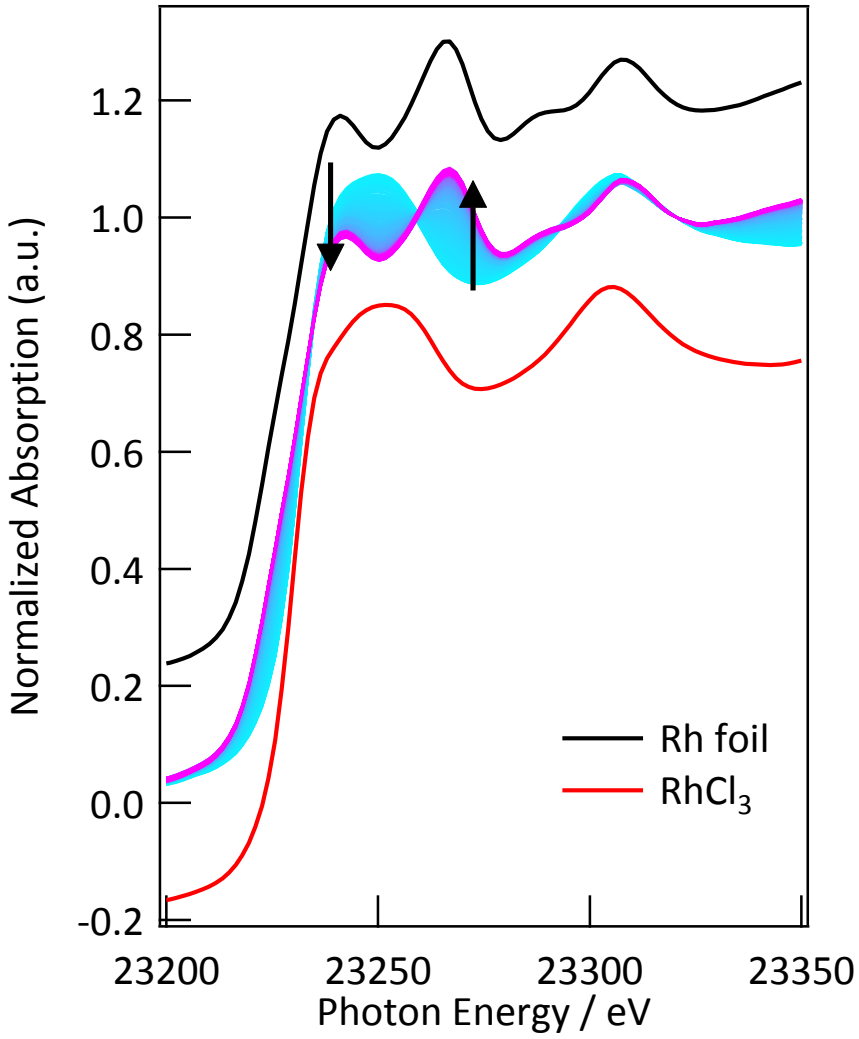


Fig. S1. Rh K-edge XANES spectra of Rh foil, a series of Rh K-edge XANES spectra of reaction solution containing $RhCl_3 \cdot 3H_2O$ at 398 K for 1 h, and PVP in EG (Rh/PVP = 1/30), and $RhCl_3 \cdot 3H_2O$. (Arrows indicate spectral change for 1 hour)

