

IN SITU STRUCTURAL ANALYSIS OF HETEROGENEOUS NOBLE METAL CATALYSTS IN SOLVENT UNDER REDUCTION-OXIDATION CONDITIONS BY QUICK XAFS

Reduction-oxidation reactions catalyzed by noble metals are industry important and environmentally friendly processes. Among the metal catalysts, palladium has been widely and intensively studied and applied to various industrial fields. We have studied reduction-oxidation reactions catalyzed by heterogeneous palladium in the liquid phase. In the course of the investigation, we expected that the local structure of palladium would change during chemical interaction between catalysts and the solvent, taking into account that reaction and deterioration rates were significantly dependent on reactants, solvents and temperatures. Herein, we report the structural change of the palladium catalyst suspended in a solution using an *in situ* cell developed by us. Generally, the measurement of a solid catalyst suspended in a liquid is difficult because of the inhibition by cell windows or solvents. In this respect, the absorption of the X-ray beam is small at the energy of the Pd *K*-edge, which renders the measurement of XAFS of a solid catalyst in a liquid cell.

The illustration and photograph of our reaction cell are shown in Fig. 1. The *in situ* reactor cell made of stainless steel could be operated under an inner pressure of 1 MPa and a temperature of up to 100 °C. The stainless cell was placed on a hot plate and the solvent was stirred with a magnetic stirrer. The

temperature of the solvent was measured with a thermocouple inserted into the center of the reactor cell. The solid catalyst loaded onto a pipe (3 cm in length) was placed on the X-ray path. Polycarbonate disks with a thickness of 1 cm were used as windows of the cell. Pressure inside the cell could be monitored using a gauge. The reducing agent (an aqueous formaldehyde solution) was poured from the vessel connected to the upper part of the cell.

In the initial stage of our research, it was difficult to obtain good spectra with a high S/N ratio due to the interference of a high background count, which was caused by air bubbles generated during stirring. To improve the quality of spectra, the shape and construction of the reaction cell, and experimental conditions were improved to decrease the number of bubbles. The most effective improvement was the optimization of the rotation of stirring.

The *in situ* cell was applied to QXAFS measurement in the course of the reduction of Pd with a formaldehyde solution. In the measurement, the 10wt% Pd/Al₂O₃ catalyst was placed on the path of an X-ray beam and Pd *K*-edge XAFS spectra were collected every 5 min in N₂ atmosphere.

Figure 2 shows examples of Pd *K*-edge Fourier transforms of Pd/Al₂O₃ measured in the formaldehyde/water solvent at a temperature ramping

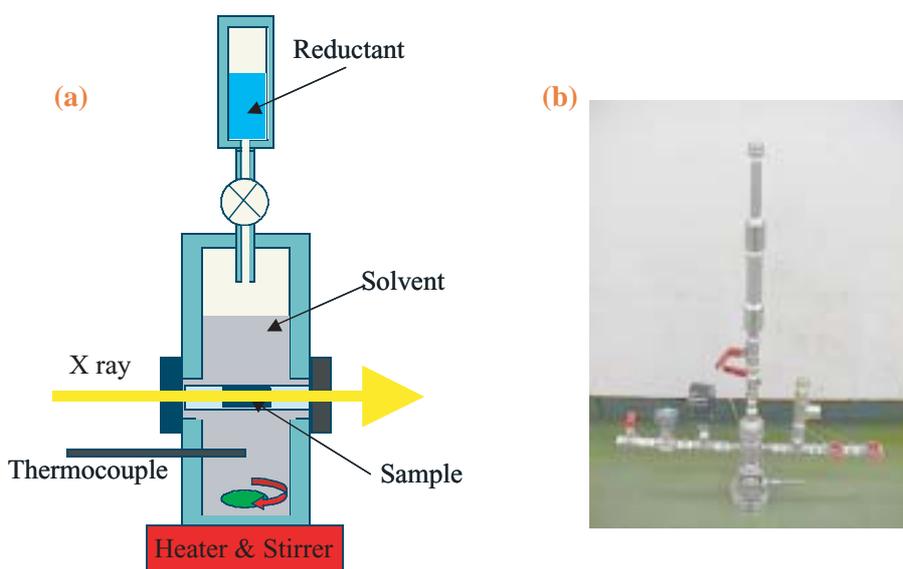


Fig. 1. Illustration (a) and photograph (b) of new reactor cell.

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rate of 10 K/min. In the Fourier transforms, the Pd-O peak appeared at 1.6 Å, indicating that palladium was oxidized at the initial stage. The intensity of the peak of Pd-O decreased accompanied by the reduction of PdO in the temperature range between 50 and 70 °C. Then the Pd-Pd peak ascribed to the Pd metal appeared at 2.7 Å above 70 °C.

