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Kinetic modelling of homogeneous low temperature multi-pollutant oxidation by ozone: The importance of SO and HCl in predicting oxidation*

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Abstract: A detailed kinetic model consisting of 126 reactions and 37 species modelled homogeneous low temperature multi-pollutant oxidation in flue gases by ozone. The kinetic model includes the oxidation and chlorination of key flue-gas components, as well as reactions involving SO. An important and previously unrecognized pathway of homogeneous Hg oxidation mechanism includes Hg reactions involving oxygen-containing compounds and chlorine-containing compounds. Analyses by sensitivity simulations revealed that the pathway Hg+Cl=HgCl and $HgCl+Cl_2=HgCl_2+Cl$ is more significant than some of the key reactions in the kinetic mechanism proposed in the literature except $Hg+NO_3=HgO+NO_2$, which indicates the possibility to promote the Hg removal by adding HCl in the inlet stream. Studies on the effects of SO show that SO violently prevents NO consumption through the pathway $SO+NO_2=NO+SO_2$, even the net NO produced under the condition of low O_3 concentration and high SO concentration.

Key words: Low temperature oxidation, Multi-pollutant removal, Kinetic modelling, Reaction mechanism
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INTRODUCTION

The concurrent removal of multi-pollutants by power plants has become a recent concern on the part of the electric utility industry. The low temperature oxidation process was originally developed as a high-efficiency NO_x control technology. The process utilizes the injection of ozone into the flue gas to convert NO and NO_2 to higher oxides of nitrogen (such as N_2O_5), which are easily removed in a wet scrubber. Perhaps even more important is the recently demonstrated capability of ozone to oxidize elemental mercury and hydrogen sulfide in the flue gas. Since low temperature oxidation is generally employed upstream of a wet scrubber, the result is an integrated emission control system capable of controlling NO_x together with Hg, SO_2, H_2S, HCl (Kilgroe and Senior, 2003; Jarvis *et al*., 2003; Fu and Diwekar, 2004). The reaction chemistry pertaining to the low temperature reactions through which multi-pollutants and O_3 react was collected.

Hg^0 is insoluble in water, HgO has low solubility in water and $HgCl_2$ is highly soluble in water. Since $HgCl_2$ is water-soluble, it can be captured in wet chemical scrubbers to prevent its release to the atmosphere. Previous studies on the mercury oxidation in combustion systems have identified that HCl can effectively remove Hg (Senior *et al*., 2000; Mamani-Paco and Helble, 2000; Edwards *et al*., 2001; Niksa *et al*., 2001). Therefore, understanding of the mechanisms of Hg oxidation and the effects of HCl on Hg oxidation in flue gases is important when considering mercury capture by ozone.

The combustion of fuel-bound sulfur (Fuel-S) proceeds as follows: Fuel-S→SO→SO_2→SO_3. The conversion of SO to dioxide is generally rapid (involving hydroxyl radicals), and the relative post flame SO and SO_2 concentrations can be deduced from

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equilibrium calculations (Bowman, 1991). If the hydroxyl pool is perturbed it is possible for sulfur oxide to be present in the flue gas. Therefore, the implications of SO breakthrough for the process were also investigated.

MODEL DESCRIPTION

A well-mixed process is one which occurs in a perfectly stirred reactor (PSR), consisting of a tank in which continuous batch chemical processing occurs, and it is modelled employing the CHEMKIN and PSR codes (Kee *et al.*, 199). In this work, kinetic information on the individual isolated reactions was obtained from other experiments and references. Some thermodynamic curve-fits were obtained from the National Institute of Standards and Technology chemical species database (Mallard *et al.*, 1998), while information on other species was obtained from the CHEMKIN database.

Salient features of the PSR code are briefly reviewed. The stirred reactor consists of a chamber with inlet and outlet ducts. The walls of the chamber are assumed to be non-catalytic, and the reactor is characterized by nominal residence time (deduced from the flow rate and the reactor volume). Heat losses are neglected in order to focus on the chemical mechanism underlying ozone oxidation. The flow is assumed steady, and the temperature and composition in the reactor volume are assumed to be the same as that at the reactor exit.

A representative stream of flue gas and ozone mixed gas was introduced into a PSR at 101.3 kPa. The mixed gas was assumed to consist of fixed amounts of CO, CO_2, Hg, H_2O, NO, NO_2, O_2, H_2, SO_2, O_3 and H_2S and varying fractions of HCl and SO. N_2 served as balance gas. In the present study, the mole fractions of species at the reactor inlet are given in Table 1. The residence time (corresponding to flow through the reactor) and the temperature were assumed to be 1 s and 400 K, respectively.

