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XAFS analysis for Au nanoparticles supported on MgO

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1 Introduction

Hydrogenation reaction catalyzed by gold nanoparticles dispersed on suitable oxide supports have been reported [1]. Among the hydrogenation reactions catalyzed by gold nanoparticles, catalytic hydrogenation of aromatic nitro compounds to its corresponding amines is very important in the context of chemical industries, pharmaceuticals, polymers and fine chemicals. Recently, we reported preparation of gold nanoparticles supported on commercially available Nano Active Magnesium Oxide Plus (NAP-MgO), characterization and application to reduction of nitroarenes in the presence of sodium borohydride in acqueous medium at room temperature [2]. In order to obtain the structural information of gold nanoparticle dispersed on NAP-MgO, EXAFS measurements were employed.

2 Experiment

Preparation of NAP-MgO-Au is described briefly. NAP-MgO (3.5 g) was calcined at 723 K for four hours in air, and then treated with chloroauric acid solution (1g, 2.54 mmol; dissolved in 100 ml of double distilled water) and stirred at 298 K for 12 h under nitrogen atmosphere to give Au(III)-exchanged NAP-Mg-Au(III) species. To this mixture, excess of sodium borohydride (3.5 g, 92.5 mmol) was slowly added and stirred under nitrogen atmosphere for another 12 h. The solid catalyst was filtered through G-3 sintered glass funnel, washed with double distilled water and then with acetone. It was then oven dried at 343 K to obtain NAP-Mg-Au(0) as a dark purple coloured powder.

Measurements of extended X-ray absorption fine structure (Au L_{III}-edge EXAFS) were carried out at the Photon Factory in the Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK－IMSS－PF). The EXAFS spectra were analyzed with the UWXAFS package. The curve-fitting analysis was carried out using the FEFFIT program in the R-space.

3 Results and Discussion

From XPS measurements, it was found that gold nanoparticles dispersed on NAP-MgO exhibit the Au(0) valence state. Therefore, it will be denoted as NAP-Mg-Au(0), hereinafter. Au L_{III}-edge EXAFS was measured for NAP-Mg-Au(0) and compared with the result for Au foil. The k^3-weighted Au L_{III}-edge EXAFS Fourier transforms and curve fitting results for NAP-Mg-Au(0) catalyst are shown in Fig. 1. From these measurements and analysis, it was found that NAP-Mg-Au(0) exhibits Au-Au metallic bonding with slightly reduced coordination numbers as in an Au foil, indicating that these are Au metallic nanoparticles. These results are in line with the results of TEM observations.

In summary, NAP-MgO-Au(0), active for the reduction of nitroarenes containing various functional groups in aqueous medium at room temperature with sodium borohydride, was successfully characterized as nanoparticles of Au(0) by Au L_{III}-edge EXAFS.

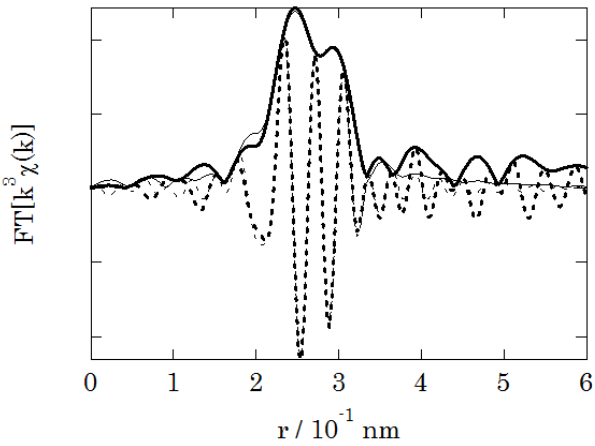

Fig. 1: k^3-weighted Au L_{III}-edge EXAFS Fourier transforms and curve fitting results for NAP-Mg-Au(0) catalyst. Amplitude: solid curves; imaginary part: dotted curves; observed data: thick curves; fitting data: thin curves.

Table 1: Summary for EXAFS analysis

	Au-Au				
	R (10^{-1}nm)	CN	DW (10^{-5}nm^2)	ΔE_0 (eV)	R_f (%)
Au foil	2.857±0.019	11.4±0.5	8.0±0.2	0.5±0.5	0.46
NAP-Mg-Au(0)	2.845±0.058	8.4±1.1	8.4±0.9	3.3±1.0	1.15

References

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