An Extended X-ray Absorption Fine Structure Study of Rhodium-Oxygen Bonds in a Highly Dispersed Rhodium/Aluminum Oxide Catalyst

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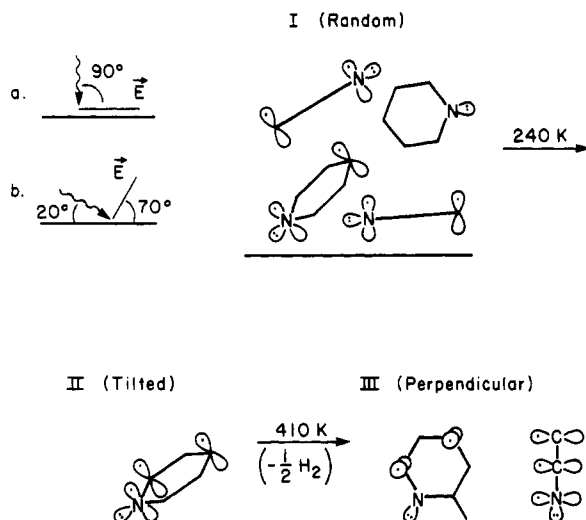**425** PUBLICATIONS **12,957** CITATIONS

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Figure 8. Proposed chemisorption states for pyridine on Pt(111). The diagrams on the left show the electric field direction that yield the NEXAFS spectra presented earlier. State I corresponds to Figure 4. State II corresponds to Figure 5 (assuming an unmixed state). State III corresponds to Figures 6 and 7.

is formed. Slowly at 240 K and more rapidly at higher temperatures the α C–H bond is cleaved and the pyridine is converted to an α pyridyl state characterized by the ring becoming perpendicular to the surface. This transformation may be reversible to an extent of approximately 10%.[26]

(26) It is interesting to note that for high coverages a pyridine desorption is evident at higher temperatures (~470 K) and thus disproportionation of the pyridine might be invoked to provide for a small degree of reversibility of the formation of the α pyridyl. More detailed thermal desorption studies and EELS results will be presented by Grassian, V. and Muetterties, E. L. (in preparation).

(27) The gas-phase 1s binding energy relative to the vacuum level of carbon in pyridine is not known but should be between 290.2 eV (C 1s for C_6H_6[28a]) and 293.5 eV (C 1s for HCN[28b]); the nitrogen 1s binding energy in pyridine is 404.9 eV.[28c] Resonances below the binding energy are bound-state resonances. For chemisorption states the onset of absorption corresponds to excitation to the Fermi level of the metal. Thus the region from the onset of absorption to the onset plus the work function are resonances below the photoemission threshold and correspond to the bound molecular resonances. The work function of pyridine covered Pt(111) for saturation coverage at 278 K is approximately 3 V.[13]

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An Extended X-ray Absorption Fine Structure Study of Rhodium–Oxygen Bonds in a Highly Dispersed Rh/Al₂O₃ Catalyst

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Analysis of in situ EXAFS measurements on a 2.4 wt % Rh/Al₂O₃ catalyst, reduced at 473 K after calcination at 623 K, shows the presence of two different rhodium–oxygen bonds (viz. 2.05 and 2.68 Å). The oxygen neighbors of rhodium at a distance of 2.05 Å disappear after reduction at 673 K. The coordination distance 2.05 Å is the same as found for Rh₂O₃ and indicates that this rhodium–oxygen bond is present due to incomplete reduction of the catalyst at 473 K. Rhodium–oxygen bonds with a coordination distance of 2.68 Å are present at both reduction temperatures. These bonds arise from a coordination of the interfacial rhodium atoms with the oxygen ions of the support. Assuming a half-spherical shape for the rhodium metal crystallites, numerical values for the average interfacial rhodium–oxygen coordination number (N = 2.5) and the crystallite diameter (d = 11 Å) are derived from the experimental EXAFS parameters.

Introduction

The interaction between metal crystallites and the support can have a significant influence on the catalytic behavior of a supported catalyst. Several models have been proposed for the structure of

the interface between the metal particle and the support. One model suggested that calcination of the catalyst before reduction is of importance to generate metal oxides which can interdiffuse with the oxidic support: Ni/SiO_2, Ni/Al_2O_3, and Co/Al_2O_3.[1–4]

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Other authors have emphasized that the presence of metal ions in the interfacial region is functional in the metal–support interaction, with these metal ions serving as anchors for the metal crystallite: Ru/SiO_2, Pt/Al_2O_3, and Pt/TiO_2.[5,6] Besson et al.[7] proposed that $Os_3(CO)_{12}$ clusters are bound to the silica support by means of an oxidative addition of supported hydroxyl groups to an Os–Os bond.

The extended X-ray absorption fine structure (EXAFS) technique has been used as a spectroscopic tool to gain information about the metal–support interface because of its sensitivity to short-range order. From EXAFS measurements on a 1 wt % Ru/SiO_2 catalyst, reduced at 673 K, Lytle et al.[8] attributed a peak in the magnitude of the Fourier transform to a Ru–O bond with a distance larger than the distance known from RuO_2 (2.03 Å). They claimed that this oxygen belonged to the support. Lagarde et al.[9] reported the presence of a Pt–O bond (the coordination distance being equal to the Pt–O distance in PtO_2) in a 1 wt % Pt/Al_2O_3 catalyst, which was reduced in situ at 753 K after calcination. The Pt–O bond was interpreted as arising from a metal–support interaction. Bassi et al. reported EXAFS measurements on a 0.2 wt % Au/MgO[10] and a 3.5 wt % Au/MgO[11] catalyst. Again, peaks in the magnitude of the Fourier transform were ascribed to Au–O bonds, which originated from a gold–support interaction.

