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Comprehensive Hg/Br reaction chemistry over Fe_2O_3 surface during coal combustion

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ABSTRACT

A combination of experiments, density functional theory (DFT) and kinetic calculations was used to systematically understand the detailed chemistry of heterogeneous mercury reaction with HBr over Fe_2O_3 surface. Fe_2O_3 shows catalytic activity for mercury reaction with HBr. The chemisorption mechanism is responsible for the adsorption of mercury species (Hg^0, HgBr and $HgBr_2$) on Fe_2O_3 surface. Heterogeneous mercury reaction with HBr over Fe_2O_3 surface follows Langmuir–Hinshelwood mechanism in which adsorbed Hg^0 reacts with active surface bromine species derived from HBr decomposition. On the basis of the experimental and DFT calculation results, a new comprehensive heterogeneous reaction kinetic model was established to describe the detailed reaction process of Hg/Br over Fe_2O_3 surface. This heterogeneous model includes 17 elementary reactions governing the elimination and formation of mercury species on Fe_2O_3 surface. This kinetic model was validated against the experimental data. The model predictions were found to be in good agreement with the experimental data. X-ray photoelectron spectroscopy (XPS) results, DFT calculations and sensitivity analysis indicate that the dominant reaction pathway of Hg/Br over Fe_2O_3 surface is a four-step process $Hg^0 \rightarrow Hg(s) \rightarrow HgBr(s) \rightarrow HgBr_2(s) \rightarrow HgBr_2$, in which gaseous Hg^0 is first adsorbed on Fe_2O_3 surface and subsequently reacts with brominated iron site to form HgBr(s), HgBr(s) can be further converted to $HgBr_2(s)$ and released into flue gas. The proposed dimensionless temperature coefficient can be used to better understand the temperature-dependent relationship between heterogeneous Hg/Br chemistry and mercury transformation.

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1. Introduction

Mercury, a global hazardous atmospheric pollutant, has been associated with several human health problems such as chronic renal failure, birth defects, and chromosome aberrations [1]. In recent years, coal-fired power plant has become the main source of anthropogenic mercury emissions [2–4]. In United States, Mercury and Air Toxics Standards (MATS) with a maximum emission concentration between 1.4 and 4.1 μg/m^3 (STP, dry) at 6 vol% O_2 was issued to limit mercury emission from the existing coal-fired power plants [5]. Therefore, it is urgent to reduce mercury emission from coal-fired power plants, which highly depends on the understanding of the underlying mechanisms of mercury transformation in flue gas [3].

Mercury removal efficiency of coal-fired power plants is closely associated with mercury speciation in flue gas [6,7]. Mercury species in coal-fired flue gas include elemental mercury (Hg^0), oxidized mercury (Hg^{2+}) and particulate bound mercury (Hg_p). Water-soluble Hg^{2+} can be easily removed by the wet flue gas desulfurization (WFGD) system, or adsorbed on fly ash particles as Hg_p and subsequently captured with high efficiency by air pollution control devices (APCD) [8,9]. However, Hg^0 is difficult to be captured and removed by APCD because of its water insolubility and chemical inertness [10–12]. Consequently, one of the largest challenges of mercury emission control in coal-fired power plants is the transformation of Hg^0 into Hg^{2+} or Hg_p.

Previous field tests have showed that bromine addition can effectively enhance mercury transformation in low-rank coal-fired flue gas with low HCl concentration [13–17]. Both homogeneous reactions and heterogeneous interactions with fly ash particles are simultaneously involved in the complicated mercury transformation process [18–20]. Several homogeneous reaction mechanisms have been proposed to predict mercury transformation in clean simulated flue gas with bromine addition [21–24]. However, the quantitative accuracy of model prediction using these proposed homogeneous mechanisms has been called into question under the realistic flue gas conditions [18,25], because fly ash can catalyze mercury transformation in actual coal-fired flue gas [10,14].

Compared to homogeneous reactions, heterogeneous gas–solid interactions are dominant for mercury transformation in coal-fired

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flue gas [18,19]. Based on the interaction between bromine species and unburned carbon (UBC) within fly ash, an eight-step heterogeneous mechanism was developed and combined with homogeneous mechanism to predict mercury transformation in coal-fired flue gas [26,27]. Moreover, a series of experimental and theoretical studies [28–31] have indicated that Fe_2O_3 within fly ash exhibits catalytic activity for mercury transformation in flue gas. About 13.5–40% of Fe_2O_3 would be exposed to the flue gases in the real situation [29,32]. Consequently, a heterogeneous Hg/Cl/Br mechanism involving the catalytic activity of Fe_2O_3 was proposed to predict mercury transformation in coal-fired flue gas [33]. However, the heterogeneous Hg/Br sub-mechanism over Fe_2O_3 surface was not validated independently for lack of experimental data, because the previous experimental studies [28–30] only investigated mercury reaction with HCl over Fe_2O_3 surface and not considered mercury reaction with HBr. The model performance is dependent on the availability of accurate experimental data [34]. Therefore, the details of heterogeneous Hg/Br reaction chemistry over Fe_2O_3 surface are highly uncertain. Also, to date, no detailed experimental data of the heterogeneous mercury reaction with HBr over Fe_2O_3 surface has been reported for the validation of heterogeneous Hg/Br sub-mechanism. In addition, there has been no studies reported on the temperature-dependent relationship between heterogeneous Hg/Br chemistry and mercury transformation.

