

An EXAFS Study of the Influence of CO Chemisorption on the Structure of Highly Dispersed Rh/TiO₂ catalysts.

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Abstract.

EXAFS measurements have been performed on the Rh K-edge of two highly dispersed Rh/TiO₂ catalysts containing 0.54 and 1.04 wt% rhodium. The structural properties of the rhodium metal crystallites have been determined after reduction and after CO chemisorption.

After reduction with H₂ at 473 K in an in-situ EXAFS sample cell the X-ray absorption spectrum showed oscillations typical for Rh-Rh metal coordination. This proved that rhodium was present as metal crystallites. By applying a special data analysis procedure the Rh-Rh EXAFS contributions could be separated from the experimental data. Further analysis of the resulting difference spectrum gave evidence for rhodium - oxygen bonds, involving interfacial zero valent rhodium atoms and oxygen anions of the support. A small fraction of non reduced RhCl₃ could also be detected in the difference spectrum.

Evacuation at 473 K and subsequent CO adsorption at room temperature on both catalysts led to a significant decrease of the rhodium-rhodium EXAFS oscillations. Data analysis showed the formation of rhodium geminal dicarbonyl species, which are bonded to three oxygen anions of the TiO₂ support. The Rh¹⁺ - O²⁻ distance in these species was found to be 2.12 ± 0.02 Å

Introduction.

The structure and oxidation state of rhodium in highly dispersed rhodium catalysts determines its catalytic activity and selectivity (1, 2, 3). Several techniques have been used to characterize such

highly dispersed supported rhodium catalysts (4-11). Electron microscopy studies (4,5) have shown that on γ -Al₂O₃ rhodium is present as small metal crystallites. On the other hand CO infrared spectra of ultra dispersed Rh/Al₂O₃ catalysts are characterized by two adsorption bands at 2095 and 2027 cm⁻¹, which correspond closely to those observed for the bridged {Rh¹⁺ (CO)₂Cl}₂ dimer and do not shift in frequency with increasing CO coverage. Several authors have therefore assigned these infrared bands to two CO molecules adsorbed on isolated Rh¹⁺ cations (6, 7, 8). Therefore, one may conclude that there is a controversy between the infrared results and the electron microscopy studies.

This seeming contradiction for the structure of highly dispersed Rh/Al₂O₃ catalysts has been explained by our recent EXAFS study (10). We observed that after reduction of an ultra dispersed Rh(0.5)/ γ -Al₂O₃ catalyst (H/Rh=1.7), EXAFS oscillations were present typical for Rh⁰-Rh⁰ metal coordination, thus proving the presence of rhodium metal crystallites. After CO admission at room temperature the rhodium-rhodium EXAFS oscillations disappeared completely. This implied that very small (d < 10 Å) rhodium metal particles supported on γ -Al₂O₃ are disrupted by the adsorbing CO molecules and are transformed into isolated rhodium dicarbonyl species. Analysis of the resulting EXAFS spectrum (11) showed that each rhodium is surrounded by two CO molecules and three oxygen ions of the support.

Although the structure of highly dispersed Rh/ γ -Al₂O₃ catalysts before and after CO adsorption seems well understood, much less is known about the state of rhodium on other supports. Infrared studies have shown that also on supports such as SiO₂ and TiO₂ after CO adsorption the two infrared bands at 2095 and 2027 cm⁻¹ are present, suggesting the formation of the Rh(CO)₂⁺ species. The relative amount of these CO infrared bands seems to be less on TiO₂ than on γ -Al₂O₃ (9). The influence of the support on the formation of these species has not been studied yet and has to be elucidated.

Because of this lack of knowledge we decided to study the state of rhodium on TiO₂ before and after CO adsorption with the EXAFS technique. The first aim of this study is to investigate the structural behaviour of small rhodium crystallites supported on TiO₂ during CO chemisorption at room temperature and to compare these findings with the properties of small rhodium crystallites supported on γ -Al₂O₃. The second aim concerns the metal-support interaction in Rh/TiO₂ catalysts. Because of the limited understanding of metal-support interaction

especially for a support as TiO_2 , we started with a structural investigation of the interface between the rhodium metal particles and the TiO_2 support.