Some questions have to be raised about the results mentioned above. The quality of some of the data is poor, and assignments were made only by comparing distances of peaks in the magnitude of the Fourier transform with those obtained from standard materials. In none of the above-mentioned cases was clear evidence given that these peaks originated from metal–oxygen bonds involved in a metal–support interaction.

Recently van Zon et al.[12] showed that a metal–support oxygen distance could be detected using EXAFS measurements on a highly dispersed and well-reduced catalyst. They studied a catalyst prepared by direct reduction in a flow reactor at 773 K followed by passivation at room temperature. Before the EXAFS measurements were carried out, the catalyst was rereduced at 773 K in an in situ EXAFS cell. By separating the Rh–Rh and Rh–support oxygen contributions from the data, they determined an Rh–O distance of 2.71 Å.

In this paper results of EXAFS measurements on a highly dispersed 2.4 wt % Rh/Al_2O_3 catalyst will be reported. This catalyst has been calcined at 623 K so that initially all rhodium was present in the oxidic state. EXAFS spectra were then measured after in situ reduction at low (473 K) and high (673 K) temperature. After reduction at 473 K, two Rh–O distances could be detected. One Rh–O distance was equal to the distance known from Rh_2O_3 (2.05 Å). Since this Rh–O distance disappeared after reduction at 673 K, it can be concluded that reduction at 473 K in the cell with preceding calcination at 623 K does not lead to a complete reduction of the catalyst. A Rh–O distance of 2.68 Å is present at both temperatures. Based upon the results of van Zon et al.,[12] this distance is assigned to a coordination of the interfacial rhodium atoms with the oxygen ions of the support. These results demonstrate that metal–support bonds can be analyzed in EXAFS data having a high signal-to-noise ratio but that
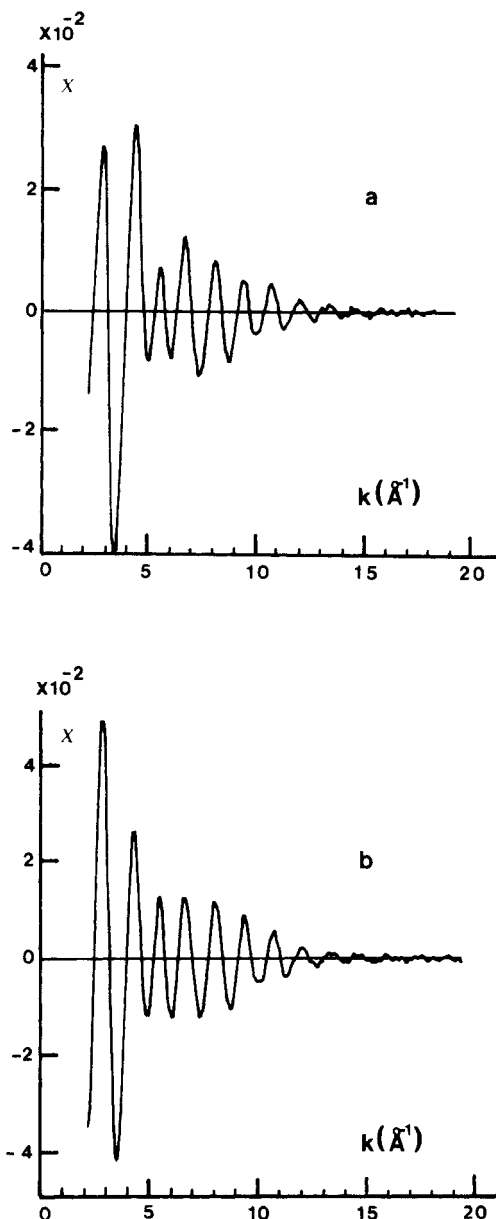

Figure 1. Raw EXAFS spectra of the 2.4 wt % Rh/Al_2O_3 catalyst: (a) T_{red} = 473 K; (b) T_{red} = 673 K.

care must be taken in the preparation of the catalyst and analysis of the data in order to separate the metal–support effects from those due to incomplete reduction.

Experimental Section

The 2.4 wt % Rh/Al_2O_3 catalyst was prepared by ion exchange on a γ-Al_2O_3 support with a solution of sulfate-free $Rh(NO_3)_3$. The support γ-Al_2O_3 (BET area of 194 $m^2 \cdot g^{-1}$) was obtained by heating boehmite (Conoco Catapal) at 723 K. The catalyst was dried in air at 383 K overnight to remove the adsorbed water and then calcined in flowing O_2 at 623 K for 2 h, after which it was stored for further use. Atomic absorption spectroscopy was used to determine the metal loading.

Hydrogen chemisorption was measured at room temperature after reduction at 473 K for 4 h, followed by outgassing at 473 K for 2–4 h. The sample was cooled under vacuum to room temperature, and hydrogen chemisorption was measured. The total absorption isotherm yields a dispersion of 1.2, assuming a H/Rh stoichiometry of 1. H/Rh values higher than 1 on Rh/ Al_2O_3 catalysts have been observed previously[13,14] and are explained by multiple adsorption.

