

## A-6.2 Decomposition of Chlorofluorocarbons by Catalysis

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**Total Budget for FY1990-FY1992** 28,882,000 Yen

**Abstract** Catalytic decomposition of CFCs was investigated. The chemical reactions studied in this project are hydrolysis and oxidative decomposition. The most active catalyst for hydrolysis is  $\text{TiO}_2\text{-ZrO}_2$  and that for oxidative decomposition is  $\text{WO}_3/\text{Al}_2\text{O}_3\text{-ZrO}_2$ . Surface properties and reaction mechanisms were also elucidated.

**Key Words:** Catalyst, Chlorofluorocarbons, 1,1,1-Trichloroethane, Carbon Tetrachloride, Hydrolysis, Oxidative Decomposition

### 1. Introduction

Recent findings of the stratospheric ozone depletion stress that the ozone depleting substances (ODS) such as chlorofluorocarbons (CFCs), halons, and some chlorinated hydrocarbons be phased out before the 21st century. The technologies for the ozone/ODS problems are (1) development of alternative materials and processes and (2) emission control of ODS by recycling and decomposition. Large quantities of banked ODS in the world, however, force us to develop technology for its decomposition urgently in the near future.

### 2. Research Objective

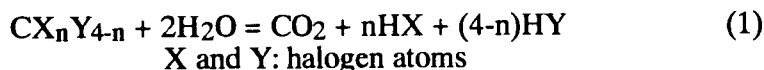
Among many technologies for CFCs, catalysis for decomposing ODS has advantages:

- (1) Energy required for the decomposition is minimum.
- (2) CFCs are decomposed continuously at atmospheric pressure.
- (3) Reaction selectivity is controlled by catalyst materials.
- (4) The device is made from small scale to large scale.
- (5) Ample experience of petro-industry is applied to the ODS decomposition.

Chemical reactions related to the decomposition of CFCs have been reported on hydrolysis, oxidation, and hydrogenolysis. This research aims at developing catalytic hydrolysis by the National Institute for Resources and Environment and catalytic oxidative decomposition i.e. catalytic combustion by Kyushu University.

### 3. Catalytic Hydrolysis

Hydrolysis of CFCs is thermodynamically favorable. This reaction converts halogen atoms in CFCs molecules to hydrogen halides and carbon atom to carbon dioxide simultaneously.



The resulting hydrogen halides are easy to be neutralized by alkali solutions in an existing technology, although materials of reactor vessel and scrubber are improved.

#### (1) Experimental

The reaction was carried out on a fixed-bed continuous flow reactor. The concentrations of CFCs and water vapor were usually 1,000 ppm and 4,000 ppm in air, respectively. One gram

of catalyst was charged to a tubular reactor (9 mm i.d.) made of quartz, calcined at 500C for 1 h under air stream. The catalysts tested in the experiments are single metal oxides, binary metal oxides, and metals supported on these oxides. The binary oxide of TiO<sub>2</sub>-ZrO<sub>2</sub> was prepared by neutralization of TiCl<sub>4</sub> and ZrOCl<sub>2</sub> in methanol solution.

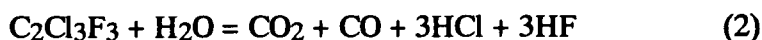
Reacted gas was taken just after the reactor before going to a scrubber. Products and unreacted CFCs were analyzed by an FID gas-chromatograph equipped with a Chromosorb 102 column. CO and CO<sub>2</sub> were converted to methane on a Ru/SiO<sub>2</sub> catalyst and analyzed by an FID gas-chromatograph.

## (2) Results and Discussion

### A. Catalytic Activities for C<sub>2</sub>Cl<sub>3</sub>F<sub>3</sub> (CFC-113)

Table 1 lists activity and selectivity in the decomposition of C<sub>2</sub>Cl<sub>3</sub>F<sub>3</sub> on some catalysts. As seen in the table, acidic catalyst of HY zeolite is more active than neutralized form of NaY zeolite, indicating that acid sites, either protonic or Lewis acid, play an important role in the reaction. As a result H-mordenite having stronger acid sites gives higher activity. Among single metallic oxides, a relatively higher activity was obtained on γ-Al<sub>2</sub>O<sub>3</sub>, which has strong acidity.

