A-2.1 Decomposition Technologies for Ozone Depleting Substances (Final Report)

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Because of the seriousness of the stratospheric ozone depletion, it is mandated to destroy ozone depleting substances (ODS). A variety of technologies are desirable for destruction of ODS from small-scale to large-scale emission sources. The present study aims at developing and assessing the technologies of corona discharge plasma, catalysis, pyrolysis, incineration, photolysis, and supercritical water, by which chlorofluorocarbons, halons, and substitute fluorocarbons (HCFCs and HFCs) were successfully decomposed. In the research period of fiscal year 1993 to 1995, the experiments were carried out with respect to evaluation of reactor performance, detailed analyses of main- and by-products, accumulation of reaction parameters, elucidation of reaction mechanisms, promotional effects of additives and so forth.

2.1.1 Decomposition of ODS by Corona Discharge

INTRODUCTION

"Plasma" is defined as a physical state where a random mixture of electrons and cations is formed from neutral atoms or molecules and the mixture is neutral. Although there are many ways to generate the plasma, we investigated corona-discharge plasma by which ODS is easily decomposed.

EXPERIMENTAL

Two methods were employed. One is the reaction between carbon tetrachloride (CCl_4) and ozone (O_3), the latter being generated by corona-discharge. The reactants were continuously fed at atmospheric pressure onto the catalysts bed (i.d. 9 mmϕ, catalyst ca. 1 g) where CCl_4 decomposition took place. Another method is to utilize a packed-bed corona-discharge reactor, which contains dielectric materials such as $BaTiO_3$. The reactor was cylindrical shape of i.d. 24.5 mmϕ and either 50 Hz or 18 kHz voltage was applied between the two electrodes (24.5 mm gap distance). The reactant of CCl_4 in air with or without humid was continuously fed, similarly to the CCl_4 and O_3 reaction.

RESULTS AND DISCUSSION

Reaction of CCl_4 and Ozone

In this reaction system, CCl_4 was decomposed on H-mordenite catalyst with the aid of O_3, where the decomposition took place even on the catalyst at 0°C. When the temperature of the catalyst increased upto 70°C, the activity gradually decreased. Further increase of the temperature, however, turned to rise the activity. Although the activity above 70°C was a sole action of H-mordenite, the decomposition of below 70°C was ascribed to the reaction between CCl_4 and O_3 on the catalyst.

Packed-Bed Corona-Discharge

When $BaTiO_3$ beads were packed, CCl_4 in a continuous flow of air was successfully destroyed. As Test 2 is compared with Test 2 in Table 1, the destruction efficiency was slightly decreased by the addition of humidity. The 18 kHz is more effective for the reaction than 50 Hz from Test 1 and Test 5. The pure $BaTiO_3$ having no dielectric shift agents of Mn was less active, probably due to stability of oxygen in the bulk, whereas $SrTiO_3$ was more active.

Combination of corona-discharge and catalysis was attempted, and the concept of this system is depicted in Figure 1 (c) and (d). In the schematics of Fig. 1 (c), catalyst was place after the corona-discharge reactor containing $BaTiO_3$, and CCl_4 was fed into the corona reactor.

Upon applying the 50 Hz voltage, the efficiency slightly increases from 59.7% to 64.6% after the catalyst (Table 1, Test 12). When an 18 kHz frequency is applied, a 100% efficiency requires 3.78 kV in the presence of the catalysts, while 4.24 kV is needed in the its absence. The catalyst works when CCl_4 is fed down to the plasma; the excited air gives 17.7% and 16.7% conversion on the catalyst (Fig. 1(d) and Test 14).

