Gas-phase Chemical Reaction of Laser Ablated Copper Atom with Carbon Tetrafluoride in Electric Field: Plasma Switching by Laser Ablation (PLASLA)

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From a viewpoint of the electric and magnetic control of a metal catalyst reaction, the chemical reaction of the metal atom generated by laser ablation with gaseous phase molecule is of great interest. The reaction of Cu generated by laser ablation with CF_4 to form CuF molecules in various excited states is studied here. Since this chemical reaction was not studied in the past, its chemical dynamics is first clarified in the present study. The analysis of the spectrum of chemiluminescence of the reaction product CuF gives the vibrational and rotation temperatures in B, C, b, and c excited states. The time-of-flight experiment gives the translational temperatures of Cu and CuF. Besides, the temperature of the blackbody radiation from the bulk site of a Cu target is obtained. Based on these data of the energy budget of the reaction system, the molecular dynamics is discussed. Furthermore, it is found that the reaction is not affected by an electric field less than 500 V. This fact indicates that no charged species such as ions are formed in the reaction system. However, in an electric field higher than 500 V, a new phenomenon named the plasma switching by laser ablation (PLASLA) is first observed. The luminescence of C_2 is observed in PLASLA.
Key words: CuF, Cu, CF_4, laser ablation, electric field, plasma

1. INTRODUCTION

The laser ablation method is widely adopted as a simple method to generate the gaseous phase atoms of various metals and hence widely applied in material chemistry. From a viewpoint of electric and magnetic control of a metal catalyst reaction of the metal atom generated by laser ablation with gaseous phase molecules, the reaction of Cu emitted by laser ablation with CF_4 to form CuF in various excited states is studied here.

In the present study, the molecular dynamics of the reaction system is first clarified by the spectroscopic analysis of the chemiluminescence of the product CuF; the rotational, vibrational, and translationa temperatures are obtained. Furthermore, we first observe plasma switching by laser ablation (PLASLA) in the reaction system in an electric field.

2. EXPERIMENTAL

A fundamental beam (1.064 μm in wavelength, 45 mJ/pulse in power, 10 Hz in a repetition rate) of a Nd^{3+}: YAG laser (Quanta-Ray DCR-2) was focused on the surface of a Cu substrate (Nilaco, 10 mm x 10 mm x 1 mm, better than 99% in purity) in a reaction chamber (aluminum, octagon with 70 mm in side and 200 mm in height) with use of a quartz lens. A copper target was rotated with a motor for homogeneous ablation. In the reaction chamber, a reactant CF_4 gas (Nihon Sanso, 99.999 % in purity) was slowly flowed by keeping its pressure at 0.2 Torr. The luminescence of CuF and Cu in the reaction chamber was introduced into a monochromator (Jobin Yvon HR-1000 with a 2000-lines/mm holographic grating with use of a quartz lens, which was able to be displaced in the direction parallel to the normal direction to the surface of the Cu target in the time of flight experiment. The output of the monochromator was detected with a photomultiplier (Hamamatsu Photonics 1P28).

For the experiment in an electric field, two copper plates (50 mm x 18 mm for each) are placed in parallel with a distance of 35 mm at a reaction site. In the experiment of the electric field effect, the photo-multiplier was covered with a μ-metal shield.

3. RESULTS AND DISCUSSION

3.1Chemiluminescence and Reaction Equation of the Present Reaction System

In the reaction of laser-ablated copper with carbon tetrafluoride, greenish luminescence is observed and is due to neutral copper and copper fluoride in b, B, C, c, and D excited states. No luminescence assigned to copper fluoride ions or copper ions is observed. In fact, we confirm that no charged species such as ions or electrons concerns the present reaction, since the luminescence spectra are invariant in an electric field of 0-500 V.

Therefore the present reaction is expressed in terms of Eq.(1).

$$Cu^* + CF_4 \rightarrow CuF^* + CF_3 \qquad (1)$$

where Cu* is the laser-ablated copper in various excited states and CuF* is copper fluoride in various excited states.

3.2 Energy Budget in the Present Reaction

All temperatures obtained in the present experimental study are shown in Fig.1. Among the temperatures, the translational temperature of Cu is highest. On the other hand, the energy necessary for the reaction in Eq.(1) corresponds to (125-250) $x10^3$ K, which is estimated from bonding energies of the reactant and product molecules. Thus it is found that the energy necessary for the present reaction is found to be equal to the lower part of the translational temperature of Cu in the inner layer. Thus it is confirmed that the translational energy of laser ablated copper has adequate kinetic energy for the reaction in Eq.(1). Probably, the collisional cooling mechanism of the product CuF with CF_4 is significant for the formation of the stable product CuF.

