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PCDD/Fs FORMATION FROM MONO-CHLOROBENZENE ON SOME METALLIC OXIDES

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Introduction

Recently, a new regulations have been enforced on the dioxins emissions from some metallurgical plants/processes in Japan. They are the steelmaking using electric arc furnaces, the sintering of iron ores, the secondary zinc and aluminum productions. They are mainly recycle processes of basic metals showing relatively larger emissions to the air, although municipal and industrial wastes incinerators still give dominant values in the Japanese emission inventory. Considerable efforts are being made in respective projects to understand the formation mechanism in individual processes and develop the ways to suppress the emissions, since the behaviors of dioxins often appear to be significantly different from those in the waste incinerators. Regarding the each process condition, metallic compounds, such as oxides and chlorides, seems to play more important role in the formation and decomposition of dioxins.

The present study aims to examine the formation of PCDD/Fs from mono-chlorobenzene (MCB) on the surfaces of several metallic oxides in their packed bed. The effects of temperature, properties of oxide particles and co-existing gases are examined.

Materials and Methods

Iron ore R consisted of hematite (Fe_2O_3) and goethite (FeOOH) and other gangue minerals (see Table 1), pure silica sand and alumina spheres (1.0 mm in particle size) are used as samples. The ore and silica sand were crushed and sieved to the size range between 0.5 and 1.0 mm. Then, they were dried at 100 °C (namely D-R and silica sand). A part of ore was further calcined at 500 °C (C-R). Specific surface areas (SSA) of D-R, C-R and silica sand are 9.9, 33.1 and 0.6 m^2/g , respectively. The sample of 20 g was set on the disk filter made of silica in a fused silica tube and hold by silica wool. All the samples and silica tube, disk filter and wool were then washed in the ultrasonic baths of distilled water, pure acetone and toluene, in this order.

Figure 1 shows the outline of the experimental apparatus. Oil bath was applied in the case for reaction temperature less than 250 °C and electric furnace for that above 250 °C. Main gas introduced through the sample bed was argon. MCB (usually 7.6 mg/Nm^3) were added to the introduced gas by using an evaporator. Concentration of MCB was usually 7.6 mg/Nm^3 , and O_2 and HCl was controlled by a mass flow controller. Total gas flow rate was fixed as 1 Nl/min . Outlet gas from the reaction tube was passed through the ice cooled gas traps. The impingers contains about 100 cm^3 of distilled water, two of dichloromethane and diethyleneglicole, in order. After the experiment, the formed/remained amounts of PCDD/Fs, CBs and CPs in both the solid sample and the traps were analyzed. The obtained data on the PCDD/Fs formation is corrected by using those for the blank experiment which was carried out without using solid samples.

Table 1. Composition of iron ore R used (mass%).

T. Fe	FeO	CaO	SiO ₂	MgO	Al ₂ O ₃	LOI*
58.0	0.25	0.55	5.17	0.27	2.58	9.15

* Loss on ignition (combined water)

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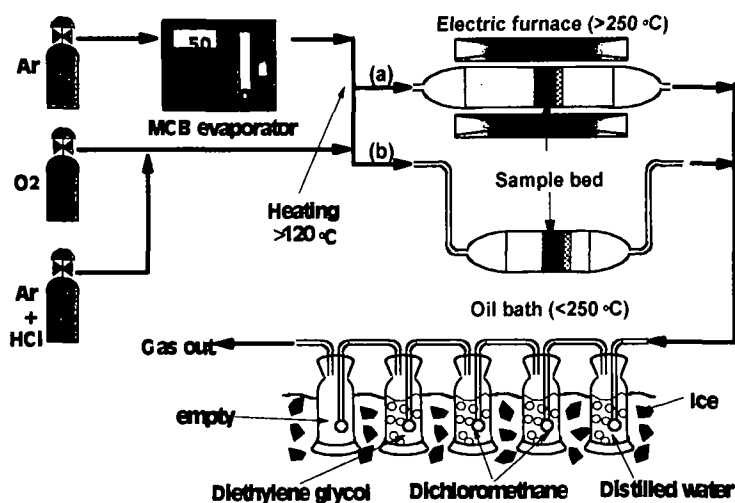


Fig. 1. Schematic diagram of experimental apparatus.

