

Study on Catalytic Elimination Technology of PCDDs/PCDFs

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1. INTRODUCTION

Severe control requirements are imposed upon PCDDs/PCDFs in flue gases from municipal solid waste incineration facilities in the West being highly toxic even with only miniscule contents. The guidelines for the prevention of PCDDs/PCDFs and related materials were issued in December 1990 and the corresponding administrative procedures are also undertaken in our country.

Catalytic oxidation decomposition has been studied as a viable technique¹⁾²⁾, however, the research on the reaction mechanisms has not been reported yet. This time we have studied the decomposition and formation of the PCDDs/PCDFs using simulated gases. The O₈CDF exchanged entirely with chlorine is used for the PCDDs/PCDFs decomposition, and the 2,4,6-T₃CP, which is said to have high PCDDs/PCDFs formation rate³⁾, is used for their formation. We also studied on the formation of CB from Bz. The Pt catalyst, which has high oxidation activity, is employed as the catalyst for this study.

We report here the basic observation obtained through the study.

2. Experimental Method

2.1 Apparatus Flow in the Experiment

Apparatus flow of the experiment is shown in Fig.1. Gas is prepared by mixing the base gas with other gases injected to the bag from gas bottles. While the prepared gas is flowing, H₂O and HCl concentration are adjusted by injecting and evaporating the HCl solution through a microfeeder into the gas preheater. Gas is further adjusted by evaporating the O₈CDF and the 2,4,6-T₃CP, after dissolving relevant amount of it with n-hexane and that, along with Bz, is directly injected using the microfeeder, into the evaporator. The gas is conducted to the catalytic layers maintained at a predetermined temperature by the electric heaters, undergoing the reaction there. Then, the reacted gas is sampled and analyzed. Materials deposited or attached to the reactor tubes and catalyst surfaces are treated as the contents of the catalyst outlet.

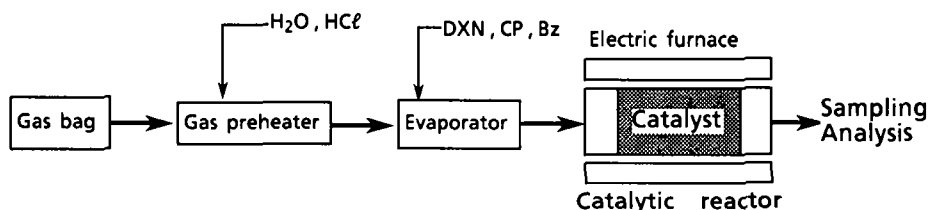


Fig.1 Schematic flow diagram

2.2 Catalyst

Properties of the catalyst used in the experiment are shown in Table 1 . The honeycomb form , which has a high contacting efficiency and a low pressure drop with the gas , is employed in the catalyst . The AP value in Table 1 is the specific value determined by the number of catalyst cells , and shows the gas contact area per unit catalyst volume .

Table 1 Properties of catalyst

	Catalyst
Form	Honeycomb
Catalyst	Pt / TiO ₂ -SiO ₂
Cell Pitch	3.7mm
Cell Number	40cell
AP value	910m ² /m ³

2.3 Conditions of Experiment

Table 2 shows the conditions of experiments .

Table 2 Conditions

	Condition 1	Condition 2	Condition 3
Main component	Bz	2,4,6-T ₃ CP	O ₈ CDF
Main component concentration	1000ppm	4000 μ g/Nm ³	100 μ g/Nm ³
Temperature[°C]	250,300	300	300
SV [h ⁻¹]	2000	1250	1250
O ₂ [%]	10	10	10
H ₂ O [%]	—	20	20
HCl [ppm]	1000	550	550

3. The PCDDs/PCDFs Formation / Decomposition - General

There are a large number of competitive reactions in the PCDDs/PCDFs formation in the exhaust gas , and the details are yet unclear down to such points as under what conditions what formation reaction takes precedence to occur . It is understood generally that the material which may become the PCDDs/PCDFs are called ' precursor ' , and also that the formation processes are called ' de novo synthesis ' under the understanding that the PCDDs/PCDFs are formed from these precursors through complicated reaction processes . Among these , the formation reactions by the flying ash has become widely acknowledged recently .⁴⁾⁵⁾

Decomposition reaction details of the PCDDs/PCDFs are unclear because it is impossible to balance the materials balances due to the extremely low concentrations of the PCDDs/PCDFs .

