Oxidation of rhodium metal clusters with nitrous oxide

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There are many studies on the reaction mechanism of rhodium catalysts and some of these are carried out in the gas phase in order to investigate intrinsic reactivity of rhodium nano-sized particles [1–3]. In the previous study, reaction rate constants of oxidation and activation energies of oxygen release of rhodium oxide clusters were evaluated from the O₂ concentration dependence and temperature programmed desorption (TPD) measurements [2,3].

Rhodium metal clusters were produced by using a laser ablation and molecular beam method. The second harmonic output of a Nd:YAG laser was focused to the rhodium metal rod and resulted plasma was thermalized by collisions with the carrier He gas of the backing pressure of 0.88 MPa. N₂O gas was doped 0–0.2% in the carrier gas by mass-flow controllers. The cluster ions were heated up to 1000 K downstream of the cluster source (post-heating), and the stoichiometry of Rh₇NₓO₇₊ (n = 2–10) was examined using mass spectrometry.

Figure 1 shows the TPD profile of Rh₇NₓO₇₊ clusters and intensity map at two different temperatures. Major products of the reaction between Rh₇⁺ and N₂O are Rh₇O₃₃(N₂O)₁₋₃⁺. TPD measurement revealed that N₂O molecules are released from Rh₇N₆O₈⁺ sequentially and N₂ released from Rh₇N₂O₆⁺.

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\begin{align*}
\text{Rh}_7\text{N}_6\text{O}_8^+ &\rightarrow \text{Rh}_7\text{N}_4\text{O}_7^+ \\
&\rightarrow \text{Rh}_7\text{N}_2\text{O}_6^+ \\
&\rightarrow \text{Rh}_7\text{O}_5^+ \\
&\rightarrow \text{Rh}_7\text{O}_6^+ \\
&\rightarrow \text{Rh}_7\text{O}_7^+ \\
\end{align*}
\]

Activation energy for the N₂O release (eq. 1) was estimated to be relatively small value of 0.2–0.3 eV.

Figure 1. (a) Temperature programmed desorption profile of Rh₇NₓO₇₊ clusters. (b) Intensity distribution map of Rh₇NₓO₇₊ clusters. Intensity is normalized for 0 ≤ x, y ≤ 10.

