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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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Since the electric and magnetic control of metal catalyst reactions is of great interest, the chemical reaction of the Cu metal atom generated by laser ablation with gaseous molecule CF_4 is studied in an electric field. The reaction product CuF molecules in various excited states are formed in the reaction and the chemiluminescence of CuF as well as the emission of Cu is observed. While the luminescence spectra of the present reaction system do not change in an electric field less than 500 V, the plasma switching by laser ablation (PLASLA) is observed in an electric field at 500 V. The spectroscopic analysis of the luminescence of the plasma indicates that C_2 is formed both in the PLASLA plasma and the DC-plasma of CF_4; that the vibrational temperature of C_2 is much less in the PLASLA plasma than in the DC-plasma of CF_4. Since the PLASLA forms C_2 under milder condition, PLASLA is considered as a new type of metal catalyst reaction.
Key words: CuF, Cu, CF_4, laser ablation, electric field, plasma

1. INTRODUCTION

In the present paper, from a viewpoint of electric and magnetic control of a metal catalyst reaction of the metal atom generated by laser ablation with gaseous molecules, the reaction of Cu emitted by laser ablation with CF_4 to form CuF in various excited states is studied in an electric field. In the past, we started from the basic study on this reaction system and first clarified the molecular dynamics of the reaction system [1-3]. By the spectroscopic analysis of the luminescence of the reaction system, we obtained the rotational and vibrational temperatures of the product CuF in B, C and b, and c states and the translational temperatures of CuF and Cu [1-3]. These studies suggest that the present reaction is due to the simple heating mechanism.

Furthermore, we first observed plasma switching by laser ablation (PLASLA) in the reaction system in an electric field [1-3]. In the present study, PLASLA will be studied more in detail. PLASLA turns out to be promising as a new type of metal catalysis reaction. In consequence, the electric and magnetic field effects are suggested in this reaction system in view of spin chemistry and MHD (magnetic hydrodynamics).

2. EXPERIMENTAL

The schematic diagram of the present experimental system is shown in Fig.1. 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 (50 mmϕ, f=300 mm). A copper target was spun with a motor for homogeneous ablation. In the reaction chamber, a reactant CF_4 gas (Nihon Sanso,

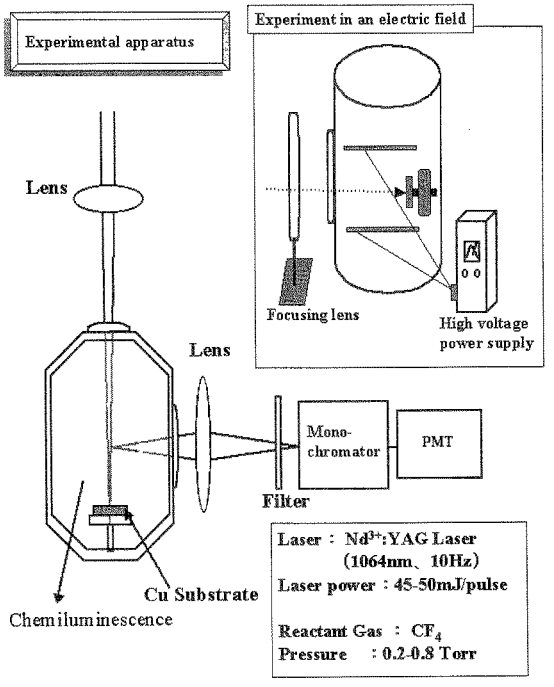

Fig.1 The schematic diagram of the present experimental system. PMT: photomultiplier.

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 or Nikon G-250 with a 1200-lines/mm grating) with use of a quartz lens (50 mmϕ, f=62.5 mm), 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). The signal from the photomultiplier was detected with use of a boxcar integrator (Princeton Applied Research model 162).

In order to confirm that no charged species such as ions and electrons affected the present chemiluminescent reaction, we did the experiments with the reaction system in an electric field. For the experiment, two copper plates (50 mm x 18 mm for each) were placed in parallel with a distance of 35 mm at a reaction site. Potential of 0-500 V was supplied between the plates with a power supplier (FLUKE 408B-874). In the experiment of the electric field effect, the photo-multiplier was covered with a μ-metal shield.

