Decomposition of Fluorinated Compounds by Water Plasma Generated under Atmospheric Pressure

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Abstract: Decomposition mechanism of CF_4, HFC32, and HFC134a in water plasmas was investigated. For the CF_4 decomposition, the feed rate and the additional oxygen had a strong effect on the decomposition rate. The oxygen addition plays important roles for CF_4 decomposition, and for HFCs decomposition with the suppression of by-product formation.

Keywords: Thermal plasma, Water plasma, PFC decomposition, HFC decomposition

1. Introduction

Fluorinated compounds such as hydrofluorocarbons (HFC) used in refrigeration and perfluorocarbons (PFC) used in the semiconductor industry have been identified as greenhouse gases due to their high global warming potential and long atmospheric lifetimes. Thus, in 1997, the Kyoto Protocol agreement confirmed to reduce the output of greenhouse gases including HFC and PFC by years 2008-2012 to 5% below 1990 levels.

Thermal plasma waste treatment has been studied for many years because of the ability of the plasma to vaporize anything and destroy any chemical bonds. The PLASCON process developed by CSIRO in Australia is one of the good examples of the industrial application [1,2]. The process has destroyed a wide range of ozone-depleting substances such as polychlorinated biphenyl (PCB), chlorofluorocarbons (CFCs), and HFC.

Researchers have studied PFC abatement by thermal plasmas [3-5]. Park et al. [6] investigated the CF_4 decomposition by Ar thermal plasmas with addition of H_2 and O_2. Supply of H_2 and O_2 as additional gases increases the CF_4 decomposition to 99%. Tsai et al. [7] studied the CF_4 destruction by adding H_2O, H_2, and O_2 in an atmospheric microwave plasma. The CF_4 decomposition rate could reach 96.8% with 1.3 kW power.

Water plasma process for destruction of hazardous wastes provides the following principal advantages; small reactor without auxiliary equipment, and lower capital cost and higher securities. Hrabovsky et al. [8] have studied the water plasma generation for industrial application. Watanabe et al. [9] developed 100%-steam DC plasma torch for the application of halogenated hydrocarbon decomposition.

In this study, PFC and HFC were decomposed by the water plasma under atmospheric pressure. The effect of PFC or HFC feed rate and the additional oxygen on the decomposition rate and the recovery of fluorine was determined. The decomposition mechanism of PFC and HFC were investigated.

2. Experimental

The decomposition system for PFC and HFC is presented in **Fig. 1**. The system includes a DC water plasma torch, a reaction tube for the decomposition of PFC and HFC, and a neutralization vessel for the absorption of fluorine. An atmospheric water plasma torch was used, which is a DC non-transferred plasma arc generator of coaxial design with a cathode of hafnium embedded into a copper cathode and a nozzle-type copper anode. The diameter of the hafnium is 1.0 mm. Water was fed into the plasma torch from the reservoir, and the water evaporates to form plasma supporting gas at the anode region.

The target PFC was CF_4, and difluoromethane (HFC32) and 1,1,1,2-tetrafluoroethane (HFC134a) were selected as HFCs. The feed rate was changed up to 1.0 L/min for PFC and HFC. The PFC or HFC without/with oxygen addition was injected through the injection hole to the center of the water plasma. The water flow rate was set at 75 mg/s. The hot mixture gases from the mixing of the plasma were rapidly quenched in 1.0 M NaOH solution. The quenching step is important to suppress the by-product formation in the plasma waste treatment.

The exhaust gas was analyzed by gas

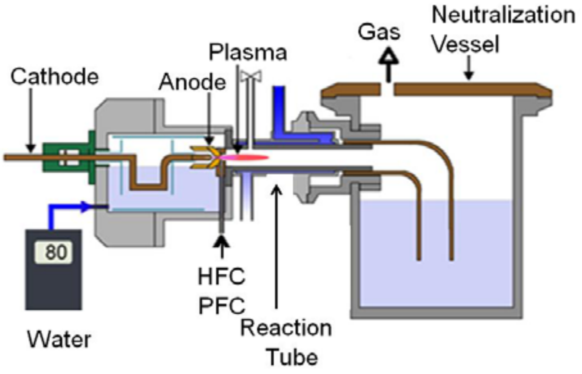


Fig.1 Schematic diagram of PFC and HFC decomposition system.

chromatography (GC, Shimadzu GC-8A) equipped with a thermal conductivity detector, and a quadruple mass spectrometer (QMS, Ametek Dycor Proline). The decomposition rate and the recovery of fluorine were calculated according to the following equations:

Decomposition rate =
1 – (PFC/HFC in exhaust gas) / (PFC/HFC feed) (1).