Results and Discussions

Figure 2 shows the effect of temperature on the amount of PCDD/Fs formation for 120 min in the case using C-R sample and O₂ 2.5 mol%. The total PCDD/Fs formation shows the largest value at 300 °C and the maximum value appears to be at around 350 °C. The ratio of PCDD to PCDF does not significantly change with temperature. The amounts of PCDD/Fs determined in solid sample and gas trap are shown in Fig. 3. PCDD/Fs in the solid sample increases rapidly at 300 °C but then decreases, while that in gas trap continuously increases. It suggests that the formation rate of PCDD/Fs increases with temperature but PCDD/Fs adsorped on the surface of the sample becomes unstable and their decomposition probably occurs in higher temperature. Figure 4 shows the homologue profiles of PCDD/Fs obtained in the same experiment. The lower chlorinated PCDD/Fs formation significantly increase with increase in temperature.

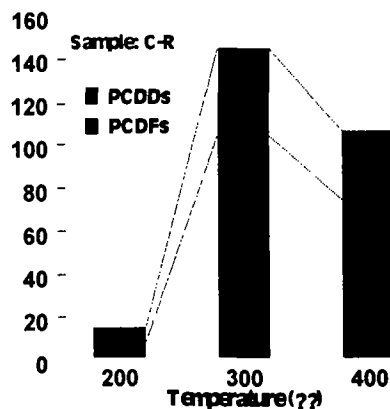


Fig. 2. Effect of temperature on the formation of PCDD/Fs.

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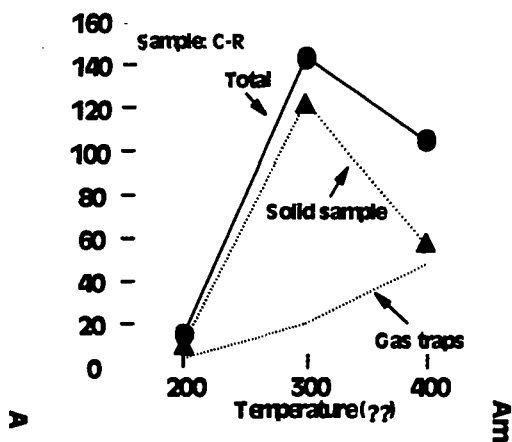


Fig. 3. Changes in formed amount of PCDD/Fs with temperature.

Increase in the formed amount of PCDD/Fs with time at 300 °C is shown in Fig. 5. It suggests that the formation rate of PCDD/Fs gradually decreases with time. Further, the transfer of the PCDD/Fs formed on the solid sample seems to start after some latent period of more than 120 min under the present condition.

Effect of O₂ concentration on the formed amount of PCDD/Fs is shown in Fig. 6. It increases with O₂ until 2.5 mol% and then gives a slight decrease above that. It can be deduced that oxygen in gas phase is important for the formation of PCDD/Fs under the

present condition but excess oxygen suppresses the formation or acts to decompose them.

The formed amounts of PCDD/Fs obtained for different solid samples at 300 °C during 2 h reaction are listed in Table 2. The order of

the formation amount is same as that of SSA except for the alumina sphere sample. In the case using the alumina sample, significantly larger amount of chlorophenols (CPs) is detected in the gas traps comparing the other samples. It means that the alumina sample have an ability

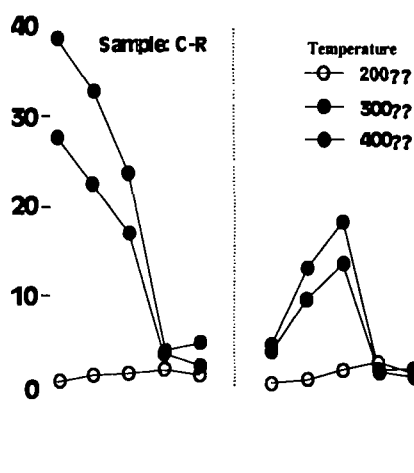


Fig. 4. Effect of reaction temperature on the homologue profiles of PCDD/Fs.

