

An EXAFS Study on the Influence of CO Absorption on the Structure of Small Rhodium Clusters Supported on γ -Al₂O₃ or TiO₂

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INTRODUCTION

Controversies exist in literature about the structure and oxidation state of highly dispersed Rh/Al₂O₃ catalysts. Some authors conclude on the basis of CO infrared data that rhodium monatomically dispersed as Rh¹⁺ ions (1-3). However, electron microscopy studies shows the presence of small metallic rhodium particles (4-5).

The carbon-oxygen stretching frequency of CO chemisorbed on Rh/Al₂O₃ (1-3) and Rh/TiO₂ (6) have been extensively studied by infrared spectroscopy. One surface species consisting of two CO molecules bound to one surface rhodium (bands at 2095 and 2027 cm⁻¹, representing the symmetrical and anti-symmetrical modes, respectively) is solely present on catalysts with a low rhodium loading. This surface species is assigned to CO adsorbed on isolated Rh¹⁺ cations (3), since the wavenumbers closely correspond to those observed for the bridged [Rh¹⁺(CO)₂Cl]₂ dimer and do not shift in frequency with increasing coverage. At high rhodium loadings two CO bands are observed, one around 2060 cm⁻¹ and another broad band between 1800 and 1900 cm⁻¹. The former band has been interpreted as arising from a CO molecule on top of a rhodium surface atom of a metal crystallite with the latter broad band due to a CO molecule bridged between neighbouring Rh surface atoms (3).

Rh/Al₂O₃ catalysts with low rhodium loading showing solely the rhodium dicarbonyl species have been studied with electron microscopy also. However, these studies showed the presence of small metallic rhodium particles. To clarify these contradicting results our group performed EXAFS studies on the influence of CO chemisorption on the topology of small rhodium clusters supported on γ -Al₂O₃ (7,8,9) and on TiO₂ (10). In this paper we will summarize the results and discuss the influence of the support and the cluster-size on the type of species which are formed during CO chemisorption.

EXPERIMENTAL

The preparation of a 0.6 wt% Rh/ γ -Al₂O₃, a 1 wt% Rh/ γ -Al₂O₃ and a 1 wt% Rh/TiO₂ has been extensively described in (8), (9) and (10) respectively. All catalysts were prepared by incipient wetting of high surface area supports with an aqueous solution of RhCl₃, dried and subsequently reduced under flowing H₂ at high temperature.

Hydrogen chemisorption measurements resulted in H/M values of 1.7, 1.65 and 1.5 for the Rh(0.6)/Al₂O₃ (8), Rh(1)/Al₂O₃ (9) and Rh(1)/TiO₂ (10), respectively.

EXAFS spectra of the rhodium K-edge were recorded in-situ at liquid nitrogen temperature on X-ray beamline I-5 at S.S.R.L., Stanford University with ring energies of 3 GeV and ring currents between 40-80 mA.

RESULTS AND DISCUSSION

The EXAFS spectrum of the reduced Rh(0.6)/Al₂O₃ catalyst shows oscillations due to rhodium nearest neighbours (7), which proves the existence of rhodium metal crystallites. The Rh-Rh coordination parameters as given in table I for the reduced catalyst were obtained by making use of rhodium-rhodium phase- and amplitude corrected Fourier transforms (11).

Table I Coordination parameters (N numbers, R distance, $\Delta\sigma^2$ Debye Waller Factor, difference with reference compound) for the 0.6 wt% Rh/ γ -Al₂O₃ catalyst. (Accuracies N \pm 10 - 20%, R \pm 0.5 - 1%, $\Delta\sigma^2$ \pm 10-30%)

TREATMENT	COORDINATION	Rh(0.6)/ γ -Al ₂ O ₃		
		N	R	$\Delta\sigma^2$ x10 ⁻³
REDUCTION	RH-RH	3.7	2.68	5
ADMISSION OF CO AT 296 K	RH-RH	-	-	-
	RH-O	3.1	2.12	3
	$\overline{\text{Rh-(C=O)}}$	1.8	1.85	7
	$\overline{\text{Rh-(C=O)}}$	1.8	3.00	7

A 3 μ -thick rhodium metal foil was used as reference for the phase and back-scattering amplitude of a rhodium-rhodium absorber-scatterer pair. The Rh-Rh coordination number (N=3.7) points to very small metal crystallites.

