An Extended X-ray Absorption Fine Structure Spectroscopy Study of a Highly Dispersed Rh/Al₂O₃ Catalyst: The Influence of CO Chemisorption on the Topology of Rhodium

H. F. J. Van't Blik,* J. B. A. D. Van Zon, T. Huizinga, J. C. Vis, D. C. Koningsberger, and R. Prins

Laboratory for Inorganic Chemistry, Eindhoven University of Technology, 5600 MB Eindhoven, The Netherlands
(Received: November 1, 1982; In Final Form: March 30, 1983)

The X-ray absorption spectrum of the Rh K edge of a highly dispersed reduced 0.57 wt % Rh/γ-Al₂O₃ catalyst shows EXAFS oscillations due to rhodium–rhodium nearest neighbors, which proves the existence of rhodium metal crystallites. Adsorption of CO at room temperature on the reduced catalyst significantly decreases the amplitude of these EXAFS oscillations. This implies that CO adsorption on very small rhodium crystallites leads to a disruption of a significant number of the metal–metal bonds.

Introduction

In the literature much attention is being paid to Rh/Al₂O₃ supported catalysts as a result of their many industrial applications. However, agreement has not been reached yet about the structure and oxidation state of the highly dispersed rhodium on the catalyst support after reduction with hydrogen. Some investigators have asserted on the basis of CO infrared data that the Rh on Al₂O₃ is monatomically dispersed and is in the Rh⁺ state.[1-5] Others have concluded from electron microscopy studies that rhodium is present in two-dimensional metallic raftlike structures.[6-8] Calculations have been reported which indicated that for small metallic clusters on supports indeed the raftlike two-dimensional form is more stable than the three-dimensional form.[9]

Infrared spectroscopy has been used as a sensitive tool to study the variations in the carbon–oxygen stretching frequencies of CO chemisorbed on Rh/Al₂O₃ catalysts.[1-7] These variations are due to subtle changes in the character of the supported rhodium. At high rhodium loading two CO bands are observed, one around 2060 cm⁻¹ and another broad band between 1800 and 1900 cm⁻¹. Both bands are assigned to CO molecules adsorbed on rhodium atom(s) on the surface of rhodium metal crystallites, the former band due to a CO molecule on top of a Rh atom, the latter band due to a CO molecule bridged between two neighboring Rh atoms. Another surface species consists of two CO molecules bound to one surface Rh (bands at 2095 and 2027 cm⁻¹, respresenting the symmetrical and antisymmetrical modes, respectively). This surface species is more pronounced for catalysts with a low Rh loading. As the wavenumbers correspond closely to those observed for the bridged [Rhᴵ(CO)₂Cl]₂ dimer and do not shift in frequency with increasing CO coverage the above-mentioned former group of authors assigned this surface species to CO adsorbed on isolated Rh⁺ cations.[1-5] Another indication that the geminal dicarbonyl refers to Rh⁺ comes from an X-ray

photoelectron spectroscopy study of a Rhᴵᴵᴵ exchange zeolite catalyst by Primet et al.[10] They have shown that after CO adsorption the Rh 3d ⁵/₂ electron binding energy changed to a value corresponding to that of a zeolite catalyst exchanged with [Rhᴵ(CO)₂Cl]₂. They ascribed this phenomenon to a reductive transformation of Rhᴵᴵᴵ–CO to Rhᴵ(CO)₂ species.

On the other hand, there are strong indications that rhodium is present as metallic crystallites after reduction with hydrogen. Detailed studies using catalytic reactions[8,11] (e.g., hydrogenolysis, which is catalyzed by metals only) have been performed on these dispersed systems as well as studies using both chemisorption and electron microscopy.[6,7] All these studies showed the existence of metallic particles. In the latter studies[6,7] also measurements after CO adsorption were carried out and the observed Rh(CO)₂ species was assigned to two CO molecules adsorbed on edge atoms in two-dimensional rafts.

The structure of rhodium in highly dispersed catalysts can be clarified by determining the coordination of Rh atoms to adjacent atoms by extended x-ray absorption fine structure spectroscopy (EXAFS).[12] EXAFS is, in contradistinction to diffraction techniques, sensitive to short-range ordering and can provide unique structural information on highly dispersed catalysts.[13] EXAFS measurements of reduced Rh/Al₂O₃ and Rh/TiO₂ catalysts have been reported before.[14] In that study it was concluded that rhodium is not entirely atomically dispersed.

