§20. Chlorofluorocarbon Treatment Process by Micro Wave Pyrolysis and its Fixation Utilizing Concrete Waste

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Various treatment methods for Fluorinated hydrocarbons (Freon) have been developed. However, these methods require high temperature to decompose Freon, and generate toxic gases such as hydrogen fluoride (HF) or hydrogen chloride (HCl). Alkali solutions, such as calcium hydroxide ($Ca(OH)_2$) solution are usually used to treat these decomposed gases. However, by using alkali solutions, secondary treatment of neutralized solution and salt sludge is required. Thus, development of more simple and effective treatment method is needed. Recently a new method which utilizes alkali metal oxide such as calcium or magnesium oxide (CaO or MgO) solid has been intensively investigated. In the study, we focused on concrete waste as an alkali metal source for fixation media of Freon decomposition gases. Waste concrete contains alkali calcium compounds, such as calcium hydroxide ($Ca(OH)_2$) and calcium silicate hydrate (e.g. $3CaO{\cdot}2SiO_2{\cdot}4H_2O$). These compounds can act as fixation media for fluorine. Furthermore, we tried to use micro wave heating method instead of conventional heating for Freon decomposition. In this year, we analyzed the reaction mechanism of HFC-134a with waste concrete particles based on experimental results obtained in the last year.

i) Materials & Methods

Waste concrete sample used in the study was obtained from Santoras Corp. The sample was grain with diameter of less than 5 mm. The calcium content ratio in the sample was measured to be about 11.3 wt%. The obtained sample was classified into three groups with sieving. HFC-134a, representative Freon, was used in the study.

Figure 1 illustrates the experimental apparatus for thermal decomposition experiments of HFC-134a. A reaction tube (SUS316, ϕ=10.2 mm) passes through an electric furnace and was kept at reaction temperature. Waste concrete sample was packed in the center part of the tube. Gaseous nitrogen and HFC-134a were supplied to the reaction tube from each cylinder with mass flow controller. HFC-134a is thermally decomposed in the reaction tube and generates decomposition gas which contains hydrogen fluoride (HF). The decomposition gas is simultaneously fixed with waste concrete, or captured by sodium hydroxide (NaOH) solution. After 10 min, exhaust gas was collected into a sampling bag, and analyzed with TG-GC/MS.

ii) Results and discussion

ii)-1 HFC-134a decomposition with conventional heating

We analyzed decomposition gas of HFC-134a at above 600°C with TG-GC/MS. HFC-134a concentration and space velocity was set at 19.82 mol% and 601 h^{-1}, respectively. Waste concrete sample with diameter of 0.6-1.2 mm was used in the experiment. The qualified chemical compounds by GC/MS analysis are summarized in **Table 1**. $CHFCF_2$ was detected as a main component of the decomposed gas at 600°C. This compound can be generated from elimination reaction of HF molecule from HFC-134a. It indicates that elimination of HF from HFC-134a and subsequent reaction with CaO in waste concrete would be the main reaction pass.

ii)-2 HFC-134a decomposition with micro wave heating

Table 2 shows the detected chemical compounds in decomposition gas of HFC-134a with micro wave heating. The detected compounds were almost same as the compounds shown in Table 1, and obtained chromatograms were quite similar. Thus, the reaction mechanism between HFC-134a and waste concrete with micro wave heating would be same mechanism as that with conventional heating.

iii) Conclusion

The composition of the decomposed gas of HFC-134a was collected and analyzed with TG-GC/MS. The results indicate that the reaction mechanism between HFC-134a and waste concrete with micro wave heating would be the elimination reaction of HF from HFC-134a and subsequent fixation with CaO in waste concrete.

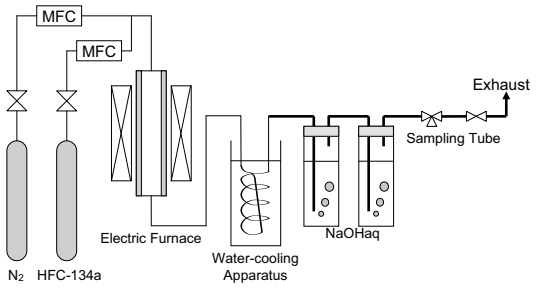

Fig. 1 Experimental apparatus for thermal decomposition experiments of HFC-134a

Table 1 Chemical compounds in decomposition gas of HFC-134a (with conventional heating)

No.	Name	Morecular formula
①	Trifluoroethylene	$CHFCF_2$
②	Sulfur dioxide	SO_2
③	1,2−propadiene	C_3H_4
④	2−methyl−1−propene	$CH_3C(CH_3)CH_3$
⑤	1,1−dimethyl−Cyclopropane	$C_3H_4(CH_3)_2$
⑥	1,2−pentadiene	C_5H_8
⑦	2−methyl−1−butene	$CH_2C(CH_3)CH_2CH_3$
⑧	Ethlidene Cyclopropane	$C_3H_4CHCH_3$
⑨	1,3−Cyclopentadiene	C_5H_6

Table 2 Chemical compounds in decomposition gas of HFC-134a (with micro wave heating)

No.	Name	Morecular formula
①	Trifluoroethylene	$CHFCF_2$
②	1,2−propadiene	C_3H_4
③	2−chloro−1,2−difluoroethylene	CF_2CHCl
④	1,1,1−trifluoro−2−chloroethane	CF_3CH_2Cl
⑤	Carbon disulfide	CS_2