Adsorption of CO at room temperature leads to a complete disappearance of the Rh-Rh EXAFS oscillations (7). This means that the metal-metal bonds in very small supported rhodium metal clusters are disrupted by CO adsorption at room temperature. The EXAFS results explain the seeming contradiction between the results obtained from CO infrared studies and from high-resolution Electron Microscopy. The EXAFS technique shows that this contradiction is only apparent, since CO adsorption changes the structure of the small metal clusters completely.

Analysis of the EXAFS spectrum obtained for the Rh(0.6)/Al₂O₃ after CO chemisorption has been carried out using phase corrected Fourier transforms with Rh₂O₃ as reference for the Rhⁿ⁺-O²⁻ and [Rh¹⁺(CO)₂Cl]₂ for the Rh-(C=O) absorber-scatterer pairs respectively (12). The results of the EXAFS data analysis, which is described in detail in (12), are summarized in table 1. It has been found that after CO chemisorption rhodium is coordinated by two CO molecules. The coordination distances between rhodium and the carbon-oxygen ligands of the carbonyl group are equal to the distances as found in the Rh(CO)₂Cl monomer. A Rh-O coordination could also be analysed with three oxygen neighbours at a distance of 2.12Å. These oxygen neighbours arise most probably from the support, implying that the Rh(CO)₂ species is adsorbed to the support with three Rh-O bonds. A coordination distance of 2.12 Å points to a valence state of rhodium higher than 0 and lower than 3+ (R=2.05 Å for

Rh₂O₃). The infrared results strongly suggest a valence state 1+ for rhodium in this species, which is further supported by the results of XPS measurements (12).

EXAFS oscillations due to rhodium-rhodium bonds can still be detected after CO chemisorption on rhodium particles with a notable size. This is illustrated in Fig. 1 for a Rh(1)/Al₂O₃ and a Rh(1)/TiO₂ catalysts.

The results of the data analysis carried out for the CO chemisorbed Rh(1)/Al₂O₃ (9) and Rh(1)/TiO₂ (10) catalysts are given in table II.

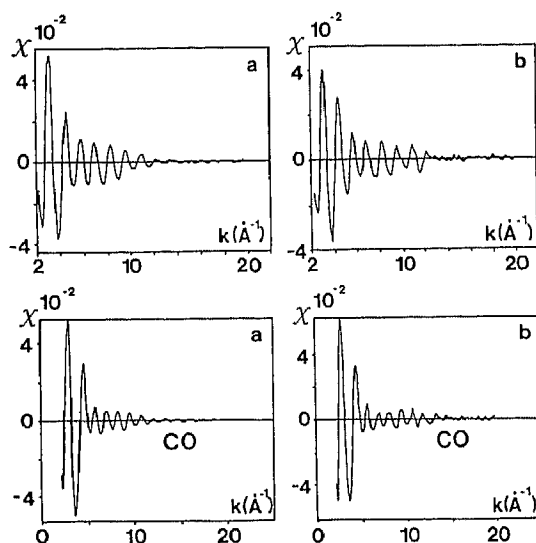


Figure 1 EXAFS spectra of Rh(1)/Al₂O₃ (a) and Rh(1)/TiO₂ (b) catalysts after reduction and after CO chemisorption at RT

Table II Coordination parameters (N number, R distance, $\Delta\sigma^2$ Debye Waller factor, difference with reference compound) for the 1 wt% Rh on γ -Al₂O₃ or TiO₂ catalysts. (Accuracies N \pm 10 - 20%, R \pm 0.5 - 1%, $\Delta\sigma^2$ \pm 10 \leq 30%)

