

## RATES OF CARBON OXIDATION AND CHLORINATED ORGANIC COMPOUND FORMATION FROM MIXTURE OF CARBONACEOUS MATERIAL AND METALLIC CHLORIDES AT LOW TEMPERATURE

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### **Introduction**

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are recognized to be synthesized during oxidation of unburnt carbon particles, "soot," without via precursors such as chlorophenols (CPs) in thermal processes. This is often referred to as "*de novo*" synthesis reaction and occurs at an oxidizing atmosphere at rather low temperatures, e.g., from 200°C to 500°C. "Soot" particles are formed through condensation reactions of hydrocarbons and are suspended in exhaust gases. They show complex states of composites containing carbon and various finely dispersed metallic and nonmetallic compounds. They are also responsible for the formation of various chlorinated organic compounds such as CPs and chlorobenzenes (CBs) at the same time<sup>1)</sup>. Thus, it is difficult to quantitatively and systematically relate the properties of "soot" to the rates of carbon oxidation and formation of chlorinated organic compounds including PCDD/Fs.

In the present study, a series of *de novo* experiments were carried out using modeled "soot" particles prepared by mixing graphite powder with a reagent grade and different metallic chlorides, i.e., CuCl, CuCl<sub>2</sub>·2H<sub>2</sub>O, FeCl<sub>3</sub>·6H<sub>2</sub>O, CaCl<sub>2</sub>·2H<sub>2</sub>O or KCl. The relationship between the rates of carbon oxidation and formation of chlorinated organic compounds is discussed on the basis of the results.

### **Experimental Materials and Methods**

Reagent grade graphite powder was first rinsed twice, with distilled water and acetone respectively, and then dried completely at 100°C. This is referred to as sample [G] in the present paper. Specific surface area and average particle size of [G] are 7.9 m<sup>2</sup>/g and 12.8 μm, respectively.

Reagents of copper (I) chloride (CuCl), copper (II) chloride dihydrate (CuCl<sub>2</sub>·2H<sub>2</sub>O), iron (III) chloride hexahydrate (FeCl<sub>3</sub>·6H<sub>2</sub>O), calcium chloride dihydrate (CaCl<sub>2</sub>·2H<sub>2</sub>O), and potassium chloride (KCl) were used as additives, which may act as both catalysts and chlorine sources during *de novo* experiment. Chlorine concentrations were set from 0 to 1 mass%. The sample [G] and metallic chloride were mixed as follows:

Acetone, ethanol or water solution of the metallic chloride was added to [G] and hand-mixed well. It was then dried at 100°C. In the case of KCl addition, the powder of KCl reagents was directly added to [G] and hand-mixed well. They were press-shaped into disk tablets and then crushed to prepare granulated samples. The granulated samples were sieved to retrieve those that were between 1 and 2 mm in size.

A schematic diagram of the experimental apparatus is illustrated in Fig. 1. Ten grams of the granulated sample were packed in a reaction tube made of heatproof glass of 27 mm internal diameter. The height of the sample bed was approximately 25 mm. The gas mixture of Ar-O<sub>2</sub> (2.5

mol%) was introduced to the sample bed with superficial velocity of 58 Nmm/s. Then the reaction tube was placed in an electric furnace. The time taken to heat up the sample bed to 300°C is approximately 15 min. After that, the bed temperature and the gas flow rate were kept constant. The time in the heating stage is represented by minus values, e.g., from -15 to 0 min.

