A new design for study on reactivity of clusters

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(Received 5 January 1998; accepted for publication 26 January 1998)

This article reports on a new apparatus, called the laser double ablation reactor, for studies on the reactivity of clusters. Structure and operative principle of the apparatus were presented. With this apparatus reactions between manganese/carbon clusters and sulfur clusters, and between silver and sulfur clusters were studied. The experiments indicate that manganese/carbon clusters appear inert when they react with sulfur clusters, while for reactions between silver and sulfur clusters, the products $\left[\text{AgS}_4\right]^+$, $\left[\text{AgS}_5\right]^+$, $\left[\text{AgS}_{12}\right]^+$, and $\left[\text{AgS}_{16}\right]^+$, mainly are obtained. In comparison to the results obtained by Fourier transform ion cyclotron resonance, it shows that the new apparatus is very efficient for study on reactions between clusters. © 1998 American Institute of Physics.

I. INTRODUCTION

Here we report on a new design by which reactions between clusters can be studied. This new design, called laser double ablation reactor (LDAR), is schematically shown in Fig. 1. In comparison with the Fourier transform ion cyclotron resonance (FTICR) spectrometer and flow tube reactor (FTR), which have been extensively applied in studies on reactions of clusters, LDAR has a very simple structure. The details of the experimental arrangement and the procedure of operation are described as follows:

As shown in Fig. 1 LDAR contains two solid samples, sample 1 and sample 2, separated from each other. Samples 1 and 2 are shaped to disks (thickness $\sim$5 mm, radius $\sim$5 mm), and a hole (radius $\sim$1 mm) is drilled in sample 2. The double frequency beam of a Nd:YAG laser (532 nm) is directed through the hole of sample 2 so as to be normal to the surfaces of samples 1 and 2. In this arrangement the laser ablates not only sample 1 but also sample 2. It has been known that laser ablation on solid samples can induce very complicated processes which occur during the photodecomposition of solid material. Throughout the lifetime of the collapsing condensed phase of the irradiated materials, neutral atoms, molecules, and ions are simultaneously emitted with sound speed. As a result, clustering between the emitted species occurs due to collisions between each other. The species emitted from samples 1 and 2, respectively, also contain clusters charged and uncharged. Some of the emitted species from sample 1 sputter through the hole of sample 2, where the reactions between the species from the two samples take place. The reaction products are then detected by the time of flight mass spectrometer (TOF MS).

On the principle of operation as above, for study on reactions between clusters emitted from samples 1 and 2, the independent clustering of the emitted species from the two samples is very important and it should be completed prior to the reactions of clusters, that is, clustering first and reaction second (CFRS). In order to satisfy the experimental condition of CFRS, the values of distance between samples 1 and 2 play an important role. Experiments indicated that with a laser fluence of 100 mJ/cm$^2$ and the 1 mm diam of the hole in sample 2, the distances in the range of 5–10 mm between samples 1 and 2 are effective. If the distance is too short, the emitted species, produced by laser ablation from samples 1 and 2 meet first, and then clustering occurs. This process is similar to that produced with one sample which contains elements in samples 1 and 2, without reactions between clusters. On the other hand, the distance between samples 1 and 2 cannot be too long. If it is, the amount of the reaction products will greatly decrease, and the detection might be in trouble.

The process of laser ablation on samples is also important for the study on reactions between clusters. Figure 2 shows two different designs of laser ablation on samples 1 and 2. In Fig. 2(a) laser beam is rightly focused on the surface of sample 1. In this arrangement, only part around the hole on the front surface of sample 2 is ablated by the laser while the inside wall of the hole is not irradiated. Figure 2(b) shows another way the beam focuses. When the focus of the laser beam is on the front surface of sample 2, the inside wall of the hole can actually be ablated by the laser. The experiments tell that the latter, Fig. 2(b), is favorable for the study on reactions of clusters, and the space inside the hole acts as a reaction cell and the reaction time can be controlled also by changing the thickness of sample 2. It should be noted that in the arrangement of Fig. 2(b), the emitted species from the hole will sputter out in opposite directions, and only the reaction products flying to TOF MS can be detected.

The following experiments were performed in order to verify the effects of the LDAR. Experiment (1) observed the changes of mass spectrum with distances between samples 1 and 2. The values of the distance satisfying the experimental condition of CFRS were found. Experiment (2) was for comparison with the results obtained by the ion cyclotron resonance (ICR).
A Nd:YAG double frequency (532 nm) laser was used in the above experiments. The laser beam was focused with a lens (f = 50 cm) and the fluence in the focused area was about 100 mJ/cm². Samples used in the experiments were prepared as the shape of disk, and all the elements contained in the samples have a purity of 99%.

