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XAFS Studies of Metal Nanoparticles Prepared by Using Microwave Heating

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Introduction

Microwave (MW) irradiation is one of the most promising techniques for the preparation of nanomaterials with controlled size and shape. In the past decade, there has been increasing interest in the use of MW irradiation instead of conventional heating in various kinds of metallic nano-sized particle syntheses [1, 2]. Recently we have developed an efficient preparation method of the size-regulated monometallic and bimetallic nanoparticles by means of MW irradiation. Here we demonstrate the structural analysis of monometallic Pd, Rh, Ru, Pt and Au nanoparticles by the use of EXAFS measurements.

Experimental

In a typical experiment for the preparation of monometallic Pd nanoparticles (Pd_EG) in ethylene glycol (EG), 555.7 mg PVP was dissolved in 50 ml of ethylene glycol as a solvent to make the polymer solution (PVP/EG) with a concentration of PVP equal to 100 mM. 0.2 ml of HCl was added to 88.66 mg of $PdCl_2$ powder to dissolve it into aqueous solutions. After the addition of HCl, 50 ml of PVP/EG solution was poured to prepare the metallic solution with the concentration of [Pd] = 10 mM. In the case of the preparation of Pd nanoparticles (Pd_gly.) in glycerol, glycerol was used as a solvent instead of EG to make PVP/glycerol solutions.

MW irradiation was carried out using an MW apparatus (MICROSYNTH PLUS, Milestone General K.K.) in a continuous wave mode at 700 W (2.45 GHz). For the preparation of Pd nanoparticles in EG, the solution temperature was raised to 471 K by heating the solution for about 2 min, and it was maintained at this temperature for about 10 min. After naturally cooling down to room temperature, the colloidal solutions were collected for the EXAFS measurements. For the preparation of Pd nanoparticles in glycerol, the solution temperature was raised to 523 K for about 3 min, and it was kept at this temperature for about 10 min. In the case of the other monometallic nanoparticles, the same experimental conditions (concentration of metal and PVP, reaction temperature, and MW heating time) were applied as in the case of Pd nanoparticles. The EXAFS measurements were carried out in a transmission mode at BL-9C and NW10A. Data analysis was performed by REX2000 (Rigaku Co.).

Results and Discussion

Table 1 shows the structural parameters such as coordination numbers (C.N.) and bond distances (r) of the monometallic Pd, Rh, Ru, Pt and Au nanoparticles prepared in EG or glycerol by using MW irradiation. In the Fourier transforms of all the colloidal samples (not shown in this report), only the peak attributed to metal-metal bond was observed between 0.2 and 0.3 nm, indicating that the starting ionic compounds were completely reduced to form metallic nanoparticles. In the case of Pd, Pt and Au nanoparticles, the C.N. obtained from the curve-fitting is nearly the same (ranging from 10.3 to 11.3). This suggests that the particle size of these nanoparticles is not strongly affected by the metal concentration and reaction temperature. However, in the case of Rh and Ru nanoparticles, the C.N. becomes larger when the metal concentration becomes higher. Moreover, C.N. of Rh-Rh bond is 9.1 (or 10.3) for EG solvent and 7.0 (or 9.3) for glycerol, suggesting that the size of Rh nanoparticles prepared in glycerol is relatively smaller. The same trend is also seen in the C.N. of Ru-Ru bond. The detailed analysis of monometallic and bimetallic Pd/Pt, Rh/Pt and Pd/Au nanoparticles is in progress.

Table 1. Structural parameters from EXAFS analysis for the colloidal dispersions of metal nanoparticles prepared by means of MW irradiation.

Sample	C.N.[a]	r / Å	dE / eV	DW / Å
Pd_EG ([Pd]=5mM)	10.7	2.74	-0.846	0.068
Pd_EG ([Pd]=10mM)	10.7	2.74	-0.757	0.065
Pd_gly. ([Pd]=5mM)	11.0	2.81	-0.750	0.077
Pd_gly. ([Pd]=10mM)	11.3	2.81	-0.836	0.073
Rh_EG ([Rh]=5mM)	9.1	2.67	-2.186	0.059
Rh_EG ([Rh]=10mM)	10.3	2.68	-0.659	0.064
Rh_gly. ([Rh]=5mM)	7.0	2.66	-4.613	0.052
Rh_gly. ([Rh]=10mM)	9.3	2.68	-1.611	0.066
Ru_EG ([Ru]=5mM)	10.5	2.66	-0.631	0.073
Ru_EG ([Ru]=10mM)	11.0	2.66	-1.32	0.075
Ru_gly. ([Ru]=5mM)	8.3	2.66	-3.009	0.071
Ru_gly. ([Ru]=10mM)	9.3	2.66	-4.00	0.076
Pt_EG ([Pt]=5mM)	10.3	2.76	-1.523	0.068
Pt_EG ([Pt]=10mM)	10.4	2.76	-1.020	0.066
Pt_gly. ([Pt]=5mM)	10.7	2.76	-1.276	0.070
Pt_gly. ([Pt]=10mM)	10.5	2.76	-1.187	0.068
Au_gly. ([Au]=5mM)	12.6	2.89	2.039	0.061
Au_gly. ([Au]=10mM)	12.1	2.88	0.678	0.060

[a] Coordination numbers of the corresponding metallic bond.

References

[1] T. Nakamura et al., *Bull. Chem. Soc. Jpn.* **2007**, *80*, 224. [2] M. Tsuji et al., *Chem. Eur. J.* **2005**, *11*, 440.

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