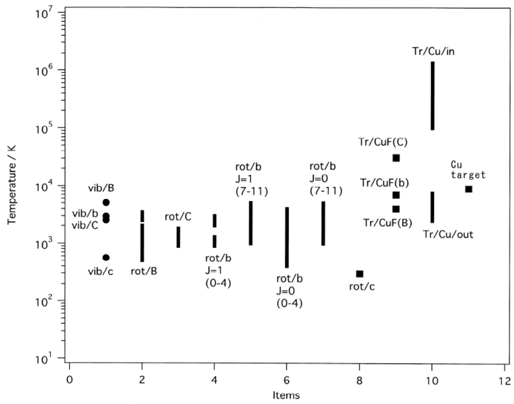

Fig.1 Internal temperatures of the product CuF and the reactant Cu. In notations, e.g., "vib/B" indicates the vibrational temperature of B state, "rot/b J=1 (0-4)" does the rotational temperatures of v'=0-4 levels in $b(^3\Pi_1)$ state, "Tr/CuF(C)" does the translational temperature of CuF in C state, "Tr/Cu/in" does the translational temperature of Cu in the inner layer, and "Cu target" does the temperature of the bulk site of the Cu target.

The translational temperature of CuF is rather similar in magnitude to the rotational and vibrational temperatures, while it is highest in these internal temperatures of CuF. This indicates that the reaction rather equally provides the translational, rotational, and vibrational energies in CuF; that the collisional energy transfer mechanism is significant in the distribution of theses temperatures. In general, the equal distribution of these internal energies indicates that the reaction is essentially thermal and has an early barrier, which is placed on the early site of the reaction coordinate and generally known popular in an exothermal reaction. In the reaction with the early barrier, the translational energy of Cu is used to go over the reaction barrier in the reactant site and the exothermal reaction energy is converted to the vibrational and rotational energy rather than the translational energy of the products in the product site beyond the barrier.

3.3 Plasma Switching by Laser Ablation (PLASLA)

While the luminescence spectra do not change in an electric field less than 500 V, DC discharged plasma is formed in an electric field greater than 500 V. As a result, the redish purple luminescence is predominant instead of the green luminescence, which is due to Cu emission and CuF chemiluminescence, by the plasma formation. The intensity of the redish purple luminescence oscillates periodically.

The plasma luminescence is stable and does not oscillate without laser ablation. This indicates that the oscillation of the plasma luminescence is due to the laser ablation. Furthermore, since the plasma luminescence is not observed without CF_4, the luminescence is due to the plasma formed by the DC discharge of CF_4.

Figure 2 shows the time chart of the total luminescence of the plasma switched by the laser ablation. In this figure, the irregularity in the switching of the plasma luminescence by the laser ablation is due to the contamination of the electrode.

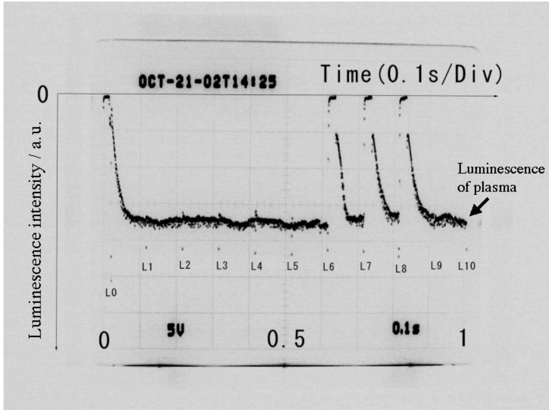

Fig.2 Total emission time chart recorded on an oscilloscope in the experiment of plasma switching by laser ablation (PLASLA). L0-L10: emission of laser ablation.

In this time chart, two kinds of luminescence are observed: luminescence of plasma and the emission of laser ablation marked with L0-L10. The chart indicates that the plasma luminescence intensity rapidly falls to zero simultaneously with the emission of laser ablation. Yet the rapid fall of the plasma luminescence intensity does not occur for laser ablations L1-L5 and L9, while it does for L0, L6-L8. After the rapid fall, the plasma luminescence recovers again. Thus the plasma switching turns out to be a nonlinear process. Since we confirmed that the plasma switching does not occur without laser ablation, it is evident that the laser ablation switches the plasma luminescence; hence we call it plasma switching by laser ablation (PLASLA).

In the further experiments, we find another type of PLASLA. While the laser ablation turns off the plasma in the previous PLASLA, the laser ablation turns on the plasma in this type of PLASA. That is, just under and very close to the threshold of DC discharge without laser ablation, the laser ablation turns on and off the plasma periodically. The induction of the plasma will be due to the ionization of the ablated copper by the impact of electrons formed in the DC discharge. The quenching of the plasma will be caused by the decrease in the concentration of charged species such as ions and electrons by their reaction with laser ablated copper.

The induction of the plasma will be due to the following processes:

$$Cu + e \rightarrow Cu^+ + e \quad (2)$$

$$Cu^+ + CF_4 \rightarrow Cu + CF_4^+ \quad (3)$$

The electrons with kinetic energy less than the ionization potential of CF_4 ionize the laser ablated copper in Eq.(2). The product copper cations react with CF_4 and form carbon tetrafluoride cations. These carbon tetrafluoride cations react with other carbon tetrafluorides to ignite the plasma. It is *the lower temperature plasma*.

The quenching of the plasma will be due to the following process:

$$Cu + CF_4^+ \rightarrow Cu^+ + CF_4 \quad (4)$$

This process decreases the concentration of cations such as CF_4^+, CF_3^+, CF_2^+, CF^+, C_2^+ etc. As a result, the plasma is quenched.

The luminescence of C_2 is observed in PLASLA.