

In Situ Observation of Wacker-type Reaction System in Organic Solvent by X-ray Absorption Fine Structure (XAFS) Analysis

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The in situ observation of a Wacker-type reaction system has been conducted by X-ray absorption fine structure (XAFS) analysis, revealing the ligand exchange on palladium from trifluoroacetato to alkene and reoxidation of a palladium/alkene complex by copper proceed in organic solvent.

Over the last several decades, a number of reports of Wacker-type oxidative functionalizations of alkenes catalyzed by palladium and copper have appeared, and to date, they have proven to be industrially and synthetically very useful protocols.^{1,2} From the synthetic, technological, and environmental view points, the use of a variety of ligands such as carboxylate, *N*-heterocyclic carbene, or heterocyclic compounds instead of halogen has recently attracted a great deal of interest in this chemistry. The key step in these reactions is revealed to be a coordination of the C=C part of the substrate to palladium. However, examples of the direct observation of homogeneous metallic species,³ especially catalytic species bearing carboxylato ligand in the reaction mixture, have been yet very limited despite many mechanistic studies about these reactions.⁴ This situation seems to be caused by the fact that convenient and conventional methods such as NMR are difficult for analysis of reaction mixtures containing copper with magnetic properties. Recently, X-ray absorption fine structure (XAFS) spectroscopy has become one of the most powerful tools for the analysis of homogeneous catalyst.⁵ This method can directly disclose both electronic structure and coordination environment of catalysts and supply informative results which may contribute to development of novel catalysts with high activity. In this article, we report the application of XAFS spectroscopy to the in situ observation of basic key interactions among the palladium carboxylate, copper carboxylate, and alkene of Wacker-type reaction systems.

The X-ray experiments were carried out on the beamline 14B2 at SPring-8 of the Japan Synchrotron Radiation Research Institute (8 GeV, 100 mA). A Si(311) two-crystal monochromator was used for Pd K-edge and Cu K-edge XAFS spectra. Ion chambers filled with N₂ (100%) and N₂ (70%)/Ar (30%) were used for the I₀ and I detectors. XAFS spectra at Pd K-edge were collected in a transmission mode, and total acquisition time was 15 min per spectrum; those at Cu K-edge were collected in fluorescent mode, requiring 20 min per spectrum. The data reduction was performed with the REX2000 program (Rigaku Co., Ltd.).

Initially, Pd(OCOCF₃)₂ (ca. 1000 ppm) was dissolved in butyl acetate (AcOBu) saturated with molecular oxygen (solution A), and an XAFS spectrum of this solution around Pd K-edge was taken at room temperature as shown in Figure 1A. When 10 equimolar amounts of 1-octene to Pd(OCOCF₃)₂ were added to the solution A, the absorption edge shifted to lower

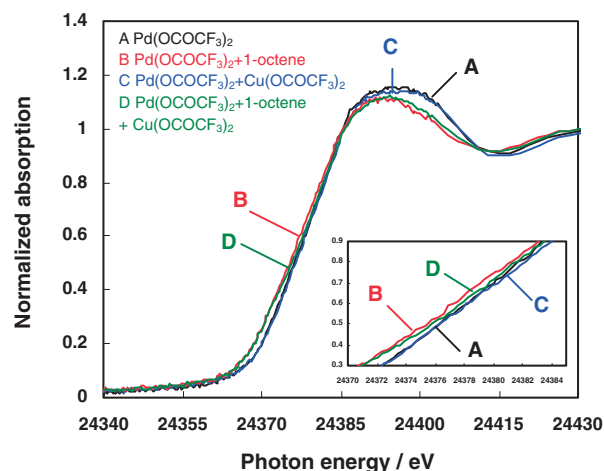


Figure 1. Pd K-edge XANES spectra with inset showing their difference (also see the text).

