

In Situ Time-Resolved Energy-Dispersive X-ray Study on the reaction mechanism on the Rh dimer catalysts

Akane SUZUKI¹, Yasuhiro INADA², Aritomo YAMAGUCHI³, Teiji CHIHARA⁴, Masaharu NOMURA⁵ and Yasuhiro IWASAWA*¹

¹Graduate School of Science, The University of Tokyo, Tokyo 113-0033, Japan

²Research Center for Materials Science, Nagoya University, Nagoya 464-8602, Japan

³Faculty of Science and Technology, Tokyo University of Science, Chiba 278-8510, Japan

⁴The Institute of Physical and Chemical Research, Saitama 351-0198, Japan

⁵Institute of Materials Structure Science, Photon Factory, KEK, Ibaraki 305-0801, Japan

Results and Discussion

Introduction

The Rh dimer/SiO₂ (1) was employed as catalyst for ethene hydroformylation. The dimer with an acyl ligand is favorable as a catalyst for ethane hydroformylation because the Rh acyl species is a reaction intermediate for the hydroformylation. Thus, we succeeded in the design of the catalytic site with the reaction intermediate[1]. However, the conventional XAFS cannot provide dynamic structural information on Rh dimer at the time scale of second or less. In this study, we attempted to elucidate the structural change of Rh dimer/SiO₂ during CO adsorption and desorption by means of time-resolved energy-dispersive XAFS(DXAFS).

Experimental

The incipient SiO₂ attached Rh dimer was prepared by the reaction of trans-[Rh(C₅Me₅)(CH₃)₂CH₂]₂ with surface OH groups of SiO₂ in the pentane solution. The obtained sample of 80 mg was pressed to a disk (7 mmφ) and placed at a holder of an in-situ DXAFS cell, and reduced at 373 K for 1 h under evacuation.

DXAFS measurements in the energy range 23.0–24.2 keV were carried out at BL-9C in KEK-PF. A four-point supporting crystal bender was newly developed for a Si(311) bent-crystal polychromator (Bragg-type) to achieve an elliptical optics for focusing incident X-rays at the sample. A self-scanning photodiode array (PDA: 1024 sensing elements: 25 μm width and 2.5 mm height for each element) manufactured by HAMAMATSU Photonics (S3904-1024FX SPL3402) was used as a position-sensitive linear detector. A fiber optical plate embrocated by a CsI(Tl) fluorescent (150 μm thickness) was directly coupled at the active area of PDA to convert X-ray to visible light. The energy calibration at each sensing element of the PDA was performed by comparison with an XAFS spectrum of a Rh foil recorded using an Si(311) channel-cut monochromator.

The incipient Rh dimer on SiO₂ was converted to the Rh dimer species in Figure.1 by stepwise transformation at the surface. Each step for the transformation was characterized by FT-IR (use of deuterium-labeled Rh dimer precursor) and conventional EXAFS.

Figure 2 shows Fourier transformed *k*³-weighted DXAFS functions for Rh/SiO₂ during CO adsorption at 313 K. The spectra were measured every 100 ms. The curve fitting analysis revealed that Structural change during CO adsorption for Rh dimer/SiO₂ (1) proceeded through three steps. During CO adsorption, at first CO molecules coordinate and in the second step the Rh-Rh bonds disappeared. In the last step, structural change from acyl ligand to CO and ethyl ligand. The present study demonstrates that the DXAFS technique is powerful and useful to monitor the dynamic structure change.

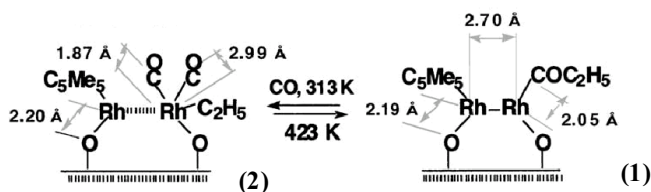


Figure 1. Transformations of the Rh dimer on SiO₂ for CO insertion and decarbonylation.

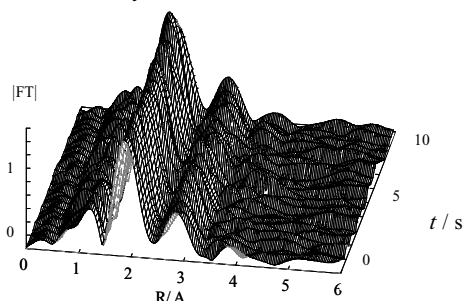


Figure 2. Fourier transformed *k*³-weighted DXAFS functions for Rh/γ-Al₂O₃ during CO adsorption at 313 K

[1] K. Asakura, K.K. Bnado, Y. Iwasawa, H. Arakawa, K. Isobe, J.

Am. Chem. Soc. 112 (1990) 9096.