

## Determination of the active structure of PdTe catalyst

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### Introduction

PdTe bimetallic systems show high activity for oxidative diacetoxylation reaction of butadiene. Liquid phase reduction method gives PdTe nanoparticles with homogeneous composition and size. However, the inner structure of PdTe bimetallic nanoparticle is still unknown. We have applied EXAFS spectra to determine the structure of PdTe bimetallic nanoparticles and found the Pd very small core surrounded by a thick PdTe shell. In this paper we followed the preparation process in liquid phase.

### Experimental

The EXAFS measurements were carried out at NW10A of PF-AR with 6.5 GeV – 50 mA. The X-rays were monochromatized with a Si(311) double crystal monochromator. The X-ray was focused to the sample by a Pt-Coated bent cylindrical mirror. The critical energy for the total reflection of the mirror was set at 42 keV. The  $I_0$  and  $I$  signals were measured by Ar filled ionization chambers. The PdTe nanoparticles were prepared by the liquid reduction method. The concentration of Pd and Te was adjusted to enable us to follow the process in a transmission mode. Consequently the concentration of the sample was more than 10 times larger than the real reaction conditions.

### Results and discussion

Figures 1 and 2 shows Pd and Te EXAFS oscillations in solutions, respectively. Figure 1 shows the EXAFS oscillations of Pd(EDTA) complex and the reaction mixture without reductant (hydrazine). The peak around 0.1–0.2 nm and 0.2–0.3 nm are almost the same among them, indicating that the Pd(EDTA) structure is maintained in the reaction mixture.

Te K-edge showed the one peak corresponding to citrate ligands as shown in Fig. 2. The coordination number and bond distance of Te–O were 4 and 0.196 nm, respectively.

When hydrazine was added to the mixture at 0 °C, the solution colour was changed and the precipitation gradually occurred. EXAFS oscillations were completely changed, indicating the destruction of complex structures.

The addition of the hydrazine increased the solution pH, causing the precipitation. This precipitation was not observed in the real mixture of the preparation solution which has less amount of Pd and Te species. We tried to obtain the XANES of the reaction mixture at 0 °C by a fluorescence XANES. They showed the similar structure before the addition of hydrazine. We are planning to obtain a fluorescent EXAFS of the hydrazine mixture in a dilute solution.

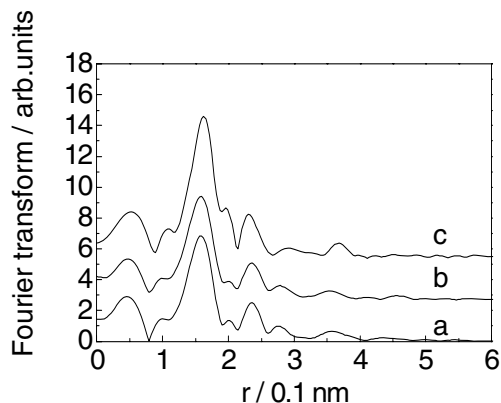


Figure 1 Pd K-edge EXAFS Fourier transforms of (a) Pd(EDTA), (b) Pd(EDTA)+citrate, (c) Pd(EDTA)+Te(citrate)

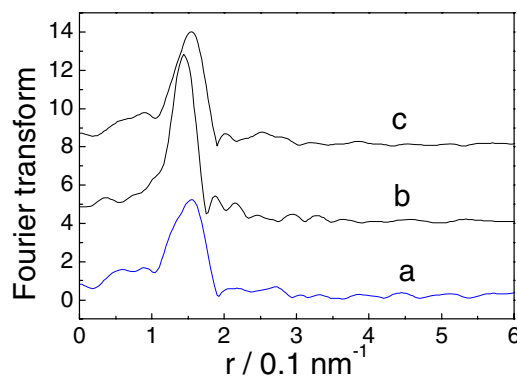


Figure 2 Te K-edge EXAFS Fourier transforms of (a) Te(citrate)<sub>2</sub>, (b) Te(EDTA)+citrate, (c) Pd(EDTA)+Te(citrate)<sub>2</sub>