

## Investigation of CO oxidation reaction on Pt(111) by dispersive NEXAFS

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## Introduction

CO oxidation reaction on Pt(111) has been widely studied to understand its mechanism for their importance. In realistic conditions, this catalytic reaction proceeds at several hundreds Kelvin. At above room temperature, however, this reaction has not been directly observed with surface spectroscopy but only with pressure measurements by mass spectroscopy. Under such conditions, the reported activation energies have been scattered from 0.39 to 1.0 eV. Recently, our group has upgraded the dispersive NEXAFS technique at an undulator beamline BL-16A so that we can measure NEXAFS spectra every a few tens ms. This technique enables us to obtain information directly from surface species involved in the reaction proceeding above room temperature. In the present work, we observed CO oxidation reaction on Pt(111) at 300-500 K, and estimated reaction rate, frequency factor, and activation energy.

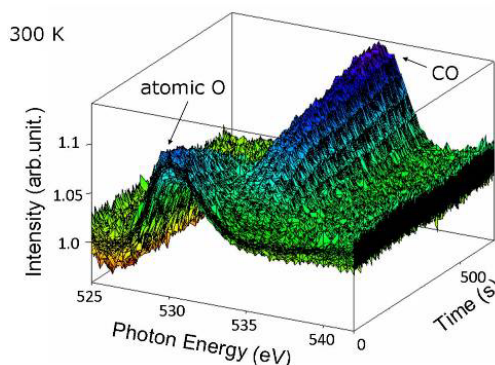
## Experimental

Clean Pt(111) single crystal surfaces were exposed to O<sub>2</sub> gas at 150 K and annealed at a temperature higher than 240 K to prepare atomic oxygen adlayers. Then the atomic oxygen precovered surfaces were exposed to CO gas (1.0×10<sup>-8</sup> Torr) at constant temperatures (300-500 K). During CO exposure, O K-edge NEXAFS spectra were measured every 33 ms continuously.

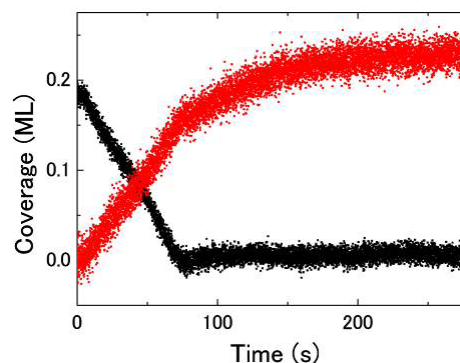
## Results and Discussion

Fig.1 shows O K-edge NEXAFS spectra during exposing CO gas at 300 K. The peaks at 530.3 eV and 534.2 eV are attributed to atomic oxygen and CO, respectively. Oxygen and CO coverages are estimated from O K-edge NEXAFS spectra as shown in Fig.2. The oxygen coverage decreases via CO oxidation reaction as increasing the CO coverage. Its reaction rate is estimated from time evolution of oxygen coverage. Assuming the first-order reaction in terms of O and CO coverages, the rate constant was obtained from the reaction rate. Fig. 3 shows temperature dependence of the rate constant. It exhibits a drastic decrease above 360 K. This change is tentatively associated with contribution from CO precursor above this temperature. Below 360 K, the frequency factor and the activation energy were estimated 10<sup>8.3±0.6</sup> ML<sup>-1</sup> s<sup>-1</sup> and 0.58 ± 0.04 eV, respectively. This value of activation energy is comparable to previous reports<sup>[1,2]</sup>. Although the activation energy value is not so different from those for other noble metals, Pt is more reactive for

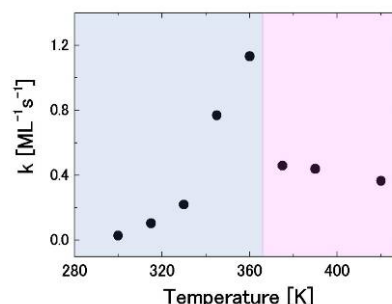
CO oxidation. This is because the frequency factor is much larger for Pt(111), which might be attributed to large difference in inter-particle interactions.



**Figure 1.** O K-edge NEXAFS spectra measured by the dispersive mode during the titration of an O overlayer with CO on Pt(111) (T = 300 K, P<sub>CO</sub> = 1×10<sup>-8</sup> Torr)



**Figure 2.** Time evolution of the coverages of O and CO observed by dispersive NEXAFS at T = 420 K.



**Figure 3.** Temperature dependence of the reaction rate constant for CO oxidation on Pt(111).

## References

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