We have carried out an X-ray absorption in situ study on a highly dispersed 0.57 wt % Rh/γ-Al₂O₃ catalyst before and after CO admission and in this Letter we present the results. Hydrogen and carbon monoxide chemisorption and CO infrared spectroscopy have been used for further characterization.

Experimental Section

The 0.57 wt % Rh/Al₂O₃ catalyst was prepared by incipient wetting of γ-Al₂O₃ with an aqueous solution of RhCl₃. The support γ-Al₂O₃ (BET area of 150 m²/g and a pore volume of 0.65 cm³/g) was obtained by heating boehmite (supplied by Martinswerk, GmbH) at 873 K. After impregnation the catalysts was dried in air at 393

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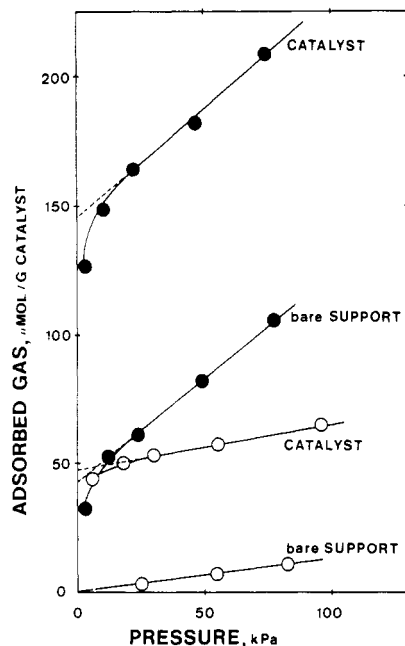
Figure 1. H_2 (O) and CO (●) chemisorption isotherms (measured at 298 K).

Figure 2. CO infrared spectrum on a 0.57 wt % Rh/γ-Al$_2$O$_3$ (measured at 298 K).

K for 20 h to remove the adsorbed water and stored for further use. The rhodium content was determined spectrophotometrically.

Chemisorption measurements were performed in a conventional glass system at 298 K. Before measuring the CO and H_2 adsorption isotherms the dried catalyst was reduced at 593 K (heating rate of 5 K/min) for 1 h under flowing hydrogen and evacuated (10^{-2} Pa) at 573 K for another hour. Temperature programmed reduction (TPR) studies confirmed that after this treatment reduction of the catalyst is complete.

Infrared spectra were recorded at 298 K with a Bruker IFS 113 V Fourier transform IR spectrometer with a resolution of 2 cm^{-1}. The catalyst was pressed into a thin self-supporting wafer following a prereduction at 593 K and passivation at room temperature and was placed in an infrared cell suitable for in situ measurements. Before CO admission (50 kPa) and evacuation (10^{-1} Pa) at 298 K the passivated catalyst was reduced and evacuated (10^{-1} Pa) at 523 K. The EXAFS experiments were performed on X-ray beam line I-5 at the Stanford Synchrotron Radiation Laboratory (SSRL) with ring energies of 3 GeV and ring currents of 40–80 mA. The EXAFS spectrum was recorded at 140 K in an in situ cell.[15] The dried catalyst was pressed into a thin (0.2 mm) self-supporting wafer and mounted in the sample cell. The reduction procedure was identical with the one preceding chemisorption measurements. After in situ EXAFS experiments of the reduced catalyst (under 100 kPa H_2) the cell was evacuated at 573 K for 1 h. After the sample was cooled under vacuum (10^{-2} Pa) to room temperature it was exposed to 100 kPa of CO and the EXAFS spectrum was again recorded in situ.

Results and Discussion

The H_2 and CO adsorption isotherms, determined at 298 K, of the bare support and the catalyst are shown in Figure 1. Following the method of Benson and Boudart[16] one obtains the total amount of chemisorbed H atoms and CO
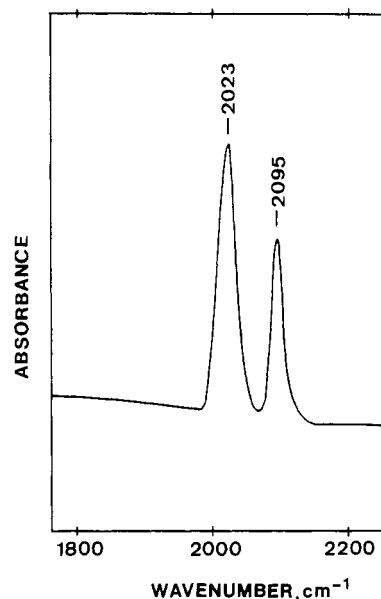
molecules by extrapolating the linear higher-pressure region of the isotherm of the catalyst to zero pressure and correcting for the extrapolated value of the bare support. The measurements result in a H/Rh ratio of 1.7 and a CO/Rh ratio of 1.9, indicating a highly dispersed system. H/Rh and CO/Rh values higher than 1 on Rh/Al$_2$O$_3$ catalysts have been observed previously[17,18] and are explained by multiple adsorption.

