

Investigation of CO oxidation on Rh(111) by dispersive NEXAFS

Kouki YANAGAWA¹, Masaaki YOSHIDA¹, Yuka KOUSA¹, Syuichi NAKAMOTO¹,
Kenta AMEMIYA², Hiroshi KONDOH¹¹Keio Univ, Hiyoshi, Yokohama 222-8522, Japan²KEK-PF, Tsukuba, Ibaraki 305-0801, Japan**Introduction**

The oxidation of CO on Rh(111) is one of the most studied catalytic reactions. It is not only one of the fundamental surface reactions, but also important as a model of automotive exhaust catalysts. The CO oxidation contributes to the catalytic conversion of CO to CO₂ and the removal of atomic O which is generated from the NO reduction. Rhodium exhibits eminent activity to the both reactions. So far, it has not been fully understood yet why rhodium plays a role as such an active catalyst to the CO oxidation. Therefore, we studied the CO oxidation with dispersive near-edge X-ray absorption fine structure (NEXAFS) so as to acquire useful information on the reaction mechanism.

Experimental

Clean Rh(111) single crystal surfaces were exposed to O₂ gas at room temperature to prepare O-precovered surface. O saturated Rh(111) could be obtained at O exposure reaching to about 10-15L. Then the oxygen saturated surface was exposed to CO gas to make CO oxidation proceed at constant temperatures (340-460 K). During CO exposure, O K-edge NEXAFS spectra were measured every 33 ms continuously. All the experiments were conducted at BL16A.

Results and Discussion

Fig.1 shows O K-edge NEXAFS spectra during exposing CO gas (1.0×10^{-7} Torr) at 340 K. The peaks at 530.3 eV and 534.2 eV are attributed to atomic oxygen and CO, respectively. The oxygen and CO coverages are estimated from O K-edge NEXAFS spectra, as shown in Fig.2. The oxygen coverage decreased via CO oxidation reaction as increasing the CO coverage. Assuming the first-order reaction in terms of O and CO coverages, the rate constants were obtained from the reaction rate. Fig. 3 shows Arrhenius plots for different CO pressures. The activation energy and the pre-exponential factor could be estimated from these plots slope and intercept, respectively, as shown in Table 1. The kinetic parameters correspond to the reference value¹⁾ within the margin of error ($E_a = 65 \pm 5 \text{ kJ} \cdot \text{mol}^{-1}$, $\nu = 10^{7.5 \pm 1} \text{ s}^{-1}$) except for $P_{\text{CO}} = 4.0 \times 10^{-7}$ Torr condition. This difference observed at 4.0×10^{-7} Torr is attributed to O island formation which was confirmed by the reaction order analysis. It should be noted that the rate constant depends on the CO pressure as shown in Fig.3. The gaseous CO might be involved in the reaction mechanism at the Rh(111) surface.

Table 1. Activation energy and pre-exponential factor taken under different conditions.

Pco[Torr]	Ea[kJ.mol ⁻¹]	ν [s ⁻¹]
2.5×10^{-8}	62±1	107.0±0.2
2.0×10^{-7}	58±4	107.0±0.6
4.0×10^{-7}	52±3	106.7±0.4

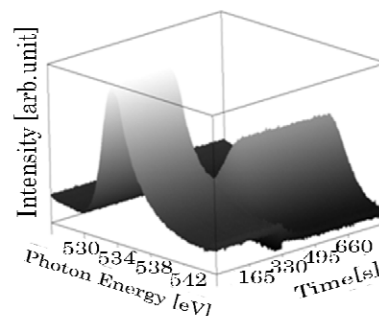


Figure 1. O K-edge NEXAFS spectra measured by the dispersive NEXAFS during the CO oxidation on Rh(111) ($T_s = 340 \text{ K}$, $P_{\text{CO}} = 1 \times 10^{-7} \text{ Torr}$).

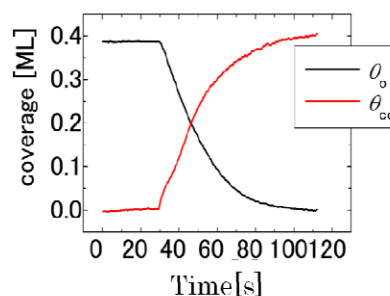


Figure 2. Time evolution of the coverages of O and CO observed by dispersive NEXAFS at $T = 420 \text{ K}$.

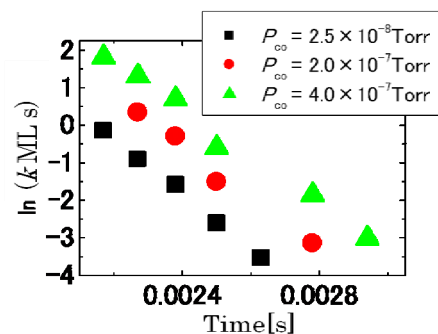


Figure 3. Arrhenius plots for different CO pressures: 2.5×10^{-8} Torr, 2.0×10^{-7} Torr, and 4.0×10^{-7} Torr.

Reference

- 1) M. J. P. Hopstaken and J. W. Niemantsverdriet, J. Chem. Phys. **113**, 5457 (2000).

* yanagawa@chem.keio.ac.jp