For the sampling of organic chlorines<sup>2)</sup>, outlet gas was made to flow through ice-cooled sampling columns of activated carbon. The columns consisted of three beds, each of which was packed with one gram of activated carbon particles. After the experiment, activated carbon was first washed with distilled water and further with an

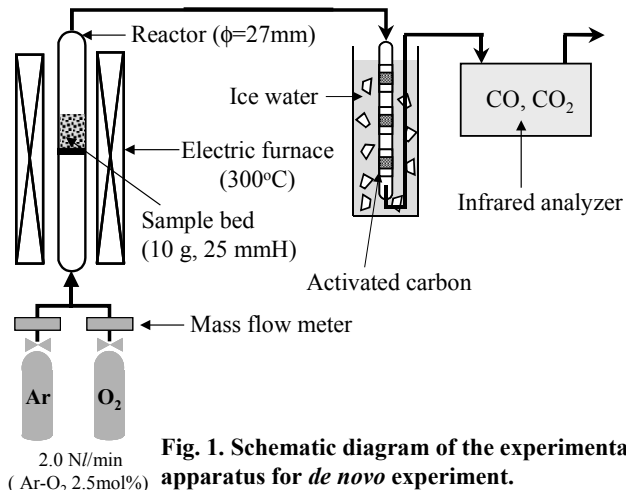


Fig. 1. Schematic diagram of the experimental apparatus for *de novo* experiment.

aqueous solution of potassium nitrate (0.8 mass%  $\text{KNO}_3$ ) to remove inorganic chlorides. Then, they were burnt in an organic halogen analyzer and the chlorine content was determined using the method of potentiometric redox titration.

Gas from the sampling column of activated carbon was then introduced to an infrared gas analyzer, and the concentrations of CO and  $\text{CO}_2$  were measured continuously.

### Results and Discussion

#### Effect of the coexistence of metallic chloride on carbon oxidation and organic chlorine formation

Figure 2 shows the plots of the total amount of carbon oxidation and detected organic chlorine in the gas traps for sample [G] and those mixed with KCl,  $\text{CaCl}_2$ ,  $\text{FeCl}_3$ , CuCl and  $\text{CuCl}_2$  (1 mass%–Cl). Sampling time for all conditions is 135 min., including the heating stage. This shows a linear

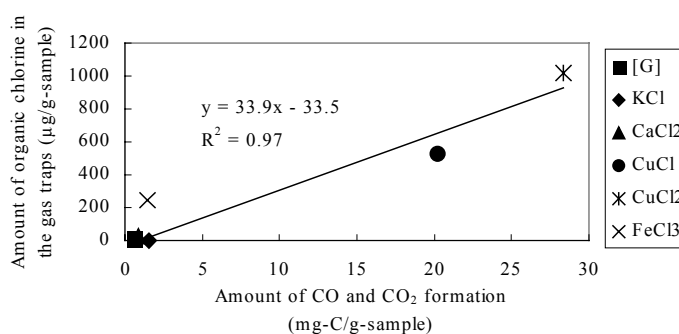


Fig. 2. Relationship between the amount of organic chlorine and carbon oxidation for various metallic chlorides additions.

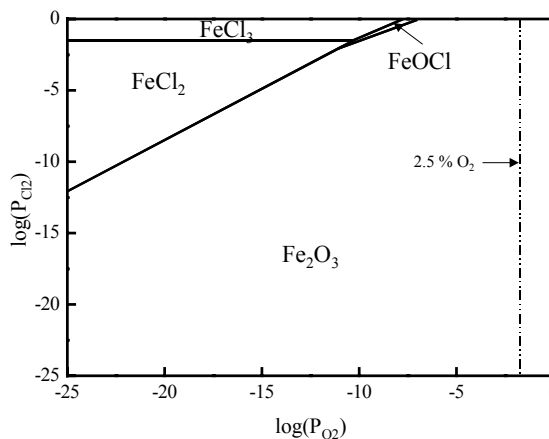


Fig. 3. Potential diagram of Fe – Cl – O at 300°C.

