Reactions of Nitrogen Monoxide Molecule on Bare and Hydrogenated Cobalt Cluster Ions – Size-Specific Reactivity Enhancement by Hydrogen-Atom Introduction

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In a heterogeneous catalytic reaction, it is often the case that even a trace amount of impurities alters the reactivity. Similarly, foreign atoms on a metal cluster are expected to influence its reactivity with a reactant molecule. In this relation, we measured the cross sections of the reactions of Coₙ⁺ (n=2−9) and CoₙH⁺ (n=2−5) with NO by use of a tandem-type mass spectrometer equipped with a reaction cell in order to elucidate the influence of H-atom introduction.

The parent cluster ion, CoₙH⁺⁺ (m=0,1), was produced by bombardment of cobalt metal targets with Xe ion-beams accelerated up to 15 keV. The cluster ions thus produced were decelerated and cooled by multiple collisions with helium atoms, mass-selected by the first quadrupole mass filter, and allowed to collide with an NO molecule in the reaction cell under single collision conditions. The product ions were mass-analyzed by the second quadrupole mass filter and detected.

Decomposition of NO (eq.1), chemisorption of NO (eq.2), and dissociation of the parent cluster ion after NO chemisorption (eq.3),

CoₙH⁺⁺ + NO → Coₙ⁺⁺N⁺ + CoOH⁺⁺ (m=0,1) (NO decomposition) (1)
CoₙH⁺⁺ + NO → Coₙ(NO)H⁺⁺, Coₙ₋₁(NO)H⁺⁺ + Co, (m=0,1) (NO chemisorption) (2)
CoₙH⁺⁺ + NO → Coₙ₋₁H⁺⁺ + Co(NO), (m=0,1) (cluster dissociation) (3)

were found to proceed. The results show that the cross sections for the NO decomposition and the cluster dissociation on Coₙ⁺⁺ are small and insensitive to the size change, while the H-introduction enhances the cross sections for the NO decomposition at n=3−4 and for the cluster dissociation at n=3. In addition, (1) the cross section for the NO chemisorption on Coₙ⁺⁺ reaches the Langevin cross section as the cluster size increases, and (2) H-atom introduction enhances the chemisorption cross section at n=3. The chemisorption was found to dominate at a size larger than 5.

In order to explain the size-specific enhancement of the reactivity by the H-introduction, the structures and the energies of the reaction intermediates and the products were calculated by use of the density functional method. The calculation shows that energetic stabilization of a dissociatively chemisorbed intermediate and the products causes to enhance the reactivity of Co₃H⁺. On the other hand, no reaction with NO was observed on Co₂⁺ and Co₂H⁺ because the reactions on both cluster ions are endothermic; actually the reaction intermediates and the products are stabilized by H-introduction. The formation of –OH or –NH groups on CoₙH⁺ is likely to contribute to such energetic stabilization.