

## In situ time-resolved XAFS study of the formation mechanism of Rh NPs in the presence of quaternary ammonium bromide

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### Introduction

Metal nanoparticles (NPs) are getting attention in both fields of fundamental science and engineering. For example, metal NPs have several catalytic activities such as hydrogenation, oxidation or C-C coupling<sup>1</sup>. In these days, various scientists' effort enabled us to control NPs' size and/or shape. Their formation mechanisms are also vigorously investigated, but are still under discussion. In this study, we observed the formation of Rh NPs in the presence of quaternary ammonium bromide<sup>2</sup> in ethylene glycol at elevated temperature by means of in situ time-resolved XAFS technique.

### Results and Discussion

Figure 1 shows a series of *in situ* time-resolved EXAFS spectra of Rh NPs formation from RhCl<sub>3</sub>·3H<sub>2</sub>O with 15 eq. Polyvinylpyrrolidone (PVP, M.W.=24000) and Tetrabutylammonium bromide (TTAB) in ethylene glycol (EG) for 1 hour at 403 K. In the first step, Cl<sup>-</sup> dissociates from a Rh precursor and the intermediate having Rh-Br bonding was formed. In the second step, the Rh-Rh peak at around 2.3 Å gradually increased in about 20 minutes through an isosbestic point. For the latter 40 minutes, the EXAFS spectra were almost unchanged, which means that the Rh NPs formation stopped under this condition. The TEM observation clarified that the obtained Rh NPs were 6 nm cubic NPs and their size distribution were very small.

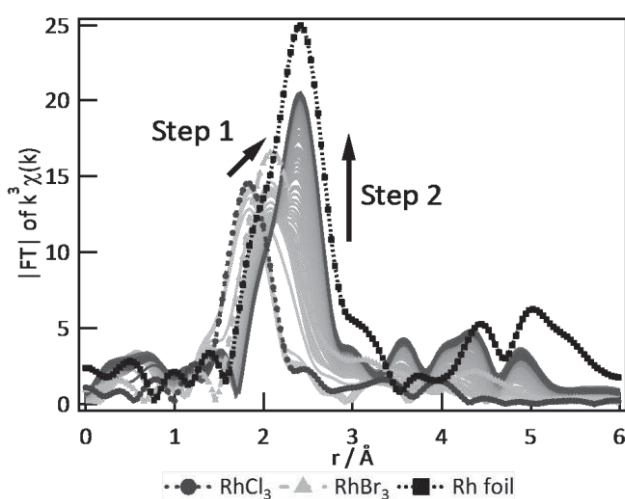


Figure 1 A series of in situ time-resolved Fourier transformed EXAFS spectra for 1 h at 403 K (Additives: PVP and TBAB) Reference spectra: RhCl<sub>3</sub> (Circle), RhBr<sub>3</sub> (Triangle), Rh foil (Square)

<sup>1</sup> N. Yan, C. Xiao and Y. Kou, *Coord. Chem. Rev.*, **2010**, 254, 1179.

<sup>2</sup> W. Y. Zhang et al., *J. Am. Chem. Soc.*, **2008**, 130, 5868.