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Reactivity of cationic niobium carbide clusters with N_2O

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Introduction

In the last two decades metal carbide clusters are extensively studied due to the fact that they can catalyse reactions in a manner similar to platinum group metals (Pt, Ru, Rh, Pd, Os and Ir), which is explained as being due to modification of the surface electronic properties by the addition of carbon. Niobium carbide clusters has been investigated by several groups using methane gas as a carbon source. It can also be prepared in the gas phase by the double laser vaporization. Using this procedure the reactivity of niobium carbide (NbC) clusters has been previously investigated with H_2 gas by Miyajima et al. [1]. In that study the authors found that Nb_nC_m clusters with composition ratio n:m=1:5 were relatively inert to H_2 gas. To further investigate the composition dependent reactivity of $Nb_nC_m^+$ clusters we measured the reactivity of $Nb_nC_m^+$ clusters with N_2O gas.

Experiment

Niobium carbide clusters were formed in a supersonic double laser ablation source coupled to a reflectron-equipped time-of-flight mass spectrometer. The niobium and graphite rods were irradiated with the focused laser pulses (~10 mJ/pulse) at a wavelength of 532 nm from Quanta Ray GCR-170 and Continuum Surelite II Nd^{3+}:YAG lasers for generating the plasma. The evaporated niobium atoms and carbon atoms were cooled in the gas phase by the He gas (>99.99995%), forming $Nb_nC_m^+$ clusters. The clusters then entered into the collision cell filled with N_2O gas. The stagnation pressure of He carrier gas used was 5 atm or 9 atm which affects strongly towards the cluster distribution.

Results and discussion

Mass Spectra of $Nb_nC_m^+$: In this study we produced two different mass distributions to observe the

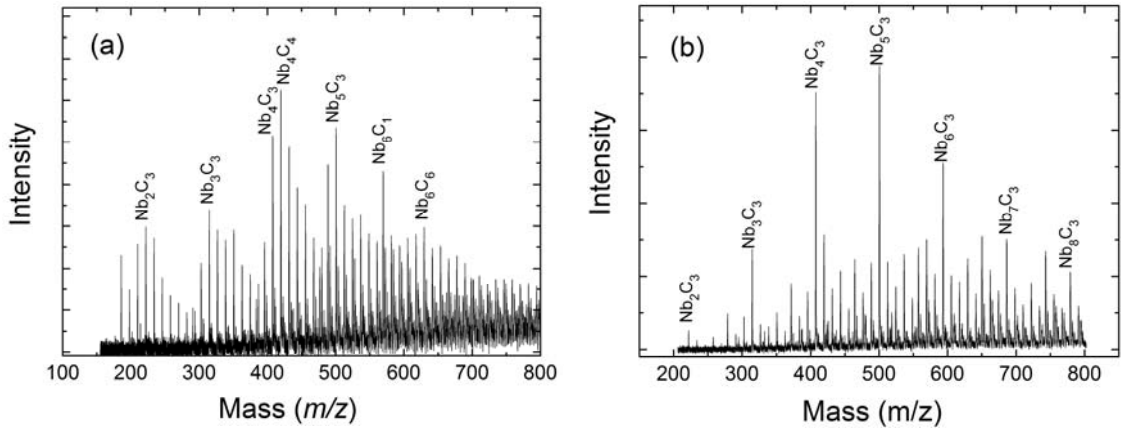

Figure 1: Mass distribution of $Nb_nC_m^+$ clusters (a) Nb_4C_4 as the highest intensity condition (b) Nb_nC_3 product rich condition.

reactivity with N_2O gas. Figure 1 shows the two types of mass distribution produced in two different conditions. In one distribution (Figure 1a; He 5 atm) ions $Nb_2C_3^+$, $Nb_3C_3^+$, $Nb_4C_4^+$, $Nb_5C_3^+$, $Nb_6C_1^+$, $Nb_6C_6^+$ show high abundance and in another type of distribution (Figure 1b, He 9 atm) $Nb_nC_3^+$ (n=2-8) show high abundance.

Reactivity with N_2O: The reactivity of $Nb_nC_m^+$ clusters were examined for both mass distributions. We observed that the same cluster for both the mass distributions behaved differently to N_2O gas at the same pressure. Figure 2 shows the color maps of intensity ratios of two types of mass distribution. Generally Nb_nC_m clusters decreased with N_2O gas addition. However, some clusters, such as Nb_2C_3 and Nb_3C_2 are inert compared to the adjacent compositions. Additionally, in the Nb_nC_3 product rich condition Nb_2C_3, Nb_3C_4, Nb_5C_7 and Nb_6C_7, Nb_8C_7 were found relatively inert. Furthermore, Nb_nC_3 clusters have reacted more compared to the other clusters. This trend is very different to the result of Nb_4C_4 as the highest intensity condition. This observation implies that geometrically different isomers are formed due to the different cluster formation environment. In Nb_nC_3 product rich condition, Nb clusters react to the neutral C_3 cluster in a growth region while in another condition Nb and C are well mixed during the cluster formation. In order to verify the production of different isomers photoionization experiment can be utilized to obtain their ionization potentials (IP) [2]. Previous IP measurement in our group was conducted under the Nb_nC_3 rich condition, and the values of IPs were close to the calculated ones for 2x2x2 cubic structure in the case of Nb_5C_3. We are further investigating the IP measurement of Nb_4C_4 as the highest intensity condition which will be presented in the conference.

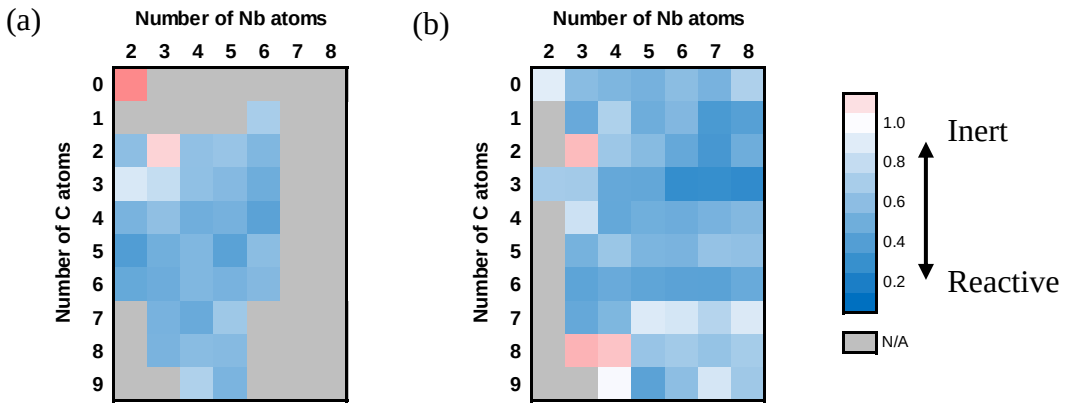

Figure 2: Color maps for two different production conditions of $Nb_nC_m^+$ clusters (a) Nb_4C_4 as the highest intensity condition (b) Nb_nC_3 product rich condition. Values are calculated from the ratio of cluster intensity: ratio = $I_{\text{with N2O}}$ /$I_{\text{without N2O}}$.

References:

[1] Ken Miyajima, Naoya Fukushima, Fumitaka Mafuné, *J. Phys. Chem. A* **2009**, *112*, 5774.

[2] Naoya Fukushima, Ken Miyajima, Fumitaka Mafuné, *J. Phys. Chem. A* **2009**, *113*, 2309.