Figure 2 shows the 2200–1800-cm^{-1} region of the infrared spectrum of CO adsorbed on the 0.57 wt % Rh/Al$_2$O$_3$ catalyst divided by the spectrum of the reduced and evacuated catalyst. One can see only two infrared bands at 2095 and 2023 cm^{-1} which are assigned to the symmetrical and antisymmetrical stretching frequencies of the Rh(CO)$_2$ species. Again this result is an indication of having a highly dispersed catalyst and is in accordance with the results of Cavanagh[3] on a 0.2 wt % Rh/Al$_2$O$_3$ catalyst and of Worley[2] and Yates[6] on a 0.5 and a 1.0 wt % Rh/Al$_2$O$_3$ catalyst.

Figure 3a shows the oscillatory EXAFS function $\chi(k)$ as a function of wavenumber k of the rhodium K edge of the reduced catalyst. The oscillations are characteristic for rhodium neighbor atoms. A careful data analysis[19] has shown that the main part of the spectrum can be attributed to the first Rh–Rh coordination shell with an interatomic distance of $r = 2.65 \pm 0.01$ Å and an average coordination number of $N_a = 5.0 \pm 0.5$. The coordination distance shows a contraction in comparison with the bulk value ($r = 2.69$ Å). This, in combination with the low coordination number, indicates a highly dispersed catalyst. However, on the basis of these EXAFS results alone one cannot distinguish between (a) a form of dispersion consisting of a mixture of rhodium metal crystallites and isolated Rh^0 atoms and/or Rh^{n+} ions and (b) a homogeneous form of dispersion in which only rhodium metal crystallites are present. The obtained average coordination number (N_a) is a product of the fraction (f) of the total number of rhodium atoms which is present in metal crystallites and the average coordination number (N_c) of rhodium atoms in the metal crystallites ($N_a = fN_c, f \neq 1$

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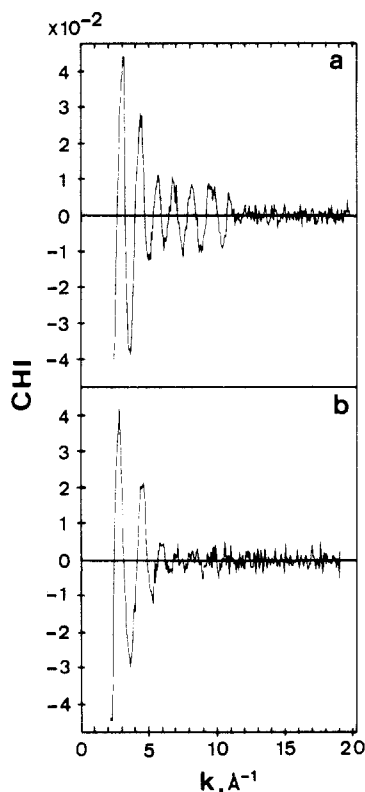
Figure 3. The normalized EXAFS oscillations $\chi(k)$ vs. k (measured at 140 K): (a) reduced catalyst (100 kPa H_2); (b) CO adsorbed catalyst (100 kPa CO).

for model a and $f = 1$ for model b. If we assume that the rhodium metal particles have a face-centered cubic structure, N_c is smaller than 12 and the fraction of isolated rhodium atoms and/or rhodium ions $(1 - f)$ must be smaller than 0.58. From TPR results we known that all rhodium has been reduced. Consequently no isolated Rh^{n+} ions can be present. On the other hand, isolated Rh^0 (d^9) atoms on the 0.57 wt % Rh/Al_2O_3 catalyst could not be detected by ESR.[20] We therefore exclude model a and conclude that the reduced 0.57 wt % Rh/γ-Al_2O_3 catalyst is highly and homogeneously dispersed with metallic rhodium particles consisting of 15–20 rhodium atoms.[6-8,11]

After CO adsorption at room temperature the amplitude of the EXAFS oscillations above $k = 5$ Å^{-1}, typical for the Rh–Rh metal coordination, has significantly decreased as is shown in Figure 3b. The remaining part of the spectrum is caused by rhodium–carbonyl bonds.