energy (solution B) (Figure 1B). This phenomenon is interpreted as the result of the increase of electron density on palladium due to the coordination of 1-octene to palladium. No change was observed in the case of addition of Cu(OCOCF₃)₂ (ca. 1000 ppm) to the solution A (solution C) (Figure 1C). On the other hand, the addition of Cu(OCOCF₃)₂ (ca. 1000 ppm) to the solution B brought about the shift of the absorption edge to a higher energy position (solution D) than that of solution B (Figure 1D). This suggests that the palladium can be reoxidized by copper in the presence of 1-octene. In this study, no difference was observed in XAFS spectra between powdery Pd(OCOCF₃)₂ and Pd(OCOCF₃)₂ in AcOBu; the coordination of AcOBu solvent to Pd center was not observed by XAFS spectroscopy. We consider that the coordination power of AcOBu is weaker than that of 1-octene and that the coordination environment of Pd(OCOCF₃)₂ in AcOBu does not change with that of powdery Pd(OCOCF₃)₂.

The Fourier transforms of *k*³-weighted Pd K-edge EXAFS spectra of the solutions A–D are shown in Figure 2. The peak at 1.60 Å found in all the spectra was attributed to a Pd–O scattering. No peak due to Pd–Pd scattering was observed in A–D, meaning that the aggregated Pd(0) cluster species did not exist in the mixture. The main characteristic feature was the reduction of the peak height of both solution B and D spectra. The structural parameters of the palladium complexes in the solution were obtained by curve fitting as shown in Table 1.⁶ The coordination number (CN) of a Pd–O bond in the absence of 1-octene was evaluated to be 4.1 (solutions A and C), whereas in the presence of 1-octene the CN was 2.4–2.2 (solutions B and D). Because the Debye–Waller factors do not undergo large fluctuation, the reduction of the CN by almost 1.8 suggests that

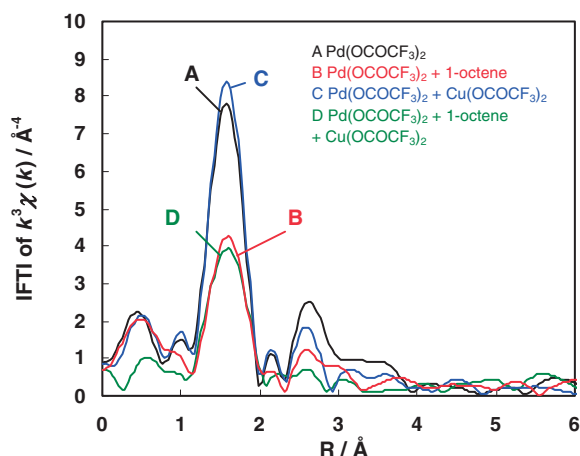


Figure 2. Fourier transforms of k^3 -weighted Pd K-edge EXAFS (also see the text).

Table 1. Curve fitting results of a Pd–O bond of solutions A–D^a

Solution	CN ^b	$r^c/\text{\AA}$	$\sigma^d/\text{\AA}$	$R^e/\%$
A	4.1(5)	2.004(6)	0.055(28)	1.1
B	2.4(12)	2.050(10)	0.067(31)	2.5
C	4.1(5)	2.017(7)	0.062(29)	0.49
D	2.2(14)	2.040(9)	0.066(32)	2.2

^a R fitting range is 1.1–2.0 \AA , and k fitting range is 2.55–11.6 \AA^{-1} . ^bCoordination number. ^c r : Interatomic distance.

^d σ : Debye–Waller factor. ^eThe so-called R factor.

1-octene molecule coordinates to palladium and that one trifluoroacetato ligand is eliminated. The oxidation of 1-octene slowly proceeded in the solution D at room temperature for a month to give 2-octanone (351 μmol determined by GLC).