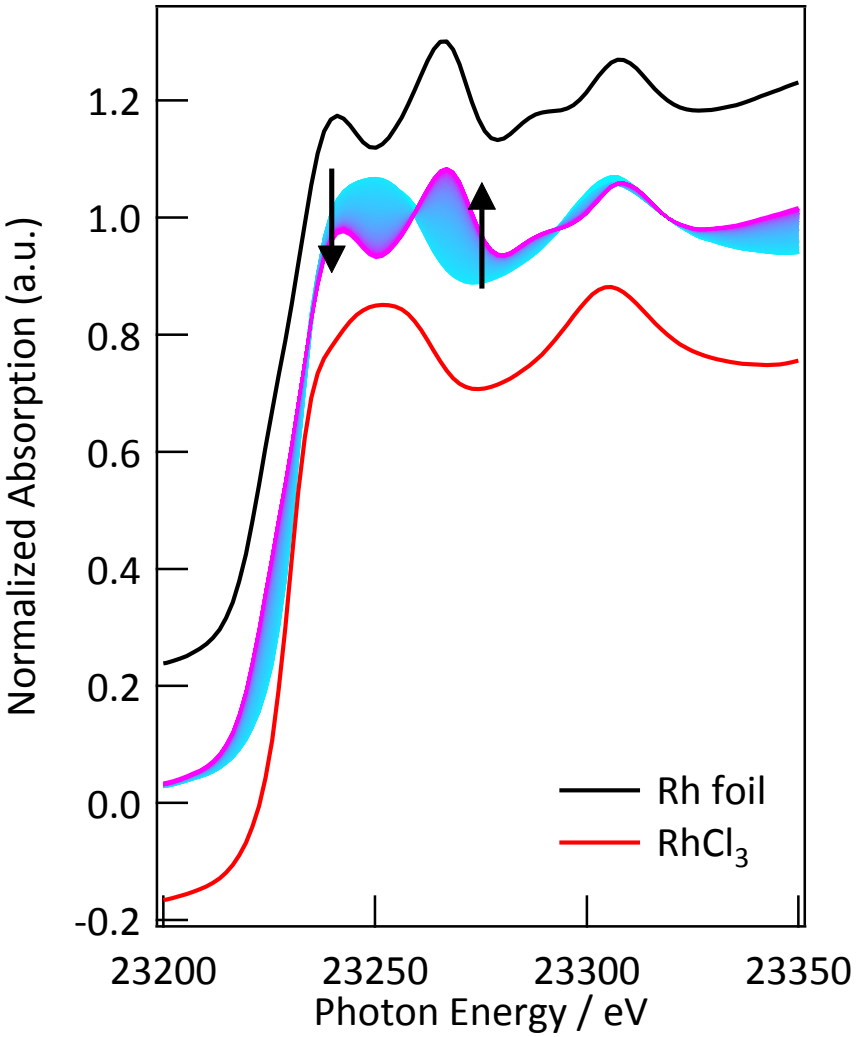


Fig. S2. Rh K-edge XANES spectra of Rh foil, a series of Rh K-edge XANES spectra of reaction solution containing $RhCl_3 \cdot 3H_2O$ at 398 K for 1 h, and PVP in EG (Rh/PVP = 2/15), and $RhCl_3 \cdot 3H_2O$. (Arrows indicate spectral change for 1 hour)

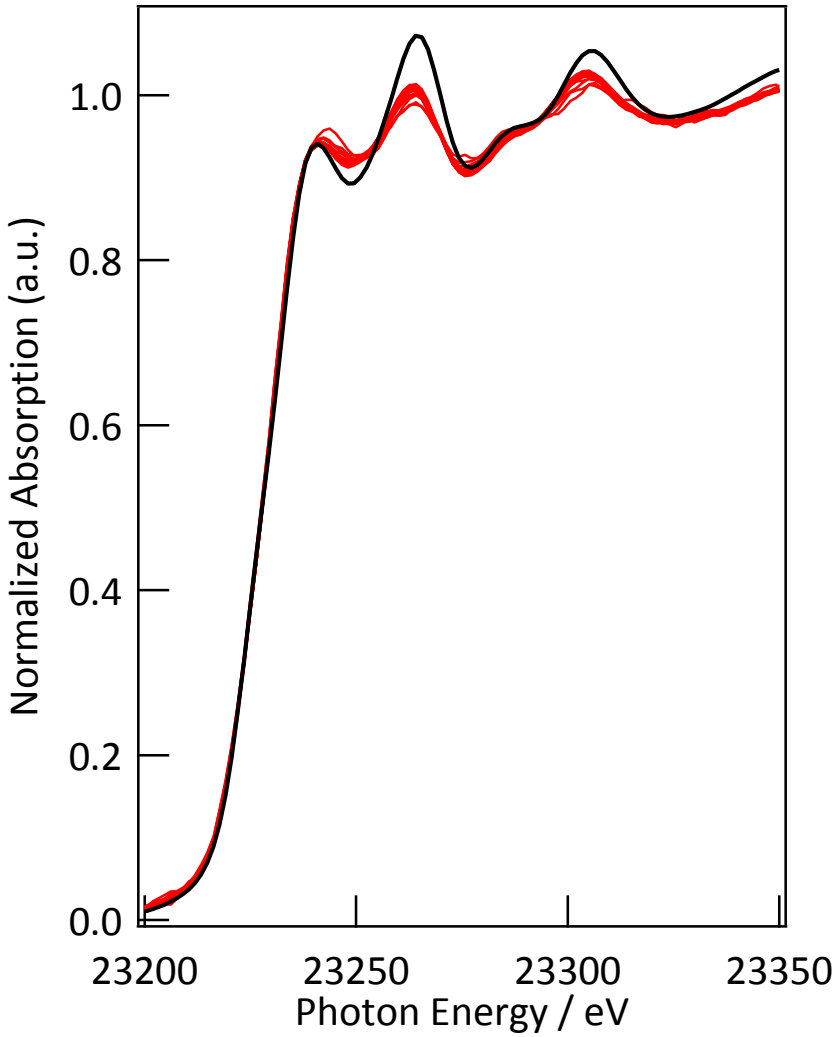
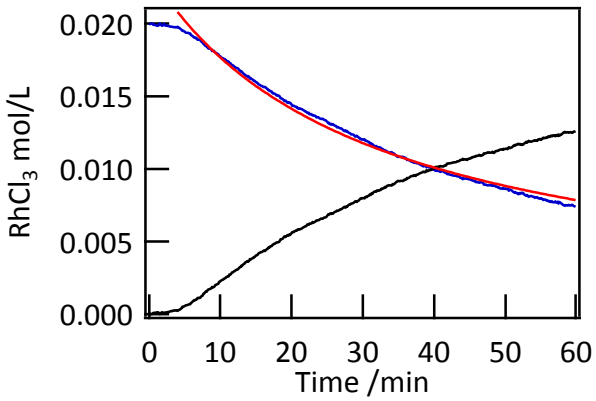
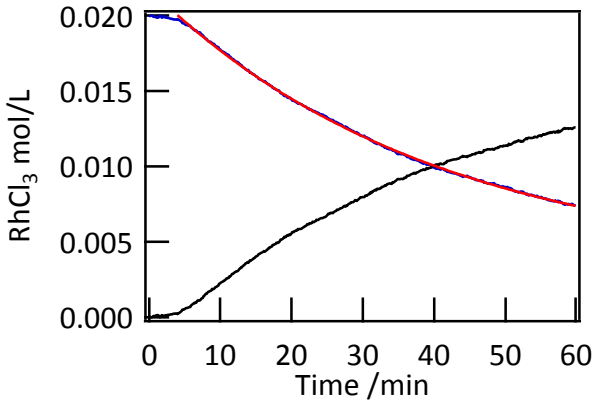


