

Formation of $\text{Ca}_1\text{Mn}_4\text{O}_5^+$ Clusters Investigated by Thermal Desorption Spectrometry

○Yufei Zhang, Daigo Masuzaki, S. Kudoh, K. Miyajima, F. Mafune
Department of Multidisciplinary Sciences, The University of Tokyo, Japan

[Abstract] Formation of a $\text{Ca}_1\text{Mn}_4\text{O}_5^+$ cluster, which is known as an active center of catalyst in the PSII system, was investigated in the gas phase. To observe thermal stability of $\text{Ca}_m\text{Mn}_k\text{O}_i^+$, thermal desorption spectrometry of $\text{Ca}_m\text{Mn}_k\text{O}_i^+$ was performed. $\text{Ca}_1\text{Mn}_4\text{O}_5^+$ was not produced and instead several oxygen rich clusters were formed such as $\text{Ca}_1\text{Mn}_4\text{O}_7^+$. In $\text{Ca}_m\text{Mn}_k\text{O}_i^+$, manganese oxide plays an important role in the whole structure and hence, Mn_mO_n^+ likely has similar reacting properties. To understand structure and properties of $\text{Ca}_m\text{Mn}_k\text{O}_i^+$, the thermal stability and the hydration effect on the Mn_mO_n^+ clusters were investigated. Before hydrated, Mn_mO_n^+ only show several oxygen rich clusters such as Mn_4O_6^+ whereas after hydrated, oxygen poor cluster Mn_4O_4^+ was produced.

[Introduction] The $\text{Ca}_1\text{Mn}_4\text{O}_5^+$ cluster is known as the active center of the catalyst in the PSII system for water splitting and plays an important role in the photosynthesis.^[1] As the main part of structure of $\text{Ca}_1\text{Mn}_4\text{O}_5^+$, Mn_4O_4^+ cluster also plays an important role. Previous study proved that the hydrated manganese clusters also have the ability of structure change.^[2] The structural change of the hydrated manganese clusters may lead to form the oxygen poor clusters. The investigation of Mn_mO_n^+ would help understanding the structures of $\text{Ca}_m\text{Mn}_k\text{O}_i^+$ and mechanism of the structure change with hydrated clusters. In this study, thermal stability of Mn_mO_n^+ and their hydration effect were investigated by the thermal desorption spectrometry.

[Methods] The calcium manganese oxide clusters were prepared by using laser ablation inside the cluster source. A calcium metal rod and a manganese metal rod were vaporized by using the second harmonic and third harmonic of the Nd:YAG pulsed laser in the high vacuum condition. The cluster ions were formed in a He gas flow containing O_2 from a pulse valve at a stagnation pressure of 0.8 MPa. The partial pressure of O_2 gas was adjusted by using the mass flow and pressure controllers.

The prepared $\text{Ca}_m\text{Mn}_k\text{O}_i^+$ were reacted with water vapor mixed with He gas and heated in the extension tube (up to 1000 K). $\text{Ca}_m\text{Mn}_k\text{O}_i^+$ were analyzed using the TOF-MS and the mass spectra were measured.

[Results and Discussion]

Thermal Stability of $\text{Ca}_m\text{Mn}_k\text{O}_i^+$ and Mn_mO_n^+ were investigated by thermal desorption spectrometry. Figure 2 shows the mass spectra of $\text{Ca}_m\text{Mn}_k\text{O}_i^+$ at 1000 K and room temperature. At room temperature, more oxygen rich clusters tended to be formed. Figure 3 shows the thermal desorption curves of $\text{Ca}_1\text{Mn}_4\text{O}_m^+$: Clearly O_2 desorption was observed as the following reactions,

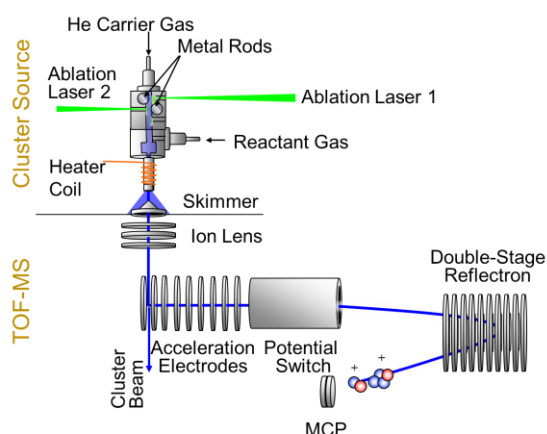


Fig. 1. Experimental Setup



However, $\text{Ca}_1\text{Mn}_4\text{O}_5^+$ was not formed even at 1000 K. This finding suggests that $\text{Ca}_1\text{Mn}_4\text{O}_5^+$ is not thermal stable in the presence of oxygen.

Thermal desorption spectrometry was conducted for Mn_mO_n^+ . Figure 4(a) shows that at room temperature, Mn_4O_4^+ did not form and instead oxygen rich clusters such as Mn_4O_6^+ and Mn_4O_7^+ were found to be produced. With an increase in the temperature, the oxygen poor clusters started to appear and Mn_4O_4^+ appeared over 850 K. This finding suggests that oxygen was strongly bonded with Mn_4O_4^+ .

