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Homogeneous and heterogeneous reaction mechanisms and kinetics of mercury oxidation in coal-fired flue gas with bromine addition

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Abstract

A detailed kinetic model consisting of homogeneous mechanism with 352 elementary reactions and a new heterogeneous mechanism on fly ash surface was developed to predict mercury oxidation in coal-fired flue gas with bromine addition. The heterogeneous mechanism involves the catalytic oxidation activity of unburned carbon (UBC) and Fe_2O_3 within fly ash, and includes 38 irreversible elementary reactions governing the adsorption, oxidation and desorption of mercury on fly ash. The competitive adsorption among flue gas compositions is also involved in the heterogeneous mechanism. Kinetic parameters of some homogeneous reactions in the Hg/Br and Hg/Cl sub-mechanisms have been updated based on the recent experimental data obtained by the improved aqueous chemistry methods. This kinetic model was validated by comparison to lab-, pilot- and full-scale experimental data. The comparison shows that the model predictions are in good agreement with the experimental data. The rate of production analysis illustrates that the heterogeneous pathway is dominant for mercury oxidation in coal-fired flue gas with bromine addition. The sensitivity analysis and reaction path analysis indicate that the dominant pathway of heterogeneous mercury oxidation by bromine on fly ash surface is $Hg^0 \rightarrow StHgBr(s) \rightarrow HgBr_2$, whereby a brominated carbon site partially oxidizes Hg^0 into StHgBr(s) which is subsequently oxidized into $HgBr_2$. NO and SO_2 weakly inhibit mercury oxidation. H_2O exhibits an inhibitory effect on heterogeneous Hg oxidation because of the elimination of brominated carbon sites.

Keywords: Heterogeneous mechanism; Mercury; Bromine addition; Kinetic model; Fly ash

1. Introduction

Mercury has been regarded as the hazardous atmospheric pollutant because of its toxicity, volatility, persistence, bioaccumulation in the ecosystem and food chain, and neurological health effects [1]. Fossil fuel combustion (particularly coal-fired power plants) is one of the main sources of mercury emissions, which contributes approximately 24% of total anthropogenic mercury emissions [2]. Therefore, it is imperative to effectively control mercury emissions from coal-fired power plants.

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Mercury mainly exists in three forms in coal-fired flue gas: elemental mercury (Hg^0), oxidized mercury (Hg^{2+}) and particulate bound mercury (Hg_p) [3,4]. During coal combustion, mercury is vaporized and released into flue gas in Hg^0 form which is difficult to be captured by the existing air pollution control devices (APCD) [5,6]. As the flue gas cools, Hg^0 can undergo a series of homogeneous and heterogeneous reactions and partially convert to Hg^{2+} [7,8]. Water-soluble Hg^{2+} can be easily removed by the wet flue gas desulfurization (WFGD) system, or adsorbed on fly ash as Hg_p and subsequently captured by APCD [9,10]. Consequently, the method to effectively oxidize Hg^0 into Hg^{2+} is critical for mercury emission control in coal-fired power plants.

The bromine addition can be applied at very lower concentrations to effectively enhance mercury oxidation [11–13]. Both homogeneous gas–gas reactions and heterogeneous gas–solid interactions are simultaneously involved in mercury oxidation in coal-fired flue gas [5]. The complete understanding of mercury oxidation mechanisms and kinetics that control the transformation of Hg^0 to Hg^{2+} is crucial for the effective mercury emission control in coal-fired power plants [14]. Some homogeneous mercury oxidation mechanisms have been proposed to predict mercury oxidation in simulated flue gas [7,15–17]. However, these homogeneous mechanisms are unable to accurately predict mercury oxidation in actual coal-fired flue gas [8,16,17], because fly ash particles can catalyze the mercury oxidation.

In recent years, some heterogeneous experiments reported that HBr addition to Powder River Basin (PRB) coal-fired flue gas can promote Hg^0 oxidation and subsequently enhance mercury capture by fly ash [11,12]. Compared to homogeneous reactions, heterogeneous interactions are dominant for mercury oxidation in coal-fired flue gas [8,14]. Niksa et al. [16,17] developed an eight-step heterogeneous mechanism for mercury oxidation by bromine on unburned carbon (UBC) of fly ash, but the catalytic oxidation activity of Fe_2O_3 within fly ash was not considered. Thus, this heterogeneous mechanism cannot accurately describe the significant mercury oxidation capacity of iron-rich fly ashes.

Previous experimental studies indicated that Fe_2O_3 within fly ash can exhibit an excellent catalytic oxidation performance for mercury oxidation in flue gas [18,19]. To date, no heterogeneous reaction mechanism of mercury oxidation by bromine on Fe_2O_3 within fly ash has been proposed. In addition, experiments showed that mercury oxidation on fly ash was affected by the competitive adsorption among HBr, HCl, SO_x and H_2O in flue gas [20]. However, the surface reaction mechanism for competitive adsorption among HBr, HCl, SO_x and H_2O on UBC and Fe_2O_3 within fly ash is still unknown.

In this study, a new detailed heterogeneous reaction mechanism for mercury oxidation by bromine and chlorine on fly ash was developed and combined with homogeneous mechanism to predict mercury oxidation in coal-fired flue gas with bromine addition. The catalytic activity of UBC and Fe_2O_3 within fly ash and competitive adsorption among HBr, HCl, SO_x and H_2O were considered. To the authors' knowledge, this is the first kinetic investigation involving the heterogeneous mechanism of mercury oxidation by bromine on Fe_2O_3 within fly ash and competitive adsorption. This study can provide a more complete understanding of homogeneous and heterogeneous reaction mechanisms and kinetics of mercury oxidation in coal-fired flue gas with bromine addition.

2. Model development

2.1. Homogeneous mechanism of C/H/O/N/S/Cl/Br/Hg

The homogeneous mechanism involves Hg/Cl chemistry, Hg/Br chemistry, Hg/Br/Cl chemistry, Hg/O chemistry, C/H/O/N/S/Cl/Br chemistry, CO chemistry, NO_x chemistry and SO_x chemistry. Mercury oxidation is directly or indirectly affected by these reaction sub-mechanisms. Rate constants of these reactions are in the modified Arrhenius form, $k = AT^n\ exp(-E_a/RT)$. The Hg/Cl and Hg/O sub-mechanisms are presented in Table 1. The Hg/Br and Hg/Br/Cl sub-mechanisms are given in Table 2. The pre-exponential factor of reaction 5 in Table 2 was calculated based on the collision theory. The temperature exponent and activation energy were obtained from reference [15]. The C/H/O/N/S/Cl/Br sub-mechanism was obtained from NIST chemical kinetics database [21] and literatures [22,23]. The NIST CO oxidation sub-mechanism [24] and the Leeds NO_x and SO_x sub-mechanisms [25] were used in this study. In total, this homogeneous mechanism includes 94 species and 352 elementary reactions.

2.2. Heterogeneous Hg/Cl/Br mechanism on unburned carbon (UBC)

HCl is the most important species for mercury oxidation in coal-fired flue gas without bromine addition. The chlorinated UBC shows higher catalytic activity for mercury oxidation on fly ash. Thus, the heterogeneous mechanism for Hg oxidation by chlorine on UBC is proposed as follows:

$$StSA(s) + HCl \rightarrow StCl(s) + H \quad (R1)$$

$$StCl(s) + Cl \rightarrow Cl_2 + StSA(s) \quad (R2)$$

$$StCl(s) + Hg^0 \rightarrow StHgCl(s) \quad (R3)$$

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