

The mechanism of CO oxidation on Pt(111) surface studied by energy-dispersive NEXAFS

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Introduction

CO oxidation on Pt(111) surface is a prototypical heterogeneous catalytic reaction and has been extensively studied by various methods. A previous STM study [1] showed that when two-dimensional islands of atomic oxygen on Pt(111) surface are exposed to gaseous CO molecules, oxidation proceeds exclusively at island perimeters after a certain "induction time". No reaction takes place during it.

Recently we developed a new technique, energy dispersive near edge x-ray absorption fine structure (NEXAFS) [2]. By using dispersed soft x-ray and position sensitive electron analyzer (GAMMADATA-SCIENTA, SES-2002), an Auger electron yield NEXAFS spectrum is obtained in one shot. We applied this new technique to monitor CO oxidation on Pt(111) and reconsidered its kinetics and reaction mechanism by a spectroscopic approach.

Experimental

The O *K*-edge energy-dispersive NEXAFS spectra were taken at BL-7A by the method described above.

Initially we prepared a Pt(111) surface covered with islands of atomic oxygen. Then the substrate was exposed to gaseous CO with a constant pressure at a constant substrate temperature. O-*K* dispersive NEXAFS spectra were taken in every forty seconds during CO exposure.

Results and discussion

Fig. 1 is a typical series of O-*K* dispersive NEXAFS during the reaction. The initial oxygen layer was annealed at 240 K and 1×10^{-8} Torr of CO gas was introduced at 240 K. Two peaks corresponding to CO π^* and atomic oxygen are observed. The latter continuously decreases as the reaction proceeds. CO₂ molecules desorb directly upon formation. Fig. 2 shows time evolution of the coverage of O and CO evaluated by curve fitting for each spectrum in Fig. 1. Apparently no "induction time" is observed and the coverage of atomic oxygen falls immediately as adsorption of CO starts in contrast to the previous observation by STM [1]. The curve for the reduction of atomic oxygen is classified into two processes at about 300 second. Oxygen reduces faster in the first process. Detailed analysis of the reaction rate revealed that the reaction rate in the first process is proportional to the coverage of atomic oxygen and that in the second process is proportional to its square root. This kinetic order for the second process suggests that the reaction takes place at island perimeters in accordance with the result of the

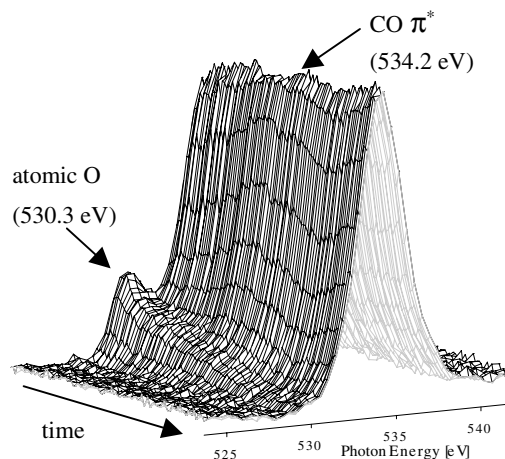


Fig. 1: Series of O-*K* energy-dispersive NEXAFS during the reaction of CO+O/Pt(111) at 240 K

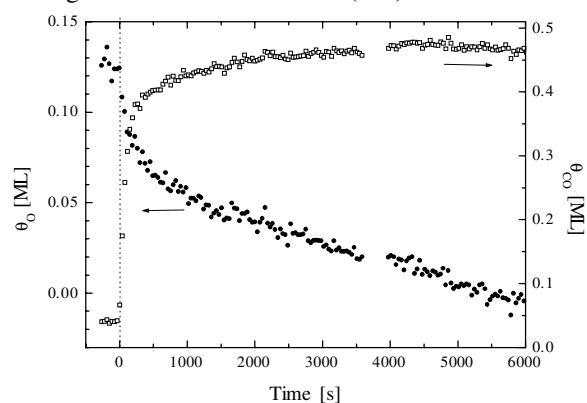


Fig. 2: Time evolution of coverage of O and CO obtained from the result of Fig. 1

STM study [1]. The first process probably takes place during the induction time for the second one.

An oxygen-covered surface annealed at higher temperature is expected to be more highly ordered. When we started a reaction for an oxygen-covered surface preannealed at a higher temperature, less amount of oxygen reacted in the first process. This suggests that the first process is associated with disordered atomic oxygen. We consider that oxygen atoms diffusing between immobile islands react in the first process faster than ones in islands and that because of their high mobility such a reaction process was undetectable with STM.

References

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