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INVESTIGATION OF HFC-134A DECOMPOSITION BY COMBUSTION AND ITS KINETIC CHARACTERISTICS IN A LABORATORY SCALE REACTOR

Thermal decomposition of HFC-134a at 900–1000 K was investigated using a laboratory scale reactor. The experimental results indicate that the lower initial HFC-134a concentration and higher reaction temperature could enhance HFC-134a decomposition efficiency. Based on the results of measurements, it seems that the reaction order is around 1. Its activation energy (E_a) and the frequency factor (A) in the investigated temperature range are 300.5 kJ·mol^{-1} and 2.96×10^{14}, respectively. The results demonstrate that 99.9% destruction efficiency could be achieved when HFC-134a/LPG is below 0.5 and the excess air ratio – above 0.6.

1. INTRODUCTION

Increasing emissions of greenhouse gas (GHG) due to human activities have led to a marked increase of the global temperature. In 1997, carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), hydrofluorocarbons (HFCs), perfluorocarbons (PFCs) and sulfurhexafluoride (SF_6) were considered the six target greenhouse gases (GHGs) under the Kyoto Protocol of the United Nations' Framework Convention on Climate Change (UNFCCC) [1]. According to the requirement of the Kyoto Protocol, the emission of CO_2, CH_4, N_2O, SF_6, HFC and PFC should be reduced in all signatory nations. On September 21th, 2007, approximately 200 countries agreed to accelerate the elimination of hydrochlorofluorocarbons entirely by 2020, and the use of HFCs in the automobile air condition is being prohibited since 2011.

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In 2007, the total amount of HFCs emission was about 125.5×10^8 g of CO_2 equivalence [2]. How to safely and efficiently dispose HFCs in the used automobile is one of serious environmental issues. At present, the main treatment methods of HFCs are thermal decomposition [3], catalytic decomposition [4–7], plasma decomposition [8–10] and combustion decomposition.

Han et al. [3] discussed C_2F_6 thermal decomposition characteristic at 950–1100 °C in a laboratory scale reactor. Their experimental results indicated that the reaction order of C_2F_6 thermal decomposition was between 0 and 1, and above 90% C_2F_6 decomposition ratio could be achieved under 1100 °C.

The catalytic oxidative decomposition of CFCs containing two carbon atoms was investigated in the presence of hydrocarbons (alkanes C_1–C_4) over silica and various acidic metal oxides. It was found that γ-alumina was the most active catalyst [11]. Zhang et al. [7] also found that platinum promoted non-sulfated TiO_2–ZrO_2 was stable and gave more than 90% of $CHClF_2$ conversion and 95% selectivity to CO_2 for over 60 h.

Mok et al. [10] carried out the experiments of destructing hexafluoroethane (C_2F_6) in a nonthermal plasma reactor packed with dielectric pellets. The maximum destruction efficiency was about 40% and the energy requirement was in the range of 8.2–45.3 MJ/g. The byproducts contained CO_2, CO, COF_2, CF_4, SiF_6, NO_2, and N_2O.

Although combustion methods were widely used to treat waste, there were few reports on decomposing HFCs by combustion. In this paper, the combustion method was applied to decompose HFC-134a and the kinetics of its decomposition was discussed.

2. EXPERIMENTAL

The experiment was carried out using a tube reactor system, which consisted of a silicon reactor, heater, thermal couples and mass flow meters (Fig. 1). Before the experiment, the reactor was electrically heated to predetermined temperature. HFC-134a was mixed with air and fed into the reactor. In these runs, the reaction temperature was in the range of 900–1000 K, and the reaction time was about 2–5 s, as summarized in Table 1. After passing the reactor, the flue gas was directed to an adsorption system to remove HF, then it was analyzed by the GC-MS.

