

An EXAFS Study of a Highly Dispersed Rh/Al₂O₃ Catalyst

D.C. Koningsberger, T. Huizinga, H.F.J. van't Blik,
J.B.A.D. van Zon, R. Prins, and D.E. Sayers¹

Laboratory for Inorganic Chemistry and Catalysis, Eindhoven University
of Technology, NL-5600 MB Eindhoven, The Netherlands

Abstract

The X-ray absorption spectrum of the Rh K-edge of a highly dispersed reduced Rh/Al₂O₃ catalyst shows EXAFS oscillations due to Rhodium-Rhodium nearest neighbors. Adsorption of CO at room temperature on the reduced catalyst significantly decreases the amplitude of the EXAFS oscillations. This implies that CO adsorption on very small metal crystallites leads to a disruption of a significant number of the Rhodium-Rhodium metallic bonds.

These results show that the Rh in this system is not monatomically dispersed but is in the form of very small crystallites whose structure is disrupted by the adsorption of CO.

I Introduction

Several conflicting proposals have been published for the structure of highly dispersed Rhodium metal on Al₂O₃. Electron microscopy studies (1) have indicated that very small two-dimensional metal rafts are present. On the other hand infrared results obtained from CO adsorbed on the metal catalyst (2) (3) have been interpreted at low Rhodium loadings, (0.5 wt%), as being due to isolated Rhodium atoms.

Uncertainties also exist about the oxidation state of Rhodium on Al₂O₃. Electron microscopy shows that metallic Rhodium clusters are present. However, the Rhodium dicarbonyl species formed after CO adsorption exhibit infrared bands, which are similar to those of Rh₂(CO)₄Cl₂, suggesting that Rhodium atoms on Al₂O₃ are in the +1 oxidation state.

To investigate the structure of these highly dispersed Rhodium catalysts X-ray absorption studies were carried out before and after CO adsorption. Preliminary results of these measurements will be presented.

II Experimental

EXAFS experiments were performed at the Stanford Synchrotron Radiation Laboratory (SSRL) on station I-5 in February 1982

¹Department of Physics, North Carolina State University Raleigh,
North Carolina, 27650, USA

(Ring Energy 3 GeV; Ring Current 40-80 mA). The EXAFS was measured at 140 K in a controlled environment cell (4).

The Rh/Al₂O₃ catalyst was prepared by pore volume impregnation of the support with an aqueous solution of RhCl₃, leading to a metal loading of 0.5 wt%. The catalyst was pressed into a thin (~ 0.2 mm) self-supporting water and mounted in the sample cell. The sample was reduced by heating at a constant rate (5 K/min) under flowing hydrogen to 593 K. The sample was held at that temperature for about one hour and cooled down to room temperature. Reduction studies in our laboratory verified that after this treatment reduction of the catalyst is complete.

After in situ EXAFS experiments (under 100 kPa H₂) the catalyst was evacuated at 573 K for one hour. After cooling in vacuum (10⁻² Pa) to room temperature the sample was exposed to 100 kPa CO and the EXAFS spectrum was again measured in situ.

To further characterize the sample H₂ and CO chemisorption measurements were also performed in our laboratory. The temperature treatments of the catalyst during these experiments were the same as those described above. Hydrogen chemisorption resulted in an adsorbed H/Rh value of 2.1 and chemisorption of carbonmonoxide resulted in a CO/Rh value of 3.0 indicating a very highly dispersed material.

III Results and Discussion

The X-ray absorption spectrum of the K edge of Rhodium shows EXAFS oscillations due to a Rhodium coordination around the Rhodium atoms (see fig. 1a). This contradicts the interpretation that the system consists solely of isolated Rh atoms, which was derived from the infrared results. However, based on a preliminary analysis the Rh-Rh coordination number is very low (~ 5), indicating a highly dispersed system.

