

EXAFS analysis of the effect of chelating agent on formation of RhTe nanoparticles

Masafumi NAKAYA¹, Noritoshi YAGIHASHI², Atsushi MURAMATSU¹, Kiyotaka ASAKURA*³,
¹Institute of Multidisciplinary Research for Advanced Materials, Tohoku University,

Sendai, Miyagi 980-8577, Japan

²Graduate School of Engineering, Tohoku University, Aoba-ku, Sendai, Miyagi 980-8579, Japan

³Catalysis Research Center, Hokkaido University, Sapporo, Hokkaido 001-0021, Japan

Introduction

The rhodium tellurium (RhTe) bimetallic nanoparticle works as the catalyst of oxidative diacetoxylation reaction of butadiene. In our previous study, RhTe nanoparticles were prepared by liquid-phase reduction in the presence of chelating agents. However, the coordination state of chelating agent on metal ion was not clarified. In this paper, we have studied the state of metal ions in water with chelating agent by using EXAFS analysis to figure out the effect of chelating agent on preparation of RhTe nanoparticles.

Experimental

The EXAFS measurements were carried out at NW10A of PF-AR with 6 GeV – 50 mA. The X-rays were monochromatized with a Si(311) double crystal monochromator. The monochromatized 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- and Kr-filled ionization chambers, respectively. The rhodium chloride and sodium telluride (or telluric acid) were dissolved into ion-exchanged water in the presence of thiosalicylic acid (TS), citric acid or 4-(2-pyridylazo)resorcinol (PAR) as chelating agent and pH of the solution was aligned to 13.

Results and discussion

Figure 1 shows the Rh K-edge FT-EXAFS spectra, in the case of addition of Rh and Te precursors into the water in the presence of TS or combination of PAR and citric acid. When TS was added into the solution, the first peak appeared at 0.16 nm and corresponded to the Rh-O or Rh-N distance. When the citric acid and PAR was added into the solution, the peak of Rh-O or Rh-N was also observed. These may suggest that the ligand of Cl is changed. The second peak at 0.27 nm was observed and corresponded Rh-Rh or Rh-Te distance in the case of addition of PAR and citric acid. On the other hand, in the case of using TS, the second peak at ca. 0.27 nm was not observed. In order to clarify the coordination state of Rh in more detail, Te EXAFS analysis was carried out.

Figure 2 shows the Te K-edge FT-EXAFS spectra, in the case of addition of Rh and Te precursors into the

water in the presence of TS or mixture of PAR and citric acid. The first peak at 0.15 nm which corresponded to Te-O was observed. The second peak was observed at 0.27 nm in the case of addition of PAR and citric acid as the chelating agent. On the other hand, when the TS was added as chelating agent, the peak at around 0.27 nm did not appear.

From these results, when the TS was added as chelating agent, Rh and Te could respectively form the complex without Rh-Te bond. Therefore, when TS is used as the chelating agent, the formation of RhTe bimetallic nanoparticles may be controlled by changing the rate of reduction reaction.

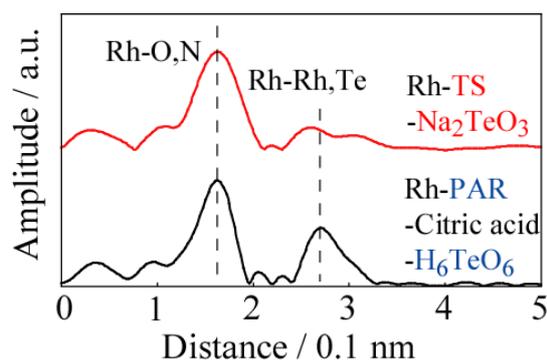


Figure 1. Rh K-edge FT-EXAFS spectra of the solution.

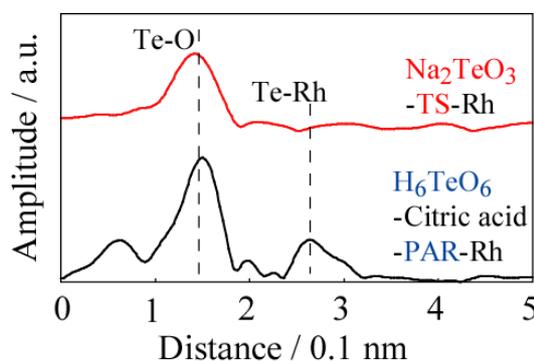


Figure 2. Te K-edge FT-EXAFS spectra of the solution.

* askr@cat.hokudai.ac.jp