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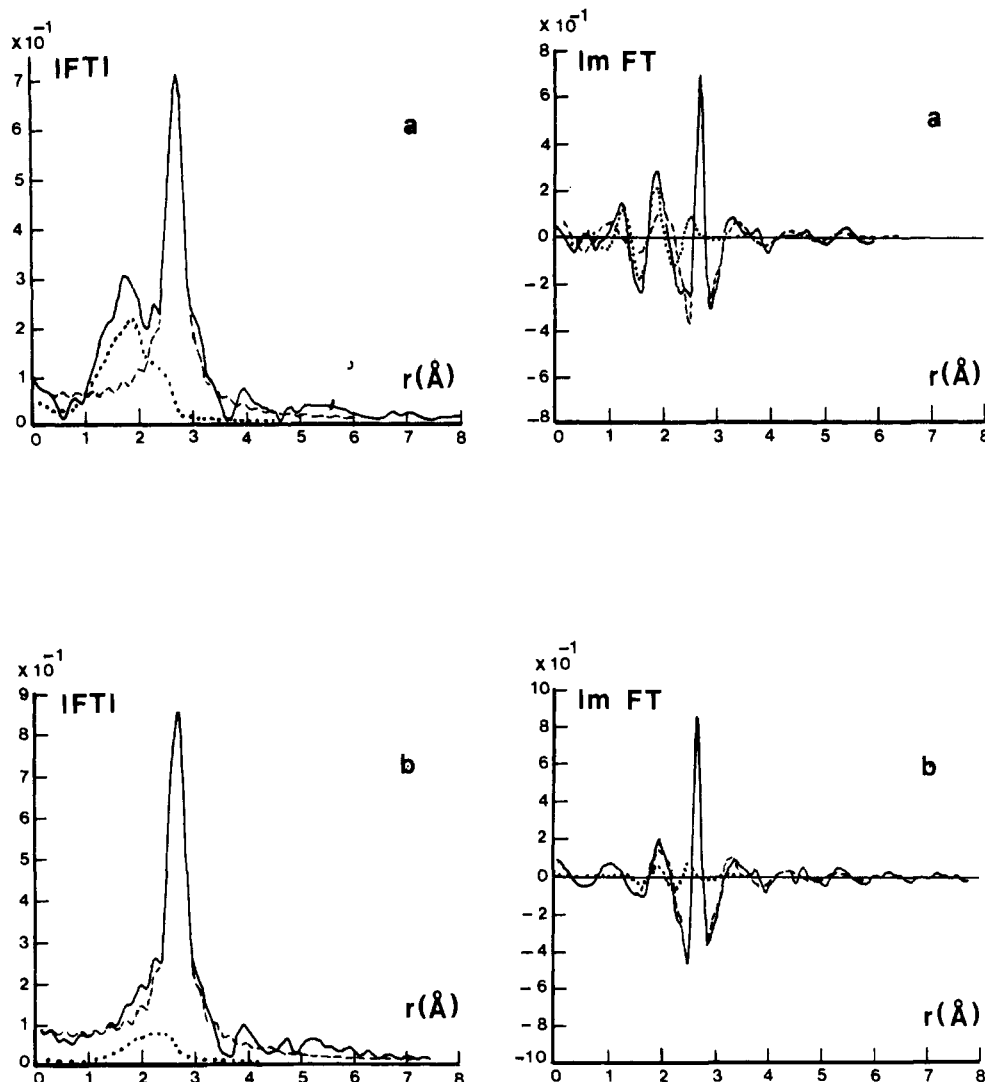
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Figure 2. Fourier transform (k^1 weighed, Rh–Rh phase and amplitude corrected, $k_{min} = 3.3$ Å⁻¹, $k_{max} = 14.5$ Å⁻¹) of experimental EXAFS data (—) and calculated Rh–Rh (– – –) and Rh–O EXAFS (···) (for parameters see Table I): (a) $T_{red} = 473$ K; (b) $T_{red} = 673$ K.

The dried catalyst was pressed into a thin self-supporting wafer and mounted in the in situ EXAFS cell.[15] The thickness of the wafer was chosen to give $\Delta\mu x \sim 1.5$ at the rhodium edge. Reduction was carried out under flowing H_2 for 2 h at 473 K, with the temperature being increased at a heating rate of 2.5 K/min. The sample was then cooled to room temperature under flowing H_2, and EXAFS spectra were recorded at 90 K with the catalyst exposed to 1 atm of static hydrogen. The same procedure was used for the subsequent reduction at 673 K.

The EXAFS spectra of the rhodium K edge were recorded in situ on X-ray beam line I-5 at the Stanford Synchrotron Radiation Laboratory (SSRL) with a ring energy of 3 GeV and ring currents between 40 and 80 mA.

Data Analysis and Results

EXAFS oscillations in k space are obtained from the X-ray absorption spectrum by a cubic spline background subtraction startig at 20 eV above the edge.[16] The EXAFS oscillations are normalized by division by the height of the edge. Reference compounds are used to obtain phase and backscattering amplitude functions and are treated in the same way. Parts a and b of Figure 1 present the EXAFS oscillations in k space of the 2.4 wt % Rh/Al₂O₃ catalyst reduced at 473 and 673 K, respectively.