Stoichiometry of the reaction indicated that the decomposition of C<sub>2</sub>Cl<sub>3</sub>F<sub>3</sub> follows the equation,



since equal quantities of CO<sub>2</sub> and CO were formed with smaller amounts of disproportionation reaction products such as C<sub>2</sub>Cl<sub>4</sub>F<sub>2</sub> and C<sub>2</sub>Cl<sub>2</sub>F<sub>4</sub>.

A series of the reaction experiments for CCl<sub>4</sub>, CCl<sub>3</sub>F, CCl<sub>2</sub>F<sub>2</sub>, CClF<sub>3</sub>, and CF<sub>4</sub> on H-mordenite catalyst made an reactivity order as CCl<sub>4</sub> = CCl<sub>3</sub>F > CCl<sub>2</sub>F<sub>2</sub> > CClF<sub>3</sub> >> CF<sub>4</sub>, as depicted in Fig. 1. CF<sub>4</sub> was not decomposed even at 800C. Since above mentioned reactivity agrees with C-Cl and C-F bond dissociation energies, the rate determining step of the decomposition may be associated with C-Cl cleavage at first stage.

### B. Deactivation of Catalysts

One of the most important factors in development of catalysts is the life of catalysts. TiO<sub>2</sub>-ZrO<sub>2</sub> catalyst was little deactivated while H-mordenite was deactivated within several hours run. X-ray photoelectron spectroscopy of H-mordenite catalysts reveals that surface Al/Si atomic ratio on used sample is smaller than that on fresh sample, indicating that Al atoms are evaporated by the formation of AlCl<sub>3</sub> and AlF<sub>3</sub> during the reaction and the loss of Al atoms in the crystal framework leads degradation of acidic nature on the catalysts.

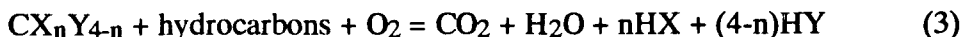
Optimal composition of TiO<sub>2</sub>-ZrO<sub>2</sub> was found to range from 0.6 to 0.9 of Ti/(Ti + Zr) atomic ratio. The catalysts was active in a 200 h continuous flow.

### C. Decomposition of 1,1,1-Trichloroethane

Transition metals were supported on TiO<sub>2</sub>-ZrO<sub>2</sub> binary oxide, and the activity in decomposition of 1,1,1-trichloroethane was investigated. As exemplified in Fig. 2, the products detected in the reaction were 1,1-dichloroethylene (DCE), trichloroethylene (TCE), CO, and CO<sub>2</sub>. DCE and TCE were first observed at lower temperatures. Upon raising the reaction temperature DCE and TCE were reduced while CO and CO<sub>2</sub> increased in their concentrations, suggesting that DCE and TCE are intermediate species in the decomposition.

## 4. Catalytic Oxidative Decomposition

Oxidative decomposition of CFCs is express as equation (3). Similarly to hydrolysis, halogen atoms in CFCs molecules are converted to hydrogen halides and carbon atom to carbon dioxide simultaneously.



X and Y: halogen atoms

(1) Experimental

The reaction was carried out on a fixed-bed continuous flow reactor. The experimental procedures are almost identical to hydrolysis reaction.

(2) Results and Discussion

A. Decomposition of C<sub>2</sub>ClF<sub>5</sub> (CFC-115)

The decomposition of C<sub>2</sub>ClF<sub>5</sub> was attempted in oxidative reaction since it has five fluorine atoms and seems the most unreactive substance among CFCs. In the reaction between C<sub>2</sub>ClF<sub>5</sub> and methane in air, γ-Al<sub>2</sub>O<sub>3</sub> having acidic character gave a 33.0% conversion. The addition of transition metal oxide to γ-Al<sub>2</sub>O<sub>3</sub> improved the activity, as shown in Fig. 3. However, all catalysts in Fig. 3 were deactivated in several hours flow, probably due to chlorination and fluorination of the catalysts. As shown in Fig. 4, no deactivation was found on WO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> catalyst.

B. Effect of Hydrocarbons

Methane, ethylene, propylene, and butane were compared in C<sub>2</sub>ClF<sub>5</sub> decomposition on ZnO/γ-Al<sub>2</sub>O<sub>3</sub>. Among these hydrocarbons, butane gave the highest conversion whereas other three hydrocarbons influenced the reaction almost similarly. Increase in partial pressure of hydrocarbons slightly enhanced the activity.