Experimental.

Two Rh/ TiO_2 catalysts (0.54 and 1.04 wt%) were prepared by incipient wetting of a TiO_2 support (BET area $110 \text{ m}^2/\text{gram}$, pore volume = $0.6 \text{ cm}^3/\text{gram}$) with an aqueous solution of RhCl_3 aq. The catalysts were dried at 393 K for 20 hrs. and subsequently heated under flowing hydrogen to 473 K (heating rate 5 K min^{-1}) and further reduced for 1 hr. at the same temperature. Thereafter they were passivated.

Hydrogen chemisorption measurements were performed after reduction at 473 K using the procedure described in (11). H/Rh values of 1.8 and 1.5 were found for the 0.5 and 1 wt% Rh/ TiO_2 catalysts, respectively. These values indicate that both catalysts are ultra dispersed.

The passivated catalysts were pressed into a thin self supporting wafer and mounted in our in-situ EXAFS cell (12). The thickness of the wafer was chosen to give a ratio of incident to transmitted intensity of 5. Reduction was carried out under flowing H_2 for 1 hr. at 473 K. (Heating rate 5 K min^{-1}). The sample was then cooled down to room temperature under flowing H_2 and EXAFS measurements were performed with the catalysts exposed to 100 kPa of static hydrogen. After these in-situ EXAFS experiments of the reduced catalysts the EXAFS cell was evacuated at 473 K for 2-hrs. After cooling to room temperature and exposing the samples to 100 kPa CO EXAFS spectra were recorded in-situ once again.

EXAFS spectra of the rhodium K-edge were recorded in-situ at 90 K on X-ray beamline I-5 at the Stanford Synchrotron Radiation Laboratory (S.S.R.L.) with ring energies of 3 GeV and ring currents between 40-80 mA.

Data Analysis and Results.

A cubic spline background subtraction starting at 20 eV above the edge (13) has been used to extract the EXAFS oscillations from the X-ray absorption spectrum. The EXAFS spectra are smoothed by removing high frequency components (noise) via Fourier filtering. We have shown (14) that the use of normal Fourier transforms and fitting in k-space is

insufficient to determine the smaller oscillations from other atoms (e.g. support oxygen), whose frequencies are close to the main frequency of the metal-metal coordination. In this paper we will make use of phase and/or amplitude corrected Fourier transforms to separate the Rh-Rh coordination from other contributions. Information about phase and backscattering-amplitude has been obtained from EXAFS measurements on reference compounds.

A. Reduced Catalysts

Fig.1 presents the EXAFS oscillations in k-space of the 0.5 and 1 wt% Rh/TiO₂ catalysts reduced at 473 K. The analysis of the EXAFS data of the Rh(1)/TiO₂ catalyst will be shown in full detail. The same procedure has been used for the Rh(0.5)/TiO₂ catalyst. The EXAFS has been Fourier transformed to r-space over a k-range from 3.3 to 10.7 Å⁻¹ (Fig.2).

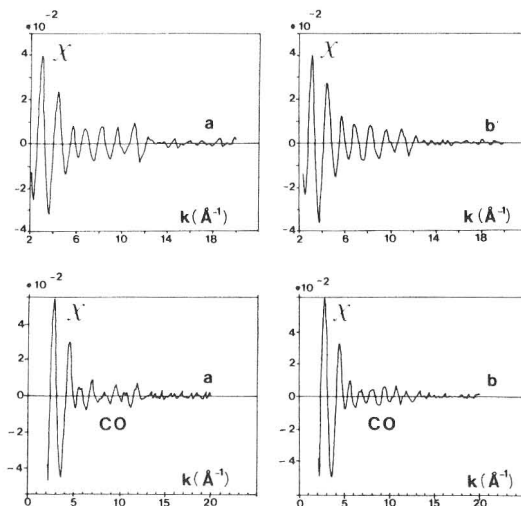


Fig.1 EXAFS spectra of the 0.5 (a) and 1 (b) wt% Rh/TiO₂ catalysts after reduction at 473 K and after CO adsorption at roomtemperature.

