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Decomposition of trifluoromethane in a dielectric barrier discharge non-thermal plasma reactor

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Abstract

The decomposition of trifluoromethane (CHF$_3$) was carried out using non-thermal plasma generated in a dielectric barrier discharge (DBD) reactor. The effects of reactor temperature, electric power, initial concentration and oxygen content were examined. The DBD reactor was able to completely destroy CHF$_3$ with alumina beads as a packing material. The decomposition efficiency increased with increasing electric power and reactor temperature. The destruction of CHF$_3$ gradually increased with the addition of O$_2$ up to 2%, but further increase in the oxygen content led to a decrease in the decomposition efficiency. The degradation pathways were explained with the identified by-products. The main by-products from CHF$_3$ were found to be COF$_2$, CF$_4$, CO$_2$ and CO although the COF$_2$ and CF$_4$ disappeared when the plasma were combined with alumina catalyst.

Key words: trifluoromethane; plasma; alumina; dielectric barrier discharge; decomposition

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Introduction

Trifluoromethane (CHF$_3$) is a colorless, odorless greenhouse gas with a global warming potential (GWP) of 11,700 and the atmospheric lifetime of the gas is 270 years. It has been widely used in semiconductor and polystyrene industries, commercial refrigeration and air conditioning, all of which result in emissions to the atmosphere. Thus, the emission of this gas should be controlled before its releases into the atmosphere. Several methods have been attempted for the treatment of fluorinated gases including recovery and reuse, incineration, catalytic oxidation, adsorption and plasma decomposition (Lee and Choi, 2004; Xu et al., 2007; Kowalczyk and Holyst, 2008; Ogata et al., 2004; Won, 2009). Incineration is one of the efficient and clean technologies; however, it requires more energy and extensive heating time to destroy chemical bonds in the fluorinated compounds. Catalytic oxidation is also an attractive and durable technology and it is capable of reducing the operation temperature, but high temperatures of above 500°C are needed to attain sufficient catalytic activity. In addition adsorption and membrane separation are technically proven, but less successful due to high cost and lower efficiency (Hoover, 1999). Recently, non-thermal plasma technology has offered an innovative approach for effective decomposition of fluorinated gases including CF$_4$, SF$_6$, CHF$_3$ and C$_2$F$_6$ (Kim et al., 2005, 2010; Chen et al., 2008; Mok et al., 2008). The main disadvantages in the non-thermal plasma technology will be high energy consumption, low destruction efficiency and unwanted by-products formation. In order to overcome these problems, current research has been focused on the combination of non-thermal plasma with catalysis (Al$_2$O$_3$, AlPO$_4$, MnO$_2$, TiO$_2$, Pt, iron oxide, zeolite, etc.) for effective decomposition of such gases.

The non-thermal plasma has been created in different plasma reactors such as microwave, electron beam, pulsed corona and dielectric barrier discharge (DBD). The DBD plasma reactor becomes very attractive due to its capability of producing abundant reactive species by the collisions of high-energy electrons with working gas molecules (Kim et al., 2010, 2011). Kim et al. (2011) reported that the combination of plasma-catalysis produced higher decomposition compared to the sum of plasma and thermal catalysis. Dissimilar results were reported during the decomposition of such fluorinated gas with the addition of oxygen in the reactor. According to Ogata et al. (2004) the increases in the O$_2$ content increased the fluorocarbon destruction. On the other hand, Mok et al. (2008) reported that the destruction of hydrofluorocarbon was maximum in the presence of small amount of oxygen (0.5%, V/V), and further increase in the oxygen content decreased the destruction efficiency.

Therefore, in the present study, we investigated the decomposition of CHF$_3$ under different O$_2$ levels, electric powers and different initial concentrations using DBD plasma reactor packed with alumina and zirconia beads. The decomposition products were analyzed by using a Fourier transform infrared (FT-IR) spectrometer and possible reaction mechanisms leading to the formation of...
carbon oxides (CO and CO\textsubscript{2}) were elucidated.

1 Materials and methods

The schematic diagram of the experimental setup for decomposing CHF\textsubscript{3} is depicted in Fig. 1. The DBD plasma reactor was made up of a ceramic tube (inner diameter: 24 mm; outer diameter: 28 mm) serving as the dielectric barrier, an 8-mm stainless steel screw acting as the discharging electrode, and a copper foil wrapping around the ceramic tube. The stainless steel screw was coaxially inserted into the ceramic tube and an alternating current (AC) high voltage was applied to generate plasma. The supplied voltage ranged from 10 to 16 kV at a frequency of 400 Hz. The reactor was covered with a heating tape to control the reactor temperature to desired values. The temperature was measured at the midpoint of the reactor wall by using a thermocouple. The reactor was packed with 3 mm alumina beads (Sigma-Aldrich Co., USA) or 3 mm zirconia beads (Daian Scientific Co., Korea) to a volume of 127 cm\textsuperscript{3}. The Brunauer-Emmett-Teller (BET) surface area of the alumina beads was measured to be 195.7 m\textsuperscript{2}/g, while that of zirconia beads was negligible. The effective reactor length for creating plasma was 145 mm.

