

AN EXAFS STUDY OF PLATINUM - OXYGEN BONDS IN THE METAL-SUPPORT INTERFACE OF A HIGHLY DISPERSED Pt/ γ -Al₂O₃ CATALYST.

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EXAFS measurements have been performed on the Pt LIII-edge of a highly dispersed (H/M~1.14) Pt/ γ -Al₂O₃ catalyst, reduced at 673 K after calcination at the same temperature. After reduction an oxidic platinum oxygen bond (2.05 Å) is present with a very low average oxygen coordination number. This bond arises from a few not reduced platinum-oxide crystallites. Platinum oxygen bonds with a coordination distance of 2.65 Å could be detected significantly due to the high quality of the EXAFS data and the use of a new data analysis procedure. These bonds are interpreted to be originating from a coordination of the interfacial platinum atoms with the oxygen ions of the support.

1. INTRODUCTION

A still unresolved question regarding supported metal catalysts is the binding mechanism between a metal crystallite and the support. In the literature several models have been put forward for the structure of the metal-support interface. Interdiffusion of the metal-oxide with the oxidic support, the presence of low valence ions in the metal-support interface or a possible binding between zero-valent metal atoms of the metal cluster and the oxygen of the support are mentioned¹ as possible mechanisms for the metal-support interaction.

The EXAFS technique has been used to gain information about the metal-support interface because of its sensitivity to short range order. Our group² reported on EXAFS measurements on a 2.4 wt% Rh/Al₂O₃ catalyst reduced at two temperatures (473 and 673 K) after previous calcination at 623 K. Reduction at 473 K gives evidence for the presence of two types of Rh-O bonds. One Rh-O bond has a coordination distance of 2.05 Å, which is equal to the distance found in Rh₂O₃. This Rh-O bond disappears after reduction at 673 K. It is therefore very likely that the short oxide like distances reported in

literature (ref. 8-11 in²) as arising from the metal-support interaction are due to an incomplete reduction of the catalyst. The second Rh-O bond, detected at both reduction temperatures is similar to the bonds (R=2.7 Å) measured for Rh/Al₂O₃ catalysts^{1,3}, which are directly reduced at high temperatures without a preceding calcination step. From these results one has to conclude that in Rh/Al₂O₃ catalyst the structure of the metal-support interface consists of bonds between rhodium atoms and oxygen ions of the support with a bond length of about 2.7 Å.

In this paper we will report on an EXAFS study of the metal-support interface of a highly dispersed Pt/Al₂O₃ catalyst. The same data analysis procedure (making use of phase and amplitude corrected Fourier transforms) as was used for the EXAFS studies on the Rh/Al₂O₃ catalysts³ will be applied. This way of data analysis, the high dispersion of the Pt/Al₂O₃ catalysts and the high quality of the EXAFS data make it possible to separate the metal-support effects from those due to incomplete reduction.

2. EXPERIMENTAL

The 1.06 wt% Pt/ γ -Al₂O₃ catalyst was prepared

by wet impregnation of a $\gamma\text{-Al}_2\text{O}_3$ support with a known amount of $\text{Pt}(\text{NH}_3)_4(\text{OH})_2$, dried at 120°C and calcined in flowing oxygen at 673 K. Details of the preparation procedure are given in⁴. Hydrogen chemisorption measurements resulted in H/Pt = 1.14⁴.

The calcined catalyst was pressed into a thin (ratio of incident-to-transmitted intensity of about 5) self supporting wafer and mounted in a in-situ EXAFS cell⁵. Reduction was carried out under flowing H_2 at 673 K for 2hrs with the temperature being increased at a rate of 2.5K/min. The EXAFS spectra were recorded at 90 K with the catalyst exposed to 1 atm of static hydrogen.

3. DATA ANALYSIS AND RESULTS

EXAFS oscillations in k-space are obtained from the x-ray absorption spectrum by a cubic spline background subtraction followed by normalisation³. Reference compounds^{6,7} (Pt -foil and $\text{Na}_2\text{Pt}(\text{OH})_6$) are used to obtain phase and back-scattering amplitude functions (see Table 1)

TABLE 1

Reference compounds;
 n: weight factor of FT
 Δk : k-range of forward FT
 ΔR : R-range of backward FT
 R_{ref} and N_{ref} : coordination distance and number of first shell in reference.

Reference compound	k^n	$\Delta k(\text{\AA}^{-1})$	$\Delta R(\text{\AA})$	$R_{\text{ref}}(\text{\AA})$	N_{ref}
Pt-foil	k^3	2.46-20	1.94-3.3	2.77	12
$\text{Na}_2\text{Pt}(\text{OH})_6$	k^1	3.02-15	0-3.12	2.05	6

and are treated in the same way³. Fig. 1 presents the raw EXAFS oscillations in k-space of the reduced $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$ catalyst.