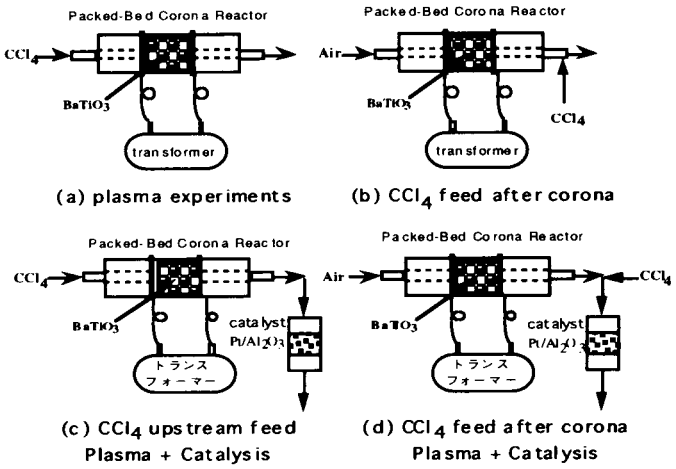

Figure 1. Schematics of Corona-Discharge Reaction Systems

Table 1. Decomposition of Carbon Tetrachloride by Packed-Bed Corona Discharge and Catalysis.

Test No.	Dielectric Material and Bead Size	Applied Volt / kV	Frequency / Hz	Humidity / ppm	Decomposition Efficiency / %	Comment
1	1-mm $BaTiO_3$	11.7	50	0	67	
2	1-mm $BaTiO_3$	11.7	50	1500	64	
3	1-mm $BaTiO_3$	11.7	50	0	80-88	CCl_4 180 ppm
4	1-mm $BaTiO_3$	11.7	50	0	0	CCl_4 fed after $BaTiO_3$
			50	1500	0	CCl_4 fed after $BaTiO_3$
5	1-mm $BaTiO_3$	4.24	18000	0	100	
6	non	11.7	50	0	9.8	
		4.24	18000	0	38.8	
7	pure 2-mm $BaTiO_3$	9.68	50	0	60.4	$BaTiO_3$ no impurity
		3.14	18000	0	87.2	
8	3-mm $BaTiO_3$	7.4	50	0	36.5	
		3.34	18000	0	93.3	
9	2-mm $SrTiO_3$	3.76	18000	0	93-100	
10	0.2% Pt on 1-mm $BaTiO_3$	11.7	50	0	40.1	calcined Pt
		13.6	50	0	57.0	
		11.7	50	1500	28.6	
		13.6	50	1500	51.7	
11	0.2% Pt on 1-mm $BaTiO_3$	2.26	50	0	5.3	reduced Pt
		2.1	18000	0	14.6	
12	1-mm $BaTiO_3$+1%Pt/Al_2O_3 (Upstream) (Downstream)	11.7	50	0	59.7	sample after $BaTiO_3$
			50	0	64.6	sample after Pt/Al_2O_3
			50	1500	56.4	sample after $BaTiO_3$
			50	1500	54.4	sample after Pt/Al_2O_3
13	1-mm $BaTiO_3$+1%Pt/Al_2O_3 (Upstream) (Downstream)	3.78	18000	1500	100	sample after $BaTiO_3$
			18000	1500	100	sample after Pt/Al_2O_3
14	1-mm $BaTiO_3$+1%Pt/Al_2O_3 (Upstream) (Downstream)					CCl_4 fed between $BaTiO_3$ and Pt/Al_2O_3
		11.7	50	0	0	sample before Pt/Al_2O_3
			50	0	17.7	sample after Pt/Al_2O_3
		5.14	18000	0	0	sample before Pt/Al_2O_3
			18000	0	16.7	sample after Pt/Al_2O_3

Reaction conditions: CCl_4 450-560 ppm in air, total flow rate 188-201 mL/min.

Another application of the catalysis is to impregnate catalyst materials with dielectric material $BaTIO_3$. Reaction system is similar to Fig. 1 (a) but the beads containing catalyst metals were

used. Although 0.2% loading of Pt does not influence (Test 10 and 11), Co and Ni effectively promote the reaction and these metals convert CO into CO_2.

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2.1.2 Study on Thermal Decomposition Behavior of Chlorofluorocarbons (CFCs)

INTRODUCTION

Waste of CFCs are sometimes mixed with unvolatile oils or solid matters. This kind of mixture needs incineration for safety disposal. However, formation of dioxins should be avoided during incineration. Here we examined thermal decomposition products of CFCs and related substances to clarify the reaction pathway of chlorinated aromatics formation.

EXPERIMENTAL

Apparatus for thermal decomposition experiments is composed of mass flow controller, vaporizer, electric furnace and products sampler. Thermal decomposition zone can be separated to two zones by inserting inner reaction tube into main reaction tube in order to examine the effect of oxidation after pyrolysis.