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Experimental conditions

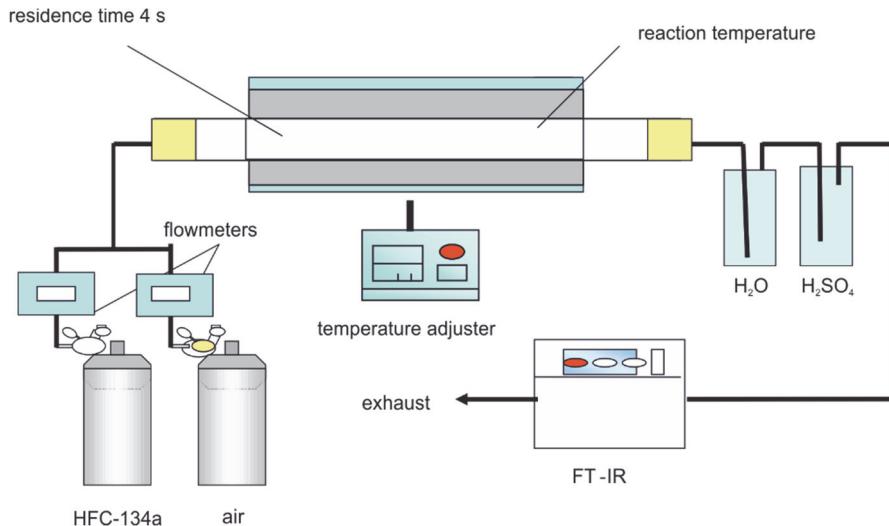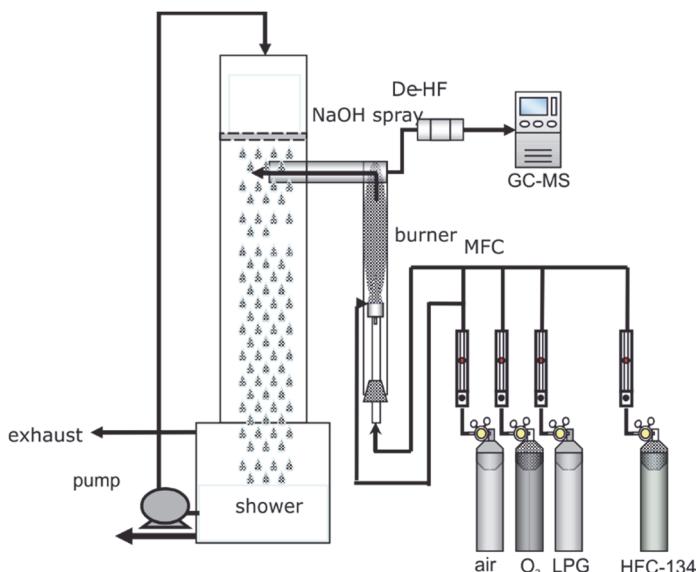| HFC-134a initial concentration, %	1.3192–1.4947
Reaction temperature, K	900–1000
Reaction time, s	4
Carrier gas	air

Fig. 1. The flow diagram of experimental apparatus

Fig. 2. Scheme of the combustion apparatus

The combustion experiments were carried out using a bench scale reactor consisting of a stainless-steel reactor, a burner, a gas supply system, a shower tower, and a reaction tank. A scheme of the experimental apparatus is shown in Fig. 2. The length and diameter of the stainless-steel reactor were 600 mm and 65 mm, respectively. In the experiments, KBSS-800 burner (Kinoshitarika Co., Japan) 10 mm in diameter was used.

HFC-134a, LPG and air were mixed at the determined ratio and fed into burner, followed by the absorption in a shower tower to remove HF and COF_2. The experimental condition of combustion is summarized in Table 2.

Experimental conditions of the combustion

Air flow rate, $dm^3 \cdot min^{-1}$	0.954–2.386
LPG flow rate, $dm^3 \cdot min^{-1}$	0.1
HFC-134a flow rate, $dm^3 \cdot min^{-1}$	0–0.1
HFC-134a/LPG ratio	0–2.0
Excess air ratio	0.6–0.9

3. RESULTS AND DISCUSSION

3.1. DECOMPOSITION CHARACTERISTIC

Dependence of the HFC-134a destruction efficiency on its initial concentration is shown in Fig. 3. The increase of HFC-134a initial concentration has a negative effect on the decomposition efficiency. At 975 K, the destruction efficiency decreases from 24.79 to 17.37% when HFC-134a initial concentration increases from 0.2% to 0.8% at the reaction time of 4 s.
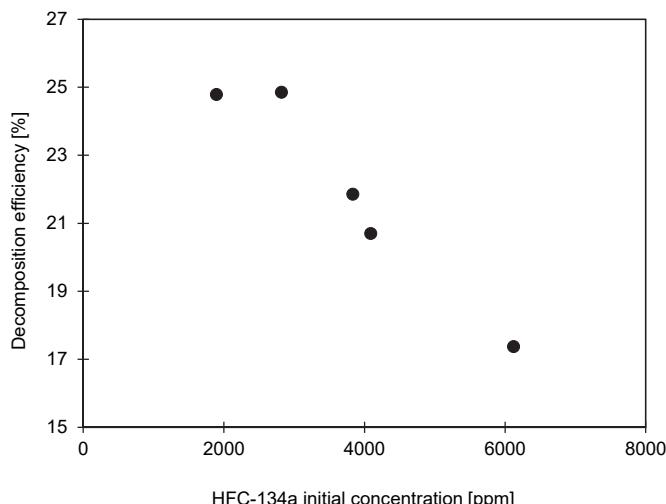