It has been shown[12] that Fourier transformation (k^1 weighed) of the EXAFS data obtained from a highly dispersed Rh/Al₂O₃ catalyst produces a strong side lobe in the R region, where con-

tributions of oxygen can be expected. However, this side lobe also has contributions due to nonlinearities in the rhodium phase shift and due to the k dependence of the rhodium backscattering amplitude. These effects can be decreased by raising the power n of the weight factor k^n in the Fourier transformation. However, when higher n values are used, the Fourier transform becomes less sensitive to contributions from oxygen, since low-Z elements (like oxygen) have most scattering power at low k values. When the phase shift and the backscattering amplitude are removed from the EXAFS function before a transformation is done, the Fourier transform simplifies to a transform of a sinelike function.[17] In a Fourier transform which is corrected for the rhodium phase shift function and backscattering amplitude (further indicated by FT′), a Rh–Rh coordination peak will show up as a single symmetrical peak localized at the actual coordination distance. Reliable data for phase and backscattering amplitude have been obtained from EXAFS measurements on rhodium foil.[18] The solid lines in Figure 2a,b show the k^1-weighed FT′ for both reduction temperatures. Clearly visible are extra contributions in the R region between 1 and 2.2 Å. Before Fourier transformation the raw EXAFS data were smoothed by removing noise (harmonic numbers higher than 200) via Fourier filtering.

Fitting in k space is a widely used technique to determine the EXAFS parameter values. However, this method is not reliable enough to determine the smaller oscillations from other atoms

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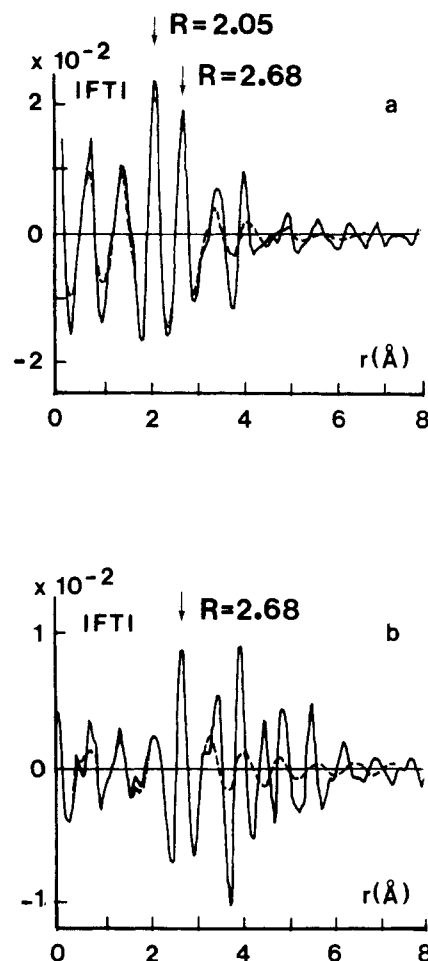(16) J. W. Cook Jr. and D. E. Sayers, *J. Appl. Phys.*, **52**, 5024 (1981).

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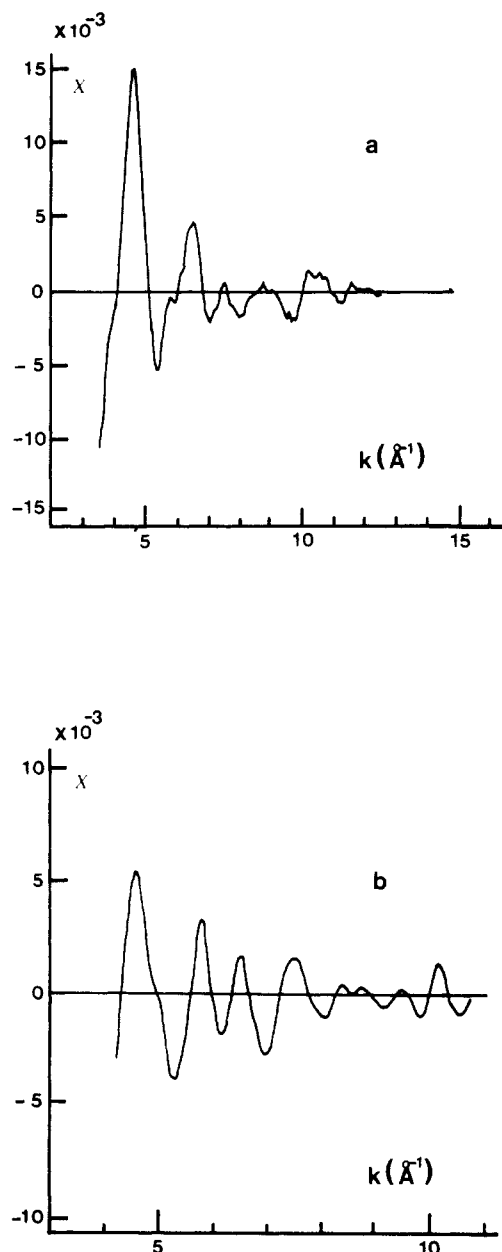
Figure 3. Residual spectra obtained after subtraction of the calculated Rh–Rh contribution from the experimental data: (a) T_{red} = 473 K; (b) T_{red} = 673 K.

Figure 4. Imaginary part of the Fourier transform (k^1 weighed, Rh–O phase corrected, k_{min} = 4 Å^{-1}, k_{max} = 10 Å^{-1}) of the difference spectrum (solid line) and calculated Rh–O EXAFS (dotted line) (for parameters see Table I: (a) T_{red} = 473 K; (b) T_{red} = 673 K.