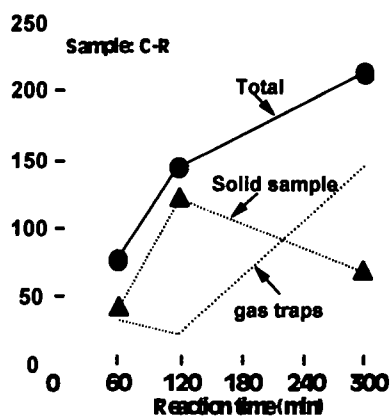


Fig. 5. Changes in formed amount of PCDD/Fs total and in solid and gas traps) with time.

Table 2. PCDD/Fs formation for different solid samples.

Sample	C-R	D-R	Silica	Alumina
SA (m ² /g)	33.1	9.9	0.6	< 0.1
Total (ng/g-sample)	144	25.4	2.52	4.70
Solid (ng/g-sample)	124	14.5	1.51	3.05
Gas trap (ng/g-sample)	20.3	11.0	1.11	1.65
Ratio [Sol.]/[Gas.] (-)	6.1	1.3	1.4	1.9

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to convert MCB to CPs. The formation of PCDD/Fs through CPs will give a relatively higher total amount of PCDD/Fs formation in spite of the lower values of SSA.

Fig. 7 shows the relation between reaction temperature and formation rate of PCDD/Fs on the basis of the surface area of the samples. The plots for the alumina sphere sample does not appear in the figure because the values are too large for it. Although some scatters are seen, the following conclusions can be pointed out on the formation of PCDD/Fs from MCB:

- 1) The amount of formation gives a peak at about 2.5 mol% O₂ and 300 °C for the all samples.
- 2) The calcined goethite (turned to hematite) shows higher ability for PCDD/Fs formation than the dried-only sample. This is because not only larger specific surface area but also its chemical and/or structural properties.
- 3) The silica sand does not act as a significant catalyst for PCDD/Fs formation while the alumina sphere gives a large formation rate. The alumina sphere has an ability to convert MCB to CPs and it may enhanced PCDD/Fs formation.

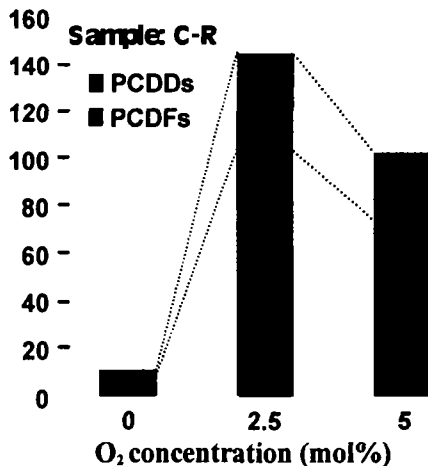


Fig. 6. Effect of O₂ concentration on the amount of PCDD/Fs formation.

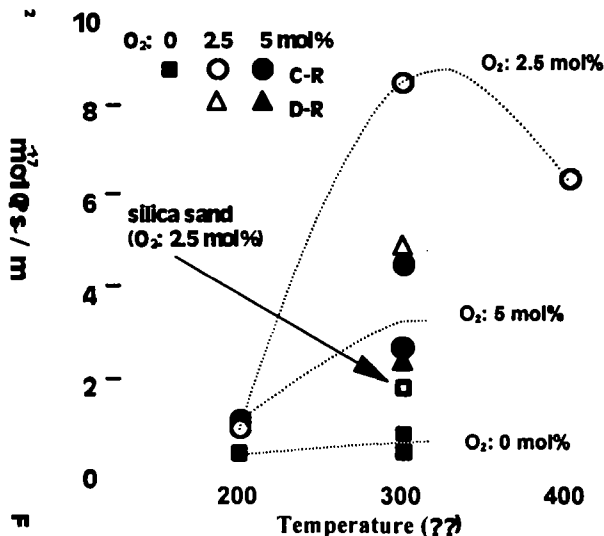


Fig. 7. Temperature dependence of apparent rate of PCDD/Fs formation estimated on different solid samples.

Acknowledgements

The authors gratefully acknowledge the financial support from the New Energy and Industrial Technology Development Organization, Japan (NEDO) to the present study (98Ea-12016, Energy and Environmental Technology).