

環境・生命工学専攻		学籍番号	023837	指導 教員	金 熙濬 木曾 祥秋 辻 秀人
申請者 氏名	林 伸哉				

論文要旨 (博士)

論文題目	地球温暖化に寄与する含フッ素化合物の分解処理特性
------	--------------------------

(要旨 1,200字程度)

現在地球温暖化は世界規模での懸念となっている。気候変動に関する政府間パネル (IPCC) の第4次評価報告書においては、「20世紀半ば以降に観測された全球平均気温の上昇のほとんどは、人為起源の温室効果ガスの増加によってもたらされた可能性がかなり高い。」と結論された。このように、地球温暖化抑制に関する技術開発は急務である。

本研究では地球温暖化に寄与するフッ素化合物として SF₆、CF₄ および HFC134a (CF₃CH₂F) を対象とした。これらのガスは高い地球温暖化係数をもつ一方で、CO₂ と比較して排出量が小さく、排出源が限定されているため、排出抑制による地球温暖化抑制への貢献度が高い。本研究では、これらの物質について熱分解実験や燃焼分解実験を行い、これらの反応を用いた分解装置の開発に必要な分解特性について知見を得た。

本研究はまず、SF₆ の純粋な熱分解反応特性を調べるため、管型反応器を用いて、He または Ar を雰囲気ガスとした場合の SF₆ 熱分解実験を行った。みかけの反応速度は SF₆ 濃度に対して一次反応であり、SF₆ 分解反応の活性化エネルギーは、雰囲気ガスを He または Ar とした場合で 354kJ・mol⁻¹、Ar とした場合で 371kJ・mol⁻¹であった。

次により実用的な条件における SF₆ 熱分解特性を調べるため、雰囲気ガスとして N₂ または O₂ を用いて熱分解実験を行った。また、反応を促進する目的で H₂O を添加して熱分解実験を行った。N₂、O₂ および Ar+H₂O 雰囲気における SF₆ 分解反応のみかけ活性化エネルギーはそれぞれ 386、408 および 304kJ・mol⁻¹であり、また、H₂O は気相での分解反応を促進することを明らかにした。

続いて、表面反応の影響を調べるため、Cu 管およびステンレス (SUS304) 管を用いて表面反応での SF₆ 熱分解実験を行い、石英管を用いて得られた結果と比較を行った。得られたみかけ活性化エネルギーは Cu 管または SUS304 管を用いた場合でそれぞれ 258 および 47.4kJ・mol⁻¹であり、石英反応管を用いて行って得られた 371kJ・mol⁻¹ よりは小さくなった。これらのことから、Cu や SUS304 反応管を用いた場合は、反応管表面が SF₆ 分解に関与することを明らかにした。

本研究では熱分解だけでなく、これまでの有機ハロゲン化合物の燃焼分解研究から得られた知見を生かして、SF₆ の燃焼分解を行った。先端混合型のバーナーを用いた SF₆ 燃焼分解実験において、SF₆/LPG が 1.3 以下の条件で、分解率 100%を達成し、分解物の主成分は SO₂ と HF であった。O₂ は直接 SF₆ 分解には関与しないことが知られているが、燃焼分解において O₂ は火炎の温度や安定性に関与する重要な因子であることを明らかにした。また、他の代表的な地球温暖化に寄与するフッ素化合物として CF₄ および HFC134a の燃焼分解実験を行い SF₆ の結果と比較を行った。その結果、SF₆ が最も燃焼分解しにくい物質であることを明らかにした。

2009年5月29日

Department of Environment and Life Engineering		ID	023837
Name	Shinya Hayashi		

Advisor	Hee-Joon Kim Yoshiaki Kiso Hideto Tsuji
---------	---

Title	Decomposition Characteristics of Fluorine Compounds Contributing Global Warming
-------	---

(800 words)

Nowadays, the global warming phenomenon is a worldwide concern. According to the fourth appraisal report by Intergovernmental Panel on Climate Change (IPCC), "Most of the observed warming over the last 50 years is likely to have been due to the increase in greenhouse gases concentrations." Therefore it is imperative that global warming policies are formulated and technologies for decreasing global warming must be developed. Among the greenhouse gases, HFC, PFC and SF₆ emissions have been limited. These gases have large GWP and long life time, and the amount of these gases are much less than CO₂. Therefore discharging control measures of these gases has effectively contributed to restraining global warming. In this thesis, SF₆, HFC134a (CF₃CH₂F) and CF₄ were chosen among the fluorine compounds which contribute to global warming. Thermal or combustion decomposition characteristics of these gases were investigated. A brief historical background is given in Chapter 1.

