In situ Time-Resolved DXAFS Studies on the Redox Mechanism of PtSn Nanoparticles on γ-Al_2O_3

In this study, the processes of formation and oxidation of PtSn nanoparticles on γ-Al_2O_3 were observed by *in situ* time-resolved dispersive X-ray absorption fine structure spectroscopy and the results were analyzed with chemical kinetics. In the formation of nanoparticles under hydrogen atmosphere, Pt and Sn were reduced through a single-step reaction at the same reaction rate to become PtSn nanoparticles. Under the oxidative condition, Pt was oxidized through a sequential reaction involving two different steps while Sn was oxidized through just a single-step reaction.

PtSn nanoparticles are multi-functional catalysts, and have been applied to a wide range of catalytic reactions. Recently, they have attracted attention as an electrode of fuel cells. PtSn nanoparticles are tolerant towards poisoning of an electrode by CO, which is one of the main drawbacks in current fuel cell systems. However, active PtSn nanoparticles are likely to collapse during long-term usage of fuel cells, and cannot maintain their initial performance. It is important to understand the basic chemical properties of PtSn nanoparticles in order to develop more tolerant and effective materials, but little is known about the reactivities of such functional nanomaterials. *In situ* time-resolved dispersive XAFS (DXAFS) is a powerful technique to study how structures and oxidation states of metal compounds change during a chemical reaction. In this study, we studied reduction and oxidation mechanisms of PtSn nanoparticles on γ-Al_2O_3 by time-resolved DXAFS. XAFS spectra of both Pt L_{III} edge and Sn K edge were measured to study the difference between Pt and Sn in reduction and oxidation processes.

In situ DXAFS experiments were conducted at AR-NW2A. The time resolution of a DXAFS spectrum was 100 ms. Reduction by H_2 and oxidation by O_2 were conducted at temperatures between 623 K and 773 K.

Figure 1 shows the results of *in situ* DXAFS experiments of Pt L_{III} and Sn K edge at 673 K. The X-ray absorption at 11566 eV is a fingerprint of the oxidation state of Pt, and the absorption at 29202 eV is that of the oxidation state of Sn. Their intensity increases when Pt or Sn is oxidized while each magnitude becomes smaller when reduced. The reaction type, such as first order or second order, of Pt or Sn during reduction or oxidation can be found by fitting the variation of the absorptions as a function of time.

Figures 1 (a) and (b) are the results of *in situ* DXAFS experiments during the formation of PtSn nanoparticles by reduction. Before reduction, Pt and Sn were oxidized (PtO and SnO_2). The variation of X-ray absorption at 11566 eV in Fig. 1 (a) was fitted well by a linear function, indicating that the reduction of Pt proceeded through a single-step process. The rate constant of Pt reduction ($k_{red,\,Pt}$) was estimated as 0.035/s·kPa by analyzing the results of DXAFS experiments under different P_{H2} conditions. Similarly, the variation at 29202 eV under hydrogen atmosphere in Fig. 1 (b) was fitted well by a single exponential function, indicating that the Sn reduction also proceeded through a single-step process. The rate constant of the Sn reduction ($k_{red,\,Sn}$) was estimated as 0.039/s·kPa by analyzing the results of DXAFS experiments under different P_{H_2} conditions.

Figures 1 (c) and (d) show the results of *in situ* DXAFS experiments during the oxidation of PtSn nanoparticles. The variation of Pt L_{III} edge under oxygen atmosphere shown in Fig. 1 (c) was not fitted by a single exponential function but was fitted well by a double exponential function. This means that the oxidation of Pt proceeded through two successive processes, where two different rate constants are needed to describe the whole reaction. These two rate constants of the Pt oxidation ($k_{ox1,\,Pt}$ and $k_{ox2,\,Pt}$) were estimated to be 4/s and 0.15/s, respectively. Regarding the oxidation of Sn, the absorption variation shown in Fig. 1 (d) was fitted by a single exponential function. This indicates that the oxidation of Sn proceeded through a single step to become SnO_2 and its rate constant was estimated to be 4/s. In the oxidation process, Pt and Sn are oxidized at the same rate at first. After Sn is completely oxidized, Pt continues to be oxidized at a slower rate than the first process.

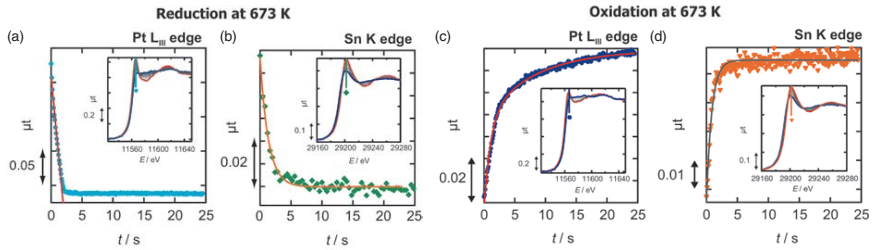

Figure 1
Results of *in situ* DXAFS experiments at 673 K; (a) the DXAFS result of Pt L_{III} edge under hydrogen atmosphere, (b) the result of Sn K edge under hydrogen atmosphere, (c) the result of Pt L_{III} edge under oxygen atmosphere, (d) the result of Sn K edge under oxygen atmosphere.

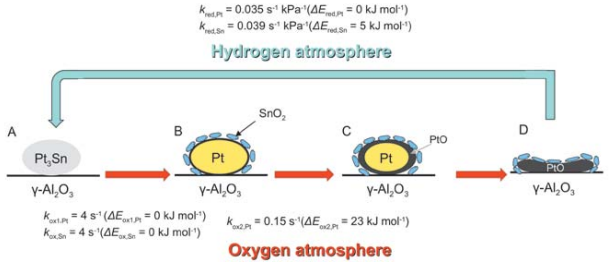

Figure 2
The whole mechanism of the formation and oxidation of PtSn nanoparticles on γ-Al_2O_3.

In our study, the whole reduction and oxidation mechanisms are shown in Fig. 2 through combining *in situ* time-resolved DXAFS experiments and kinetic analyses [1]. In the reduction process, Pt and Sn are reduced at the same time. On the other hand, SnO_2 supported on γ-Al_2O_3 without Pt was hardly reduced. Pt helps the Sn reduction to form PtSn nanoparticles. In the oxidation process, the oxidation mechanism of Pt is a two-step reaction while that of Sn is a single-step reaction. The second oxidation rate of Pt is much slower than the first one. Pt nanoparticles were observed during the oxidation by *in situ* EXAFS and TEM experiments [1]. The deceleration of Pt oxidation and the existence of Pt nanoparticles are attributed to SnO_2, which comes from the oxidation of Sn in PtSn nanoparticles and surrounds the Pt nanoparticles. The surrounding SnO_2 prevents the Pt nanoparticles from reacting with O_2 so the second oxidation of Pt becomes slower than the first and Pt nanoparticles can temporarily exist under oxidative conditions.

REFERENCE

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BEAMLINES

9C, AR-NW10A and AR-NW2A

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