(e.g. support oxygen), whose frequencies are close to the frequency of the main peak. However, by use of the phase- and amplitude-corrected Fourier transorm described above, the Rh–Rh contribution may be more localized and separated from other contributions. The data analysis has been started with the catalyst reduced at 673 K because of its less complex structure compared with the catalyst reduced at 473 K. By means of first guess parameters, obtained by a log ratio plot, a Rh–Rh EXAFS function is calculated (using the experimental Rh–Rh phase and amplitude, obtained from the rhodium foil) and subtracted from the experimental data. As a check on the Rh–Rh start parameters, the residual spectrum is transformed (Rh–Rh phase and amplitude corrected). The initial parameters have to be adjusted if significant Rh–Rh oscillations are present in the imaginary part of this transform. We have found that the final Rh–Rh parameters, obtained in this way, are not too much different from the initial parameter values. However, these small differences in Rh–Rh parameters can lead to significant Rh–Rh oscillations in the residual spectrum, which make the proper analysis of this spectrum difficult. After a correct choice of the Rh–Rh parameters and with a sufficiently high signal-to-noise ratio of the original data, the residual spectrum (see Figure 3b) can now reveal the identity

of the scatterer(s), causing the differences between R = 1 and 3 Å. Since the catalyst has been prepared from Rh(NO$_3$)$_3$, the only possible scatterer for the reduced catalyst can be oxygen. A Fourier transform (corrected for Rh–O phase shift, obtained from EXAFS measurements on Rh$_2$O$_3$[18] performed on the residual spectrum shows that the imaginary part of this transform is symmetric for 2 < R < 3 Å (see Figure 4b, solid line) and peaks at 2.68 Å in the maximum of its magnitude. This confirms the presence of oxygen as scatterer at a coordination distance of 2.68 Å. This is further verified by back-transformation to k space of the peak at 2.68 Å (see Figure 5b, solid line). Fitting in k space (using phase shift and backscattering amplitude of Rh$_2$O$_3$) results in parameter values for a single Rh–O bond. Peaks due to higher Rh–Rh coordination shells are also visible in Figure 4b. These peaks will not be analyzed in this paper. As a final check on both sets of parameters (Rh–Rh and Rh–O), an EXAFS function calculated with the obtained Rh–O parameters is subtracted from the experimental data, resulting in a spectrum which should contain only the frequency of rhodium scatterers. A Rh–Rh phase- and amplitude-corrected Fourier transform on this spectrum should therefore result in a symmetric imaginary part which peaks positively in the maximum of the magnitude. If necessary, better Rh–Rh parameters can be obtained from back-transformation of this transform to restart the whole procedure. In this recurring way the Rh–Rh and Rh–O parameters have been determined as given in Table I.

The same procedure has been applied to the EXAFS data of the Rh/Al$_2$O$_3$ sample, reduced at 473 K. Two distinct peaks can be observed (Figure 4a) in the Fourier transform of the difference spectrum for 1 < R <3 Å. Back-transformation of this transform gives an EXAFS signal, which can be fitted with two different Rh–O coordinations (see Figure 5a and parameters Table I). The
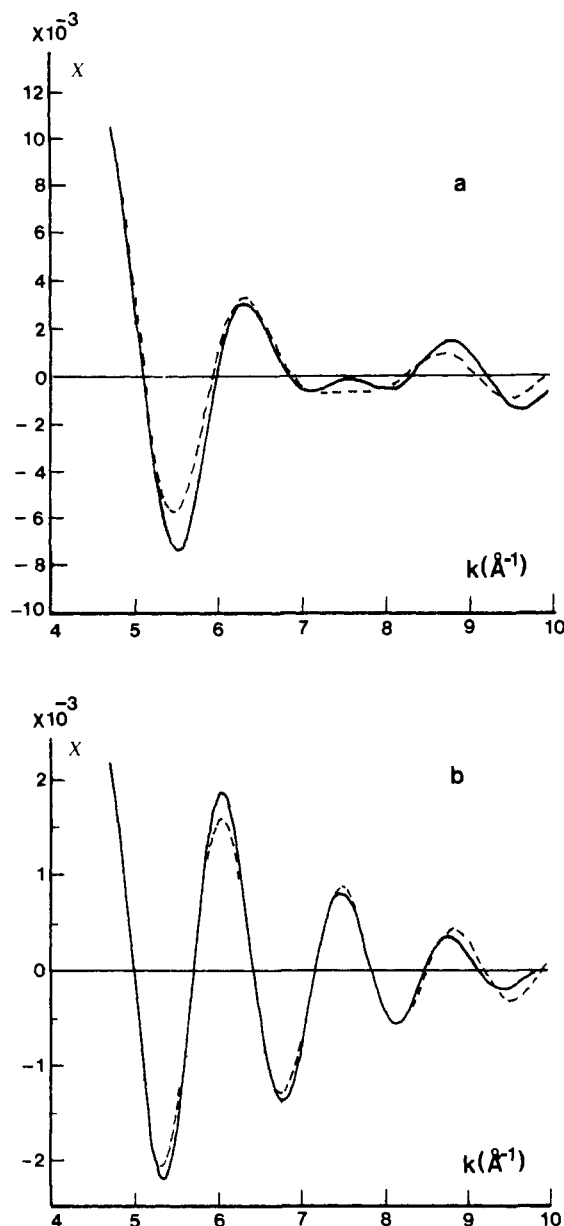
Figure 5. EXAFS obtained by back-transformation of Figure 3 (solid line) and calculated Rh–O EXAFS (dotted line) (for parameters see Table I): (a) T_{red} = 473 K (R_{min} = 1.2 Å, R_{max} = 3.2 Å); (b) T_{red} = 673 K (R_{min} = 1.9 Å, R_{max} = 3.2 Å).