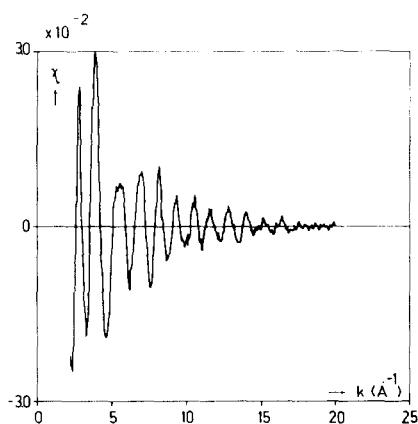


FIGURE 1
 Raw EXAFS spectrum of the 1.06 wt% $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst reduced at 673 K.

To compensate for EXAFS amplitude reduction at high K-values one normally uses a k^3 -weighted Fourier transform to obtain a radial Pt-Pt structure function. However, when using high weight factors the Fourier transform becomes less sensitive to contributions from oxygen, since low Z elements (like oxygen) have most scattering power at low k-values. Figure 2 shows the k^1 -weighted FT of the experimental EXAFS data which are first smoothed by removing noise (harmonic numbers higher than 200) via Fourier filtering. The main peak of the Fourier transform shows a complicated structure, which is partly due to interference of the Pt-Pt EXAFS with the oscillations caused by the presence of metal oxygen bonds. However, the most important contribution to this complicated structure arises from the k-dependent behaviour of the backscattering amplitude and the nonlinearities in the phase shift function of the Pt-Pt absorber-scatterer pair. This last contribution can be almost completely eliminated by using a Fourier transform (denoted by FT') which is corrected for the Pt-Pt phase shift and back-scattering amplitude. In a FT' the Pt-Pt coordi-

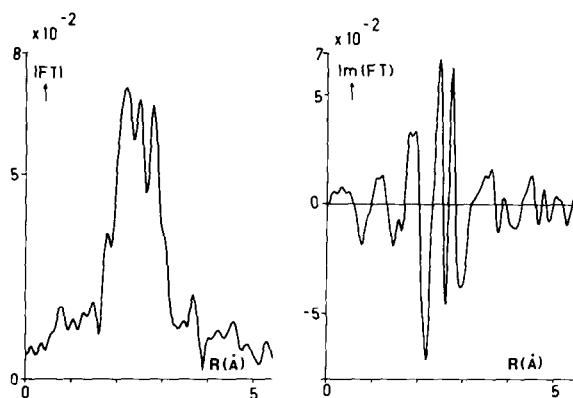


FIGURE 2
Fourier Transform (k^1 -weighted, $\Delta k=2.6-17.4 \text{ \AA}^{-1}$) of experimental EXAFS data.

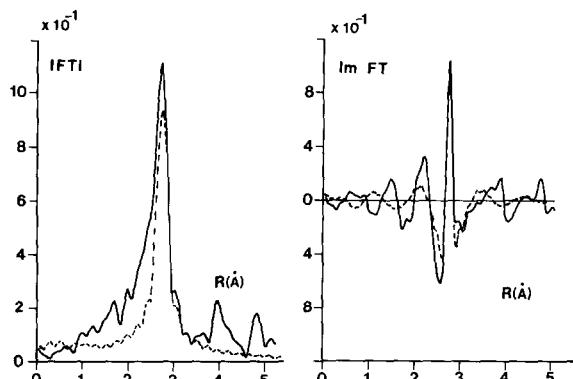


FIGURE 3
Fourier transforms (k^1 -weighted, $\Delta k=3.4-17.4 \text{ \AA}^{-1}$, Pt-Pt phase and amplitude corr.) of experimental EXAFS data (solid line) and calculated Pt-Pt EXAFS (dotted line) (see text).

nation will appear as a single symmetrical peak localised at the actual coordination distance so that metal oxygen bonds can more easily be identified. The solid lines in Figure 3 give the k^1 -weighted FT' (Pt-Pt phase and amplitude corrected) of the experimental EXAFS.

The Pt-Pt phase shift and backscattering amplitude have been obtained from EXAFS measurements

TABLE 2
Coordination parameters (N: number, R: distance, $\Delta\sigma^2$: Debye-Waller factor, difference with reference compound). Accuracies: N \pm 10-20% R \pm 0.5-1%, $\Delta\sigma^2 \pm$ 10-20%.

Pt(1.06)/ γ -Al ₂ O ₃				
Treat- ment	Coord- nation	N	R (\AA)	$\Delta\sigma^2$ $\times 10^3 (\text{\AA}^2)$
Reduct- ion at 673 K	Pt°-Pt°	5.2	2.765	3.3
	Pt ⁴⁺ -O ²⁻	0.35	2.05	0
	Pt°-O ²⁻ _S	1	2.65	0

on platinum foil⁶. Clearly visible are extra (platinum-oxygen) contributions in the R-region between 1 \AA and 2.5 \AA.