Fig. S3. A series of Fourier transformed spectra of calculated k^3-weighted Rh K-edge EXAFS from Run **B** and Rh foil (black) from 12 min to 60 min.



($\chi^2 = 4.6 \times 10^{-5}$)

Fig. S4. Fitting result of the consumption curve of Rh^{3+} with Finke's two step mechanism



($\chi^2 = 2.4 \times 10^{-6}$)

Fig. S5. Fitting result of the consumption curve of Rh^{3+} with simple exponential curve

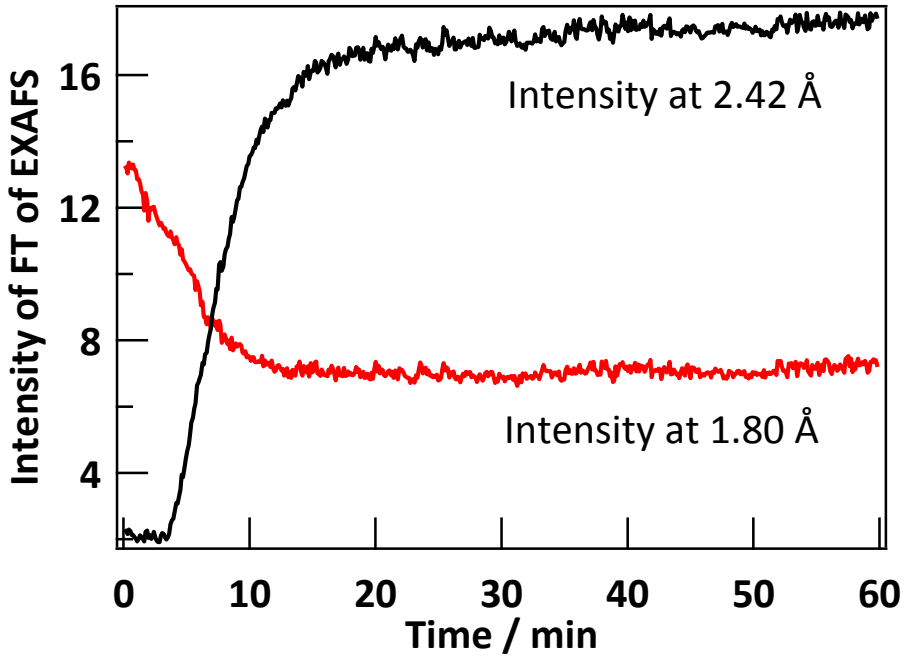


Fig. S6. The temporal change of intensity of Fourier transformed EXAFS spectra (Run A)

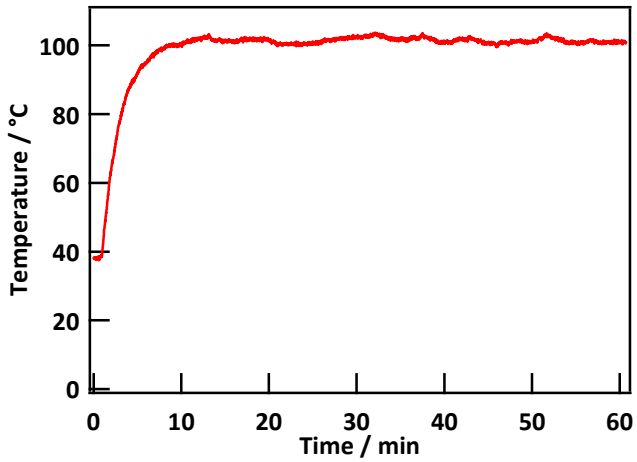


Fig. S7. A temperature profile of the in situ DXAFS measurement (Run B)