TABLE I: Coordination Parameters[a]

| | | Rh(2.4)/Al$_2$O$_3$ | | |
treatment	coordination	N	R, Å	$10^{-3} \Delta\sigma^2$, Å^2
reduction at 473 K	Rh^0–Rh^0	5.2	2.69	5.5
	Rh^{3+}–O^{2-}	1	2.05	0
	Rh^0–O$_s^{2-}$	1.3	2.68	0
reduction at 673 K	Rh^0–Rh^0	6.3	2.69	5.3
	Rh^0–O$_s^{2-}$	1.2	2.68	0

[a] N = number of neighbors, R = distance, $\Delta\sigma^2$ = Debije–Waller factor, difference with reference compound. Accuracies: $N \pm$ 10–20%, $R \pm$ 0.5–1%, $\Delta\sigma^2 \pm$ 10–20%.

reliability of the Rh–O parameters obtained for both reduction temperatures has been checked by comparing the Fourier transforms of the difference spectra with the transforms of the Rh–O EXAFS functions calculated with the parameters given in Table I. It can be seen in Figure 4 that within the R region used for back-transformation to k space both transforms are very similar.

The Fourier transforms of the calculated Rh–O coordination(s) can now be compared in Figure 2 with the transforms of the

corresponding calculated Rh–Rh coordination and those of the experimental data. As a final check for the reliability of the Rh–Rh and Rh–O parameters derived in this work, the EXAFS functions of both coordinations have been added and transformed. The equivalence of these transforms with those of the corresponding experimental data can be seen in Figure 6. It is also shown that the calculated Rh–Rh + Rh–O EXAFS functions are identical with the EXAFS functions obtained by back-transformation (R_{min} = 0.8 Å, R_{max} = 3.2 Å) of the Fourier transform of the corresponding experimental data.

Discussion

The analysis of the EXAFS data obtained on the 2.4 wt % Rh/Al$_2$O$_3$ catalyst 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 Rh$_2$O$_3$. This Rh–O bond disappears after reduction at 673 K. Therefore, we conclude that this bond originates from Rh$_2$O$_3$ species which are still present after the reduction at 473 K. The second Rh–O bond, with a coordination distance of 2.68 Å detected at both reduction temperatures, is similar to the bonds measured for a 0.5 and 1.0 wt % Rh/Al$_2$O$_3$ catalyst (R = 2.71 Å) reported previously.[12,18] This Rh–O bond has been assigned to a coordination of the interfacial rhodium metal atoms with support oxygen ions. However, in contrast to the calcination and reduction procedure employed for the 2.4 wt % catalyst, the 0.5 and 1.0 wt % Rh/Al$_2$O$_3$ catalysts were directly reduced at 773 K without a preceding calcination step. Thus, even a preceding calcination at 623 K of the Rh-(2.4)/Al$_2$O$_3$ catalyst, followed by a complete reduction, does not lead to the presence of normal cation–anion distances, which have been supposed in the literature[8–11] to be representative for an interaction between metal crystallites and support. From the results reported earlier[12,18] and from results obtained in this work, one has to conclude that in Rh/Al$_2$O$_3$ catalysts 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. This means that the rhodium metal crystallites are not bound to the support via a rhodium oxide layer with Coulombic rhodium–cation oxygen–anion interactions. It has been suggested by van Zon et al.[12] that this interaction is possibly via an ion-induced dipole interaction.

The fraction of rhodium still present in the rhodium oxide phase after reduction at 473 K can be calculated by assuming that partially reduced rhodium metal crystallites are not present. This is a reasonable assumption since it is generally accepted that the nucleation phase of the reduction of small metal oxide particles is rate determining. Thus, once the reduction process starts, the small crystallite is completely reduced. It is also known[19] that highly dispersed Rh/Al$_2$O$_3$ catalysts are neither monatomically dispersed nor have a form of dispersion consisting of a mixture of rhodium metal crystallites and isolated Rh^0 atoms. Thus, it follows that after reduction at 473 K rhodium is present only in oxidic or in metallic particles. Both the Rh^0 atoms and the Rh^{3+} ions contribute to the edge jump and thus influence the normalization. This implies that the real coordination numbers (N_r(Rh^0–Rh^0) and N_r(Rh^{3+}–O^{2-})) are related to the measured coordination numbers (N_m(Rh^0–Rh^0) and N_m(Rh^{3+}–O^{2-})) by

$$N_r(\text{Rh}^0\text{–Rh}^0) = N_m(\text{Rh}^0\text{–Rh}^0)/(1 - f) \quad (1)$$

$$N_r(\text{Rh}^{3+}\text{–O}^{2-}) = N_m(\text{Rh}^{3+}\text{–O}^{2-})/f \quad (2)$$

with f being the fraction of rhodium present in the Rh$_2$O$_3$. Since the crystallographic coordination number N_r(Rh^{3+}–O^{2-}) in rhodium(III) oxide equals 6 and the measured coordination number N_m(Rh^{3+}–O^{2-}) = 1 (cf. Table I), it follows by eq 2 that, after reduction at 473 K, 17% of the rhodium atoms are still present in the rhodium oxide phase. Given the fact that f = 0.17 and N_m(Rh^0–Rh^0) = 5.2, the real rhodium coordination number N_r(Rh^0–Rh^0) (after reduction at 473 K) is calculated to be 6.3

