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EXAFS analysis of DNA-protected platinum nanoparticles prepared by chemical reduction with sodium borohidride

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1 Introduction

Noble metal catalysts are key materials for various kinds of catalytic processes such as energy transformation, chemical production, and environmental protection. In this study, we prepared a colloidal Pt dispersion using deoxyribonucleic acid (DNA) as a protecting polymer and analyzed the Pt particles by X-ray absorption spectroscopy.

2 Experimental

DNA dry powder from salmon sperm was obtained from Wako Pure Chem. Ind. and used without further purification. An appropriate amount of DNA powder was dissolved into 100 mL of pure water with vigorous stirring. After 16 h stirring, H_2PtCl_6 (99.9%, Wako Pure Chem.) in water was added to the solution. Then, a small portion of $NaBH_4$-containing aqueous solution was added dropwise to the $PtCl_6$-DNA solution. Here, molar ratio of $NaBH_4$ to H_2PtCl_6 was 40.

XAFS measurements of the Pt L3 edge were performed at room temperature (23 °C) in the transmission mode at the Photon Factory, High Energy Accelerator Research Organization (KEK-PF).

3 Results and discussion

In the Pt L3 edge XANES spectra of the DNA-stabilized Pt particles, the first peak due to the transition to 5d3/2 and 5d5/2 orbitals was observed at around 11565 eV. The peak is known as a “white line” and its intensity correlated with the oxidation state of Pt species: the white line intensity increased with the increase in the oxidation state of Pt [1]. The white line intensity for the DNA-stabilized Pt nanoparticles was lower than that for PtO_2, but the intensity was higher than that for Pt foil, suggesting that the Pt particles were composed of reduced Pt metal and oxidized Pt species.

Figure 3 shows Pt-L3 edge EXAFS spectra of the Pt species in the colloidal dispersion and reference samples. The peak of Pt-Cl bond was observed for the spectra of PtCl64- complex, whereas the peak of Pt-Cl bond was not detected for the DNA-protected Pt particles, indicating that Cl-containing Pt complex were not present in the dispersion. A strong peak due to Pt-Pt bond was observed at 2.64 Å for Pt foil and at around 2.94 Å for PtO_2. In contrast, the peaks of Pt-Pt bond were not observed for DNA-protected Pt nanoparticles. These implied that the Pt particles consisted of highly disordered Pt clusters. The structures of DNA-protected Pt particles were different from those of PVP-protected Pt particles prepared by the same preparation methods. It has been reported that the Pt particles protected by PVP showed distinct peaks of Pt-Pt bond in the EXAFS spectra [2], indicating the formation of reduced Pt particles. The findings described above suggested that in the case of DNA-protected Pt particles, the strong interaction between DNA and Pt particles inhibited the growth of Pt particles .

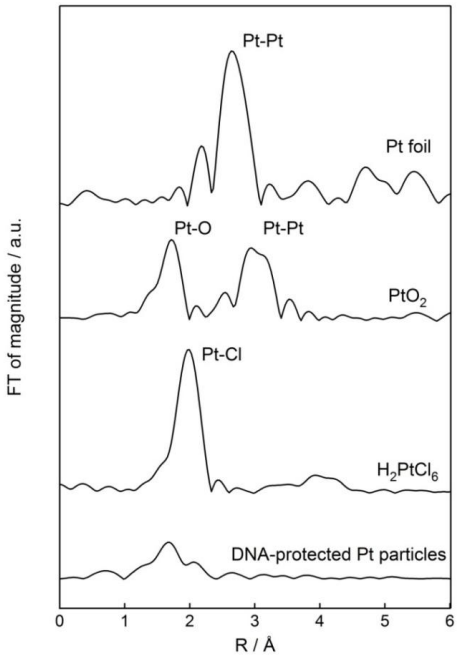

Figure 1 Pt L3 edge EXAFS spectra of DNA-protected Pt nanoparticles and reference samples.

4 Conclusion

In this study, we reported that DNA-protected Pt particles prepared by $NaBH_4$ reduction in aqueous solution consisted of reduced Pt metal and oxidized Pt species and exhibited much different spectrum from Pt foil and PtO_2.

References

[1] H. Yoshida *et al.*, *Catal. Today* **153,** 156 (2010).
[2] M. Harada *et al.*, *J. Coll. Int. Surf.* **308,** 568 (2007).
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