Table 1 Concentrations of individual gases used in the simulated mixed gas streams

Gas	Concentration in final gas stream
CO	100×10^{-6}, volume fraction
Hg	12 μg/m^3
NO	300×10^{-6}, volume fraction
O_2	0.06, volume fraction
H_2	10×10^{-6}, volume fraction
O_3	600×10^{-6}, volume fraction
SO	Variable
CO_2	0.12, volume fraction
H_2O	0.001, volume fraction
NO_2	20×10^{-6}, volume fraction
SO_2	1600×10^{-6}, volume fraction
H_2S	80×10^{-6}, volume fraction
HCl	Variable
N_2	Balance

RESULT AND DISCUSSION

Effects of HCl on mercury oxidation

Chemical kinetic sensitivity analysis indicates that the mercury oxidation occurring due to reactions with NO_3, H_2O_2, O_3 and Cl, persisted into the oxidation region. The primary gas-phase Hg oxidation product is believed to be HgO, the specie favored by equilibrium conditions. The reaction Eq.(1) is the dominant path of Hg consumption, with Cl playing an important role in Hg consumption too.

As discussed in literature (Hall *et al.*, 1990; Widmer *et al.*, 1998; Sliger *et al.*, 2000), HCl promotes mercury oxidation. Modelling indicates that essentially all the mercury oxidized via the Cl atom reaction is converted to the intermediate HgCl, Hg destruction due to the reaction Eq.(3), the intermediate HgCl is converted to the final oxidation form, $HgCl_2$, primarily by reaction Eq.(4), with little input from the reaction Eq.(5). Therefore, Cl is important early in the oxidation zone, but Cl_2 becomes important in the final conversion to $HgCl_2$. The atom Cl is produced throughout the residence time in the reactor by reaction Eq.(6). The majority of Cl_2 produced comes from the recombination of Cl atom. Therefore, the initial Cl production rate also ultimately affects Cl_2 production.

$$NO_3+Hg=HgO+NO_2, \tag{1}$$
$$O_3+Hg=HgO+O_2, \tag{2}$$
$$Hg+Cl=HgCl, \tag{3}$$
$$HgCl+Cl_2=HgCl_2+Cl, \tag{4}$$
$$HgCl+Cl=HgCl_2, \tag{5}$$
$$HCl+NO_3=Cl+HNO_3. \tag{6}$$

The chemical kinetic model accurately reflects the influence of HCl on mercury oxidation. Fig.1 shows the effect of HCl on oxidation for runs with O_3 volume fraction at 600×10^{-6} and temperature at 400 K. Since modelling indicates that mercury oxidation via chlorine-containing compounds is dependant on Cl formation, the dependence explains both the relationship between HCl concentration and NO_3 concentration, higher mercury oxidation fractions via chlorine-containing compounds are expected at higher HCl concentration, when more Cl is produced. The dependence trend of mercury oxidation on HCl concentration was observed in both the experimental data (Hall *et al.*, 1991; Widmer *et al.*, 2000; Sliger *et al.*, 2000) and the chemical kinetics modelling.

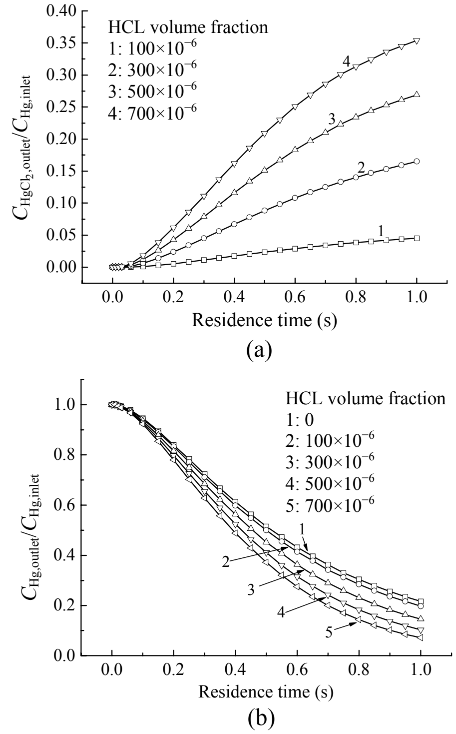

Fig.1 The variation of $C_{HgCl_2,outlet}/C_{Hg,inlet}$ (a) and $C_{Hg,outlet}/C_{Hg,inlet}$ (b) with residence time for different HCl concentration. SO volume fraction at 600×10^{-6}

Effects of SO on multi-pollutant oxidation

There is strong correlation between the SO concentration and removal of multi-pollutant, as illustrated in Fig.2. Key reactions systematically identified determine the consumption (and production) pathways for the relevant species. Significant reactions involving $NO/H_2S/SO_2$ at low temperatures include:

