-fired power plants. It can be seen from the 5 min test that the initial adsorption rates were over 75% in the early stage of the mercury removal process. Thus the CuO_x–Al_2O_3 sorbents demonstrate good mercury removal capacities and excellent catalytic oxidation capacities. CuO_x–Al_2O_3 are good mercury sorbents for coal-fired power plants. Larger Cu loading is favored for higher mercury removal rates.

3.2. Effect of HCl concentration

Many previous studies have shown that HCl can promote mercury oxidation [8,19,20]. The effect of HCl is due to the formation of active chlorine [7,11,21–24]:

$$4HCl + O_2 \overset{CuOx}{\leftrightarrow} Cl_2 + 2H_2O \tag{4}$$

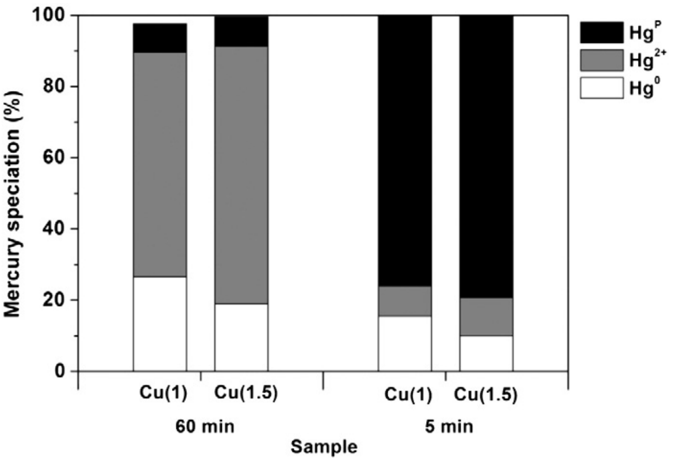

Fig. 1. Mercury speciation of the sorbents (140 °C, complete flue gas with 50 ppm HCl).