

Size-dependent reactivity of transition-metal-doped silver clusters: A study of electronic and geometric structures

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Transition-metal-doped coinage metal clusters provide us with a model system for investigating s-d electron interaction in the finite-size regime, which is known as the Kondo effect in the bulk. The first cluster experiment was performed by photofragmentation of positively charged Au [1] or Ag [2] cluster cations doped with a series of open 3d transition-metal atom, where highly abundant magic sizes were observed in the fragment mass spectra. These sizes were explained to have enhanced stability due to a closed electronic shell with 18 valence electrons formed by delocalized 3d electrons along with s electrons of the dopant and the host atoms. These studies pointed out that the clusters tend to promote delocalization of 3d electrons when a closed electronic shell can be formed. Recently X-ray spectroscopy has been performed to discuss s-d electron interaction [3,4]. Size-dependent change in the electronic structures has been investigated also by a computational study [5]. In this context, corresponding anionic clusters have been studied as well by photoelectron spectroscopy [6-8], although it is limited only to several systems. Studies of anions are important to examine influence of the number of electrons in the system compared with cations.

To extend these studies in a systematic way, the present study employs chemical reaction to probe electronic structures both for cations and for anions; reactivity is expected to be reduced upon electronic-shell closure. We have carried out reactivity measurement of 3d-transition-metal (M) doped silver cluster cations (Ag_NM^+) and anions (Ag_NM^-) toward oxygen. Figure 1 shows the result obtained for $\text{Ag}_{N-1}\text{Ni}^+$ along with that of bare Ag_N^+ ; the value of N is shifted by one so as to compare clusters with the same number of constituent atoms. A dramatic drop in the

reactivity was observed for $\text{Ag}_{N-1}\text{Ni}^+$ at $N = 9$; the reactivity at $N > 9$ is at the same level as those of Ag_N^+ . This behavior is explained by encapsulation of the Ni atom at larger sizes, i.e., screening the active site. A reactivity minimum was observed at $N = 10$, which is attributable to an 18-electron closed shell, suggesting delocalized Ni 3d electrons [9]. We will report our results obtained for a series of dopant atoms ($M = \text{Sc-Ni}$) for cations and several preliminary results for anions.

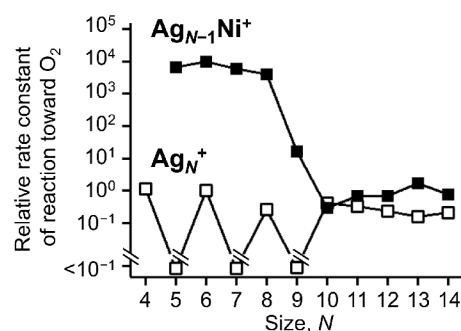


Figure 1. Relative reaction-rate constants of $\text{Ag}_{N-1}\text{Ni}^+$ and Ag_N^+ toward an O_2 molecule

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