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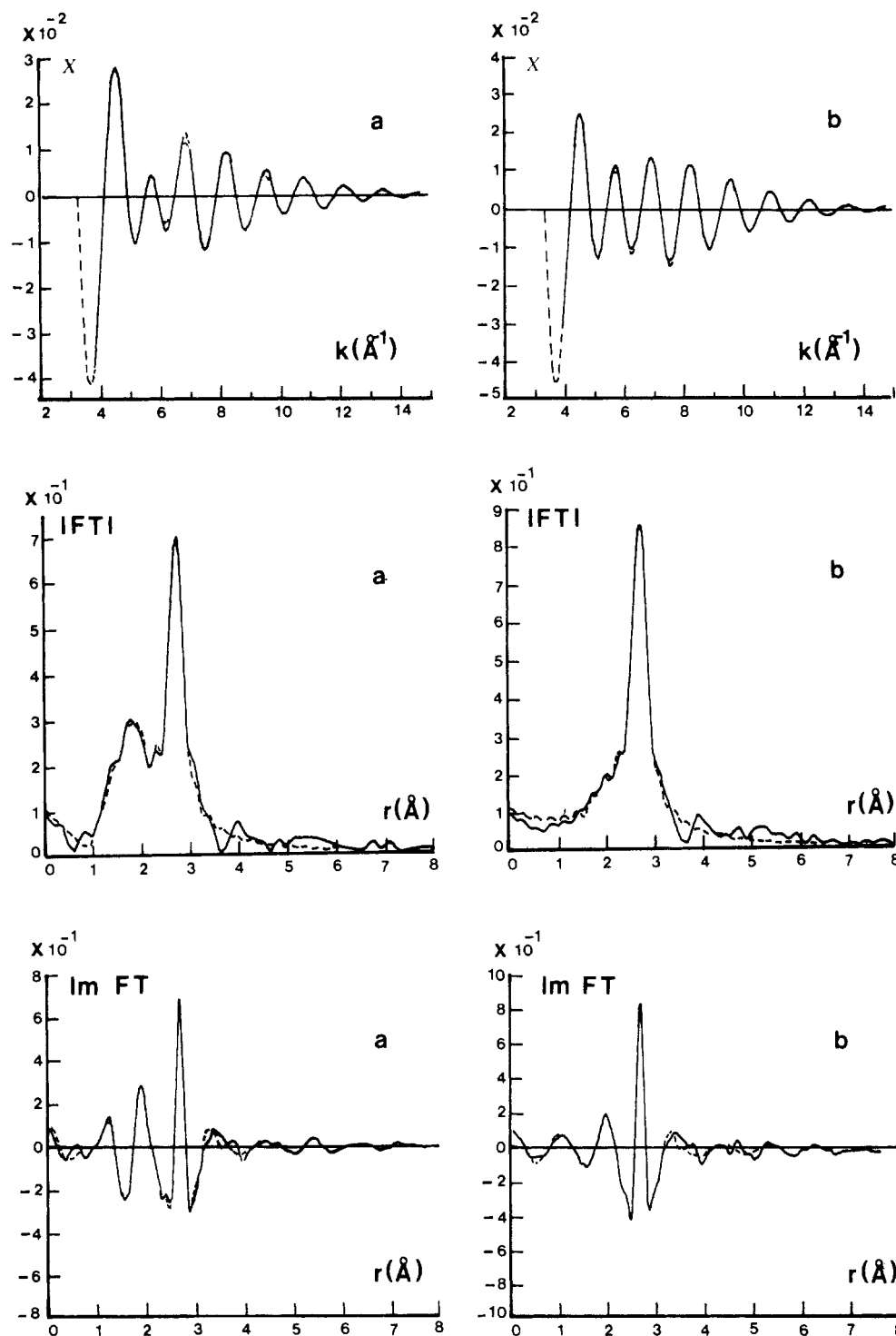
Figure 6. EXAFS obtained by back-transformation (R_{min} = 0.8 Å, R_{max} = 3.2 Å) of Figure 2 (solid lines) and calculated EXAFS (Rh–Rh + Rh–O) (dotted line). Fourier transformation (k^1 weighed, Rh–Rh phase and amplitude corrected, k_{min} = 3.3 Å^{-1}, k_{max} = 14.5 Å^{-1}) of experimental EXAFS data (solid line) and calculated EXAFS (Rh–Rh + Rh–O) (dotted line): (a) T_{red} = 473 K; (b) T_{red} = 673 K.

(eq 1). This value can be compared with the real rhodium–rhodium coordination number found after reduction at 673 K. In this case only one type of rhodium atom is present, implying that $N_r(Rh^0–Rh^0)$ = $N_m(Rh^0–Rh^0)$ = 6.3. This number is equal to the value obtained after reduction of the catalyst at 473 K. This shows that the reduction at 673 K has not led to a noticeable sintering of the metal crystallites. This also indicates that the presence of partially reduced metal crystallites with a metal oxide layer between the metal particle and the support is very unlikely, since a further reduction of these particles at higher temperatures should give an increase of the coordination number.