The transforms are k^1 -weighed and corrected for the Rh-Rh phase and backscattering-amplitude. Reliable data for phase and backscattering-amplitude have been obtained from measurements on rhodium foil (14). A Fourier transform of an EXAFS spectrum, which belongs to a single Rh-Rh phase and amplitude should give a single symmetrical peak

localised at the actual coordination distance. It can be seen in Fig.2 that the peak is not symmetrical and that extra contributions in the R-region between 1Å and 2Å are present.

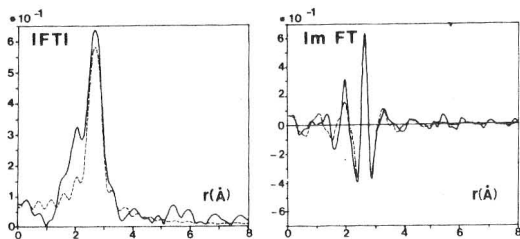


Fig.2 Fourier transform (k^1 , Rh-Rh phase and amplitude corr., $k_{min}=3.3 \text{ \AA}^{-1}$, $k_{max}=10.7 \text{ \AA}^{-1}$) of experimental EXAFS data (solid line) and calculated Rh-Rh EXAFS (dotted line) for Rh(1)/TiO₂ (|FT|:magnitude of transform Im FT:imaginary part of transform)

The Rh-Rh EXAFS is now separated from the experimental data by calculating with first guess parameters a Rh-Rh EXAFS function with the aid of the experimentally determined Rh-Rh phase and amplitude. This EXAFS function is subtracted from the experimental data and the residual spectrum is transformed. The Rh-Rh parameters used for the calculation are adjusted until the frequency components of the Rh-Rh coordination in the imaginary part of the transform of the residual spectrum (Rh-Rh phase corrected) have disappeared completely. Parameter values for the Rh-Rh coordination as given in table 1 for both catalysts were obtained using this criterion. The Fourier transform of the Rh-Rh EXAFS calculated with these parameters is shown in Fig.2.

Treat- ment	Coordi- nation	Rh(0.5)/TiO ₂			Rh(1)/TiO ₂		
		N	R	$\Delta\sigma^2$ $\times 10^{-3}$	N	R	$\Delta\sigma^2$ $\times 10^{-3}$
Reduction at 473 K	Rh-Rh	4.4	2.66	5.3	5.9	2.66	7.4
	Rh-O	2.0	2.72	0	1.6	2.72	0
	Rh-Cl	0.3	2.31	0	0.5	2.31	0
Admission of CO at 296 K	Rh-Rh	1.1	2.68	4	1.6	2.68	4
	Rh-O	2.5	2.10	3	2.1	2.12	3
	Rh-(C=O)	1.7	1.85	4	1.5	1.83	4
	Rh-(C=O)	1.7	3.00	5	1.5	3.00	5

Table 1: Coordination parameters (N:number, R:distance, $\Delta\sigma^2$:Debye Waller factor, difference with reference compound) for the 0.5 and 1 wt% Rh/TiO₂ catalysts (Accuracies: N:10-20%, R:0.5-1%, $\Delta\sigma^2$:10-30%)

The identity of the scatterer responsible for the differences between the Fourier transforms of the experimental and calculated Rh-Rh EXAFS has been further investigated by applying a Fourier transform (corrected for the phase of a rhodium-oxygen absorber-scatterer pair) on the residual spectrum (experimental EXAFS-calculated Rh-Rh EXAFS) (cf. Fig.3).