Table 1

Catalyst	Conversion of C <sub>2</sub> Cl <sub>2</sub> F <sub>3</sub> / %	Selectivity to CO <sub>2</sub> and CO / %
HY-zeolite	85	99
NaY-zeolite	15	97
H-mordenite	98	99
H-ZSM-5	88	99
γ-Al <sub>2</sub> O <sub>3</sub>	85	85
SiO <sub>2</sub> -TiO <sub>2</sub>	40	100
TiO <sub>2</sub> -ZrO <sub>2</sub>	100	100
Fe <sub>2</sub> O <sub>3</sub>	16	100
SiO <sub>2</sub>	8	100
ZrO <sub>2</sub>	1	99
TiO <sub>2</sub>	0	-

Reaction conditions; C<sub>2</sub>Cl<sub>2</sub>F<sub>3</sub> 1000 ppm, H<sub>2</sub>O 4000 ppm, balance air; WHSV - 30 L (hg-cat)<sup>-1</sup>; after 2h reaction.

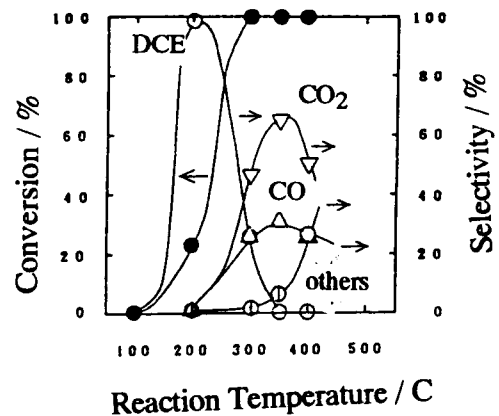


Fig. 2

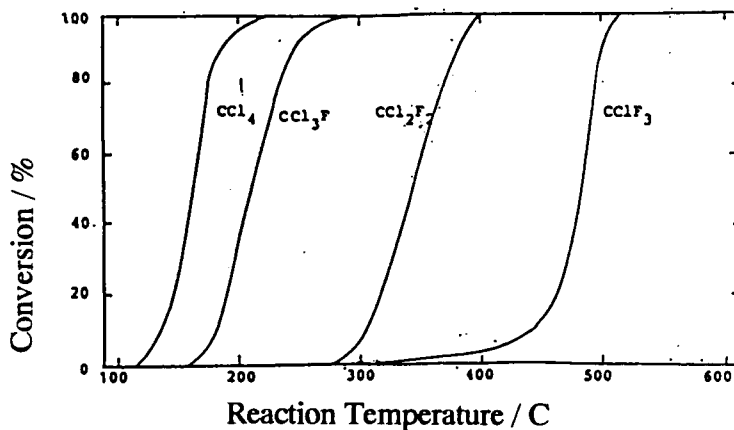


Fig. 1

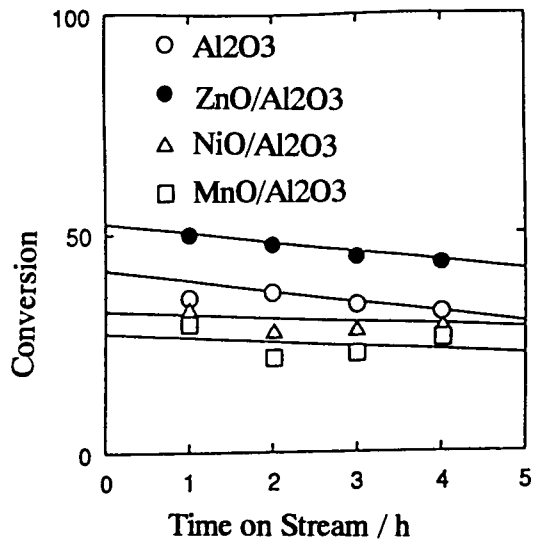


Fig. 3

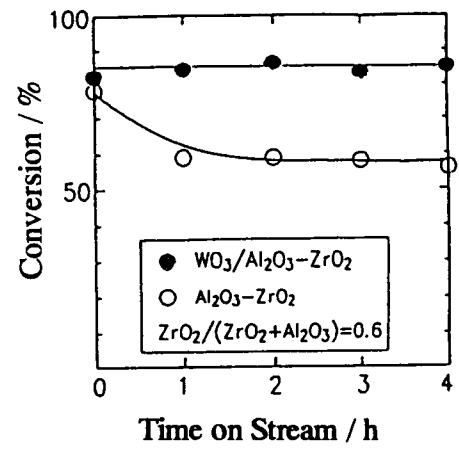


Fig. 4