# In situ time-resolved energy-dispersive XAFS study on the structural changes of $Rh/Al_2O_3$ during CO adsorption and desorption

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## Introduction

Information on the structural change of metal clusters dispersed on oxide surfaces provides a clue to grasp the mechanism for catalyst reactions and dynamic processes at catalyst surface. The structure of Rh clusters in a highly dispersed $Rh/\gamma\text{-}Al_2O_3$ catalyst before and after CO adsorption has been studied by means of the conventional XAFS [1]. However, the conventional XAFS can not provide dynamic structural information on Rh clusters during CO adsorption and desorption. In this study, we tried to elucidate the structural change of $Rh/\gamma\text{-}Al_2O_3$ during the CO adsorption and desorption by means of time-resolved energy-dispersive XAFS (DXAFS).

## Experimental

A 2wt% $Rh/\gamma\text{-}Al_2O_3$ catalyst was prepared by incipient wet impregnation of $\gamma\text{-}Al_2O_3$ (BET surface area: 150 $m^2g^{-1}$) with an aqueous solution of $RhCl_3{\cdot}3H_2O$, followed by dry at 393 K for 30 h. Before CO adsorption, the dried catalyst was reduced at 613 K for 1.5 h under a flow of hydrogen and then evacuated at 573 K for 1 h.

DXAFS measurements were carried out at BL-9C in KEK-PF. A Si(311) bent crystal was used to focus polychromatic X-ray beam and a 1024-pixel position sensitive detector was used to record DXAFS spectra.

## Results and Discussion

Figure 1 shows Fourier transformed $k^3$-weighted DXAFS functions for $Rh/\gamma\text{-}Al_2O_3$ during CO adsorption at 298 K. The spectra were measured every 0.8 s (0.4 s exposure time). The curve fitting analysis revealed that Rh-Rh bonds disappeared dramatically with an increase of the CNs of Rh-C and Rh-O (0-2.4 s). Then CN of Rh-CO and Rh-O increased slowly (7.2 s). Thus the structural transformation during the CO adsorption process proceeds through two steps. The present study demonstrates that the DXAFS technique is powerful and useful to monitor the dynamic structure change.

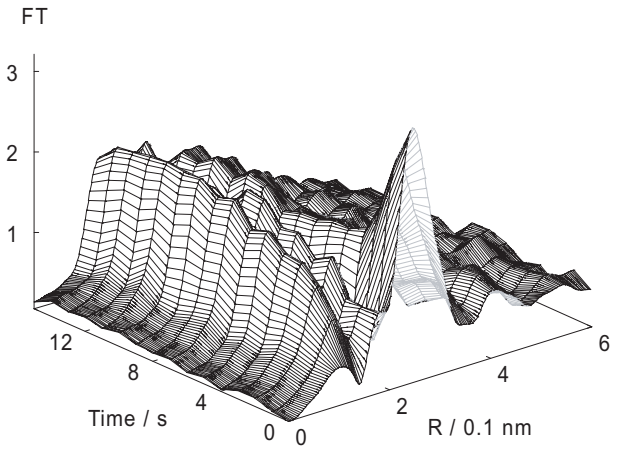


Figure 1. Fourier transformed $k^3$-weighted DXAFS functions for $Rh/\gamma\text{-}Al_2O_3$ during CO adsorption at 298 K

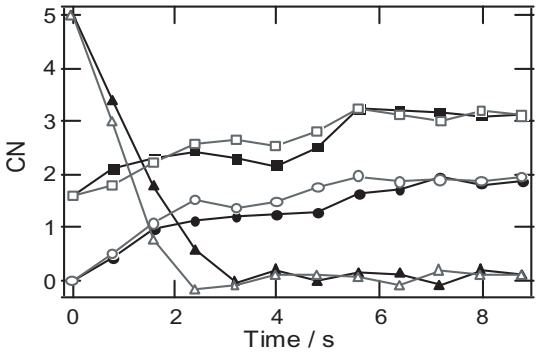


Figure 2. Change of coordination numbers (CN) of Rh-CO (○,●), Rh-Rh (△,▲) and Rh-O (□,■) during CO adsorption at 298 and 333 K .

[1] H. F. J. van't Blik et al., J. Am. Chem. Soc., **107**, 3139 (1985).

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