relation between them except in the case of  $\text{FeCl}_3$  addition. Both carbon oxidation and organic chlorine formation are significantly promoted by  $\text{CuCl}_2$  and  $\text{CuCl}$  additions. However, in comparison,  $\text{FeCl}_3$  addition only promotes organic chlorine formation. Figure 3 shows the potential diagram of Fe – Cl – O system at  $300^\circ\text{C}$ . This shows that oxide  $\text{Fe}_2\text{O}_3$  is stable in a larger region than copper (see Fig. 6). Considering the lower rate of carbon oxidation, the oxygen potential at the surface of graphite is higher than that for the  $\text{CuCl}$  and  $\text{CuCl}_2$  additions during reaction. Therefore,  $\text{FeCl}_3$  will release  $\text{Cl}_2$  and will convert to the oxide state,  $\text{Fe}_2\text{O}_3$ . According to Mul's report<sup>3)</sup>, the catalytic ability of  $\text{Fe}_2\text{O}_3$  for carbon oxidation is lower than that of  $\text{FeCl}_3$ . This can be a reason for the deviation of  $\text{FeCl}_3$  from the line shown in Fig. 2.

#### Effect of chlorinated state of copper

Figure 4 shows the relationship between the total amount of oxidized carbon and organic chlorine formation for the samples with  $\text{CuCl}$  and  $\text{CuCl}_2$  additions (0 to 1 mass%–Cl). Sampling times for these cases vary from 15 to 135 min., including the heating stage. Correlation coefficients,  $R^2$ , show high values, 0.98 and 0.93 for  $\text{CuCl}$  and  $\text{CuCl}_2$  additions, respectively. The slope for the latter is slightly greater than the former.

Table 1 shows the changes in Cu and Cl concentrations in the solid samples in the case of  $\text{CuCl}_2$  addition, with time. Cu and Cl concentrations in the solid sample decrease to 88% and 49%, respectively during the heating stage, and the molar ratio of Cl/Cu decreases to 1.11. This suggests that the reaction



has occurred in the heating stage. Also, the amount of organic chlorine formation during the heating stage (-15 to 0 min.) is  $321 \mu\text{g/g-sample}$  and it occupies about 31% of the total amount (-15 to 120 min.). On the other hand, for the  $\text{CuCl}$  addition, the value is small, i.e.,

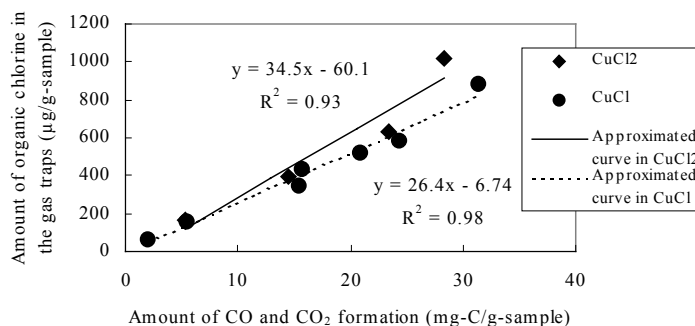


Fig. 4. Relationship between the amount of organic chlorine and carbon oxidation in the case of  $\text{CuCl}$  and  $\text{CuCl}_2$  additions.

Table 1. Remaining ratios of Cu and Cl, and the molar ratio of Cl/Cu for  $\text{CuCl}_2$  additions.

	Cu (%)	Cl (%)	Cl/Cu (mol/mol)
Initial	100	100	2.00
0 min	88	49	1.11
20 min	88	42	0.95
60 min	81	35	0.86
120 min	68	30	0.88

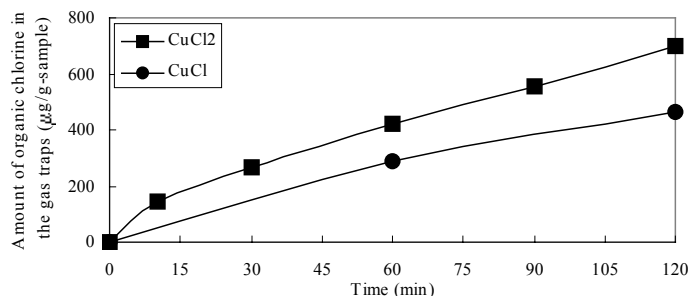


Fig. 5. Changes in the amount of organic chlorine formation in the case of  $\text{CuCl}$  and  $\text{CuCl}_2$  additions.