This result clearly shows the dramatic influence of CO adsorption on the highly dispersed Rh/Al_2O_3 catalyst. A disruption of rhodium–rhodium metallic bonds takes place as a result of the chemisorption of CO molecules. Such a disruption is understandable when considering the bond energies of Rh–Rh and Rh–CO bonds. With an Rh–Rh bond energy of $533/12 = 44.5$ kJ and an Rh–CO bond energy of 185 kJ,[21] one calculates that rhodium particles with an average coordination number below $185/44.5 = 4.2$ might be susceptible to disruption. In view of the many assumptions underlying such a calculation it is not too disturbing to observe experimentally that a cluster with an average coordination number of 5 shows disruptions on CO adsorption.

Changes of a highly dispersed Rh/Al_2O_3 catalyst caused by CO adsorption have also been observed by Yates and
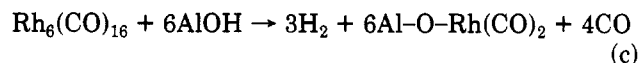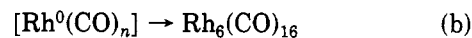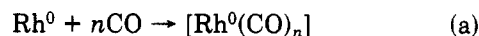
co-workers.[6] They observed a sintering of the rhodium after adsorption of CO and a subsequent reduction at low temperature and assigned it to increasing mobility of rhodium atoms on which CO is adsorbed.

There are two possible ways to explain the effect of CO adsorption: either the Rh–Rh distances in the resulting cluster have increased and have a too large spread to see any EXAFS oscillations at higher k value, or the $Rh(CO)_2$ species are indeed rather far apart on the support. In view of the mild conditions under which the small metal particles have been treated we prefer the former explanation in which the metal cluster expands under the influence of CO. This hypothesis has been proposed before by Yates et al.[7] who called it the theory of the "breathing raft".

From the EXAFS results one cannot directly tell whether the oxidation state of Rh in the $Rh(CO)_2$ species is zero or 1+. However, if the oxidation state is 1+ the adsorption of CO has to be oxidative. If the support is not dehydroxylated completely the following overall reaction can be considered:

$$2Rh + 4CO + 2AlOH \rightarrow H_2 + 2Al-O-Rh(CO)_2$$
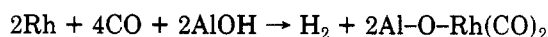
This reaction is not entirely speculative because it can be thought of as a summation of three reactions which are known in literature:[22,23]

$$Rh^0 + nCO \rightarrow [Rh^0(CO)_n] \qquad (a)$$

$$[Rh^0(CO)_n] \rightarrow Rh_6(CO)_{16} \qquad (b)$$

$$Rh_6(CO)_{16} + 6AlOH \rightarrow 3H_2 + 6Al-O-Rh(CO)_2 + 4CO \qquad (c)$$

The "$Rh^0(CO)_n$" species can polymerize to small Rh_4 or Rh_6 clusters when the CO/H_2O ratio is high, whereas at low CO/H_2O ratio sizeable metallic particles will be formed.[23] Reaction c has been proposed as a possible explanation for the formation of rhodium(I)–carbonyl species from surface OH groups and $Rh_6(CO)_{16}$ by Smith et al.[22]

In conclusion, the results of an EXAFS study of the K edge of a highly dispersed 0.57 wt % Rh/γ-Al_2O_3 catalyst show that the reduced system is highly dispersed, but not dispersed as rhodium atoms or ions. The metal crystallites consist of 15–20 rhodium atoms. This demonstrates that there is no fundamental difference between reduced Rh/Al_2O_3 catalysts with low Rh loading and those with high Rh loading. At all loadings rhodium metal crystallites are present on the support surface. Only the size and morphology of these crystallites vary with Rh loading. Adsorption of CO at room temperature on the 0.57 wt % Rh/γ-Al_2O_3 catalyst results in a significant disruption of the Rh crystallites, ultimately leading to isolated rhodium dicarbonyl species. This is confirmed by our CO infrared observations.

The results of this study explain the seeming contradiction between the results obtained from infrared studies and those obtained from high-resolution electron microscopy. This contradiction is only apparent because as our EXAFS measurements prove CO adsorption changes the system completely. After reduction and before CO admission there are small Rh crystallites present, whereas after CO admission there are isolated $Rh(CO)_2$ species present on the support. The presented evidence for a large difference in structure between a Rh catalyst before and after adsorption of CO might not be an isolated case, but

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might be an example of a more general phenomenon of a drastic change in catalyst structure upon adsorption of an adsorbate. Such cases might especially be expected for adsorbates which adsorb with large heats of adsorption on small catalyst crystallites.

Registry No. Rh, 7440-16-6; CO, 630-08-0.