Recovery of fluorine =
(absorbed F in NaOH solution) / (total F feed) (2).

3. Experimental Results

3.1 PFC decomposition

We have focused on CF_4 decomposition because CF_4 is one of the most stable gases among PFCs and its decomposition is extremely difficult. The effect of the feed rate on the recovery of fluorine and the CF_4 decomposition rate is shown in **Fig. 2**. The recovery of fluorine and the CF_4 decomposition rate over 65% was obtained at 0.215 L/min of CF_4 feed rate and at 7 A of the arc current. As the feed rate increases, the CF_4 decomposition rate and the recovery of fluorine decrease because the maximum feed rate for the decomposition depends on the enthalpy of the plasma.

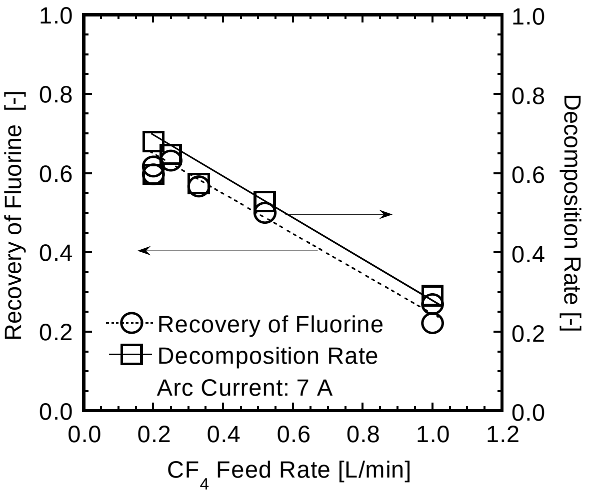


Fig.2 Effect of feed rate on fluorine recovery and CF_4 decomposition rate.

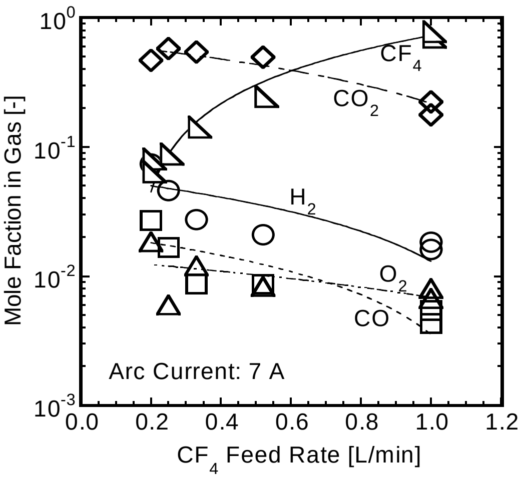


Fig.3 Composition of gaseous product after CF_4 decomposition with different feed rates.

The compositions of the exhaust gas as a function of CF_4 feed rate are shown in **Fig. 3**. No by-products were detected by GC except the undecomposed CF_4. The produced gas after the CF_4 decomposition were CO_2 (50%), CF_4 (35%), H_2 (5%), CO (3%) and O_2 (1%) at 0.215 L/min feed rate of CF_4.

3.2 HFC decomposition

For the HFCs decomposition, HFC32 and HFC134a were decomposed by the water plasma generated under atmospheric pressure. The effect of the feed rate on the recovery of fluorine and the decomposition rate is shown in **Fig. 4**. The HFC32 was decomposed by the water plasma at 7 A of the arc current. When the HFC 32 feed rate was up to 1.0 L/min, the decomposition rate was over 90%. As the HFC32 feed rate increases, the recovery of fluorine decreases. It indicates the amount of by-products formation increases with an increase of the HFC32 feed rate. The mole fractions of H_2, CO, CO_2, CH_4, and HFC32 in the exhaust gas as a function of the feed rate are shown in **Fig. 5**. The undecomposed or recombined HFC32 was detected by GC. The trace of the by-products such as CH_3F and CHF_3 was not observed by GC in the HFC32 decomposition by the water plasma.