TREATMENT	COORDINATION	Rh(1)/ γ -Al ₂ O ₃			Rh(1)/TiO ₂		
		N	R	$\Delta\sigma^2$ x10 ⁻³	N	R	$\Delta\sigma^2$ x10 ⁻³
REDUCTION	Rh-Rh	5.9	2.68	5	5.9	2.66	7.4
ADMISSION OF CO AT 296 K	Rh-Rh	1.6	2.68	4	1.6	2.68	4
	Rh-O	2.2	2.12	5	2.1	2.12	3
	Rh-(C=O)	1.5	1.85	5	1.5	1.83	4
	Rh-(C=O)	1.5	3.00	5	1.5	3.00	5

An EXAFS function for the CO chemisorbed Rh(1)/TiO₂ sample has been calculated (10) with the coordination parameters shown in table II using the phases and backscattering amplitudes obtained from the reference compounds. This function and its Rh-O phase corrected Fourier transform are given in Fig.2 with dotted lines. A good agreement exists as well as in k-space as in r-space between the experimental data and the results obtained from the data analysis.

The influence of the clustersize upon the formation of a specific surface species during CO chemisorption at RT is clearly demonstrated by our EXAFS results. The Rh¹⁺(CO)₂ is solely created on very small clusters. Rhodium catalysts with a somewhat lower dispersion still showed the presence of some metallic rhodium crystallites after CO chemisorption. Apparently, the larger particles present in these catalysts cannot be broken up by CO adsorption. These particles give rise to the linear and multicentre Rh-CO species as mentioned in the introduction.

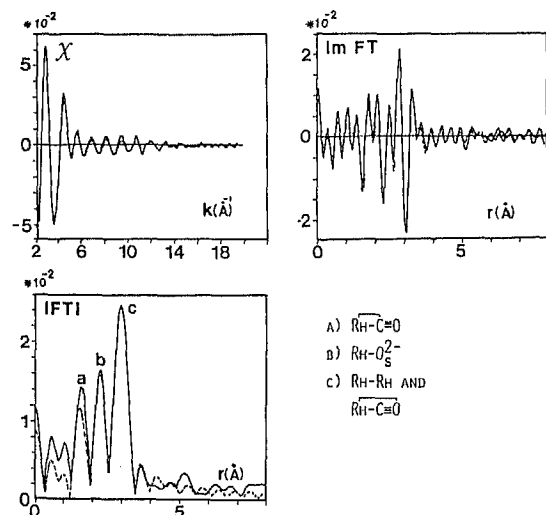


Figure 2 Experimental EXAFS data (solid line) and calculated EXAFS₀(Rh-C≡O+ Rh-O+Rh-Rh) (dotted line) and corresponding transforms (k⁰, Rh-O phase corr, k_{min}⁰=3.4 Å⁻¹, k_{max}⁰=9.2 Å⁻¹) for Rh(1)/TiO₂ catalyst

The structure of the surface Rh¹⁺(CO)₂ can be directly derived from the coordination parameters as given in Table I. However, the coordination numbers for the Rh¹⁺(CO)₂ species found in Table II are averaged over all rhodium atoms and should be corrected for the amount of rhodium that remains metallic. Reversely, the fraction metallic rhodium can be estimated by using the fact that the real Rh-(C≡O) coordination number in the geminal dicarbonyl species is 2 and the expected coordination with support oxygen ion is 3. The fraction metallic rhodium is related to the real (N_R) and measured (N_m) coordination number by f=1-N_m/N_R. This fraction is found to be 25% for both the Rh(1)/Al₂O₃ and the Rh(1)/TiO₂ catalysts using the values given in Table II.

The coordination distance for the Rh-O_s (O_s support oxygen) bond is the same for γ-Al₂O₃ and TiO₂ supported catalysts. Also the Rh-(C≡O) coordination is not influenced by the support, indicating that also on TiO₂ the ad-

sorption of CO has to be oxidative leading to Rh^{1+} valence state. In summary, the support determines the particle size distribution, which in turn influences the amounts of geminal dicarbonyl and linear/multicentre CO species formed during CO adsorption.

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