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Burning velocities and kinetics of $H_2/NF_3/N_2$, $CH_4/NF_3/N_2$, and $C_3H_8/NF_3/N_2$ flames

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ABSTRACT

The combustion characteristics and reaction mechanism of mixtures containing nitrogen trifluoride (NF_3) were investigated. Burning velocities for $H_2/NF_3/N_2$, $CH_4/NF_3/N_2$, and $C_3H_8/NF_3/N_2$ flames were determined for the first time at various equivalence ratios and N_2 mole fractions. The burning velocities of the latter two flames were similar and showed peaks at equivalence ratios of ~1.0, while those of the $H_2/NF_3/N_2$ flames had the pronounced peak at low equivalence ratios where the formation of the wrinkled flames was observed. A detailed kinetic model was constructed to simulate the laminar burning velocities of $H_2/NF_3/N_2$ and $CH_4/NF_3/N_2$ flames. The model accurately reproduced the experimental results. Analyses of the reaction mechanism revealed the major reaction pathways that involve the decomposition of NF_3, the oxidation and chain-fluoridation of H_2 and CH_4, and the formation of N_2.

1. Introduction

Nitrogen trifluoride (NF_3) is the most thermodynamically stable compound among the nitrogen–fluorine species [1] and is widely used as a cleaning and etching agent in the semiconductor and electronics industries [2]. The widespread use of NF_3 for cleaning in chemical vapor deposition processes has rapidly increased the demand for this compound. Because of the strong oxidizing ability of NF_3, several severe accidents have recently occurred in Japan. To ensure the safe use of NF_3, assessment of its combustion characteristics is of fundamental importance. Since the oxidizing ability of gases is mainly determined by their oxidation reactions, it is essential to investigate the reaction mechanism for the combustion of mixtures of NF_3 and flammable gases.

Only a limited number of studies have been carried out on the combustion of mixtures involving NF_3. Croomes [3] investigated the oxidation reaction of n-butane in NF_3–O_2 mixtures, and found that fluorine atoms react preferentially with hydrogen atoms to produce hydrogen fluoride. Lisochkin and Poznyak [4] reported the flammability limits of mixtures of NF_3 with NH_3, CCl_3H, CCl_4, CF_2ClCCl_2H, and C_8F_{16}. Although these studies provided some information on the combustion mechanisms and properties of fuel–NF_3 mixtures, there have been no studies carried out with the aim of elucidating of the reaction mechanism. Also, the burning velocity, which is one of the fundamental combustion properties and can be used to investigate the reaction mechanism, has never been reported for fuel–NF_3 mixtures.

This study aims to obtain the burning velocities of mixtures of NF_3 with H_2, CH_4, and C_3H_8 and develop and validate a kinetic mechanism to explore its oxidation reactions. The burning velocities have been measured for $H_2/NF_3/N_2$, $CH_4/NF_3/N_2$, and $C_3H_8/NF_3/N_2$ flames. A detailed kinetic model was constructed to simulate the laminar burning velocities of $H_2/NF_3/N_2$ and $CH_4/NF_3/N_2$ mixtures, which was used to investigate the reaction pathways and chain-reaction mechanisms for the oxidation of H_2 and CH_4 by NF_3.

2. Experimental method

The burning velocities were measured in a closed spherical vessel. Figure 1 shows a schematic diagram of the experimental apparatus. A spherical stainless-steel vessel with a volume of 15 L was equipped with gas inlet and outlet ports, electrodes, a pressure transducer, and, in some experiments, an acrylic (PMMA) window. The electrodes were linked to a high-voltage source and generated a spark gap of 1.5–3 mm at the center of the vessel. A strain-gauge-type pressure transducer (Kyowa, PHL–A) was installed on the wall of the vessel and connected to a strain amplifier (Kyowa, CVD-700A).

A sample mixture with a known composition, prepared by the partial pressure method, was introduced into the vessel and ignited by an electrical spark between the electrodes. Pressure profiles after ignition were measured by the pressure transducer,

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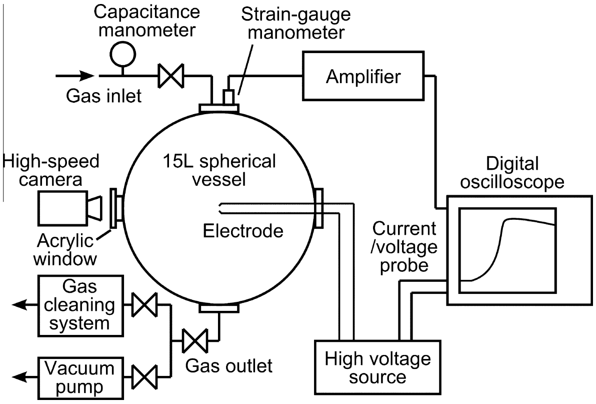

Fig. 1. Schematic diagram of the experimental apparatus.

amplified, and recorded on a digital oscilloscope (Hioki 8861). The gas composition is expressed using the equivalence ratio, ϕ, and the mole fraction of N_2. The equivalence ratios were defined as $2X(H_2)/3X(NF_3)$, $8X(CH_4)/3X(NF_3)$, and $20X(C_3H_8)/3X(NF_3)$ for the $H_2/NF_3/N_2$, $CH_4/NF_3/N_2$, and $C_3H_8/NF_3/N_2$ mixtures, respectively, where X is the mole fraction of the species in the sample mixture. The initial gas was maintained at room temperature (295 ± 5 K) and the initial pressure was 101.3 kPa. The nominal purity of the gases used was more than 99.9% for NF_3, H_2, and CH_4 and more than 99.5% for C_3H_8.