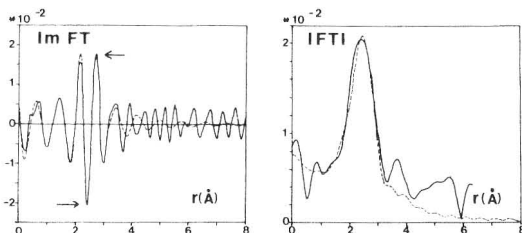


Fig.3 Fourier transform (k^1 , Rh-O phase corr., $k_{min}=4 \text{ \AA}^{-1}$, $k_{max}=10 \text{ \AA}^{-1}$) of difference spectrum (solid line) and calculated Rh-O + Rh-Cl EXAFS (dotted line) for Rh(1)/TiO₂.

The Rh-O phase has been obtained from EXAFS measurements on Rh₂O₃ (14). The imaginary part of the Fourier transform for the Rh(1)/TiO₂ catalyst peaks both positively and negatively at positions which are indicated in Fig.3. Since the phase function of a Rh-Cl pair differs approximately π radians from the phase function of a Rh-O absorber scatterer pair, one should analyse the difference spectrum in terms of both Rh-Cl and Rh-O coordinations. Backtransformation of Fig.3 ($r_{min} = 1.2$, $r_{max} = 3.5$) to k -space gives an EXAFS signal, which can be fitted with the parameters as given in table 1. Information about phases and back-scattering amplitudes of Rh-O and Rh-Cl pairs has been obtained from EXAFS measurements on Rh₂O₃ and RhCl₃ (14). The reliability of the Rh-O and Rh-Cl parameters found by the fitting procedure in k -space has to be checked by comparing the Fourier transform of the difference spectrum with the transform of the Rh-O+Rh-Cl EXAFS function calculated with the parameters given in table 1. The same procedure has been applied to the Rh(0.5)/TiO₂ catalyst leading to the parameters given in table 1.

As a final check for the reliability of the Rh-Rh, Rh-O and Rh-Cl parameters derived in this work the calculated EXAFS functions of the three coordinations have been added and transformed. The equivalence of the total EXAFS function and its transform with those of the corresponding experimental data can be seen in Fig.4 for the Rh(1)/TiO₂ catalyst. The results for the Rh(0.5)/TiO₂ catalyst are similar.

Fig.5 gives the k^3 -weighed Fourier transform (Rh-O phase corrected, $k_{\min} = 3.4$, $k_{\max} = 9.2$) of the experimental EXAFS data of CO adsorbed Rh(1)/TiO₂ catalysts. Three peaks can be distinguished. Peak A is mainly caused by Rh-C coordination and peak C is partly due to Rh-O coordination of the adsorbed carbonyl species(15). The other part of peak C belongs to rhodium-rhodium coordination present in the crystallites, which are not or only partially disrupted by the chemisorption of CO (15). The fraction of rhodium involved in the rhodium-oxygen bonds between the metal particles (still left after CO chemisorption) and the support is very low. This means that peak B must originate from a bond between the Rh(CO)₂ species and the support. Since the slope of the phase functions of Rh-O and Rh-C hardly differ, the R-values in Fig.5 belonging to Rh-O and Rh-C coordinations correspond with real distances.

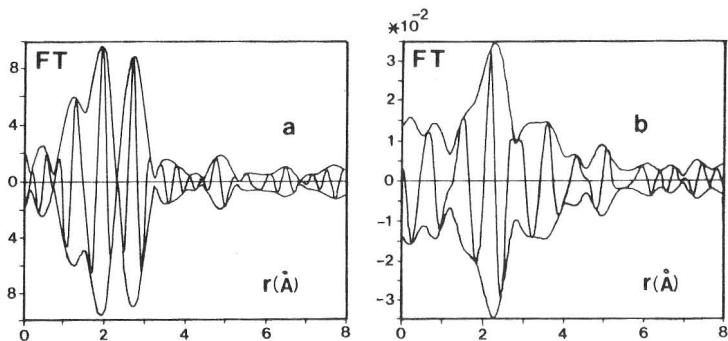


Fig.6 Fourier transform ($k_{\min}=3.4 \text{ \AA}^{-1}$, $k_{\max}=9.2 \text{ \AA}^{-1}$)