The effect of HFC134a feed rate on the recovery of fluorine and the decomposition rate is shown in **Fig. 6**. The flow rate of HFC134a varied from 0.215 to 1.0 L/min. The decomposition rate remained about 98% when the HFC134a flow rate increased. However, the recovery of fluorine decreases while increasing the HFC134a feed rate. The compositions of the exhaust gas as a function of the feed rate are shown in **Fig. 7**. H_2, CO, and CO_2 were mainly produced in the exhaust gas. The by-product of CH_2F_2 and the undecomposed HFC134a were detected when decomposition of HFC134a at 7A.

4. Discussion

The decomposition mechanisms of CF_4, HFC32, and HFC134a were investigated from the experimental results. The bond dissociation energies of C-C, C-H, and C-F bonds are 348, 412, and 484 kJ/mol, respectively. The primary step to decompose HFC134a is the breaking of C-C bond in HFC134a at high-temperature region.

$$CF_3CH_2F \rightarrow CF_3 + CH_2F \qquad (3).$$

In contrast, H and F radicals are generated from the HFC32 and CF_4 decomposition at high-temperature region. Besides, from the comparison between Figs. 2 and 4, HFC32 was easily decomposed by the water plasma than CF_4 owing the smaller dissociation energy of C-H. The decomposition mechanism of HFC32 and CF_4 can be expressed as the following reactions.

$$CH_2F_2 \rightarrow CHF_2 \rightarrow CF_2 \rightarrow CF \quad (4).$$
$$CF_4 \rightarrow CF_3 \rightarrow CF_2 \rightarrow CF \quad (5).$$

The by-products formation mechanisms were discussed for the decomposition of CF_4, HFC32, and HFC134a. As shown in Fig. 2, the negligible difference between the recovery of fluorine and the decomposition rate indicates that there is no by-product formation after the decomposition of CF_4. The QMS spectrum of the gas components after the decomposition of CF_4, HFC32, and HFC134a at 1.0 L/min feed rate are shown in **Fig. 8** (a), (b), and (c), respectively. As shown in Fig. 8 (a), CF_x-H radicals was not detected by MS for the CF_4 decomposition. The $CF_{x(x:\ 1\text{-}3)}$ radicals do not react with H, but the $CF_{x(x:\ 1\text{-}3)}$ radicals easily recombine with F.

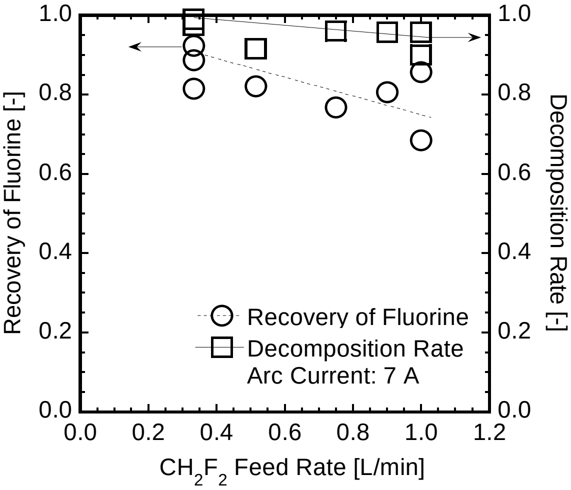


Fig.4 Effect of feed rate on fluorine recovery and HFC32 decomposition rate.