Fig. 3. Dependence of the HFC-134a decomposition efficiency
on its initial concentration

The decomposition efficiency of HFC-134a can be described by the following equation:

$$-\frac{d[C]}{dt} = k[C]^n \tag{1}$$

where C is the HFC-134a concentration at time t, k is the specific reaction rate constant, n is the order of reaction.
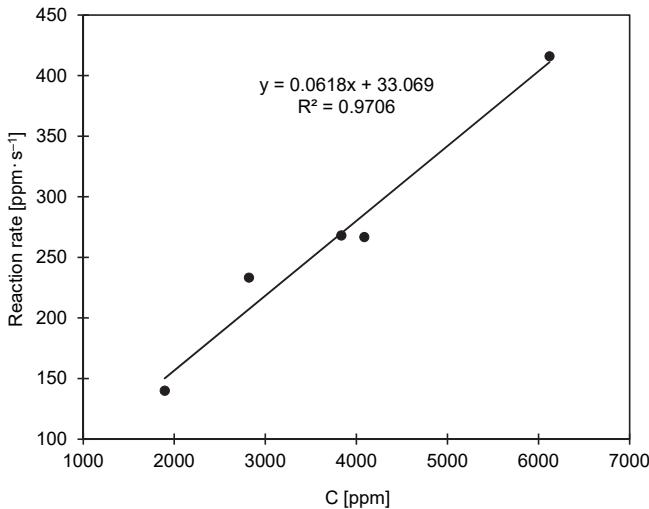

Fig. 4. Dependence of the reaction rate on the initial concentration of HFC-134a

In Figure 4, the dependence of the reaction rate (dC/dt) on the initial concentration of HFC-134a is shown. The linear dependence indicates that the reaction order is approximately 1. Thus, Eq. (1) can be rearranged as

$$k = -\frac{1}{[C]}\frac{d[C]}{dt} \tag{2}$$

The reaction rate constant may follow the Arrhenius equation:

$$k = A\exp\left(-\frac{E_a}{RT}\right) \tag{3}$$

where A is the frequency factor, E_a is the activation energy, R is the universal gas constant and T is the absolute temperature.

After some rearrangement we obtain

$$\ln k = -\frac{E_a}{R}\frac{1}{T} + \ln A \tag{4}$$

The slope and intercept of the plot $\ln k$ vs. $1/T$ (Fig. 5) were used to calculate the kinetic parameters of the reaction. The activation energy was obtained 300.05 kJ·mol^{-1} and the frequency factor – 2.96×10^{14}.
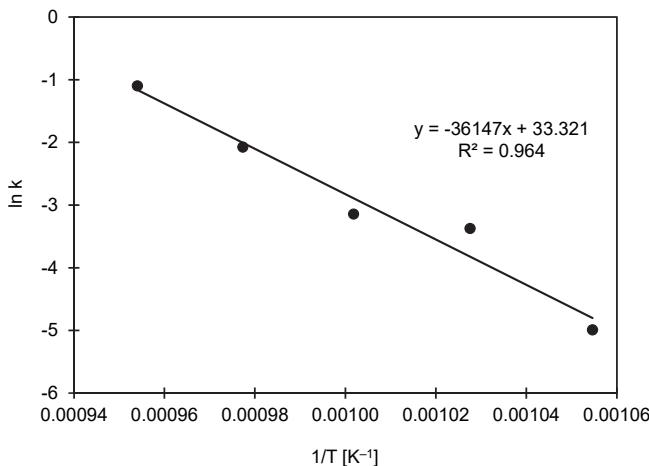