3. RESULTS AND DISCUSSION

3.1 Chemiluminescence of Reaction System in Low Electric Field

In Fig.2, the luminescence spectra measured in an electric field of 0-500 V are shown. It is confirm that no charged species such as ions or electrons concerns the present reaction, since the luminescence spectra are unchanged in an electric field of 0-500 V. This indicates that no charged species such as ions and electrons concern the present reaction. 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 Plasma Switching by Laser Ablation (PLASLA)

While the green luminescence, which is due to the luminescence of Cu and CuF, is observed 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 by the plasma formation is predominant instead of the green luminescence. The oscilloscope trace of the redish purple luminescence intensity is shown in Fig. 3, indicating the oscillation of the plasma luminescence. Since the plasma luminescence is stable and does not oscillate without laser ablation, 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.

In the time chart in Fig. 3, two kinds of luminescence are observed: the 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 for L0, L6-L8, while the rapid fall of the plasma luminescence intensity does not occur for laser ablations L1-L5 and L9. After the rapid fall, the plasma luminescence recovers again. Thus the plasma switching turns out to be a nonlinear process. Since the plasma switching does not occur without laser ablation, it is evident

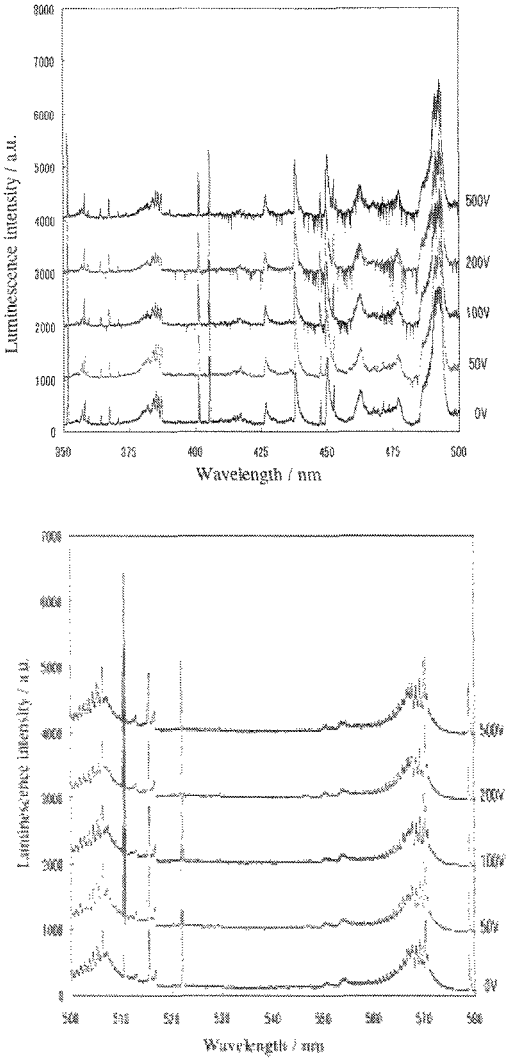

Fig.2 Luminescence spectra observed in the reaction of laser ablated copper with carbon tetrafluoride in an electric field of 0-500 V.

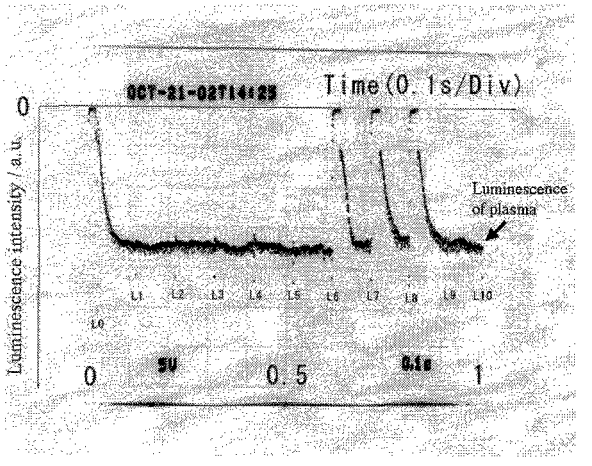

Fig.3 Total emission time chart recorded on an oscilloscope in the experiment of plasma switching by laser ablation (PLASLA). L0-L10: pulsating luminescence of laser ablation at 10 Hz.

that the laser ablation switches the plasma luminescence; hence we call it plasma switching by laser ablation (PLASLA).

3.3 Stable PLASLA

As shown in Fig.3, it is found that the laser ablation turns off the DC-plasma. As a next step experiment, we try to form a more stable PLASLA by the improvement of the experimental system: especially the accurate setup of the parallel electrodes and the precise setup of the potential between the electrodes as well as the precise control of the gas pressure of CF_4 in the reaction chamber.