A. Experiment (1)

Sample 1 was made of manganese and carbon powders with molar ratio Mn:C = 1:1 (thickness ~7 nm, radius ~5 mm). Sample 2 was made of sulfur element (thickness ~7 nm, radius ~5 mm). The diameter of the hole in sample 2 was 1 mm. The experiments were performed under conditions of only changing the distance between samples 1 and 2. Figures 3(a) and 3(b) are mass spectra of negative ions resulting from distances of 2 and 5 mm between samples 1 and 2, respectively. For comparison, the mass spectra of the sample containing manganese, carbon, and sulfur (molar ratio Mn:C:S = 1:1:1), and of the sample containing manganese and carbon (molar ratio Mn:C = 1:1) without sulfur are presented in Figs. 4 and 5, respectively.

It was known that negative ions \([\text{S}_n^-] , \ [\text{C}_n^-] , \ [\text{SC}_n^-] , \ [\text{S}_2\text{C}_n^-] , \ \text{and} \ [\text{MnS}_n^-]\) were produced in Fig. 4 without \([\text{MnC}_n^-]\), while cluster ions \([\text{MnC}_n^-]^-(n = 2, 4, \sim 12)\) were produced in Fig. 5. The fact that there were no cluster ions \([\text{MnC}_n^-]\) produced when the sulfur element was contained in the samples indicates that there is competition between the clusterings of sulfur with manganese and carbon with manganese, and the former overwhelms the latter. Figure 3(a)
was obtained in the distance of 2 mm between samples 1 and 2 and there were no cluster ions \([\text{MnC}_n]^\text{−}\) produced. This feature of Fig. 3 was the same with that of Fig. 4 without \([\text{MnC}_n]^\text{−}\) produced, indicating that the distance 2 mm between samples 1 and 2 is not long enough to satisfy the condition of CFRS. In the distance of 2 mm, the vaporized species from samples 1 and 2 are mixed clustering, which is like that of one sample containing manganese, carbon, and sulfur elements. Setting the distance between samples 1 and 2 to be longer up to 5 mm, the mass peaks \([\text{MnC}_n]^\text{−}\) appear as displayed in Fig. 3, indicating that the distance 5 mm between samples 1 and 2 has already satisfied the condition of CFRS. According to the experimental results shown above it can be confirmed that the values of the distance satisfying the condition of CFRS should be >5 mm.

B. Experiment (2)

Sample 1 was made of silver and sample 2 was made of sulfur. The distance between samples 1 and 2 was set at 6 mm. The distribution of the mass spectrum was shown in Fig. 6. It is evident that the mass peaks \([\text{AgS}_4]^\text{+}\), \([\text{AgS}_8]^\text{+}\), \([\text{AgS}_{12}]^\text{+}\), and \([\text{AgS}_{16}]^\text{+}\) are very distinct as magic numbers. For comparison, the mass spectrum obtained from the sample made of silver and sulfur powders (molar ratio Ag:S = 1:1) is presented in Fig. 7. It is also evident that the compositions of Fig. 7 are mainly \([\text{AgS}_n]^\text{+}\) and \([\text{AgS}_{3(n-4)}]^\text{+}\) \((n = 1−4)\) rather than \([\text{AgS}_l]^\text{+}\) \((l = 4, 8, 12, 16)\) indicating that the experiments shown in Fig. 6 satisfied the condition of CFRS.

Willett studied the reactions between Ag⁺ and S₈ by FTICR and got the following results:

\[
\text{Ag}^+(g) + \text{S}_8(g) \rightarrow [\text{AgS}_4]^+(g) + \text{S}_4(g) \\
[\text{AgS}_4]^+(g) + \text{S}_8(g) \rightarrow [\text{AgS}_8]^+(g) + \text{S}_4(g) \\
[\text{AgS}_8]^+(g) + \text{S}_8(g) \rightarrow [\text{AgS}_{16}]^+(g).
\]

It is clear that the reaction products obtained with LDAR are similar to those shown above, but the kinds of reaction products are more than that obtained with ICR. For example, the reaction product \([\text{AgS}_{12}]^\text{+}\) which was obtained with LDAR, disappeared from the reaction products obtained with ICR.

The defect of LDAR is that gas-phase samples cannot be used. For remedying the defect it might be a good idea to select solid compounds in which the gas-phase atoms or molecules to be used are contained.