To investigate the hydration effect on the stability and structure of Mn_mO_n^+ , thermal desorption spectrometry with hydrated Mn_mO_n^+ were conducted. According to the Figure 4(a), Mn_4O_4 was only formed after 850 K by reduction of Mn_4O_6^+ , however for the hydrated clusters in Figure 4(b), the Mn_4O_4 series clusters were formed at room temperature, suggesting that Mn_4O_4^+ tend to be formed readily when hydrated. When the reduction from $\text{Mn}_4\text{O}_6(\text{D}_2\text{O})_1^+$ to $\text{Mn}_4\text{O}_4(\text{D}_2\text{O})_1^+$ occurred over 850 K, as shown in Figure 4(b) water was still bonded after the reduction occurred which suggests that water molecule may dissociatively adsorbed.

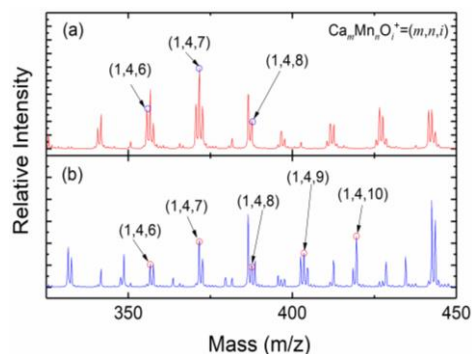


Fig. 2. Mass spectrum of $\text{Ca}_m\text{Mn}_k\text{O}_i^+$ clusters (a) 1000 K, (b) room temperature

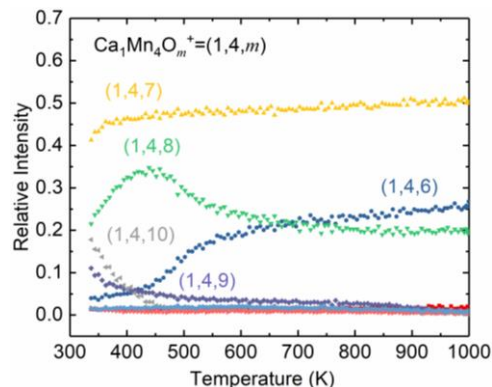


Fig. 3. Thermal desorption curve of $\text{Ca}_m\text{Mn}_k\text{O}_i^+$ clusters

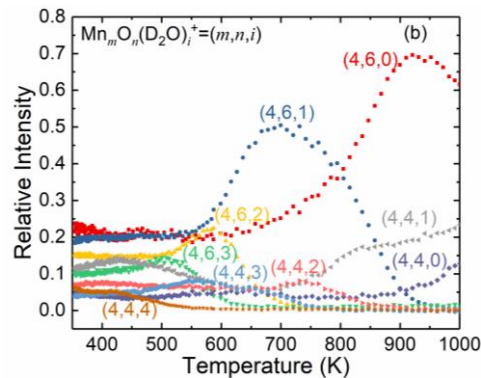
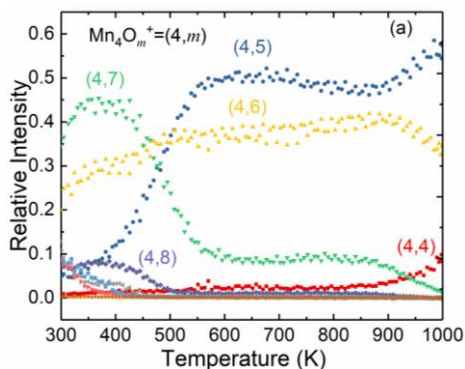


Fig.4. (a) TDS curve of Mn_4O_m^+ clusters (b) TDS curve of $\text{Mn}_4\text{O}_{4,6}(\text{D}_2\text{O})_i^+$ clusters

Figure 5 shows most stable structures of different clusters, Comparison between (a) and (c) shows that water molecule is dissociatively adsorbed on Mn_4O_4^+ , and after attached with O_2 and calcium, structures are greatly changed. According to those phenomenon, structural change of the hydrated clusters may have occurred. Further calculation and experiments on hydrated $\text{Ca}_m\text{Mn}_k\text{O}_i^+$ will be discussed.

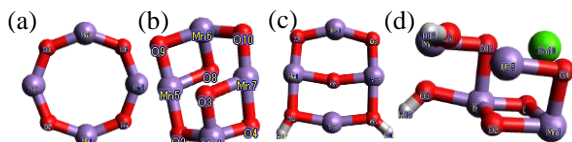


Fig.5. (a) Mn_4O_4^+ (b) Mn_4O_6^+ (c) $\text{Mn}_4\text{O}_4(\text{H}_2\text{O})^+$ (d) $\text{Ca}_1\text{Mn}_4\text{O}_5(\text{H}_2\text{O})^+$

[Reference]

- [1] Umena, Y. *et al. Nature.* 2011, 473,55-60
- [2] Sandra M. Lang *et al. Nano. Lett.* 2013, 13, 5549-5555