

In situ XAFS Study on Molecular Catalyst for Hydrogen Evolution Reaction Confined within Organic Molecular Layer on Si(111) Surface

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1 Introduction

Catalysts play crucial roles in many chemical and energy conversion processes. Often precious metals and rare metals are the major components of active catalysts and many efforts have been made to maximize the utilization of these atoms such as increasing their dispersion in heterogeneous catalysts. Although 100% atom efficiency is expected at molecular and single atom catalysts, molecular catalysts are usually used in solution and have limited applications because of difficulty in separating the product and catalyst. It is very difficult to prepare single atoms and maintain them without their being converted into metal clusters or particles because they are more energetically stable. One would expect, however, that if the metal complexes are confined on or within a solid substrate at well isolated positions, they may act as molecular catalysts without aggregation. Recently, an organic molecular layer with viologen groups and Pt complexes was constructed on a Si(111) surface and very efficient photoelectrochemical hydrogen evolution current was achieved.^[1] Here, we demonstrate that Pt complexes placed at precisely controlled position within the molecular layers act as molecular electrocatalysts for hydrogen evolution without being converted into metal clusters or particles.^[2]

2 Experiment

Si(111) electrode was modified with five layers of viologen moiety with PtCl_4^{2-} to yield a $(\text{Pt-V}^{++})_5\text{-Si}(111)$ as previously reported.^{[1],[2]}

XAFS measurements were performed at BL12C of the Photon Factory. Pt L_3 -edge XAFS spectra were recorded under electrochemical conditions at room temperature. X-rays were monochromated using a Si(111) double-crystal monochromator. The fluorescence signals were detected using a 19-element pure Ge solid state detector (GL0110S; Canberra, USA). The EXAFS analyses and

calculations were carried out using REX 2000 (Rigaku, Japan) and FEFF 8.0, respectively.

3 Results and Discussion

After PtCl_4^{2-} was incorporated into the five layers of viologen moieties by ion exchange reaction, small fraction of Cl^- ligands were exchanged by oxygen species, e.g., OH^- and H_2O . As the potential was made more negative, the Cl^- ligands were gradually replaced by oxygen species and all the Cl^- was exchanged at -0.6 V. Hydrogen evolution reaction (HER) current started to flow from -0.8 V. Since this potential is 1.3 V more positive than the redox potential of PtCl_4^{2-} , e.g., $+0.51$ V, one would expect that the Pt complex is reduced to Pt particles which act as HER catalyst. However, EXAFS oscillation was still similar to that at -0.6 V and no Pt-Pt interactions were observed, indicating that Pt particles were not formed even when HER took place. Thus, it was proved that the Pt complexes act as molecular catalysts confined within organic molecular layers. It is considered that the formation of Pt particles was inhibited since the complexes were separated by the molecular layers. Once HER started, white line intensity of the XANES spectra decreased, suggesting the formation of a hydride complex as an intermediate of HER, although more detailed experimental and theoretical examinations are required to clarify the mechanism.

References

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