Next, we investigated XAFS spectrum at Cu K-edge. $\text{Cu}(\text{OCOCF}_3)_2$ (ca. 1000 ppm) was dissolved in AcOBu saturated with molecular oxygen (solution E) at room temperature. The Cu K-edge XANES spectrum is shown in Figure 3E.⁷ Neither the addition of 1-octene (10 equimolar amounts to copper) (solution F) nor that of $\text{Pd}(\text{OCOCF}_3)_2$ (ca. 1000 ppm) (solution G) to the solution E affects the position of Cu K-edge absorption edge as shown in Figures 3F and 3G. However, only in the case of the addition of both of them to the solution E (solution H), the absorption edge dramatically shifted to low energy (Figure 3H), indicating that the copper was reduced. This reveals that the copper species does not act as an oxidant unless a palladium/alkene complex is generated.

Figure 4 shows the Fourier transforms of k^3 -weighted Cu K-edge EXAFS spectra of the solutions E–H. The peak located at 1.64 \AA observed commonly for all the samples was due to a Cu–O scattering. The peak height was slightly reduced when both 1-octene and $\text{Pd}(\text{OCOCF}_3)_2$ were simultaneously added. As mentioned in XANES analysis, EXAFS also indicated the interaction between $\text{Cu}(\text{OCOCF}_3)_2$ and $\text{Pd}(\text{OCOCF}_3)_2$ /1-octene complex.

In summary, by using XAFS analysis, we have succeeded in the in situ observation of Wacker-type reaction, revealing the ligand exchange on palladium from trifluoroacetato to alkene

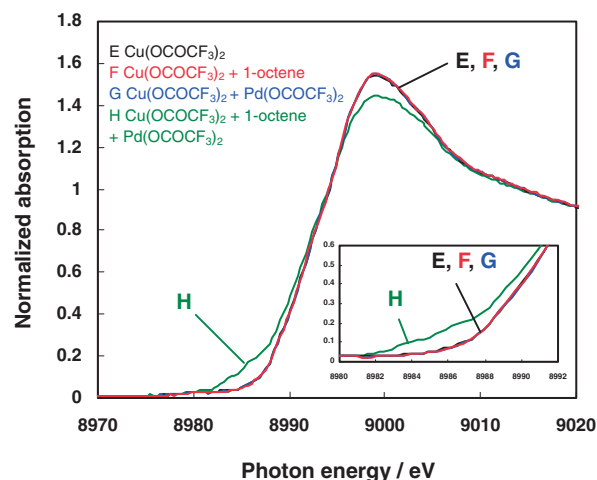


Figure 3. Cu K-edge XANES spectra with inset showing their difference (also see the text).

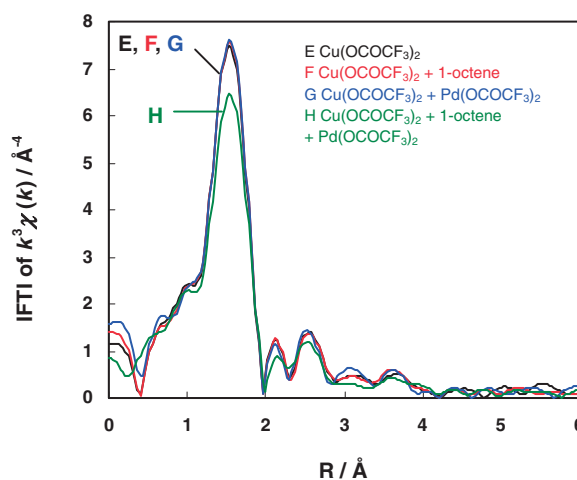


Figure 4. Fourier transforms of k^3 -weighted Cu K-edge EXAFS (also see the text).

and reoxidation of a palladium/alkene complex by copper proceed in organic solvent.

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- 6 For a Pd–O pair, the empirical parameters extracted from the spectrum of Pd(OCOFCF₃)₂ were used.
- 7 The XANES spectrum of Cu(OCOFCF₃)₂ was found to be identical with that of powdery Cu(OCOFCF₃)₂.