Characterization of Supported [Ru₆C] Cluster Catalyst on TiO₂ for the Decomposition Reaction of Nitric Oxide

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The structure of cobalt-molybdenum catalysts was reported in the Activity Report 1999. Unfortunately, they were unstable and of low surface area. The adoption of active species to surface (i.e. supporting on high surface-area metal oxides) was unsuccessful. Instead, we discovered supported catalysts of Ru/TiO₂ for ammonia synthesis, selective catalytic decomposition of NOₓ, and NOₓ decomposition by carbon monoxide.

To define the uniform structure of surface Ru site and realize best catalytic performance, catalysts were prepared by reacting [Ru₆C(CO)₁₆]²⁻ cluster crystal with TiO₂ powder. Ru content was 1.5wt%. The Ru cluster crystal was synthesized by Ishiguro, Dr. Nakajima, and Dr. Wakatsuki at Riken. In this report, the active structure of [Ru₆C]/TiO₂ catalyst is described for the catalytic NO decomposition utilizing ligand carbonyl or introduced gas-phase CO.

Catalytic NO decomposition rate in CO gas at 423 K was greater when the [Ru₆C]/TiO₂ catalyst was treated with NO at 423 K for partial decarbonylation rather than at 523 or 623 K. The reactivity was higher compared to the conventional Ru, Pt, or Co catalysts. Based on the gas-phase analysis, sixteen or fifteen carbonyl ligands remained when attached on TiO₂ surface from THF solution in argon. Twelve or eleven carbonyl ligands remained when the cluster catalyst was reacted in NO (P = 4.0 kPa) at 423 K. The structure was investigated by the Ru K-edge EXAFS at beamline 10B in a transmission mode at 13 – 290 K. The samples prepared in a closed circulating system were transferred to a Pyrex glass cell and sealed by fire.

In the Fourier transform (Figure 1b), the peaks at 1.5, 2.3, and 3.5Å (phase-shift uncorrected) were ascribed to Ru-C, Ru-Ru + Ru(-C-)O, and Ru(-C-)Ru bonds, respectively. Using the empirical structural parameters, curve-fit results are $r_{\text{Ru-C}} = 1.91$Å with $N = 3.0$, $r_{\text{Ru-Ru}} = 2.87$Å with $N = 3.5$, $r_{\text{Ru(-C)-O}} = 3.05$Å with $N = 3.0$, and $r_{\text{Ru(-C)-Ru}} = 3.99$Å with $N = 0.7$. The inclusion of Ru-O surf bond was not necessarily needed in the first shell fit. These results correspond to isolated cluster crystal [Ru₆C(CO)₁₂(NO)₃]⁻, where three bridging carbonyl ligands and three terminal NO ligands share a [Ru₃] face. The correlation between the in-situ cluster structure and the reactivity of NO decomposition is under investigation.

![Figure 1. Ru K-edge EXAFS of [Ru₆C]/TiO₂ catalyst treated in NO at 423 K.](a) χ oscillation weighted by $k^3$ and (b) its associated Fourier transform.](a) χ oscillation weighted by $k^3$ and (b) its associated Fourier transform.

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