Although the details of formation and decomposition are unknown , it may be understood that the leading reactions are as shown in Fig.2 .

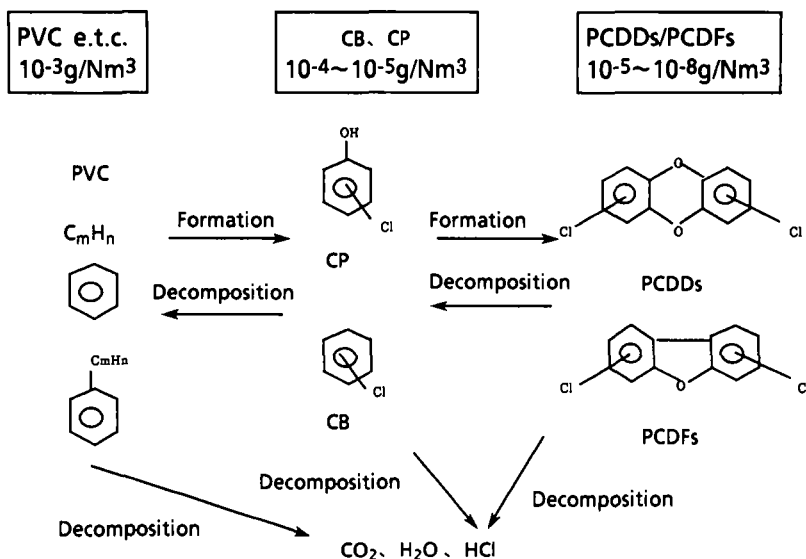


Fig.2 Schematic of formation / decomposition mechanism

4. Experiments

4.1 Formation of CB from Bz

CB formations from Bz are shown in Table 3 .

Table3 C₆H₆ rejection and C₆H_xCl_x yield

Composition	250°C	300°C
C ₆ H ₆ rejection [%]	41.6	97.5
C ₆ H _x Cl _x yield [%]	5.8	19.7
C ₆ H _x Cl _x yield [%]		
C ₆ H ₅ Cl	4.7	3.9
m-C ₆ H ₄ Cl ₂	0.6	3.6
p-C ₆ H ₄ Cl ₂	<0.2	1.9
o-C ₆ H ₄ Cl ₂	<0.1	0.4
1,3,5-C ₆ H ₃ Cl ₃	0.1	4.5
1,2,4-C ₆ H ₃ Cl ₃	0.1	3.8
1,2,3-C ₆ H ₃ Cl ₃		
1,2,3,5-, 1,2,4,5-	0	<0.1
C ₆ H ₂ Cl ₄	0	1.1
1,2,3,4-C ₆ H ₂ Cl ₄	0	0.5

Although the rejection rate of Bz increases with an increase in temperature , not all of it is decomposed into CO₂ and H₂O , though the rate of Bz chlorination is increased . At 300°C , approximately 20% of the rejected Bz became CB . When the formed CB is observed in view of the homologues , it can be seen that M₁CB to T₃CB occupy the major portions . According to Kokado's research , it was shown that the formation rate of T₄CDD from the 1,3,5-T₃CB is high in the air , and it can be seen that the CB , a precursor material to PCDDs/PCDFs , is formed in the Pt catalyst from Bz.

4.2 The PCDDs/PCDFs formation from 2,4,6-T₃CP

The PCDDs/PCDFs formation from 2,4,6-T₃CP are shown in Table 4. From this it can be seen that O₈CDF is formed, even though only slightly, in the blank, as well. The formation rates were of the order 10⁻³ to 10⁻⁴. When considered by subtracting the formation in the blank, it can be inferred that no formation was made by the catalyst. Further, it can be seen that CB is increased in the case of the catalyst. Although this may be inferred owing to the CP decomposition, but it cannot be definitely confirmed, as described later, because there was an increase in the amount of CB while the Bz ring balance did not agree and also because there was the possibility of influence by the n-hexane solvent.