The objective of present work is to update the heterogeneous chemistry of mercury reaction with HBr over Fe_2O_3 surface. Fe_2O_3 samples were prepared to experimentally investigate the heterogeneous mercury reaction with HBr over Fe_2O_3 surface. The density functional theory (DFT) calculations were carried out to identify the mercury reaction mechanism and provide kinetic parameters for the key heterogeneous reactions. A new comprehensive kinetic model was developed to describe the heterogeneous mercury transformation process, and validated against experimental data. A dimensionless temperature coefficient (ψ) was proposed to explore the role of reaction temperature in heterogeneous Hg/Br chemistry. To the best of the authors' knowledge, this is the first experimental and DFT study exploring the heterogeneous mechanism of mercury reaction with HBr over Fe_2O_3 surface. This study can provide a fundamental understanding for the reaction mechanism and kinetics of mercury transformation in coal-fired flue gas with bromine addition.

2. Experimental section

2.1. Fe_2O_3 preparation and characterization

Fe_2O_3 samples were synthesized by a precipitation method [35] at the room temperature. $Fe(NO_3)_3$•$9H_2O$ was used as the iron precursor and dissolved in deionized water under stirring. Aqueous ammonia, a kind of precipitating agent, was added dropwise to the $Fe(NO_3)_3$ solution until the precipitation was complete. The precipitate was filtrated and washed three times with deionized water. The collected precipitate was dried at 110 °C for 12 h and subsequently calcined in a muffle furnace at 550 °C for 3 h. Finally, the calcined Fe_2O_3 samples were ground and sieved to 180 mesh.

A nitrogen adsorption apparatus (ASAP-2020, Micromeritics) was used to measure the Brunauer–Emmett–Teller (BET) surface area of prepared Fe_2O_3. Prior to BET measurement, Fe_2O_3 samples were degassed at 200 °C for 2 h. Powder X-ray diffraction (XRD) measurement of the Fe_2O_3 samples was conducted using a diffractometer (XRD-7000, Shimadzu, Japan) equipped with Cu Ka ($\lambda = 1.5406$ nm) radiation. The powder XRD pattern in the 2θ range of 20–80° was recorded at a step of 0.03 °/min. X-ray photoelectron spectroscopy (XPS) analysis was carried out on a Thermo ESCALAB 250 instrument with Al Kα ($h\nu = 1486.6$ eV) as the excitation source. The binding energy was calibrated using C1s peak at 284.6 eV. Spin–orbit coupling arises from the coupling of the magnetic fields produced by an electron spinning around its own axis (defined by spin quantum number, m_s) and that produced by an electron spinning around its nucleus (defined by angular momentum quantum number, l) if following a nonsymmetric orbital ($l > 0$). The spin orbit coupling can be described by the inner quantum number (j) [36]. In this work, the spin–orbit coupling was considered when we fitted the core level spectra of Fe, Br and Hg. The inner quantum numbers of (1/2 and 3/2), (3/2 and 5/2), and (5/2 and 7/2) were considered for fitting the core level spectra of Fe, Br, and Hg, respectively.

2.2. Heterogeneous reaction tests

It was reported that mechanistic investigations will most likely require laboratory-scale experiments under simulated flue gas conditions [37], because the complexity of real coal-derived flue gas under the commercial operating conditions may prevent the elucidation of the reaction mechanism. Therefore, in this work, the laboratory studies of specific reactions were used to elucidate the heterogeneous mechanism of mercury conversion over Fe_2O_3 surface in the presence of HBr. Heterogeneous mercury reaction experiments were conducted in a fixed-bed quartz reactor (i.d. 10 mm) placed in a temperature controlled tubular furnace. The schematic diagram of experimental system is shown in Fig. 1. Hg^0 vapor was generated from mercury permeation device and introduced into the simulated flue gas (4% O_2, 12% CO_2, 5 ppm HBr, N_2 as the balance gas). To avoid the disturbance of other flue gas species (moisture, SO_2, NO and HCl) to the study of surface reaction kinetic mechanism, these species were intentionally not included in the synthetic flue gas. To provide a constant Hg^0 concentration (about 45 μg/m^3), the sealed U-shaped tube with a mercury permeation device was immersed in a fixed temperature (45°C) water bath. The total flue gas flow rate was maintained at 1 L/min, which corresponded to a space velocity of about 5×10^4 h^{-1}. 0.5 g of Fe_2O_3 samples and 1.5 g of quartz sand were loaded into the quartz reactor. The mixture of Fe_2O_3 samples and quartz sand was supported by the quartz sieve plate of reactor, and was packed by quartz wool to avoid sample loss. The quartz wool and sand have been demonstrated to be inert towards mercury conversion. To decrease the flow resistance of flue gas, the bed layer was not compacted. The length of reaction zone for heterogeneous mercury transformation was approximately 16 mm. Hg^0 concentration in simulated flue gas was continuously monitored using a mercury analyzer (VM3000, Mercury Instruments, Germany). The impinger containing 10 wt% KCl and 0.5 wt% $Na_2S_2O_3$ solution was used to capture oxidized mercury. Another impinger containing 10 wt% NaOH solution was used to remove acid gas HBr, avoiding the corrosion of mercury analyzer.

At the beginning of every mercury transformation experiment, the simulated flue gas stream passed through bypass to determine the stable inlet Hg^0 concentration (C_{in}). After the experimental system obtained a stable C_{in} for 30 min, the gas stream was switched to reactor to measure the outlet Hg^0 concentration (C_{out}). A stable equilibrium situation of heterogeneous Hg/Br reaction would be reached when C_{out} stabilized for more than 30 min. Subsequently, the gas stream was switched from reactor to bypass to verify the stability of C_{in}. Thus, the reduced amount of Hg^0 across Fe_2O_3 samples was ascribed to Hg^0 conversion. The conversion of mercury (E_{con}) can be defined as follows:

$$E_{con}(\%) = (1 - C_{out}/C_{in}) \times 100\% \quad (1)$$

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