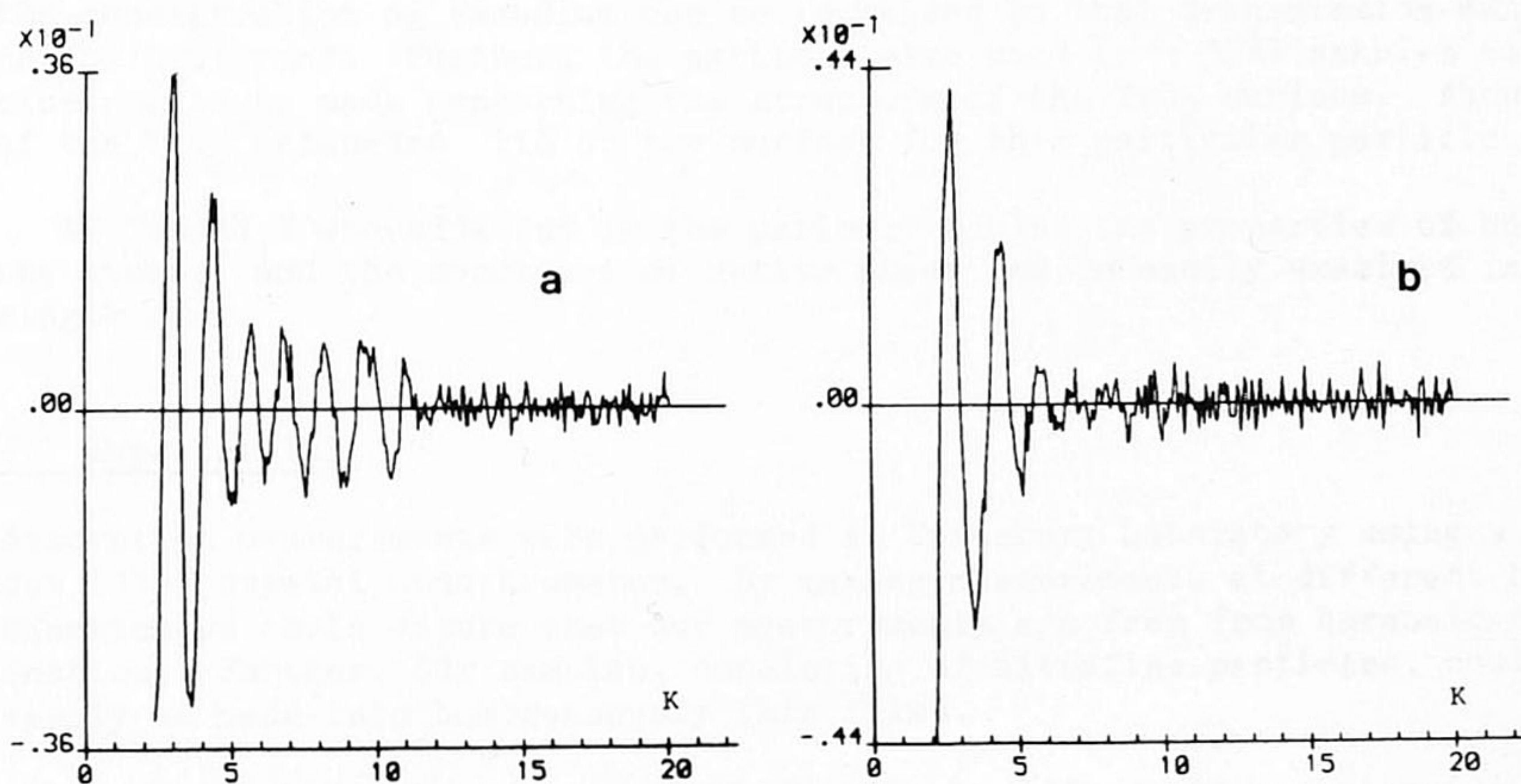


Fig. 1. Rh(0.5)/Al₂O₃

a) H₂, 593 K

b) H₂, 593 K + vac. 573 K + CO, 300K

After CO adsorption at room temperature the amplitude of the EXAFS oscillations attributed to a Rh-Rh metal coordination is significantly decreased (see fig. 1b). From this one can conclude that the greater part of the Rhodium-Rhodium metallic bonds are disrupted by the adsorption of CO molecules. This may also explain why the infrared bonds of chemisorbed CO molecules have been interpreted only in terms of isolated Rhodium dicarbonyl species.

In summary, preliminary results of an EXAFS study of the K edge of a highly dispersed Rh/Al₂O₃ catalyst shows that the reduced system is highly but not monatomically dispersed. Adsorption of CO at room temperature resulted in a significant disruption of the Rh crystallites. A more detailed analysis of this system is currently underway.

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Literature

1. D.J.C. Yates, L.L. Murrell and E.B. Prestridge, *J. Catal.*, 37 (1980) 975.
2. J.T. Yates, T.M. Duncan, S.D. Worley and R.W. Vaughan, *J. Chem. Phys.*, 70 (1979) 1219.
3. R.R. Cavanagh and J.T. Yates, *J. Chem. Phys.* 74 (1981) 4150.
4. D.C. Koningsberger and J.W. Cook Jr. (see Proceedings of this Conference).