Table4 Dioxine formation from 2,4,6-T₃CP

PCDDs				PCDFs			
PCDD	Conc. of inlet [ng/Nm ³]	Conc. of outlet [ng/Nm ³]		PCDF	Conc. of inlet [ng/Nm ³]	Conc. of outlet [ng/Nm ³]	
		Blank	Pt			Blank	Pt
T ₄	77	30	2.4	T ₄	2.5	4.8	11
P ₅	26	9.1	4.0	P ₅	3.7	5.0	9.0
H ₆	4.3	11	11	H ₆	4.8	14	12
H ₇	17.5	4.1	3.9	H ₇	19.5	21	23
O ₈	12.2	5.6	5.2	O ₈	28	190	93
Σ	137.0	59.8	26.5	Σ	58.5	234.8	148

CB				CP			
CB	Conc. of inlet [ng/Nm ³]	Conc. of outlet [ng/Nm ³]		CP	Conc. of inlet [ng/Nm ³]	Conc. of outlet [ng/Nm ³]	
		Blank	Pt			Blank	Pt
D ₂	53000	33000	120000	D ₂	3950	1100	400
T ₃	4700	2800	130000	T ₃	4000000	1200000	100000
T ₄	3035	0	10000	T ₄	6900	4500	980
P ₅	235	210	40000	P ₅	1355	1700	850
H ₆	230	0	18000	Σ	4000000	1200000	100000
Σ	61500	36000	410000				

4.3 Decomposition of O₈CDF

The PCDDs/PCDFs decompositions can be thought of, by dividing broadly, three types of decomposition cutting the bonds of C=C, C-O, C-Cl, respectively. Among these, the reaction cutting the C-Cl bonds simply a dechlorination, and can be inferred that the PCDDs/PCDFs are formed again with the addition of chlorine.

The O₈CDF decomposition is shown in Table 5. From this it can be seen that the decomposition with the catalyst is not a dechlorination reaction. Further, CP is not increased, leading to it being inferred that no CP is formed

after decomposition, though contrary to this, CB is greatly increased. However, it cannot be determined that they were formed with the decomposition of the O₈CDF, as the Bz ring balance does not agree entirely.

Table5 O₈CDF decomposition

PCDDs				PCDFs			
PCDD	Conc. of inlet [ng/Nm ³]	Conc. of outlet [ng/Nm ³]		PCDF	Conc. of inlet [ng/Nm ³]	Conc. of outlet [ng/Nm ³]	
		Blank	Pt			Blank	Pt
T ₄	4.4	0	0	T ₄	5.2	2.5	0
P ₅	7.6	2.5	0	P ₅	24.5	11	0
H ₆	13.1	6.3	7.9	H ₆	730	220	7.9
H ₇	65	7.0	5.7	H ₇	22500	34000	5.7
O ₈	590	18	13	O ₈	68500	35000	13
Σ	680	33.8	26.6	Σ	91760	69234	26.6

CB				CP			
CB	Conc. of inlet [ng/Nm ³]	Conc. of outlet [ng/Nm ³]		CP	Conc. of inlet [ng/Nm ³]	Conc. of outlet [ng/Nm ³]	
		Blank	Pt			Blank	Pt
D ₂	29000	35000	130000	D ₂	1100	2600	91
T ₃	2550	3100	100000	T ₃	4050	5300	240
T ₄	230	250	76000	T ₄	125	200	280
P ₅	125	120	42000	P ₅	350	410	1000
H ₆	81.5	39	23000	Σ	5650	8500	1600
Σ	32000	38000	370000				

5. CONCLUSION

The following points became clear through this research on decomposition basis of the PCDDs/PCDFs with a catalyst using simulated gas.

- (1)The CB, a precursor to the PCDDs/PCDFs, is formed while decomposing Bz in the Pt catalyst.
- (2)The PCDDs/PCDFs are not formed from the 2,4,6-T₃CP in the Pt catalyst.
- (3)The PCDDs/PCDFs decomposition in the Pt catalyst is not a dechlorination reaction.

6. REFERENCES

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