

Time-Resolved Energy-Dispersive XAFS Study on the Structural Changes of Rhodium Clusters on an Alumina Surface during CO adsorption

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Introduction

While reaction kinetics and dynamics of molecules adsorbed on catalyst surfaces have been extensively studied, little is known about the dynamic structural change of active metal sites in supported metal cluster / nanoparticle catalysts, such as the time scale of integration and disintegration of the active structure induced by reaction gases and the sequence of bond rearrangements involved in the dynamic event on the surfaces. reports novel issues found by the time-resolved DXAFS characterization of the structural disintegrity of Rh clusters on an Al₂O₃ surface, namely, the time scale and sequence of dynamic bond rearrangements in the clusters and at the interface.

Experimental

A 2 wt%-Rh/Al₂O₃ catalyst was prepared by an incipient wet impregnation method with an aqueous solution of RhCl₃•3H₂O, followed by drying at 393 K for 30 h to remove the solvent. The obtained sample was pressed to a disk and placed at a holder of an in-situ DXAFS cell, and reduced at 613 K for 1.5 h under a flow of hydrogen followed by evacuation at 573 K for 1 h. DXAFS measurements in the energy range 23.0–24.2 keV were carried out at BL-9C in KEK-PF.

Results and Discussion

The time-resolved DXAFS analysis reveals three elementary steps for the surface dynamic structural rearrangement of Rh clusters involving an depicted in Fig. 1. Before CO exposure (t = 0) Rh atoms in the cluster and interact with the surface oxygen atoms of Al₂O₃ at the distance of 0.213 nm. The CN and R of Rh–Rh were 5.0 and 0.265 nm, respectively and these structural parameters assume that the Rh cluster consists of 7 atoms (first layer) and 3 atoms (second layer) as shown in Fig. 1, which shows the CN of 5.4 for Rh–Rh bond. The CN value of 1.6 for Rh–O indicates that each Rh atom in the lower layer interacts with two O atoms of the Al₂O₃ surface. At the first step of the dynamic processes (0–600 ms) CO rapidly adsorbs on the Rh cluster to show the CN of 0.7 for Rh–CO, which

indicates that one CO molecule adsorbs on each Rh atom of the second layer. At this stage no Rh–Rh bond breaking occurred. At the second step after 600 ms the Rh–Rh bonds became weaker by further CO adsorption and the Rh cluster was completely disintegrated at 3000 ms, where the ratio of adsorbed CO to Rh was one. The existence of the isosbestic point (a) in Fig. 2 indicates that the second step consists of a one-to-one direct conversion, namely from [Rh₁₀(CO)₃] (B) to [Rh–CO]₁₀ (C) in Fig. 1. The [Rh–CO] can migrate across the Al₂O₃ surface to react OH groups. The fragmentation of the Rh cluster permits the adsorption of further CO molecules on the Rh atoms at the third step (3000–6000 ms) to form [Rh(CO)₂](D) which interacts with three surface O atoms as shown in Fig. 1. This process is also a direct transformation process as evidenced by the second isosbestic point (b), where the Rh atoms are more strongly interacted with the surfaces because of a decrease in the Rh–O distance from 0.213 to 0.200 nm.

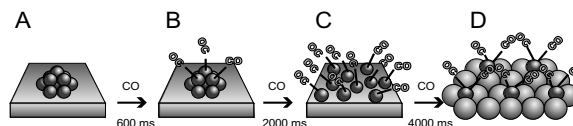


Fig. 1. Illustrative mechanism and time scale at 298 K for the disintegration of Rh clusters on Al₂O₃ during CO adsorption time-resolved by DXAFS.

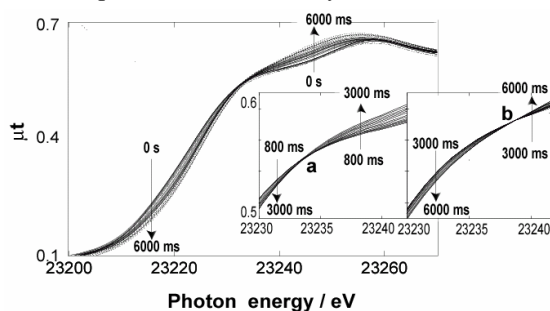


Fig. 2. The k^3 -weighted EXAFS oscillations at the Rh K-edge during the carbonylation process at 298 K measured by DXAFS every 100 ms. Pco=26.7 kPa, Cat. Weight= 80 mg.