

XAFS Analysis for Preparation Process of PdCu Alloy Catalyst

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1. Introduction

Palladium-containing supported alloy catalysts are widely used for oxidation reaction of carbon dioxide (PdCu alloy catalyst), steam reforming reaction (PdZn alloy catalyst), and so on. The preparation of the alloy catalyst is started by the co-impregnation or stepwise impregnation of the Pd and other metal species on supporting materials. The supported precursors are usually reduced to generate the mixed-metal alloy catalyst under hydrogen gas flow at elevated temperature. However, the formation mechanism of the alloy catalyst during the reduction process is still unclear. Thus, in this study, the chemical states of the Pd and Cu species were analyzed by *in situ* XAFS technique under the hydrogen atmosphere in order to understand the chemical transformation of Pd and Cu species during the preparation process of the PdCu alloy catalyst.

2. Experimental

The co-impregnated precursor supported on Al₂O₃ was prepared using an aqueous solution of HCl, in which same amounts of PdCl₂ and Cu(NO₃)₂•H₂O were contained. After Al₂O₃ powder was suspended in the solution, the mixture was stirred for 30 min at 30 °C and dried at 80 °C for 73 h. The loadings of Pd and Cu were 5 and 3 wt%, respectively.

In-situ QXAFS measurements at the Cu and Pd K edges were carried out in transmission mode at BL-3 of the SR Center (Ritsumeikan University), BL-12C of PF (KEK), and NW10A of PF-AR (KEK). The precursor powders were heated up to 650 °C with the increasing rate of 10 °C/min under the dilute hydrogen gas flow (10 vol% balanced by He, 200 cm³/min).

3. Results and discussion

The XANES spectrum change at the Pd K edge is shown in Fig. 1. The initial spectral matched to that of PdCl₂, and the edge energy shifted to the lower energy with the increasing temperature. The spectrum was changed at 140 °C to that of Pd metal, indicating that

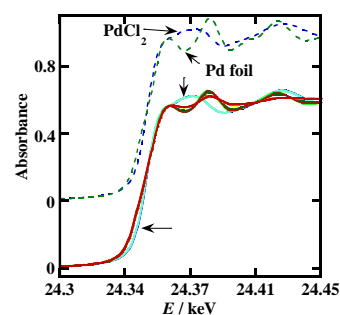


Figure 1. XANES spectral change at the Pd K edge.

the reduction of Pd(II) proceeded at this temperature

In contrast to Fig. 1, the spectral change at the Cu K edge was much complex as seen in Fig. 2. The initial spectrum corresponded to CuCl₂ was changed to that of CuCl at *ca.* 180 °C, and was further changed with the edge shift to the lower energy at *ca.* 200 °C, indicating that the Cu(I) center was reduced to Cu(0). A similar stepwise reduction from Cu(II) to Cu(0) via Cu(I) was observed for the supported CuCl₂ on Al₂O₃ without Pd, for which the reduction to Cu(0) was completed at *ca.* 400 °C. It was found that the existence of Pd(0) particles facilitated the reduction of the Cu species because of the adsorbed H atoms. Furthermore, the spectrum was slightly changed at temperature higher than 200 °C as shown in Figure 2(b). Because the valence of Cu has already reduced to 0 at that temperature range, the spectral change was assigned to the mixing of metallic Cu and Pd atoms in a supported particle.

The structure parameters were determined by the curve-fitting analysis of the EXAFS data. The optimized coordination numbers, $N_{\text{Cu-Cu}}$ and $N_{\text{Cu-Pd}}$, around the Cu center are shown in Fig. 3 as a function of temperature. After the reduction of Cu(I) at *ca.* 200 °C, the $N_{\text{Cu-Pd}}$ value increased with temperature whereas the $N_{\text{Cu-Cu}}$ value decreased. This means the atomic mixing between the metallic Pd and Cu species.

In summary, the proposed formation mechanism of the PdCu alloy catalyst is as follows (see Fig. 4). The Cu(II) precursor is reduced to Cu(0) via a Cu(I) intermediate, and the reduction is facilitated by the previously reduced Pd(0) species. Then, the atomic mixing between the metallic Pd and Cu species forms the PdCu alloy particles.

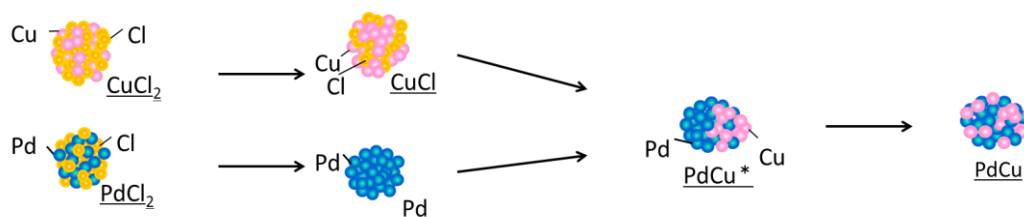


Figure 4. Proposed formation mechanism of the PdCu alloy catalyst

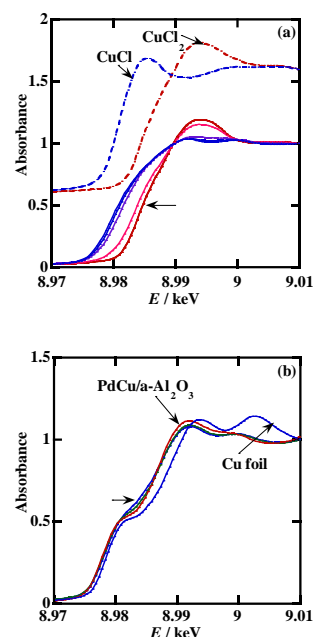


Figure 2. XANES spectral change at the Cu K edge in the temperature range from r.t. to 180 °C (a) and from 200 to 650 °C (b).

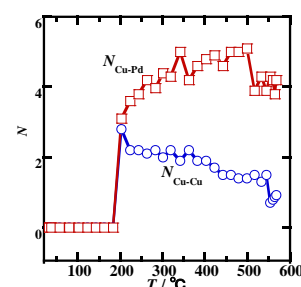


Figure 3. Temperature dependence of the coordination number around a Cu center.