$$NO+O_3=NO_2+O_2, \tag{7}$$

$$NO_2+O_3=NO_3+O_2, \tag{8}$$

$$O_3+H_2S=H_2O+SO_2, \tag{9}$$

$$SO+O_3=SO_2+O_2. \tag{10}$$

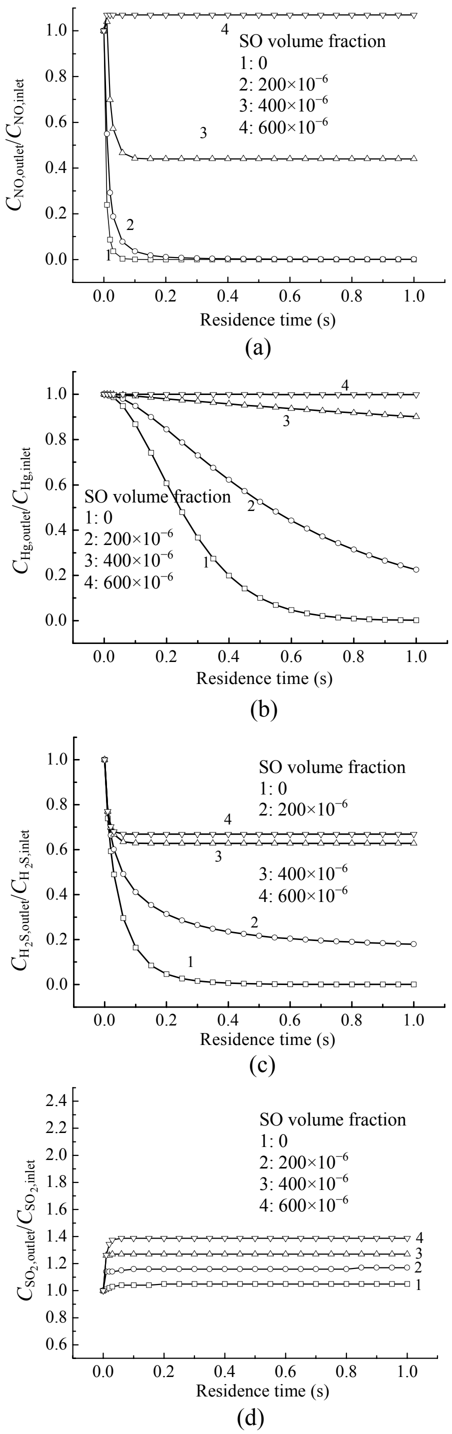

Fig.2 The variation of multi-pollutant with residence time for different SO concentration. HCl volume fraction at 600×10^{-6}. (a) NO; (b) Hg; (c) H_2S; (d) SO_2

When the SO volume fraction changes from 0 to 400×10^{-6}, the rate of reaction Eq.(7) exceeds that of reaction Eq.(11). SO has less effect on multi-pollutant oxidation and is also responsible for ozone consumption through reaction Eq.(10).

$$SO+NO_2=SO_2+NO. \tag{11}$$

When lower levels of SO are included in the inlet stream ($<200\times10^{-6}$), NO is almost completely converted to NO_2, and then partly to NO_3. With higher SO concentration ($>600\times10^{-6}$), significant SO_2 occurs through the reactions Eqs.(9) and (10). However, most of the SO consumption and the SO_2 production occur due to the reaction Eq.(11), which under these conditions becomes a dominant route for NO formation. The net effect of the reaction is to reconvert NO_2 to NO. In the presence of increased amounts of O atoms (due to ozone decomposition) a secondary path of NO oxidation occurs through the reaction

$$O+NO+M=NO_2+M, \tag{12}$$
$$O+NO=NO_2. \tag{13}$$

In the absence of O atoms formed due to SO oxidation it is the reverse direction of reactions Eqs.(12) and (13). Reaction pair Eqs.(12) and (13) are three-body reactions, and the corresponding high-pressure limit forms. These were implemented as separate reactions to account for uncertainties in the rate of either reaction belonging to the pair.

Reaction Eq.(11) produces a net increase in NO concentration, since the rate of this reaction exceeds that of reaction Eq.(7). Therefore, at high concentrations of SO net NO production is possible. The rate of reaction Eq.(8) and NO_3 concentration decrease with increasing SO concentration, the Hg and H_2S consumptions occur at lower reaction rate.

Residence times

The residence time corresponding to flow through the reactor does not seem to have great effect on NO/H_2S consumption and SO_2 production. As shown in Fig.2, NO, H_2S and SO_2 rapidly reach the equilibrium between the forward and reverse rates for the chemical reactions for the inlet stream composition considered in the study. Therefore, longer residence times do no necessarily contribute towards larger NO/H_2S conversion by ozone during the well-mixed process considered here. However, the Hg oxidation is still slow even though at low SO concentrations.

CONCLUSION

A parametric investigation of low-temperature multi-pollutant oxidation was conducted using a perfectly stirred reactor model with the input stream consisting of a representative flue gas and ozone gas mixture.

The oxidation of Hg via chlorine-containing compounds plays an important role. The primary pathway includes Hg+Cl=HgCl and $HgCl+Cl_2=HgCl_2+Cl$. The results support the conclusion that control on Hg is essential for effective removal of Hg by chlorine species.

The oxidation of NO due to ozone oxidation occurs largely through the reaction $NO+O_3=NO_2+O_2$, in the presence of SO, net NO formation occurs through the reaction $SO+NO_2=SO_2+NO$.

In the presence of high SO levels in the feed stream even with moderate ozone input ($SO=600\times10^{-6}$, $O_3=600\times10^{-6}$), it is determined that the NO inlet mole fraction can be increased at the outlet, Hg oxidation almost does not occur and H_2S oxidation can be reduced to 33%.

Higher residence time does not imply higher NO/H_2S removal. Equilibrium between the forward and reverse rates for the chemical reactions is rapidly achieved.

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