The feed gas was composed of three gases, i.e., CHF\textsubscript{3} nitrogen and oxygen. The total flow rate of the feed gas was in the range of 0.5 to 1.0 L/min. The initial concentration of CHF\textsubscript{3} was changed from 1000 to 4000 ppm and the oxygen content ranged from 0 to 6.0% (V/V). The temperature effect on the decomposition of CHF\textsubscript{3} was examined in the range up to 450°C. The DBD plasma reactor was also operated without packing material to contrast the results with those obtained in the presence of packing materials. The identification and quantification of CHF\textsubscript{3} and associated by-products were carried out by a FT-IR spectrometer (IFS 66/S, Bruker, Germany). The CHF\textsubscript{3} and the by-products were assigned in the spectra and the measured absorbance was converted into concentration using standard compilations (Hanst and Hanst, 1993). The decomposition efficiency (R) is defined as:

\[ R = \left(\frac{C_0 - C}{C_0}\right) \times 100\% \]  

2 Results and discussion

2.1 Effect of electric power on decomposition efficiency of CHF\textsubscript{3}

The variations of CHF\textsubscript{3} decomposition as a function of electric power are shown in Fig. 2. The complete decomposition of CHF\textsubscript{3} was observed during the combined application of plasma with alumina beads. As expected, higher electric power resulted in a higher decomposition rate of CHF\textsubscript{3} at lower temperature. When the reactor temperature was 319°C, the decomposition efficiency approached 100% at 60 W while at 298°C it could reach 100% at 90 W. The fluctuation can be attributed to the fact that increasing power towards increases the concentration of reactive species and it is responsible for CHF\textsubscript{3} decomposition, thus accelerating the conversion rate. The non-thermal plasma alone (without packing material) decomposed CHF\textsubscript{3} up to 71% at the reactor temperature of 258°C. The maximum decomposition efficiency obtained with zirconia as the packing material was 55% at 308°C. In the absence of plasma, alumina catalyst alone decomposed CHF\textsubscript{3} up to 97% at 351°C. As per the statement by Holzer et al. (2002), the short living reactive species formed by the plasma discharge are available for the further oxidation of hydrocarbons in the inner pore volume of the alumina beads. This is probably due to the longer residence time of intermediates during diffusion through the pore system. The consequence is a significantly higher decomposition in the presence of porous alumina beads compared with zirconia beads.

2.2 Effect of initial concentration on decomposition efficiency of CHF\textsubscript{3}

The concentration dependence of the CHF\textsubscript{3} decomposition is shown in Fig. 3. The initial concentration was varied from 1000 to 4000 ppm with the feed gas flow rate of 1.0 L/min. The packing material was alumina beads. Taking a wide variation of 1000–4000 ppm into account, the
initial concentration effect on the decomposition of CHF$_3$ was not remarkable. The complete destruction of CHF$_3$ was achieved within 312°C when the initial concentration was 1000 ppm, whereas it took 354, 369 and 411°C, for the initial concentrations of 2000, 3000 and 4000 ppm, respectively. The decreases of the decomposition efficiency at the higher concentration of CHF$_3$ might be due to decreases in the relative amount of reactive species at the given electric power.

2.3 Effect of oxygen content on decomposition efficiency of CHF$_3$

The effects of oxygen content on the decomposition of CHF$_3$ are shown in Fig. 4. The oxygen content was changed from 0 to 6% by volume at a feed gas flow rate of 0.5 L/min. The CHF$_3$ concentration was 2000 ppm and the electric power was 60 W. The packing material was alumina beads. The CHF$_3$ decomposition efficiencies gradually increased as the addition of O$_2$ up to 2% and then decreased as O$_2$ content further increased. The tendency is caused by the decreases of energetic species, due to surplus reaction between energetic species (excited nitrogen atoms and nitrogen molecules produced by plasma) with excess oxygen. Then, a significant energy is consumed for the formation of nitrogen oxides like NO and N$_2$O, which most probably leads to a decrease in decomposition efficiency.

The following equations may explain in detail:

\[ N(^2D) + O_2 \rightarrow NO + O \]  \hspace{1cm} (2)

\[ N_2(A^3 \Sigma_u^+ + O_2) \rightarrow N_2O + O \]  \hspace{1cm} (3)

The same trend was observed during non-thermal plasma decomposition of fluorinated gases by Kim et al. (2005) and Mok et al. (2008).

