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Observation of Pt-NiO$_{1-x}$ nanostructure formation on Pt$_3$Ni(111) surface with ambient pressure XPS and STM

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With the combination of ambient pressure XPS and STM, a formation of Pt-NiO$_{1-x}$ nanoclusters on Pt$_3$Ni(111) is observed. Initially, under UHV condition, a Pt-skin surface is formed. Then, as oxygen gas is introduced, NiO$_{1-x}$ clusters forms on surface as Ni atoms segregate to the surface. When CO and oxygen gases are introduced at room temperature, the Pt-NiO$_{1-x}$ nanoclusters, the product of NiO$_{1-x}$ clusters and Pt skin, is observed with the presence of CO oxidation reaction. In comparison of density functional theory calculations, it is identified that interfacial Pt-NiO$_{1-x}$ nanostructures is responsible for a highly efficient step in the CO oxidation reaction.

1. Introduction

Pt alloys have been actively studied in the community of fuel cell research to overcome the main technical obstacle of Pt in oxygen reduction rate (ORR) at the cathode in PMFC. Also, the high cost of Pt limits the practical use of Pt in commercial application. In early 2007, it is reported that the performance of ORR can be significantly increased when Pt is alloyed with certain 3*d* transition metals (TM), e,g, Pt$_3$Ni, Pt$_3$Fe, Pt$_3$Co. In model electrochemical studies, the formation of Pt skin layer is observed and the altered electronic structures from Pt skin layer is regarded as the origin of improved chemical reaction.

However, many following studies show that the Pt skin layer is not stable under reaction conditions and the controlling of the Pt-skin layer has become a major task. The major issue on stability of Pt-skin layer comes from the surface segregation of subsurface TM layer under electrochemical environments.

In an effort to resolve this issue and identify the nature of the enhanced catalytic reactivity on Pt$_3$Ni alloys, ambient pressure XPS and STM are employed to probe the surface properties of the alloy under reaction condition, i.e. CO oxidation.

2. Experiment

The AP-XPS measurements are carried out at soft-ray beamline BL13 at Photon-Factory of High Energy Accelerator Research Organization (KEK-PF) in Tsukuba, Japan, Tempo beamline at Soleil, France, and BL9.3.2 at Advanced Light Source of Lawrence Berkeley National Laboratory, USA. The AP-STM measurements was carried out at KAIST, Daejon in Korea. The clean surface of Pt$_3$Ni(111) was prepared with ion sputtering and annealing procedure. During observations using the AP-STM system, the measured tunneling current between the positive-bias applied Pt$_3$Ni(111) sample and the sharply etched tungsten tip was recorded by ~15 mL of the reaction cell integrated into the STM scanner (SPECS GmbH) at various catalytic reaction conditions.

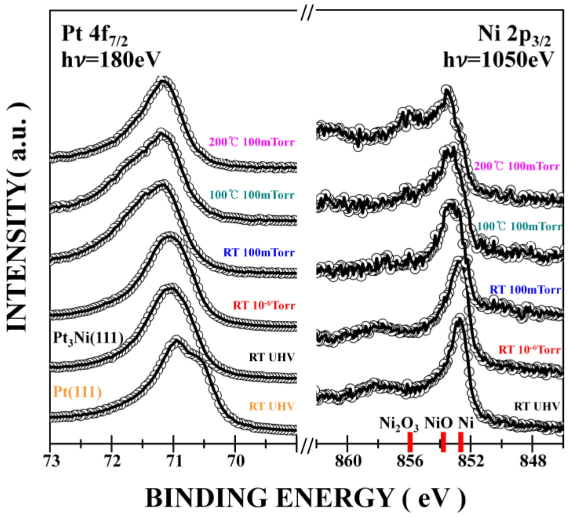

Fig. 1 Pt 4f and Ni 2p spectra taken with AP-XPS under various oxygen pressure.

3. Result and discussion

First, a well-ordered Pt-skin/Pt$_3$Ni(111) structure is observed upon UHV cleaning procedure. Then, immediately after the introduction of oxygen gas, AP-STM images clearly show the segregation of Ni elements to topmost surface layer and the formation of Pt-NiO$_{1-x}$ nanostructure oxide. The oxidation states of this Pt-NiO$_{1-x}$ nanostructure, probed with AP-XPS, display the various oxidation state of Ni. (Fig. 1) When CO gas is introduced to Pt-skin layer, no surface Pt-NiO$_{1-x}$ nanostructure is formed, indicating oxygen gas pulls the Ni subsurface layer to top surface. Finally, when CO and oxygen are introduce together at room temperature, the presence of Pt-NiO$_{1-x}$ nanostructure remains as the product of CO$_2$ starts to appear.

In conclusion, using AP-STM and AP-XPS, we confirmed the presence of the interfacial Pt-NiO$_{1-x}$ nanostructure on Pt-TM alloys and the segregated NiO$_{1-x}$ cluster is thermodynamically favored for efficient CO$_2$ evolution.

4. References

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