- a) $\text{EXAFS}_{\text{exp}}^3 - \text{EXAFS}_{\text{calc}}(\text{Rh-C}\equiv\text{O})$
(k^3 , Rh-Rh phase and amplitude corr.)
- b) $\text{EXAFS}_{\text{exp}} - \text{EXAFS}_{\text{calc}}(\text{Rh-C}\equiv\text{O}) - \text{EXAFS}_{\text{calc}}(\text{Rh-Rh})$
(k^1 , Rh-O phase corr.)

The imaginary part of the Fourier transform between 1.2-1.8 Å (cf. fig.5) belongs only to the Rh-C absorber-scatterer pair. Parameters for the Rh-C≡O coordination are found by calculating an EXAFS using

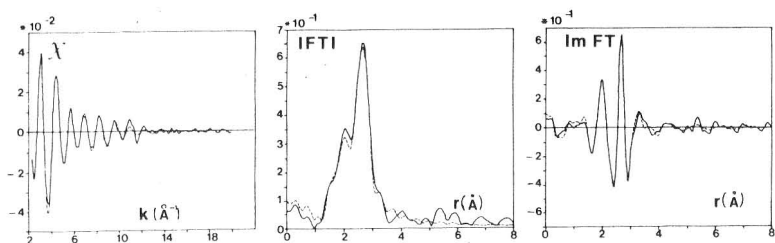


Fig.4 Experimental EXAFS data (solid line), calculated EXAFS (Rh-Rh + Rh-O + Rh-Cl) (dotted line) and corresponding Fourier transforms (k^1 , Rh-Rh phase and amplitude corr., $k_{\min}=3.3 \text{ \AA}^{-1}$, $k_{\max}=10.7 \text{ \AA}^{-1}$) for Rh(1)/TiO₂

.B. CO adsorption at room temperature

The influence of CO adsorption at room temperature on the EXAFS spectrum of the reduced catalysts can be seen in Fig.1. The amplitude of the EXAFS oscillations above $5-6 \text{ \AA}^{-1}$, typical for a rhodium-rhodium coordination has decreased, directly demonstrating that at least part of the Rh-Rh bonds have been disrupted by CO adsorption. We will apply the same method of analysis on the EXAFS data of the CO chemisorbed Rh/TiO₂ catalysts as was used for the corresponding Rh/Al₂O₃ system (11) (15). Infrared measurements on highly dispersed Rh/TiO₂ catalysts resulted in the same infrared bands as obtained on the [Rh(CO)₂Cl]₂ dimer. As EXAFS reference data for the geminal dicarbonyl species Rh(CO)₂ we use therefore EXAFS measurements on [Rh(CO)₂Cl]₂ from which the Rh-Cl contributions are subtracted.

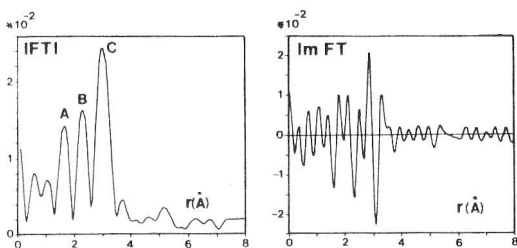


Fig.5 Fourier transform (k^3 , Rh-O phase corr., $k_{\min}=3.4 \text{ \AA}^{-1}$, $k_{\max}=9.2 \text{ \AA}^{-1}$) of experimental EXAFS data of CO adsorbed Rh(1)/TiO₂ catalyst

the phase and backscattering amplitude of the geminal dicarbonyl reference sample. This calculated EXAFS should have an overlap in the imaginary part of its transform between 1.2 and 1.8 Å with the corresponding transform of the experimental data. The optimized parameter values for the Rh-(C≡O) coordination are given in table 1 for both catalysts.