60  $\mu\text{g/g}$ -sample, and it occupies only 11% of the total amount. This may be because a larger amount of active Cl is available in the heating stage due to the  $\text{CuCl}_2$  addition.

Figure 5 shows the variations in the accumulated amount of organic chlorine formation after the heating stage, for the cases of  $\text{CuCl}$  and  $\text{CuCl}_2$  additions, with time. The slopes of both curves are similar, except for the initial few minutes. This indicates that most of  $\text{CuCl}_2$  changes to  $\text{CuCl}$ , and then behaves as  $\text{CuCl}$  after heating. This also agrees with the results of Table 1.

Figure 6 shows the potential diagram of Cu – Cl – O system at  $300^\circ\text{C}$ . Following X-ray Photoelectron Spectroscopy (XPS) analysis of the samples after *de novo* experiments, it has been found that copper exists not in the metallic but in the chloride state. The range of chlorine potential in this case can, therefore, be estimated as  $\log(P_{\text{Cl}_2})$ :  $-19$  to  $-3$ . Hence, the corresponding range of  $\log(P_{\text{O}_2})$  is  $-23$  to  $-3$ . This range is much lower than the oxygen concentration of the gas made to flow through the sample bed. Such “moderate” reducible conditions at lower temperatures promote the formation of organic compounds. Further investigations are needed to clarify the above phenomena including the detailed analysis of copper valence on the carbon surface using XPS.

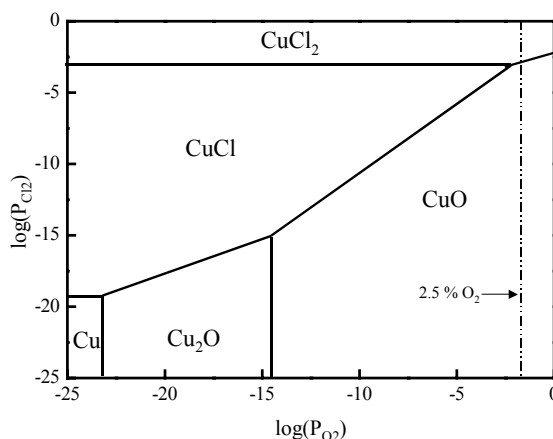


Fig. 6. Potential diagram of Cu – Cl – O at  $300^\circ\text{C}$ .

### Conclusions

*De novo* experiment was conducted using a mixture of graphite powder and metallic chlorides, i.e.,  $\text{CuCl}$ ,  $\text{CuCl}_2$ ,  $\text{KCl}$ ,  $\text{CaCl}_2$  and  $\text{FeCl}_3$ . The formation rates of  $\text{CO}$  and  $\text{CO}_2$ , and organic chlorine including PCDD/Fs were analyzed:

1. Additions of  $\text{CuCl}$  and  $\text{CuCl}_2$  promote both carbon oxidation and organic chlorine formation;
2. A linear relationship was found between carbon oxidation and organic chlorine formation except for the sample with  $\text{FeCl}_3$  addition;
3. There is a large difference in the case of  $\text{CuCl}$  and  $\text{CuCl}_2$  addition with regard to the amount of organic chlorine formation in the heating stage. However, this becomes similar under constant temperature conditions;
4. Oxygen and chlorine potentials at the surface of carbon during *de novo* experiment were roughly estimated based on the valence analysis of copper using XPS.

### Acknowledgements

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### References

1. L. Stieglitz, H. Vogg, G. Zwick, J. Beck, H. Bautz: *Chemosphere*, 23(1991), 1255
2. K. Kawamoto, N. Yasuda, H. Miyata, T. Sadatsuka: *Proc. 11<sup>th</sup> Annual Conf. Japan Soc. Waste Manag. Exp. (In Japanese)*, (2000), 691
3. G. Mul, F. Kapteijn, J. A. Moulijn: *Applied Catalysis B: Environmental*, 12(1997), 33