The burning velocity, S_u, of the sample mixture was determined by the pressure profile method developed by Metghalchi and Keck [5] and Hill and Hung [6]. According to Hill and Hung, the time profile of the mass burned fraction, x, can be expressed as

$$\frac{dx}{dt} = \frac{3S_u}{R}\left\{1-(1-x)\left(\frac{P_0}{P}\right)^{1/\gamma}\right\}^{2/3}\left(\frac{P}{P_0}\right)^{1/\gamma} \tag{1}$$

where R is the inside radius of the vessel, P_0 is the initial pressure of the gas, P is the instantaneous pressure in the vessel, and γ is the specific heat ratio of the unburned gas. The mass burned fraction can be calculated by assuming that it has a linear relationship [6] with the pressure increase, i.e.,

$$x = \frac{P-P_0}{P_e-P_0} \tag{2}$$

Here, P_e is the equilibrium pressure under an adiabatic constant-volume condition. The temperature and pressure dependences of the burning velocity can be expressed as

$$S_u = S_{u0}\left(\frac{T}{T_s}\right)^{\alpha}\left(\frac{P}{P_s}\right)^{\beta} \tag{3}$$

where S_{u0} is the burning velocity under the reference condition of $T_S = 298$ K and $P_s = 101.3$ kPa, and α and β are coefficients used to express the temperature and pressure dependences, respectively. Substituting Eqs. (2) and (3) into Eq. (1) and integrating the resultant equation from $t = t_0$ to an arbitrary time t yield

$$P = P_{t=t_0} + \int_{t_0}^{t} \frac{3S_{u0}(P_e-P_0)}{R}\left[1-\frac{P_e-P}{P_e-P_0}\left(\frac{P_0}{P}\right)^{1/\gamma}\right]^{2/3}\left(\frac{T}{T_s}\right)^{\alpha}\left(\frac{P}{P_s}\right)^{\beta}\left(\frac{P}{P_0}\right)^{1/\gamma}dt \tag{4}$$

Because the unburned gas is assumed to be compressed isentropically and $T_0 \approx T_s$ and $P_0 \approx P_s$, Eq. (4) can be reduced to be

$$P = P_{t=t_0} + \int_{t_0}^{t} \frac{3S_{u0}(P_e-P_0)}{R}\left[1-\frac{P_e-P}{P_e-P_0}\left(\frac{P_0}{P}\right)^{1/\gamma}\right]^{2/3}\left(\frac{P}{P_s}\right)^{c}dt \tag{5}$$

where c represents a pressure–temperature dependence coefficient given as

$$c = \alpha + \beta - \frac{\alpha-1}{\gamma} \tag{6}$$

The burning velocity, S_{u0}, and the coefficient c were obtained by a least-squares fit of the observed pressure–time profile to Eq. (5). The equilibrium pressure, P_e, was determined by using NASA-CEA2 program [7]. Figure 2 shows pressure profiles following the ignition of the $H_2/NF_3/N_2$, $CH_4/NF_3/N_2$, and $C_3H_8/NF_3/N_2$ mixtures at $X(N_2) = 0.8$ and $\phi = 1.0$. All the profiles could readily be fitted to Eq. (5). The bold curves represent the pressure profiles calculated using Eq. (5) with the fitted parameters.

To assess the accuracy of the pressure profile method, the burning velocities of CH_4/air mixtures were also measured. They were determined to be 17.8, 37.2, and 27.0 cm s^{-1} at equivalence ratios of 0.7, 1.0, and 1.3, respectively. These values are in close agreement with reported values ([8] and references therein).

In some experiments of the $H_2/NF_3/N_2$ and $CH_4/NF_3/N_2$ mixtures, the burning velocity was also determined by directly observing the flame propagation. Light emission from the flame was monitored with a high-speed monochrome video camera (Vision Research, Phantom v7.3) through the PMMA window with a sample rate of 5 kHz and exposure for 0.1 ms. The time evolution of the flame radius was determined by following the emission front in the flame images. This analysis was only performed for flames with a radius of less than 50 mm. For such flames, the total pressure in the vessel remained nearly constant (the actual pressure rise was less than 3%).

The flame speed, V_s, can be evaluated from the measured flame radius as $V_s = dr/dt$. This flame speed corresponds to the stretched one, which is related to the unstretched laminar flame speed [9], V_l, as

$$V_s = V_l - L\kappa \tag{7}$$

where L is the Markstein length and κ is the stretch rate, defined as $\kappa = 2V_s/r$. Then, the unstretched laminar burning velocity, S_l, can be determined as

$$S_l = V_l\frac{\rho_b}{\rho_u} \tag{8}$$

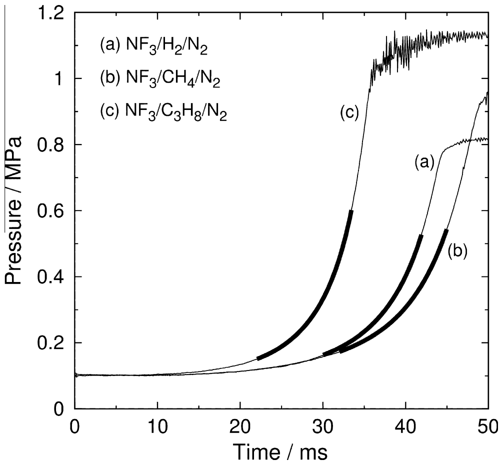

Fig. 2. Time profiles of the pressure following the spark ignition of $NF_3/H_2/N_2$ (a), $NF_3/CH_4/N_2$ (b), and $NF_3/C_3H_8/N_2$ (c) mixtures at $X(N_2) = 0.80$ and $\phi = 1.0$. The bold lines are the profiles calculated using Eq. (5) with the fitted parameters.