The Pt-Pt coordination parameters have been determined following the procedure extensively described in³. The results are given in Table 2. The k^1 -weighted FT' (Pt-Pt phase and amplitude corrected) of the Pt-Pt EXAFS calculated with these parameters is given in Figure 3 with the dotted lines.

To further determine the coordination parameters of the platinum-oxygen bonds the calculated Pt-Pt EXAFS is subtracted from the smoothed experimental data (see Figure 4a). A Fourier transform (corrected for the Pt-O phase shift^{6,7}) on this residual EXAFS spectrum shows that the imaginary part of this transform peaks in the maximum of its magnitude at two distinct R-values for $1.5 < R < 3 \text{ \AA}$ (see figure 4b, d). Peaks due to higher Pt-Pt coordination shells are also visible but will not be analysed in this paper. Back transformation to k-space of the Fourier transform presented in Figure 4 separates the contribution of the platinum oxygen bonds from that of the higher Pt-Pt coordination shells (see Figure 4c solid line). Fitting in k-space (see Figure 4c dotted line) (using phase shift and backscattering amplitude of $\text{Na}_2\text{Pt}(\text{OH})_6$ ^{6,7}) results in parameter values for the two different Pt-O coordinations (see Table 2). The reliability of these Pt-O para-

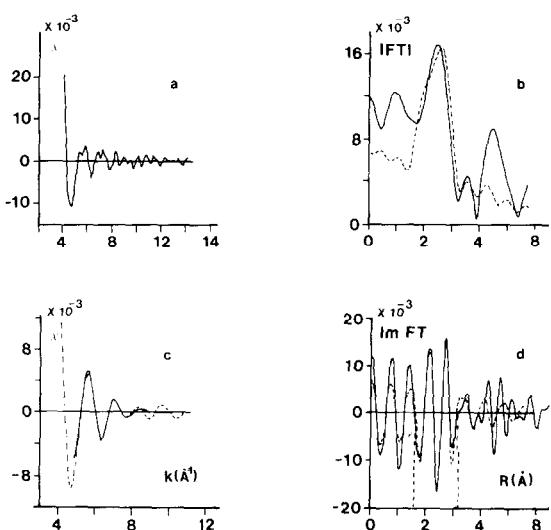


FIGURE 4
 a) Residual EXAFS spectrum (see text). Fourier transform (k^1 -weighted, $\Delta k = 4.3\text{-}9 \text{ \AA}^{-1}$, Pt-O phase corr.). Fourier transform (b: Magnitude, d: Imaginary part) of residual EXAFS spectrum (solid line) and calculated Pt-O coordinations (dotted line) (see text), c) EXAFS obtained after back transformation ($\Delta R = 1.6\text{-}3.3 \text{ \AA}$) (solid line) and best fit (dotted line).

meters has been checked by comparing the Fourier transform (Magnitude and Imaginary part) of the residual EXAFS spectrum with the Fourier transform of the Pt-O EXAFS function calculated with the Pt-O parameters given in Table 2 (Figure 4b, d dotted line). It can be seen in Figure 4 that within the R-region used for backtransformation to k-space both transforms are very similar.

4. DISCUSSION

The analysis of the EXAFS data on the 1.06 wt% Pt/ Al_2O_3 catalyst reduced at 673 K gives evidence for the presence of two types of Pt-O bonds. The Pt-O bond with a coordination of 2.05 Å is equal to the distance found in $\alpha\text{-PtO}_2$. The average measured coordination number is very low. A forthcoming paper⁶ will report on the change of the structure of this Pt/ $\gamma\text{-Al}_2\text{O}_3$ catalyst as a function of the reduction

temperature. Based upon these preliminary results, the very low average Pt-O coordination number found in this paper and the results obtained on the Rh/ Al_2O_3 catalysts¹⁻³, we conclude that the Pt-O bond with 2.05 Å originates from a few not reduced platinum-oxide crystallites.

The second Pt-O bond with a coordination distance of 2.65 Å is of a similar type as found for fully reduced Rh/ Al_2O_3 catalyst¹⁻³. This Pt-O bond will therefore be assigned to a coordination of the interfacial platinum metal atoms with support oxygen ions. This means that also for supported platinum catalysts the metal crystallites are not bound to the support via a platinum oxide layer with coulombic platinum-cation oxygen-anion interactions but via an interaction between the platinum metal atom (atomic radius ~1.38) and the oxygen anion (radius ~1.4 Å) of the support.

In conclusion, by applying a new data analysis procedure³ on EXAFS data of high quality it is possible to separate metal-support effects from those due to incomplete reduction. The results show that for supported platinum catalysts the metal-support interaction is possibly through an ion-induced dipole ($\text{O}^{2-}\rightarrow\text{Pt}^0$) interaction of the metal particle with the support.

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