RESULTS AND DISCUSSION

When trichlorofluoromethane (CFC-11) was decomposed under nitrogen stream, the major products were benzene, toluene, styrene, naphthalene and their fluorinated derivatives. Few chlorinated compounds were found in this case. By oxidation of pyrolysis products of CFC-11, chlorinated phenols and dibenzofurans were formed (Table 2). Chlorinated aromatics, which were almost hidden behind fluorinated aromatics, were also found by this experiment. The amount of chlorinated phenols produced was comparable with those from similar decomposition experiment for chloroform.

Thus CFCs were possible sources to form chlorinated phenols as well as chlorinated hydrocarbons. Chlorinated phenols could be converted to dioxins in post flame reactions. These result matches with the report of incineration experiments by R.E. Hall et. al. (US-EPA) that dioxins are mainly formed in post furnace reactions under existence of Cu.

Thermal decomposition of bromofluorocarbon-1301 (halon-1301) resulted in formation of fluorinated hydrocarbon (CF_4 and C_2F_6).

LIST OF PUBLICATIONS

1) T. Imagawa, M. Takeuchi and A. Miyazaki; "Analysis of by-products in thermal

decomposition experiments of ozone-depleting substances", *Journal of Environ. Chem.*, **5**, (2), 384-385 (1995).

Table 2 Concentrations of Thermal Decomposition Products.

unit: ppmv

	from CFC-11	from $CHCl_3$		from CFC-11	from $CHCl_3$
Benzene	24.5	140	Naphthalene	3	6.9
Fluorobenzene	17	0	Fluoronaphthalene	2.5	0
Difluorobenzene	5.1	0	Chloronaphthalene	0.2	1.7
Chlorobenzene	0.92	28	Chlorophenol	0.5	0.42
Dichlorobenzene	ND	7.1	Dichlorophenol	0.66	0.14
Trichlorobenzene	ND	0.8	Trichlorophenol	0.2	0.023
Tetrachlorobenzene	ND	0.07	Dibenzofuran	0.52	0.83

2.1.3 Catalytic Decomposition of Ozone Depleting Substances

INTRODUCTION

The general consensus has been to phase out the use of the most harmful CFCs because CFC emissions are largely responsible for the decline in the stratospheric ozone. Therefore, the development of the safe disposal of the CFCs which are in use now and which are still being produced is important.

We have investigated the catalytic oxidative decomposition of CFC-115 in the presence of butane[1)~3)]. In our previous paper[3)], WO_3/Al_2O_3-ZrO_2 catalyst exhibited a very high activity and kept the activity for a long time. In this work, we investigated the effect of the catalyst composition on the activity for CFC-115. In addition, we also investigated the oxidative decomposition of CFC-12, which has been employed in the largest quantities among all the CFCs, in the presence of butane with WO_3/Al_2O_3-ZrO_2 catalysts.

EXPERIMENTAL

The WO_3/Al_2O_3-ZrO_2 catalyst was prepared according to our previous paper[3)]. The oxidative decomposition was carried out in a fixed-bed reactor. A mixture of CFC, butane and air (flow ratio, 1:1.2:150) was used as a feed gas, and the weight of the catalyst was 2.0 g. The products were analyzed by gas chromatography.

RESULTS AND DISCUSSION

Oxidative Decomposition of CFC-115: *The effect of catalyst composition*

The oxidative decomposition of CFC-115 in the presence of butane was carried out to investigate the effect of Zr/Al molar ratios on the catalytic activity of WO_3/Al_2O_3-ZrO_2 catalysts having various Zr/Al ratios. The activities were almost the same in the wide range of Zr/Al molar ratios above 0.25. The effect of tungsten (VI) oxide content on the catalytic activity was also investigated. Despite the increase in tungsten (VI) oxide content, the CFC-115 conversions were almost constant at the tungsten (VI) oxide contents more than 0.15mmol/g.