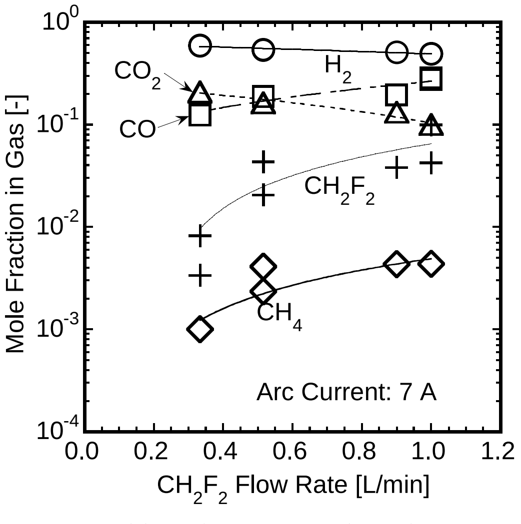


Fig.5 Composition of gaseous product after HFC32 decomposition with different feed rates.

In contrast, as shown in Figs. 4 and 6, the difference between the recovery of fluorine and the decomposition rate indicates that the by-products were generated for the decomposition of HFC134a and HFC32. In comparison with NIST data of CH_2F_2, the intensities peak of $32(CH_2F^+)$ and $33(CHF_2^+)$ in Fig. 8 (b) and (c) correspond to CH_2F_2 and CHF_3, respectively. It indicates the by-products of CH_2F_2 and CHF_3 were generated when HFC32 and HFC134a were decomposed by the water plasma. The by-products formation mechanism can be expressed as follows:

$$CHF + F \rightarrow CHF_2 \quad (6).$$
$$CHF_2 + F \rightarrow CHF_3 \quad (7).$$
$$CH_2F + F \rightarrow CH_2F_2 \quad (8).$$

The effects of additional oxygen on the decomposition rate and the recovery of fluorine were

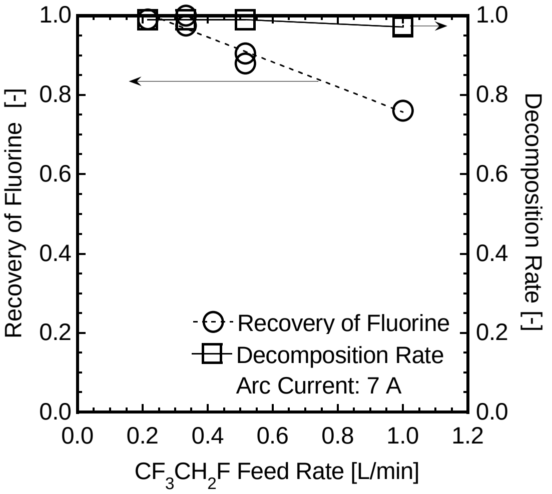


Fig.6 Effect of feed rate on fluorine recovery and HFC134a decomposition rate.

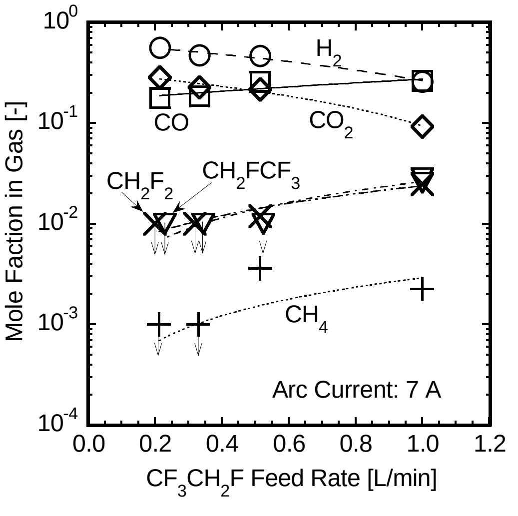
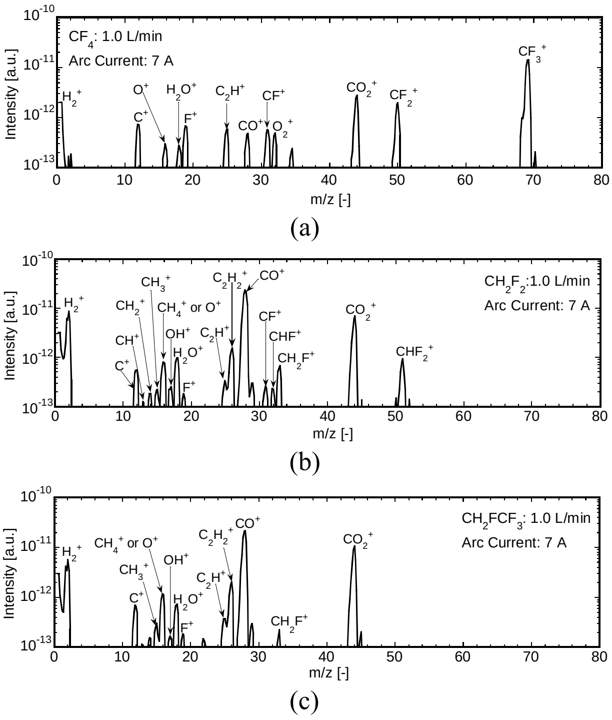


