

## Structures and Reactions of Transition Metal Oxide Cluster Ions

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Metal oxide clusters are regarded not only as local structure models of solids or surfaces but also as candidates of novel functional materials. In this study we have applied ion mobility mass spectrometry to investigate geometrical structures of oxide cluster ions of the first row transition metals such as Ti, V, Cr, Fe, Co, Ni, Cu and Zn. We have also examined CO-adsorption reactions on the cluster ions with the same setup.

In the present experiment, cluster ions formed in vacuum were injected by pulsed electric field into an ion drift cell, in which He gas was filled and an electrostatic field was applied. The cell was cooled by liquid N<sub>2</sub> circulation. The ions exited from the cell were analyzed in a time-of-flight (TOF) mass spectrometer. We thus obtained a series of TOF mass spectra at different arrival times, which were defined as the time duration between the ion injection pulse and the acceleration pulse in the TOF mass spectrometer. Collision cross sections (CCSs) of the ions were determined experimentally from the obtained arrival time distributions. Finally, geometrical structures are assignable by comparison of CCSs obtained in this experiment with those deduced for structures predicted by quantum chemical calculations.

For the oxide cluster ions of late transition metals such as (FeO)<sub>n</sub><sup>+</sup>, (CoO)<sub>n</sub><sup>+</sup>, and (NiO)<sub>n</sub><sup>+</sup>, structural transitions were commonly observed from two-dimensional (2D) cyclic or sheet structures to three-dimensional (3D) compact tower or cage structures at the size *n* smaller than 10; both types of isomers coexist at *n* = 6-8 for (FeO)<sub>n</sub><sup>+</sup> (Fig. 1) [1] and at *n* = 5 for (NiO)<sub>n</sub><sup>+</sup> [2], whereas 3D structures were clearly observed from *n* = 6 for (CoO)<sub>n</sub><sup>+</sup> (Fig. 2) [3]. By contrast, the most stable isomers have 3D structures for the oxide cluster ions of early transition metals such as (TiO<sub>2</sub>)<sub>n</sub><sup>+/-</sup> (*n* ≥ 3) and (V<sub>2</sub>O<sub>5</sub>)<sub>n</sub><sup>+/-</sup> (*n* ≥ 2).

In addition, kinetics of CO adsorption reactions were examined by introducing CO gas which was diluted in He buffer gas in the ion drift cell. We have found from the experiment that some of the ions show isomer-dependent reactivity; e.g., polycyclic isomer ions of N<sub>7</sub>O<sub>6</sub><sup>+</sup> have much higher rate constant than 3D isomers.

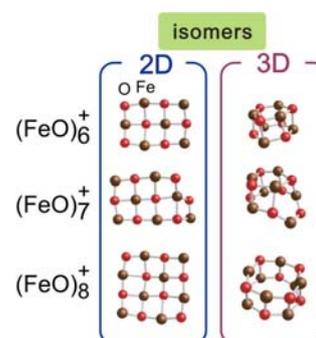


Figure 1: Observed isomer structures for (FeO)<sub>n</sub><sup>+</sup>, *n* = 6-8 [1].

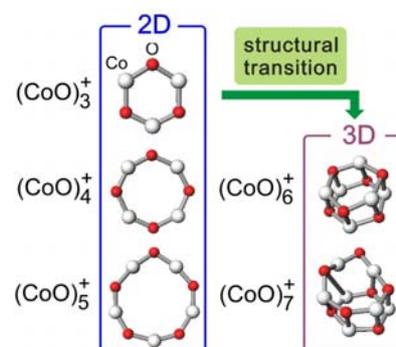


Figure 2: Structure change with cluster size for (CoO)<sub>n</sub><sup>+</sup>, *n* = 3-7 [3].

[1] K. Ohshimo, T. Komukai, R. Moriyama, and F. Misaizu, *J. Phys. Chem. A* **118**, 3899 (2014).

[2] K. Ohshimo, S. Azuma, T. Komukai, R. Moriyama, and F. Misaizu, *J. Phys. Chem. C* **119**, 11014 (2015).

[3] K. Ota, K. Koyasu, K. Ohshimo, and F. Misaizu, *Chem. Phys. Lett.* **588**, 63 (2013).