After subtraction of the calculated Rh-(C≡O) contribution from the experimental EXAFS data, the Rh-Rh contribution can be determined by applying a Rh-Rh phase and amplitude corrected Fourier transformation on the resulting difference spectrum (Fig.6a for Rh(1)/TiO₂). The imaginary part between 2.3 - 3.3 Å is characteristic for a Rh-Rh absorber-scatterer pair. The imaginary part peaks positively in the maximum of the magnitude of Fourier transform at R = 2.68 Å. The Rh-Rh parameter values are determined by fitting an EXAFS function in k-space obtained by inverse transformation of Fig.6a from r min = 2.3 to r max = 3.7 Å. The Rh-Rh parameters for both catalysts found by this procedure are given in table 1.

The scatterer responsible for the contribution between 1 - 2.3 Å in Fig.6a is found as follows. The sum of Rh-Rh and Rh-C≡O EXAFS signals calculated with the parameters as given in table 1 are subtracted from the experimental data. The k¹-weighed Rh-O phase corrected Fourier transform of the difference spectrum is shown in Fig.6 for the Rh(1)/TiO₂ catalyst. The imaginary part of the Fourier transform has a positive peak (R= 2.12 Å) at the maximum of the magnitude of the Fourier transform indicating the presence of an oxygen scatterer. Back-transformation (r min = 0.8, r max = 3.0 Å) and fitting in k-space resulted in Rh-O parameters, which are given in table 1.

As a final check for the CO adsorbed Rh(1)/TiO₂ catalyst the three EXAFS functions (Rh-C≡O, Rh-Rh and Rh-O) calculated with the parameters given in table 1 have been added. It can be seen in Fig.7 that this EXAFS function fits the experimental data. The imaginary part and magnitude of the associated k³ Fourier transform correspond within the limits of accuracy (cf. table 1) with the Fourier transform of the experimental data. The same results are obtained for the CO adsorbed Rh(0.5)/TiO₂ catalyst.

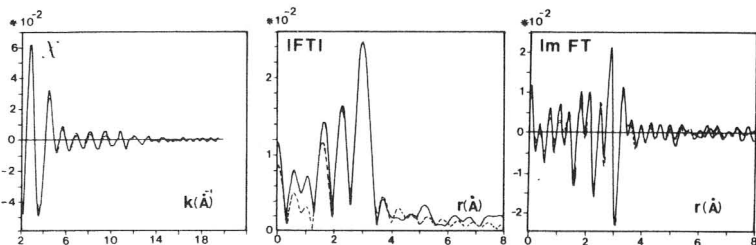


Fig.7 Experimental EXAFS data (solid line) and calculated EXAFS (Rh-C=O + Rh-O + Rh-Rh) (dotted line) and corresponding transforms (k^3 , Rh-O phase corr., $k_{min}=3.4 \text{ \AA}^{-1}$, $k_{max}=9.2 \text{ \AA}^{-1}$) for Rh(1)/TiO₂ catalyst

Discussion

The analysis of the EXAFS data obtained on the Rh/TiO₂ catalyst after in-situ reduction at 473 K gives evidence for the presence of a small fraction of non reduced RhCl₃, in agreement with the results of TPR₀ experiments (16). A Rh-O bond with a coordination distance of 2.72 Å is clearly present on both catalysts. This bond is similar to the bonds measured for Rh/γ-Al₂O₃ catalysts (14, 17). The Rh-O bond has been assigned to a coordination of rhodium atoms with oxygen anions of the support (radius of Rh-atom: 1.34 Å, of O²⁻ anion: ~1.4 Å). The measured number of oxygen neighbours for this Rh-O bond increases with decreasing coordination number of the rhodium metal-metal bond (see table 1), which also has been found for Rh/γ-Al₂O₃ catalysts (14). For three dimensional particles the fraction of metal atoms present in the interface between the metal particles and the support increases with decreasing particle size. This means that just like for Rh/γ-Al₂O₃ catalysts (11, 14) a two-dimensional raftlike structure (one atom layer) is excluded since in that case the support oxygen coordination number would be independent of the particle size.