Oxidative Decomposition of CFC-12: *The effect of reaction temperature on catalytic activity*

We investigated the relationship between catalytic activity and reaction temperature. Figure 2 shows initial conversions of CFC-12 and butane at various reaction temperatures. The conversions of CFC-12 and butane increased with on increase in temperature. The catalyst deactivation was observed below 400°C and it was more remarkable at lower reaction temperatures. The color of the catalyst changed from white to black below 400°C. Accordingly, it is considered that the deactivation might be attributed to the coke deposit on the catalyst caused by the polymerization of butane at low temperatures. These results suggest that

the improvement of activity for butane is necessary to attain a high activity for CFC-12 at lower temperatures.

WO_3/Al_2O_3-ZrO_2 catalysts doped with various metals were investigated for the oxidative decomposition of CFC-12 to increase the activity for the butane combustion and to depress the coke deposit at lower temperatures. The Pt-doped catalyst improved the conversion of butane and CFC-12.

For the purpose of confirming the role of Pt metal in the oxidative decomposition of CFC-12, the oxidation of CFC-12 was carried out in the absence of butane over the Pt-doped catalyst. Figure 3 shows the relationship between activity for the CFC-12 decomposition at 350°C and time on stream. The activity of non-doped catalyst decreased remarkably with passage of time on stream. On the other hand, the Pt-doped catalyst completely decomposed CFC-12 for a long time. Therefore, it is considered that Pt participated directly in the reaction between CFC-12 and oxygen.

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2) H.Nagata, T.Takakura, S.Tashiro, M.Kishida, K.Mizuno, I.Tamori, K.Wakabayashi, *Appl. Catal. B*, **5**, 23 (1994).
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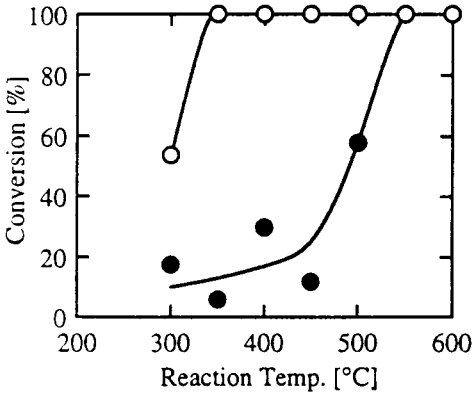

Fig. 2 Correlation between conversion and reaction temprature. ○:CFC-12; ●:C_4H_{10}; Feed gas condition, CFC-12:C_4H_{10}:Air=1:1.2:150; Flow rate, 152.2cc/min; Weight of cat., 2g.

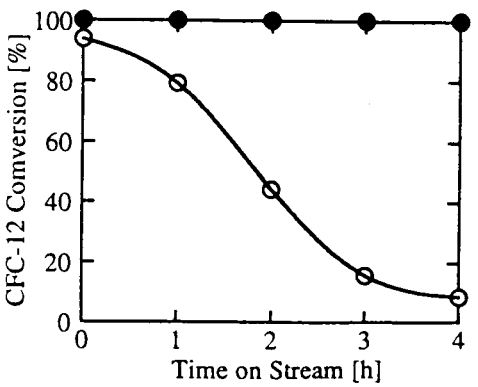

Fig. 3 The activity of metal doped WO3/Al2O3 -ZrO2 catalysts in the oxidation at 350°C. ○: none; ●:Pt; Feed gas condition, CFC-12:Air =1:150; Flow rate, 151cc/min; Weight of cat., 2g.

2.1.4 Combustion Decomposition of ODS

INTRODUCTION

Among the several ODS destruction technologies so far proposed, the incineration method is considered to be closest to the practical utilization. In this study, various ozone depleting substances such as CFCs, HCFCs, HFCs, Halon, methyl chloroform have been treated in a burner to demonstrate the ability of the burning method.

RESULTS AND DISCUSSION

A cylindrical type burner with inner diameter of 10 mm was used in the experiments, which is set in a stainless steel chamber. The flow rates of the gases were individually controlled and measured by mass flow controllers. For the less volatile gases, the samples were supplied by carrying them with air to the burner. Methane was used as fuel. The burnt gases were analyzed by gaschromatography.