Thermal decomposition of SF₆ in He or Ar bath gases with a quartz tubular reactor is discussed in Chapter 2. In order to obtain fundamental data such as decomposition rate constant and activation energy of SF₆ decomposition, flow rate of gases (related to residence time), reaction temperature, reactor diameter and SF₆ initial concentration were varied. It was found that the rate of SF₆ decomposition reaction was first-order in both He and Ar base gases, and the rate-determining step of SF₆ decomposition was gas phase reaction. The activation energies of SF₆ decomposition in gas phase were 354kJ·mol⁻¹, 371kJ·mol⁻¹ for He and Ar base gases respectively. Comparing with activation energies obtained by other researchers using shock tube reactor, the maximum difference was 25%. It is interesting to note that the activation energies are roughly in accordance with that obtained by shock tube reactor.

In Chapter 3, the effects of the type of bath gas and additives on SF₆ decomposition were investigated. N₂ and O₂ were chosen as bath gases and H₂O and methanol (MeOH) were chosen as additives. It was found that the rate of SF₆ decomposition reaction was first-order in N₂, O₂, He+H₂O, N₂+H₂O, O₂+H₂O, Ar+H₂O and Ar+MeOH bath gases. It was observed that the reaction rate constant was increased by using H₂O or MeOH additives. The rate-determining step of SF₆ decomposition in N₂, O₂ and Ar+H₂O bath gases was gas-phase reaction. Therefore it was concluded that H₂O enhanced the gas-phase reaction. The activation energies of SF₆ decomposition were 386, 408 and 304 kJ·mol⁻¹ for N₂, O₂ and Ar+H₂O bath gases respectively. It was found that O₂ did not enhance the SF₆ decomposition rate. Mass spectrum analysis of the decomposition components in SF₆+O₂ gas mixture at 1373K revealed the presence of SO, SO₂, SOF, SO₂F, SOF₂ and SO₂F₂.

In Chapter 4, the thermal decomposition of SF₆ in Ar with Cu tubular reactor or SUS304 tubular reactor was investigated. The rate of SF₆ decomposition reaction was first-order with both Cu and SUS304 reactors. In the case of Cu or SUS304 reactor, the rate-determining step of SF₆ decomposition was surface reaction or gas diffusion. The activation energies of SF₆ decomposition were 258 and 47.4 kJ·mol⁻¹ for Cu and SUS304 reactors respectively. These activation energies were smaller than the values obtained with gas phase reaction-limited regime. Therefore, it can be concluded that the surface of Cu or SUS304 reactor participated in SF₆ decomposition reaction.

Chapter 5 shows the results of SF₆ decomposition by combustion using a nozzle-mixing burner. At SF₆/LPG less than 1.3, 100% decomposition rate was achieved. In the case of SF₆/LPG equal to 1.3, the decomposition product which include "S" was SO₂, but in the case of SF₆/LPG of 2.0, SO₂F₂ was also detected. This implies that at SF₆/LPG of 1.3, SF₆ would be completely decomposed to SO₂. When SF₆/LPG was 1.3 and primary O₂ concentration was 70%, SF₆ decomposition rate was 100%. But as primary O₂ concentration was decreased to 60%, it was impossible to generate the flame. Although O₂ concentration hardly affected SF₆ decomposition rate, it contributed to the stability of the flame. Hence O₂ concentration is an important factor in SF₆ decomposition by combustion. In addition, the introduction of up to 0.22L·min⁻¹ water vapor to the combustion field increased the SF₆ decomposition rate. However, above 0.22L·min⁻¹ water vapor, the decomposition rate decreased. Therefore, the effect of water vapor on SF₆ decomposition is larger than that of O₂.

In Chapter 6, CF₄ and HFC134a decomposition by combustion was studied. In diffusion combustion method, CF₄ decomposition rate was over 99.98% when CF₄/LPG was below 2.0. But above CF₄/LPG of 2.0, the decomposition rate decreased. Furthermore, CF₄ decomposition rate decreased when the flow rate of secondary O₂ was increased. Using nozzle-mixing burner, the decomposition rate was over 99% even with CF₄/LPG of 2.0 when the primary oxygen concentration was 15% and the secondary oxygen concentration was 60%. The decomposition rate became more strongly dependent on the primary oxygen concentration, as the secondary oxygen concentration was decreased. Comparing between diffusion method and nozzle-mixing method, it was found that nozzle-mixing method is more useful. With a nozzle-mixing burner, a decomposition rate of more than 98.8% was achieved at HFC134a/LPG less than 4. Also, HFC134a decomposition rate was over 98% even with HFC134a/LPG of 5. But in the case of HFC134a/LPG above 4, the number of F atoms is larger than H atoms. Therefore, it is considered that fluorocarbons are produced as by-products.

(909 words)