

Size-specific reactivity of transition-metal-doped silver clusters toward oxygen: Geometric and electronic effects

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Transition-metal atoms exhibit distinct chemical and physical characteristics due to unpaired d electrons. In bulk materials, however, these features of atoms are modified because the d electrons interact with other electrons on neighboring atoms. It is not obvious whether the d electrons localize on the transition-metal atom, or they are delocalized and hybridized with other orbitals. To investigate interaction between d and s electrons, we focus on the 3d-transition-metal-doped silver clusters Ag_NM as a model system. A previous study of abundance spectra of clusters generated by laser vaporization and subsequent photo-dissociation showed that 3d electrons tend to delocalize when a closed electronic shell is formed by the entire cluster with contribution of 3d electrons as well as 4s and 5s [1]. In the present study, we focus on reactivity of such doped clusters, which should be influenced sensitively by the nature of 3d electrons.

In the experiment, a series of silver cluster ions doped with a single transition-metal atom (Ag_NM^+) were produced in a magnetron-sputter ion source, and were mass-selected by a quadrupole mass filter. The mass selected clusters were introduced into a linear ion trap filled with a buffer He gas of 2×10^{-3} Pa and a pressure-controlled oxygen gas as a reactant. Product ions were extracted from the ion trap after a given time for reaction, and were analyzed by a time-of-flight mass spectrometer. Reaction-rate constants were derived from extinction rates of the parent clusters. Optimization of geometrical structures was performed by DFT calculations using the Gaussian 09 package to discuss structure–reactivity correlation.

Ag_NNi^+ cluster ions with $N \leq 7$ were dissociated promptly within 10 ms in the presence of O_2 at 10^{-4} Pa. Major products were $\text{Ag}_{N-2}\text{NiO}_2^+$ and $\text{Ag}_{N-1}\text{NiO}_2^+$. On the other hand, larger ones with $N \geq 8$ remained mostly intact even in O_2 at 2×10^{-3} Pa; adsorption of O_2 molecules was the only reaction channel. Figure 1 shows that relative reaction-rate constants of Ag_NNi^+ clusters with $N \leq 7$ were about four orders of magnitude higher than those of Ag_{N+1}^+ . In contrast, those with $N \geq 8$ were comparable with those of Ag_{N+1}^+ . Geometric structures of the clusters were obtained by DFT calculation as illustrated in Fig. 1. There is a Ni atom on the surface of the clusters with $N \leq 7$. In contrast, the Ni atom is encapsulated by Ag atoms in the clusters with $N \geq 8$. The result of DFT calculations implies that this dramatic decrease in the reactivity of $N \geq 8$ is attributed to encapsulation of the Ni atom, which might be an active site if it is on the surface. On the other hand, Ag_9Ni^+ exhibited minimal reactivity, which possesses 18 valence electrons with Ag 5s, Ni 3d, and Ni 4s. This minimal reactivity might be due to its closed electronic structure, formed by the 18 electrons. It was thus found that both geometric and electronic features cause size specificity in reactivity of Ag_NNi^+ clusters. Results for $M = \text{Mn}, \text{Fe},$ and Co will also be presented.

- [1] E. Janssens, S. Neukermans, H. M. T. Nguyen, M. T. Nguyen and P. Lievens, *Phys. Rev. Lett.* **94**, 113401 (2005)

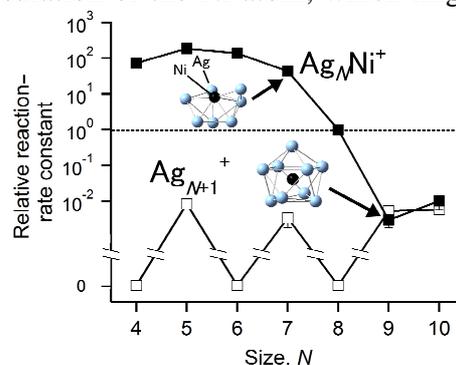


Figure 1: Relative reaction-rate constants of Ag_NNi^+ and Ag_{N+1}^+ ($N = 4\text{--}10$) with O_2 .