16A/2009G146,2011G105

The CO oxidation reaction on Ir(111) surface studied by dispersive-NEXAFS

Shuichi NAKAMOTO[1], Masaaki YOSHIDA[1], Yuka KOUSA[1], Shogo KOUZAI[1],
Ryohei SUMII[2], Hitoshi ABE[2], Kenta AMEMIYA[2], Hiroshi KONDOH[1]
[1]Keio Univ., Hiyoshi, Yokohama 222-8522, Japan
[2]KEK-PF, Tsukuba, Ibaraki 305-0801, Japan

Introduction

Platinum group metals have been widely used as catalysts that remove nitrogen oxides (NO_x) and the carbon monoxide in automobile exhaust. It is reported that iridium-metal catalysts exhibit high efficiency in the selective reduction of NO with CO under the oxygen atmosphere. The origin of the high efficiency has not been revealed yet, and it is important to clarify the mechanism of the reaction in order to improve the efficiency further. Here, we have studied CO oxidation reaction ($O_{ad} + CO_{ad} \rightarrow CO_{2g}$) on Ir(111) surface by dispersive near edge x-ray absorption fine structure (dispersive-NEXAFS) spectroscopy.

Experimental

The experiments were carried out at BL-16A2 of the Photon Factory. First, an atomic-oxygen covered surface was prepared on a clean Ir(111) surface. The surface was then exposed to gaseous CO (5.0×10^{-8}-4.0×10^{-7} Torr) at a constant temperature (350-550 K). Dispersive-NEXAFS spectra were taken at every ~30 ms under the progress of the reaction.

Results and Discussion

Fig. 1 shows the dispersive-NEXAFS spectra measured during CO oxidation reaction on Ir(111). The rate constants were obtained by analyzing the time dependence of CO and atomic O coverages. Fig. 2 shows the Arrhenius plot, indicating that the frequency factors and the activation energies are different between high and low temperature regions (Table 1), and the rate constant of CO oxidation reaction depends on CO pressure only in the high temperature region. In addition, the CO adsorption curves exhibit some flexional points at the boundary temperatures between the high and low temperature regions (Fig. 3). It is likely that the adsorbed oxygen atoms undergo a phase transition at a certain oxygen coverage, and the reaction path would be switched over at the transition.

Table 1: Comparison of frequency factor and activation energy between high and low temperature regions. The results for Pt (111) are shown as reference.

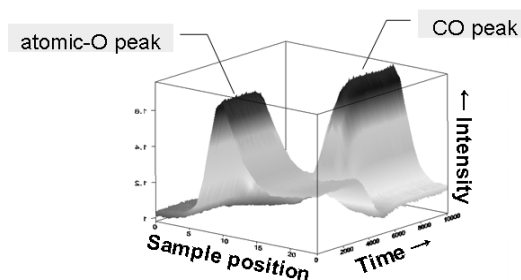|	A_0 / $ML^{-1}s^{-1}$	Ea / eV
Ir(111) high temp.	$10^{3.1 \pm 0.4}$	0.27 ± 0.02
Ir(111) low temp.	$10^{8.7 \pm 0.7}$	0.77 ± 0.05
Pt(111)	$10^{8.9 \pm 2.1}$	0.62 ± 0.14

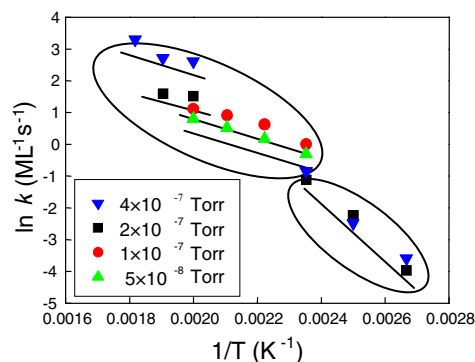Fig. 1 Dispersive NEXAFS spectra taken at 425 K under 5×10^{-8} Torr CO gas.
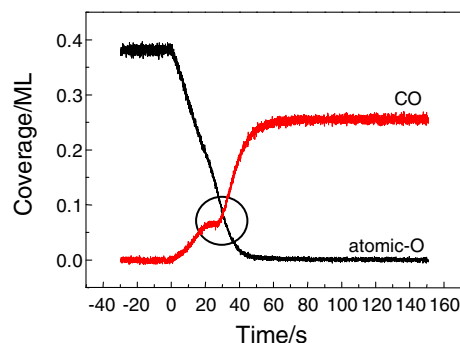

Fig. 2 Arrhenius plot of the rate constant.

Fig. 3. Flexional point observed for a CO coverage curve at a boundary temperature (450 K).

References

[1] T. Fujitani, et al, J. Phys. Chem. B, 109 (37), 17603-17607(2005)
[2] Y. Kousa et al, 90th Annual Meeting of The Chemical Society of Japan 2009, 2E1-05.

*kondoh@chem.keio.ac.jp