2.4 Byproducts formation and chemical mechanisms

The FT-IR spectra of the gas from inlet and outlet of the reactor are shown in Fig. 5. The major CHF$_3$ decomposition products generated in the plasma reactor were CO$_2$, CO, CF$_4$ and COF$_2$. In addition, a small amounts of N$_2$O and NO$_2$ were also identified from the effluent gas stream. The N$_2$O is classified as a greenhouse gas (Chang and Peng, 2010), but its GWP value of 310 is much less than that of CHF$_3$. The decomposition of CHF$_3$ by non-thermal plasma goes through several steps which are summarized in Fig. 6. The primary processes lead to producing trifluoromethoxy radical and difluoromethoxy radical, which can react with oxygen to form peroxy radicals. The peroxy radicals react with each other to form alkoxy radicals, and furthermore the alkoxy radicals are promoting to carbonyl fluoride (Barker, 1995; Mallard et al., 1998). The reaction of COF$_2$ with excited oxygen atom leads to CO$_2$ and a part of CO$_2$ can be reduced to CO. As per the statement by Kim...
et al. (2011), the COF$_2$ is one of the key intermediate compounds leading to the formation of CO$_2$ and CO. As shown in Fig. 5, the COF$_2$ was detected during plasma-alone treatment (without packing), but there was no COF$_2$ during the combined application of plasma with catalyst. It means that COF$_2$ was efficiently oxidized to carbon oxides when catalyst was packed in the reactor.

The concentrations of CO and CO$_2$ produced in the reactor packed with alumina were measured at different oxygen contents of 0, 2%, 4% and 6% (V/V), which are given in Fig. 7. It can be noted that the concentrations of CO$_2$ and CO slightly increased with the increases of oxygen level. The addition of oxygen leads to an increase in the amount of oxidative species, thus consecutively react with the secondary products. Further, the secondary products are completely oxidized slowly with excess energy and finally more carbon oxides were formed as by-products. Unexpectedly, CO$_2$ and CO were observed even without oxygen in the feed gas. In this case, since the only oxygen source was the alumina beads, the formation of CO$_2$ and CO might be explained by the following reaction:

$$\text{Al}_2\text{O}_3 + 2\text{CF}_3 \rightarrow 2\text{AlF}_3 + \text{CO}_2 + \text{CO} \quad (4)$$

The formation of AlF$_3$ was observed when the decomposition of CF$_3$ with Al$_2$O$_3$ as packing material under the temperature less then 600°C (Xu et al., 2005). However the generation of AlF$_3$ leads to a progressive decrease in the catalytic activity of alumina beads.

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**Fig. 5** FT-IR spectra before and after plasma treatment. Electric power: 60 W, O$_2$: 2%, V/V.

**Fig. 6** Possible reaction pathways for the decomposition of CHF$_3$. 
Figure 8 shows the concentration of CF$_4$ obtained at different oxygen contents. It is believed that the formation of CF$_4$ is caused by the reaction between CF$_3$ and F radicals. The concentration of CF$_4$ gradually decreased as the temperature increased. In the presence of oxygen, CF$_4$ completely disappeared at 300–320°C, depending on the oxygen content. On the other hand, without oxygen, it still remained even at a temperature as high as 330°C. It clearly indicates that the concentration of CF$_3$ also depends on the oxygen level during the decomposition of CHF$_3$.

![Graph showing concentration of CO and CO$_2$ obtained in different oxygen levels. Flow rate: 0.5 L/min; initial CHF$_3$: 2000 ppm; electric power: 60 W; reactor temperature: 275°C.](image)

**Fig. 7** Concentrations of CO and CO$_2$ obtained in different oxygen levels. Flow rate: 0.5 L/min; initial CHF$_3$: 2000 ppm; electric power: 60 W; reactor temperature: 275°C.

![Graph showing concentration of CF$_4$ as functions of oxygen level and temperature. Flow rate: 0.5 L/min; initial CHF$_3$: 2000 ppm; electric power: 60 W.](image)

**Fig. 8** Concentration of CF$_4$ as functions of oxygen level and temperature. Flow rate: 0.5 L/min; initial CHF$_3$: 2000 ppm; electric power: 60 W.

### 3 Conclusions

The decomposition of CHF$_3$ was investigated in the dielectric barrier discharge non-thermal plasma reactor. The effects of electric power, initial concentration and oxygen content were examined and the decomposition mechanisms were discussed. The experimental results revealed that the decomposition efficiency increased with increasing electric power and it was shown that the reactor packed with alumina beads acting as a catalyst decomposed CHF$_3$ more effectively than zirconia. The decomposition efficiency gradually decreased with increasing initial concentration. The addition of O$_2$ to the feed gas greatly improved the decomposition efficiency, however, an increase in the oxygen content above 2% (V/V) rather led to a decrease in the decomposition efficiency. The main CHF$_3$ destruction products were found to be CF$_4$, COF$_2$, CO$_2$ and CO. In addition, NO$_2$ and N$_2$O were also identified in the effluent gas. The CF$_2$ and COF$_2$ completely disappeared during the combined application of non-thermal plasma with alumina. The combination of catalyst with non-thermal plasma facilitates the decomposition. The problems of non-thermal plasma process, i.e., lower decomposition efficiency and the formation of unwanted by-products for fluorinated carbons may be minimized by introducing the alumina catalyst.

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### References