The oscilloscope trace of the DC-plasma luminescence in Fig. 4a indicates a stable DC-plasma of CF_4 is formed without laser ablation of copper in an electric field of 500 V. On the other hand, Fig. 4b indicates the oscilloscope trace of luminescence in the reaction system of the laser ablated copper and CF_4 in the zero electric field. The figure indicates the periodic luminescence at a repetition rate of 10 Hz.

An electric field of 400 V is not adequate to form the DC-plasma of CF_4 without laser ablation of copper, since the electron from the electrode cannot ionize CF_4 by the impact. However, the laser ablation of copper induces the DC-plasma of CF_4 in the electric field, as shown in Fig. 4c. In this figure, the oscilloscope trace of the luminescence of the DC-plasma and the laser ablation indicates the stable switching of the DC-plasma by the laser ablation. In the trace, the first laser ablation induces the DC-plasma, the second one quenches it, the third one induces it again, the fourth one quenches it, and so on. Thus we succeed in forming the very stable PLASLA in the present reaction system. The laser-ablated copper can be ionized in this electric field, while CF_4 cannot, since the ionization potential of Cu is less than CF_4. The ionized copper reacts with CF_4 to form the ionized carbon tetrafluoride. As a result, the DC-plasma is formed in this electric field, i.e., under more mild condition. In the present reaction, the copper will concern only this initial process, since the laser-ablated copper has very high translational temperature and hence it will stay in the reaction region for a very short time. Therefore these facts imply to be a catalyst for the copper.

While we consider that the pre-ionization of Cu, as described above, is essential for the mechanism of the plasma induction in the PLASLA, we feel difficult to fix the mechanism of the plasma quenching in the PLASLA. One of the possible mechanisms is that the ablated copper is ionized by the reaction with ionic species in the plasma and decreases the ion concentration in the plasma to quench the plasma. Another mechanism is that the ionization of the ablated copper will accelerate the ionic

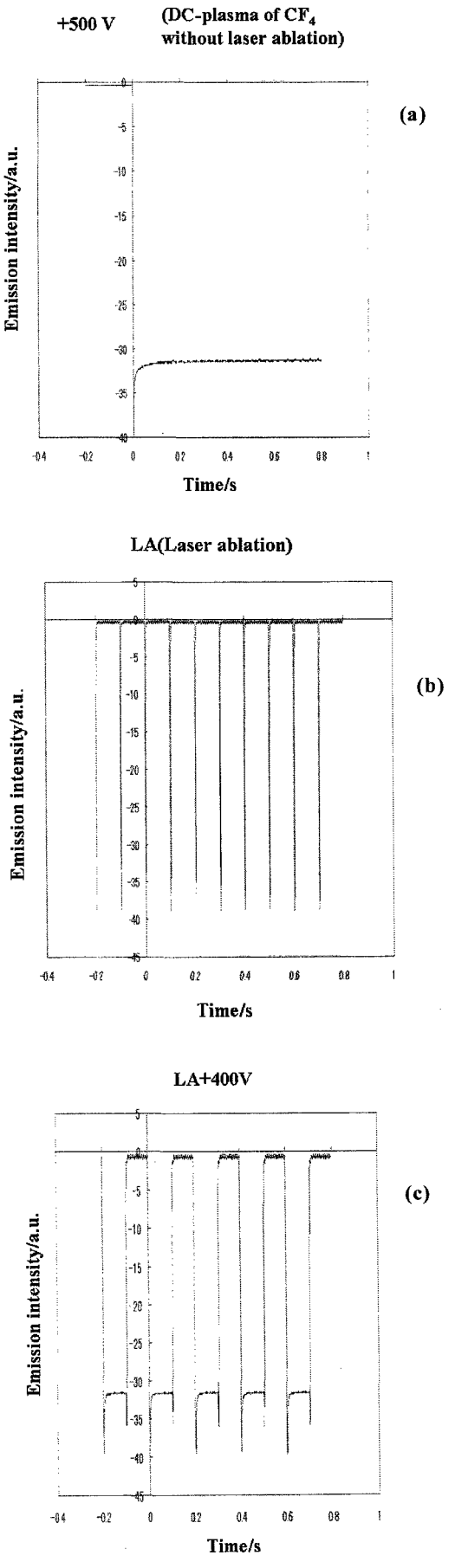

Fig.4 (→) (a) Upper right; the oscilloscope trace of the luminescence of the DC-plasma of CF_4 without laser ablation in an electric field of 500 V. (b) Middle right; the oscilloscope trace of the luminescence of the laser ablation in the presence of CF_4 in an electric field of 0 V. (c) Lower right; the oscilloscope trace of the luminescence of PLASLA in an electric field of 400 V.

reaction in the plasma and the over current will occur in the plasma to stop it.