Fig. 5. Dependence of $\ln k$ on $1/T$

3.2. COMBUSTION EXPERIMENT

Figure 6 demonstrates the dependence of the HFC-134a destruction efficiency by the combustion method on HFC-134a/LPG ratio under various operation conditions (Table 2). In this run, the flow rate of LPG is kept at 0.1 dm^3/min, HFC-134a flow rate varies from 0 to 1.0 dm^3/min, and the excess air ratios are 0.6, 0.8 and 0.9. The experimental results indicate that the HFC-134a destruction efficiency is as high as 99.98% when HFC-134a/LPG ratios are in the range of 0–0.4. It is almost independent of HFC-134a/LPG ratio when the excess air ratio is above 0.8. Under the excess air ratio, the destruction efficiency sharply decreases from 99.98% to 92.40% when HFC--134a/LPG ratios increase from 0.4 to 1.0. It was also found that the HFC-134a destruction efficiency increases with the increase of the excess air ratio when the HFC--134a/LPG ratio is above 0.4. For example, HFC-134a destruction efficiency decreases from 99.98% to 95.00% when the excess air ratio decreases from 0.9 to 0.6 under the HFC-134a/LPG ratio equal to 0.8.
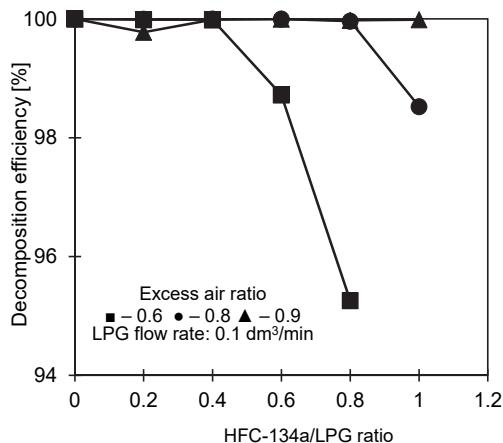
Fig. 6. Dependence of the excess air ratio on the HFC-134a decomposition efficiency
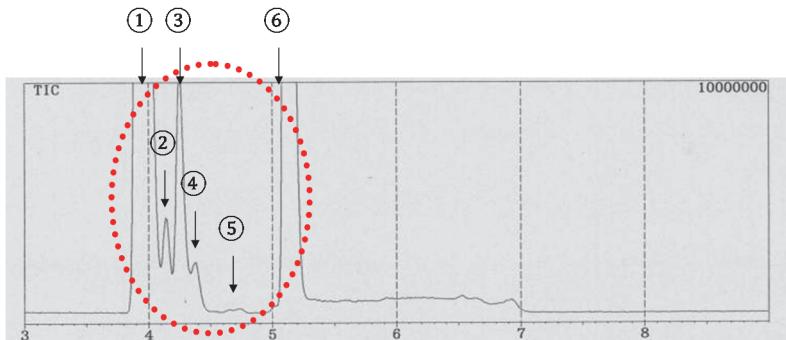

Fig. 7. Components of flue gas after decomposition of HFC-134a:
1 – O_2, 2 – $C_2H_2F_2$, 3 – C_3H_8, 4 – C_2H_3F, 5 – $C_3H_3F_3$, 6 – $C_2H_2F_4$

In order to further understand the decomposition of HFC-134a, the flue gas after water shower is also analyzed by the GC-MS. The components of the flue gas are presented in Fig. 7. The results indicate the presence of such byproducts as $C_2H_2F_2$, C_2H_3F, $C_3H_3F_3$ and $C_2H_2F_4$. However, the concentrations of $C_2H_2F_2$ and C_2H_3F are very low. Moreover, there is residual HFC-134a in the flue gas (peak 6), which is consistent with the result shown in Fig. 6: the decomposition efficiency is about 98.75% when the flow rate of LPG is 0.1 dm^3/min, the excess air ratio is 0.9, and the HFC-134a/LPG ratio is 0.5.

4. CONCLUSIONS

The results of the experiments demonstrate that the increase of HFC-134a initial concentration has a negative effect on its decomposition efficiency, and the decomposition reaction is the first order reaction. The activation energy and frequency factor of the decomposition reaction in the range of 900–1000 K are 300.05 KJ·mol^{-1} and 2.96×10^{14}, respectively.

The highest decomposition efficiency is 99.9% when HFC-134a/LPG ratio is below 0.5. The efficiency increases with the increase of the excess air ratio and decreases with the increase of HFC-134a/LPG ratio.

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