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Characterization of Supported [Ru_6C] Cluster Catalyst on TiO_2 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/TiO_2 for ammonia synthesis, selective catalytic decomposition of NO_x, and NO_x decomposition by carbon monoxide.

To define the uniform structure of surface Ru site and realize best catalytic performance, catalysts were prepared by reacting $[Ru_6C(CO)_{16}]^{2-}$ cluster crystal with TiO_2 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 [Ru_6C]/TiO_2 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 [Ru_6C]/TiO_2 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 TiO_2 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 $r_{\text{Ru-C}}$ = 1.91Å with N = 3.0, $r_{\text{Ru-Ru}}$ = 2.87Å with N = 3.5, $r_{\text{Ru(-C-)O}}$ = 3.05Å with N = 3.0, and $r_{\text{Ru(-C-)Ru}}$ = 3.99Å 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 $[Ru_6C(CO)_{12}(NO)_3]^-$, where three bridging carbonyl ligands and three terminal NO ligands share a [Ru_3] face. The correlation between the *in-situ* cluster structure and the reactivity of NO decomposition is under investigation.

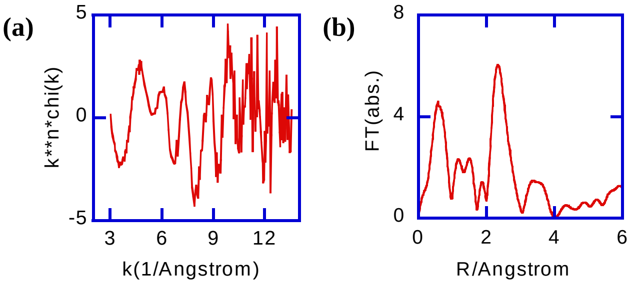

Figure 1. Ru K-edge EXAFS of of [Ru_6C]/TiO_2 catalyst treated in NO at 423 K. **(a)** χ osicillation weighted by k^3 and **(b)** its associated Fourier transform.

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