The structural change of Pd was monitored sequentially at 65 °C immediately after the addition of the formaldehyde solution from the upper vessel. The spectrum was collected every 5 min. As can be seen from the figure, the reduction of palladium progressed with time and the growth of the Pd metal continued over 30 min from the beginning of the reaction, after which it progressed slowly.

In summary, a new *in situ* liquid cell was applied to the observation of the reduction of Pd-supported catalysts. By using this technique, we could demonstrate the applicability of the cell in the measurement of solid catalysts suspended in a solution.

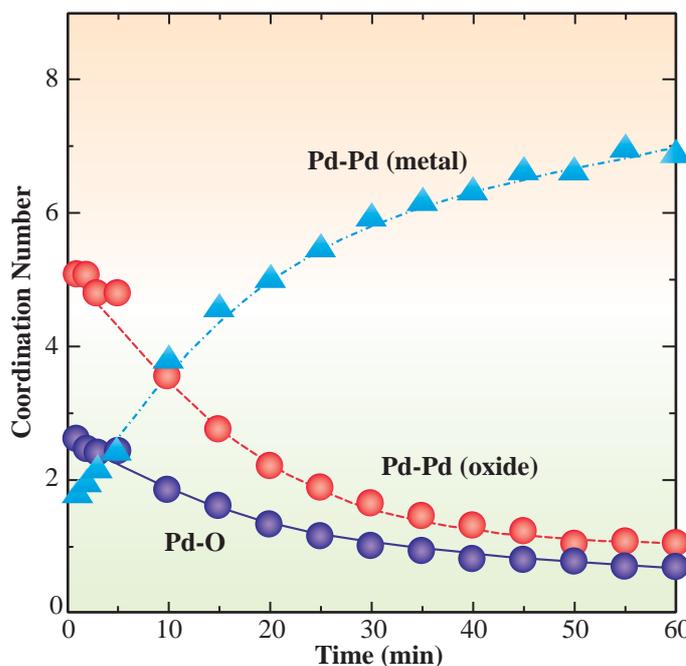


Fig. 2. Pd K-edge EXAFS Fourier transforms of 10wt% Pd/Al₂O₃ measured during reduction with formaldehyde in N₂ atmosphere. Temperature was changed stepwise from 30°C to 80°C.

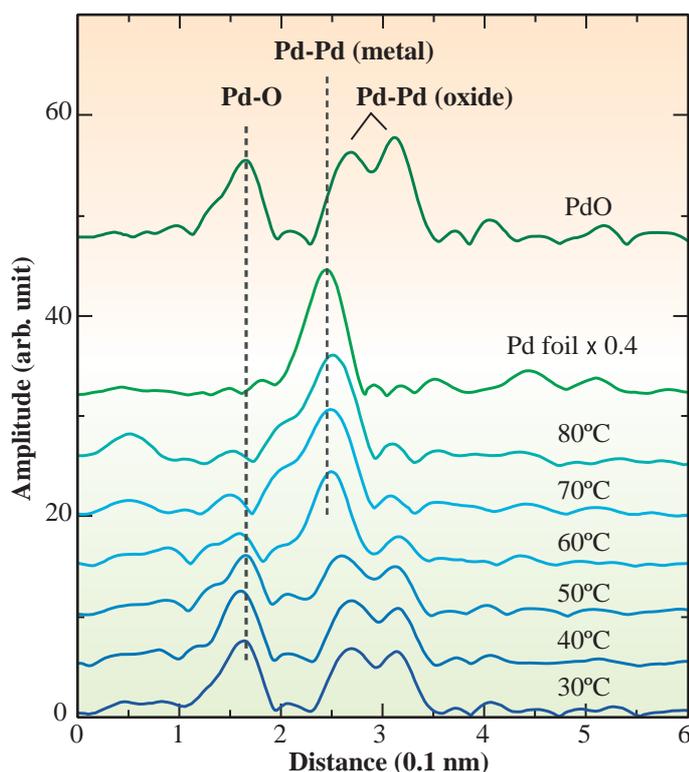


Fig. 3. Coordination numbers of Pd-O, Pd-Pd (oxide) and Pd-Pd (metal) of 10wt% Pd/Al₂O₃ plotted as function of reaction time. Formaldehyde solution was used as the reductant. Temperature, 65 °C.

Tsutomu Fujita^{a,*}, Kazu Okumura^b and Yasuo Takenaka^a

^a Mitsubishi Rayon Co. Ltd.

^b Faculty of Engineering, Tottori University

*E-mail: fujita_ts@mrc.co.jp