

Ambient-Pressure XPS Study on CO oxidation Reaction on Pd(111) under near realistic conditions

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Introduction

Catalytic CO oxidation reaction on Pd has been studied over the past decades, because of the importance for industrial technology such as automotive exhaust converter and methane combustion system for gas-powered turbines. Recently, the chemical states of Pd (i.e. metallic Pd, Pd oxide) are correlated to catalytic activity under reaction conditions. Under UHV condition, generally, metallic Pd is more active than PdO or other oxides, and the reaction proceeds in Langmuir-Hinshelwood mechanism. On the other hand, several groups reported Pd oxides exhibit higher activity both for CO oxidation reaction^[1] and methane oxidation reaction under ambient-pressure conditions. In this work, we studied CO oxidation reaction on Pd(111) under near ambient-pressure conditions by ambient-pressure X-ray photoelectron spectroscopy (AP-XPS).

Experimental Section

Clean Pd(111) surfaces were exposed to O₂ and CO gas up to near 1Torr at 400 °C, and CO oxidation reaction proceeded. During the gas exposure, XP spectra were obtained under various pressures. Production of CO₂ was monitored by the quadrupole mass spectroscopy (QMS).

Results and Discussion

Fig. 1 shows (a) QMS results, (b) Pd3p/O1s XP spectra and (c) O2s XP spectra. Each QMS measurement condition (A, B, C, D) corresponds to the XP spectrum with the same label, and “no dose” denotes the one taken before the gas exposure. Under condition A, with exposing O₂ gas, CO partial pressure decreased, in contrast the CO₂ partial pressure increased. CO oxidation reaction was ongoing under this condition. Four new peaks were observed in Pd3p/O1s spectrum. The 529.3 eV and 529.8 eV peaks are attributed to Pd₅O₄ surface oxide with two oxygen components, whereas the 537.5 eV and 538.5 eV peaks are of gas-phase O₂. Six new peaks were observed in the corresponding O2s spectrum. The 20.2 eV and 21.9 eV peaks are attributed to Pd₅O₄, the 23.9 eV peak is a subsurface oxide, and the others are due to gas-phase O₂. Under condition B, the O₂ partial pressure was stable, but the production rate of CO₂ was decreased, obviously indicating that the chemical state of Pd surface was changed. This change is explained by the growth of a 529.8 eV peak ascribed to the PdO oxide, which is also observed in the Pd3p/O1s XP spectrum. Under condition C, as increasing O₂ gas, the PdO peak

grew further resulting in a much lower activity. Under condition D, where only CO gas was dosed, the 529.3 eV(b) and 20.2 eV (c) peaks disappeared. It indicates that the surface oxide was preferentially expended under this reductive condition. We conclude the surface oxide, presumably Pd₅O₄, is the most active under the ambient pressure conditions used here.

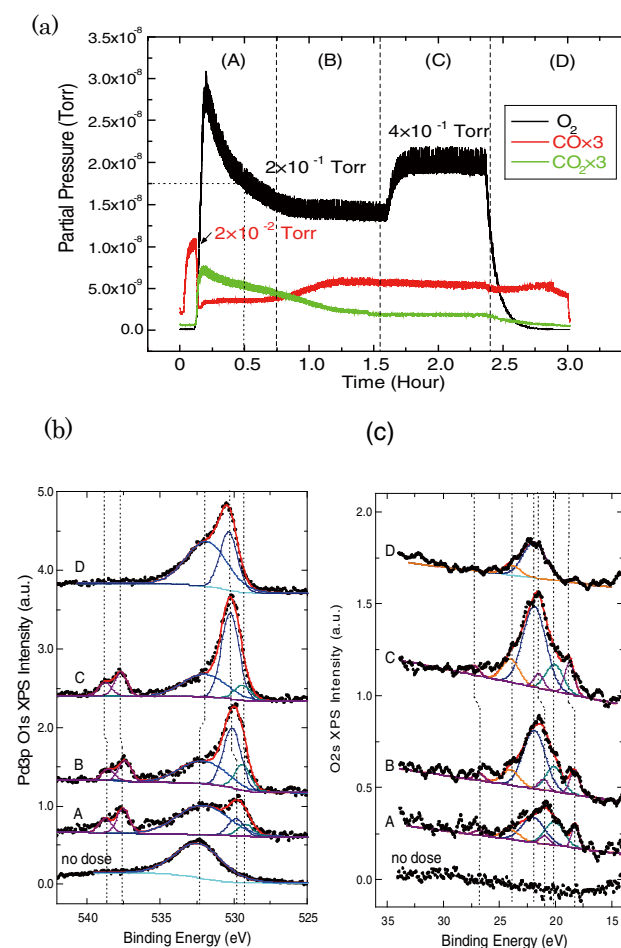


Figure.1 (a) QMS result, (b) Pd3p/O1s XP spectra and (c) O2s XP spectra during CO oxidation reaction.

Reference

[1] B. L. M. Hendriksen, S. C. Bobaru, J. W. M. Frenken, Surf. Sci. 2004, 552, 229.

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