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

$$Cu + e \rightarrow Cu^+ + e \quad (2)$$
$$Cu^+ + CF_4 \rightarrow Cu + CF_4^+ \quad (3)$$

In the quenching of the plasma, the following process will be significant besides processes in Eqs. (2) and (3):

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

3.4 Spectroscopic study of PLASLA

The spectroscopic analysis of the luminescence of the DC-plasma indicates the progression of C_2 in a wavelength region of 300-480 nm. The similar progression is observed in the complex time-resolved spectrum of the luminescence of the PLASLA at a delay time of 0.5 μs, while the spectra at delay times of 8 μs and 0.25 ms are similar to the chemiluminescence spectrum. The luminescence intensities of the DC-plasma and the PLASLA in various vibrational levels of C_2 are plotted, as shown in Fig.5.

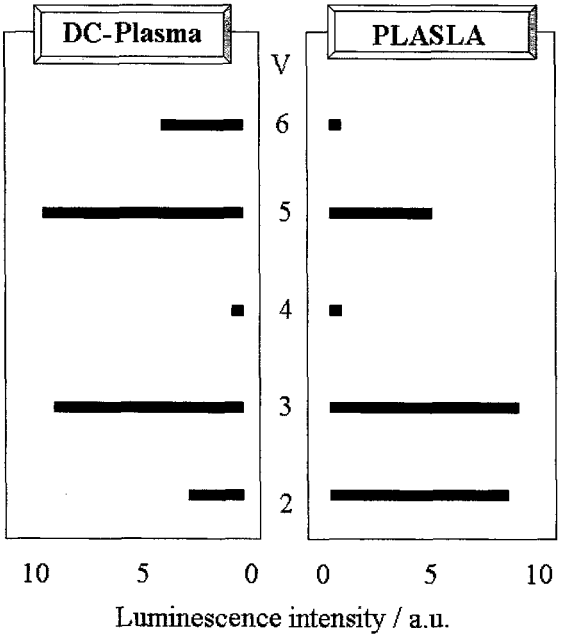

Fig.5 The vibrational distributions of C_2 in the DC-plasma and the PLASLA, where v denotes the vibrational quantum number.

In this figure, both vibrational distributions cannot be fit to a Boltzmann distribution. Yet, the vibrational temperature of C_2 is evidently lower in the PLASLA than in the DC-plasma. This fact indicates that C_2 can be formed under milder condition in the PLASLA than in the DC-plasma. Hence PLASLA is suggested to be a new type of metal catalysis. Since a black carbon-like material is prepared on the electrodes in the present DC-plasma and PLASLA experiments, the polymeric carbon material is finally formed from C_2 in both the plasma. Therefore PLASLA is promising for a new type of metal catalysis reaction in material science.

3.5 Magnetic Field and Electric Field Effects on the Present Reaction

In the present reaction, the laser-ablated copper in doublet states reacts with carbon tetrafluoride in the singlet ground state to form copper fluoride in singlet and triplet states and carbon trifluoride in doublet states. In view of spin chemistry, it is of great interest to study the spin exchange in the reaction and its control by a magnetic field [4, 5]. The present study gives the significant basic information for the objective. It is noticeable that no charged species concerns the present reaction, since we can do the experiments of the magnetic field effect without a magnetic hydrodynamic (MHD) effect.

Furthermore, PLASLA observed first in the present study is of great interest in view of laser CVD. In particular, the cooperative electric and magnetic control of the macroscopic structure of the reaction system will open a new technique in material science [6].

4. CONCLUSION

In the present paper, we study the reaction of laser-ablated copper with carbon tetrafluoride to form the product copper fluoride, which emits the chemiluminescence, in an electric field. As a result, we first observe the very stable plasma switching by laser ablation (PLASLA). It is found that the vibrational temperature of C_2 is lower in the PLASLA than in DC-plasma. This indicates that C_2 can be formed under the milder condition in the PLASLA. Hence, PLASLA is suggested to be a new type of catalysis.

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