In the experiments, such substances as CCl_4, CFC-13, CF_4, CFC-116, Halon-1301, HCFC-22, HCFC-123, HFC-134a, HCFC-141b, HCFC-142b, HFC-152a and CH_3CCl_3 have been treated in a burner flame. For any of these substances, the burning velocities decreased

with addition of the substances, and stabilization of the flame became difficult. In the case of CCl_4, CFC-13, and C_2F_6, supplied substances were almost completely destroyed in the pre-mixed flame for the ODS/methane ratio smaller than 0.2. For CF_3Br, the undestroyed amount of CF_3Br was lower than the detection limit of gaschromatography for CF_3Br/methane ratio less than 0.06. On the other hand, degree of destruction of CF_4 was smaller than 50% even if CF_4/methane ratio was as small as 0.02, while HCFCs and HFCs can more easily be destroyed. The degree of destruction was unity if ODS/methane ratio is equal or less than 0.4, 0.2, and 1.0, respectively, for HCFC-22, HCFC-123, and HFC-134a. For HCFC-141b, HCFC-142b, and methyl chloroform, the situation is much the same. Among others, HFC-152a is flammable itself and can be destroyed without any additional fuel.

As an example of field application of the combustion method, CFC-12 has been treated in a fluidized-bed type industrial waste incinerator. It has been found that CFC-12 is completely destroyed in the incinerator if the supply ratio is controlled less than 2% of the total wastes. Also, the levels of harmful by products such as HCl, HF, and others can well be controlled under the level of UNEP guideline.

2.1.5 Photodecomposition of ODS

Several CFCs and organochlorine compounds were photolyzed in the presence of air by illumination with 185 nm light. The photolysis reaction followed the first order kinetics. The rate constants indicated that organochlorine compound is more degraded than CFC, and CFC with less number of fluorine is the more degradable. HCFC and HFC were photo-catalytically degraded on TiO_2 or ZnO by the illumination with either 254 nm or near-UV light (310-390 nm). The degradation products were CO_2, HCl and HF, and no intermediate products were detected. To assess the photo-catalytic degradability of different HCFCs, their quantum yields of photo-catalytic degradation was measured. They ranged from 0.1 to 0.01. It was found that the order of these values of six HCFCs was proportional to that of their estimated life times in the atmosphere. Photocatalytic degradation of new alternative HCF ($CF_3CF_2OCH_3$) on TiO_2 was 3.5 times faster than the photolysis by 185nm light. In conclusion TiO_2 illuminated by low pressure mercury lamp which contains 185 nm and 254 nm lights is recommendable for the destruction of CFCs and HCFCs.

2.1.6 Decomposition of ODS with Supercritical Water

INTRODUCTION

As the supercritical water (SCW) is highly reactive and stable at high temperature, it attracts much attention as reaction medium to decompose hazardous waste and refractory substances. In this work, we studied the hydrolysis of CFCs in SCW, in which the CFCs are completely hydrolyzed and the hydrogen halides produced are neutralized with alkali in the reactor and, therefore, hazardous waste is not emitted.

RESULTS AND DISCUSSION

The experiments were carried out using a flow-type reactor made of Hastelloy C-276 (6.35 mm O.D. x 1.0 mm thickness). The concentration of CFC was 4.8 g/L H_2O. The effluent was cooled and depressurized to separate the liquid and gas phases that were analyzed afterwards with ion chromatography and gas chromatography, respectively, in order to determine the decomposition rate.

The hydrolysis rate constant of CFC-11 was determined under the assumption of pseudo-first-order reaction. It was enhanced with pressure and the tendency corresponded to the rise of the density, dielectric constant and ion product of SCW.

Since the reactor corrosion caused by hydrogen halides was extremely severe, sodium hydroxide was added into SCW to reduce the corrosion and promote the decomposition. Higher conversions were obtained as the concentration of alkali increased. Excess amount of alkali to the number of halogen atoms in the CFC molecule was effective to reduce the corrosion, as well as to improve the decomposition. In accordance to these results, 99.9% CFC-11 can be decomposed in a few minutes residence time.

CFC-113 was hardly hydrolyzed by pure SCW, but its decomposition was highly accelerated with sodium hydroxide. Extending reaction time will result in the complete decomposition. Furthermore, the addition of methanol in the equivalent amount to the concentration of sodium hydroxide solution has made the CFC decomposition effective.