Fig.7 Composition of gaseous product after HFC134a decomposition with different feed rates.



(a)

(b)

(c)

Fig.8 Mass spectrum of gaseous product after decomposition of 1.0 L/min PFC or HFC by water plasma; (a) CF_4, (b) HFC32, (c) HFC134a.

evaluated. The recovery of fluorine and the decomposition rate as a function of O_2/CF_4 and O_2/HFC134a are shown in **Fig. 9**. The experiments were performed at 7 A under atmospheric pressure. O_2 flow rate remained at 0.215 L/min, but the adding flow rate of CF_4 was decreased from 1.0 L/min to 0.215 L/min. The CF_4 decomposition rate and the recovery of fluorine CF_4 decomposition rate and the recovery of fluorine were increased with increasing of the ratio O_2 to CF_4. It indicates the CF_4 decomposition rate is promoted with the addition of O_2 because of enhanced oxidation of CF_x. When O_2/CF_4 is at 0.6, the decomposition rate of CF_4 reaches 86%. More addition of O_2 has little effect on CF_4 decomposition rate because the excess addition of O_2 reduces the plasma enthalpy flow as well as the residence time.

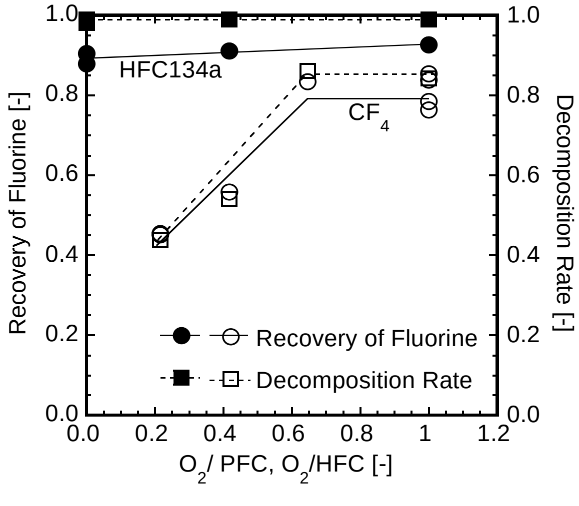


Fig. 9 Effect of O_2/PFC and O_2/HFC on fluorine recovery and decomposition rate.

In the case of HFC134a, the flow rate remained at 0.515 L/min, but the adding O_2 flow rate increased to 0.515 L/min. Variations in O_2/HFC134a had little affect the HFC134a decomposition rate. However, the recovery of fluorine increases with an increase of O_2/HFC134a. The decomposition enhancement by addition of O_2 results in the suppression of by-product formation. The radicals generated from the breaking of C-C bond in HFC134a convert into CO by adding O_2.

$$CF_3 + O \rightarrow CO + 3F \qquad (9).$$

$$CH_2F + O \rightarrow CO + HF + H \qquad (10).$$

5. Conclusions

Fluorinated compounds of CF_4, HFC32, and HFC134a were decomposed by the water plasma. The addition of O_2 enhances the CF_4 decomposition. The experimental results reveal the mechanisms of the decomposition and the by-products formation. The addition of O_2 plays important roles for CF_4 decomposition with enhanced decomposition, and for HFCs decomposition with the suppression of by-product formation.

Acknowledgment

This work was supported by the Grant-in-Aid for Scientific Research (20310038).

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