It is possible to estimate the real number of support oxygen anions, which are on the average in contact with one interfacial rhodium atom. Assuming a half spherical shape for the rhodium particles, the average Rh-Rh coordination number can be related to the diameter d of the particle (14). Diameters of 8 and 10 Å are found for the 0.5 and 1 wt% Rh/TiO₂ catalysts, respectively. With the aid of the following relation (14): $N_R = N_M d/4R$ (N_R and N_M are the real and measured coordination numbers for the Rh-O bonds, R is the radius of a rhodium atom) the

number of support oxygen anions coordinating one interfacial rhodium metal atom is calculated to be about 3 for both catalysts.

The Rh-O bond of 2.72 Å is clearly much longer than the distance observed in rhodium metal oxide. Short oxide-like coordination distances have been detected with EXAFS (18) (19) and were supposed to be responsible for an interaction between the metal crystallites and the support. However, even EXAFS measurements on highly dispersed Rh/γ-Al₂O₃ catalysts (17) which were calcined at 623 K and fully reduced at 673 K did not lead to the detection of oxide-like distances. Combining the EXAFS results obtained in this work with the results of our other EXAFS studies (14, 17) we concluded that rhodium metal crystallites are not bound to γ-Al₂O₃ or TiO₂ supports (non SMSI conditions) via a coulombic rhodium-cation oxygen-anion interaction but via a Van der Waals type interaction.

The EXAFS data clearly show that most of the rhodium metal crystallites are broken up during CO adsorption at room temperature. However, the adsorption did not lead to a complete disappearance of the Rh⁰-Rh⁰ EXAFS oscillations. CO adsorption upon an ultra dispersed Rh(0.5)γ-Al₂O₃ catalyst {N (Rh-Rh) = 3.7} resulted in a complete disappearance of the EXAFS oscillations due to rhodium metallic bonds (11), whereas rhodium catalysts with a somewhat lower dispersion {N (Rh-Rh) = 5.3 and 5.9} still showed the presence of some metallic rhodium crystallites. Apparently, the larger particles present in these catalysts cannot be broken up by CO adsorption because the available adsorption energy is not high enough to break all rhodium-rhodium bonds.

The analysis of the structure of the rhodium species formed during CO adsorption is in agreement with the results obtained with I.R. measurements (9) and proves the information of RhCO₂⁺ species. The coordination numbers for the Rh(CO)₂⁺ species given in table 1 are averaged over all Rh atoms and should be corrected for the amount of rhodium that remains metallic. On the other hand, the real coordination number of rhodium in the geminal dicarbonyl species is 2 and the expected coordination with the support oxygen anions is 3 (11). Therefore, the fraction of the rhodium atoms which remains metallic can now be estimated. The real (N_R) and measured (N_M) coordination numbers are related to this fraction by $f = 1 - \frac{N_M}{N_R}$. Using the values given in table 1 for the Rh(CO)₂⁺ species this fraction is found to be 15% and 25% for the 0.5 and 1 wt% Rh/TiO₂, respectively.

The support does not influence the structure of the geminal dicarbonyl species formed during CO adsorption. The coordination distance for the Rh-O bond ($R=2.12 \text{ \AA}$) is the same for $\gamma\text{-Al}_2\text{O}_3$ and TiO_2 supported systems. This means that the valence state of the rhodium ion in the $\text{Rh}(\text{CO})_2$ species on TiO_2 is also $1+$ and that also on TiO_2 the adsorption of CO has to be oxidative. A mechanism for an oxidative adsorption has been suggested (11) as being due to dissociation of carbon monoxide. This mechanism is not directly influenced by the support which could also explain the support independent results. However, the support determines the particle size distribution which in turn influences the amounts of geminal dicarbonyl and linear/bridged CO species formed during CO adsorption.

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