The number of support oxygen ions which are in contact with one interfacial rhodium atom can be estimated as follows. The ratio between the number of interfacial metal atoms, N_{int}, in a

particle with (assumed) half-spherical shape and the total number of atoms, N_t, present in this particle is given by[18]

$$N_{int}/N_t = 4R_{at}/d \qquad (3)$$

with d the diameter of the particle and R_{at} the atomic radius of the rhodium atom. The relationship between the real $N_r(Rh^0–O_s^{2-})$ and the measured $N_m(Rh^0–O_s^{2-})$ coordination number of the rhodium support–oxygen bond can now be derived:

$$N_r(Rh^0–O_s^{2-}) = N_m(Rh^0–O_s^{2-})d/(4R_{at}) \qquad (4)$$

From calculations which relate the average rhodium–rhodium coordination number to the diameter d for half-spherical-shaped particles,[18] a diameter of about 11 Å is derived from the coordination number N = 6.3. By using this value, R_{at} = 1.34 Å, and

$N_m(Rh^0-O_s^{2-}) = 1.2$, we obtain $N_r(Rh^0-O_s^{2-}) = 2.5$. Possible structures for the metal–support interface are discussed in ref 18.

In summary, we have found experimental evidence for a coordination of interfacial rhodium atoms with oxygen ions of the support. The bond length is 2.68 Å with an estimated average coordination number of 2.5 atoms. Short oxide-like coordination distances have not been detected in fully reduced rhodium catalysts. The metal–support interaction is possibly through an ion-induced dipole interaction due to the registry of the metal particle with the support. The results presented in this work show that metal to support–oxygen bonds in supported metal catalysts can be detected when both the dispersion of the metal particles and the signal-to-noise ratio of the EXAFS data are high enough.

Kinetic Analysis of the Anomalous Behavior in the Fluorescence Quenching of Phenanthryl Groups Covalently Linked to Polyelectrolytes

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The fluorescence quenching of amphiphilic polyanions containing phenanthryl chromophores (APh) by bis(2-hydroxyethyl) terephthalate (BHET) was investigated in aqueous solutions over a concentration range of the phenanthryl residue of 8×10^{-5}–3×10^{-3} M. The steady-state experimental data were analyzed in terms of a kinetic model based on a stepwise association for the incorporation of BHET, an amphiphilic quencher, into the hydrophobic microdomains of the amphiphilic polymer. The polyanion with a phenanthryl content of 41 mol % (APh-41) showed fluorescence quenching for which Stern–Volmer-type plots gave a downward curvature. The initial slope was extremely steep and was dependent on the residue concentration of the phenanthryl chromophore. The quenching process was reasonably approximated as entirely static in nature. The first-step association constant for the BHET incorporation was estimated to be $K_1 = 1.1 \times 10^3$ M^{-1}, which is in fair agreement with the binding constant of $K = 1.2 \times 10^3$ M^{-1} obtained by the equilibrium dialysis technique. The analysis also led to estimates of the average aggregation number of the phenanthryl chromophores as $n = 2.6$ for APh-41, through which energy migration could take place. The rate constant for the intradomain fluorescence quenching was estimated by computer curve fitting to be $k_{q,1} = 5.5 \times 10^7$ s^{-1}. Under conditions where the BHET concentration is high enough for all the microdomains to incorporate the quencher, the fluorescence decay curve showed apparently single exponential nature, yielding $k_{q,1} = 4.8 \times 10^7$ s^{-1} which is comparable to the computed value. In contrast, the amphiphilic copolymer with a phenanthryl content of 2 mol % showed entirely dynamic quenching because of the absence of hydrophobic association of the quencher with the polymer.

Introduction

Polyelectrolytes chemically modified with polycyclic aromatic groups have been demonstrated to form microscopically phase-separated structures in aqueous solutions because of their strong amphiphilic nature.[1-4] Within a polymer chain of these polyelectrolytes the attractive hydrophobic interaction between the hydrophobic groups competes with the repulsive electrostatic interaction between the segmental electric charges as conceptually illustrated in Figure 1. The consequence of the competition critically determines the conformation of the macromolecular chains. In case the hydrophobic interaction prevails over the segmental Coulombic repulsion, the hydrophobic groups would end up forming hydrophobic microdomains. In this situation the charged segments would surround the periphery of the microdomains, thus the amphiphilic polyelectrolytes may provide a

"unimolecular" micelle.[5,6] This is actually the case for polyelectrolytes with a higher content of aromatic segments as will be discussed later. On the other hand, if the content of the hydrophobic segments is not high enough, the segmental Coulombic repulsion allows the polymer chain to expand, as usually occurs in the common polyelectrolytes. In the expanded conformation a hydrophobic group would be isolated from another along an electrolyte main chain and completely exposed to an aqueous environment. The photochemical behavior of the polycyclic aromatic groups is considerably dependent on whether the polymer conformation is expanded or miceller like. In a recent article concerning the photophysics of poly(methacrylic acid) containing pendant 9,10-diphenylanthracene, the emission properties and quenching rate constants of the photoactive group were shown to be strongly affected by the conformation of the polymer.[7] We have reported that the fluorescence quenching of the photoexcited phenanthryl groups in amphiphilic random copolymers of 9-

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