

On the detection with EXAFS of metal-support oxygen bonds in a highly dispersed rhodium on alumina catalyst

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(Received 27 July 1983; accepted 8 February 1984)

An intriguing but still unresolved question regarding supported metal catalysts is the binding mechanism between the metal crystallite and the support. Several models have been proposed for the structure of the interface between a metal particle and an oxidic support. Interdiffusion of the metal oxide with the oxidic support (Ni/SiO₂, Ni/Al₂O₃, Co/Al₂O₃),¹⁻⁴ the presence of low valence ions in the interface between particle and support (Ru/Al₂O₃, Ru/SiO₂, Pt/TiO₂, Pt/Al₂O₃)^{5,6} or a possible binding between zero-valent metal atoms of the metal cluster and the oxygen of the support (Os₃(CO)₁₂)⁷ are mentioned as possible mechanisms for metal-support interaction.

Information about the metal-support interface can be obtained by the EXAFS technique, which is an excellent tool to study short range order about a specific type of atom. In most supported metal catalysts, group VIII metals are involved. The detection of oxygen by the EXAFS technique is therefore possible due to the large differences in the backscattering amplitudes of oxygen (low *Z* element) and the group VIII element (high *Z*). In this communication, the results of an EXAFS study of a highly dispersed reduced 0.5 wt.% rhodium on an alumina catalyst will be presented, showing clear evidence of a rhodium-support oxygen interaction.

The catalyst was prepared by the incipient wetting technique. A known amount of γ -Al₂O₃ (Ketjen, BET area 200 m² g⁻¹, pore volume of 0.6 cm³ g⁻¹) was wetted with an aqueous solution of RhCl₃. After impregnation, the catalyst was dried in air (393 K, 20 h), reduced with flowing H₂ (heating rate 5 K/min, 773 K, 2 h), cooled down to 300 K and passivated (oxidation at room temperature). Hydrogen chemisorption experiments on the reduced catalyst resulted in a H/Rh of 1.75 ($\pm 10\%$), demonstrating very high dispersion of the metal and multiple adsorption of hydrogen. The reduction was complete as proven by temperature programmed reduction measurements.⁸ The catalyst was mounted as a pressed wafer in an EXAFS cell designed for *in situ* measurements⁹ and was reduced under flowing hydrogen at 773 K. The x-ray absorption spectra, performed on the *K* edge of rhodium, were measured at room temperature on beam line I-5 at the Stanford Synchrotron Radiation Laboratory.

Since any contribution from the support will be small, even for a highly dispersed catalyst, the EXAFS spectra must be carefully analyzed to obtain reliable values for the coordination parameters. To obtain this information for the metal-metal and metal-oxygen bonds with the support, a

modification of the usual data analysis procedures has been applied.

Typically, a k^n -weighted Fourier transform (FT) ($n = 1, 2, 3$) of a rhodium-rhodium EXAFS shows a satellite on the left-hand side of the Rh-Rh peak. This sidelobe is caused by the k -dependent behavior of the backscattering amplitude and by nonlinearities in the phase shift function. For a k^{-1} -weighted Fourier transform, this sidelobe may have an intensity up to 30% of the intensity of the main peak and therefore interfere drastically in the *R* region where distances due to support oxygen are to be expected. Reduction of sidelobe effects is desirable for a reliable identification of support oxygen. The use of a Fourier transform which is corrected for phase shift and backscattering amplitude (denoted by FT') compensates almost completely for the sidelobe effect.¹⁰ In a FT' (corrected for the rhodium phase and backscattering amplitude) the rhodium-rhodium contribution will appear as a single localized peak without sidelobes so that the support oxygen can more easily be identified. The structural parameters of the rhodium-support oxygen bond can be obtained after subtracting the Rh-Rh contributions from the experimental data.

Figure 1(a) shows a k^{-1} -weighted FT' of the rhodium catalyst, transformed from $k = 3.3 \text{ \AA}^{-1}$ to $k = 12.7 \text{ \AA}^{-1}$. The phase shift and backscattering amplitude have been obtained from EXAFS measurements on rhodium foil.¹¹ The main contribution in Fig. 1(a) originates from a nearest

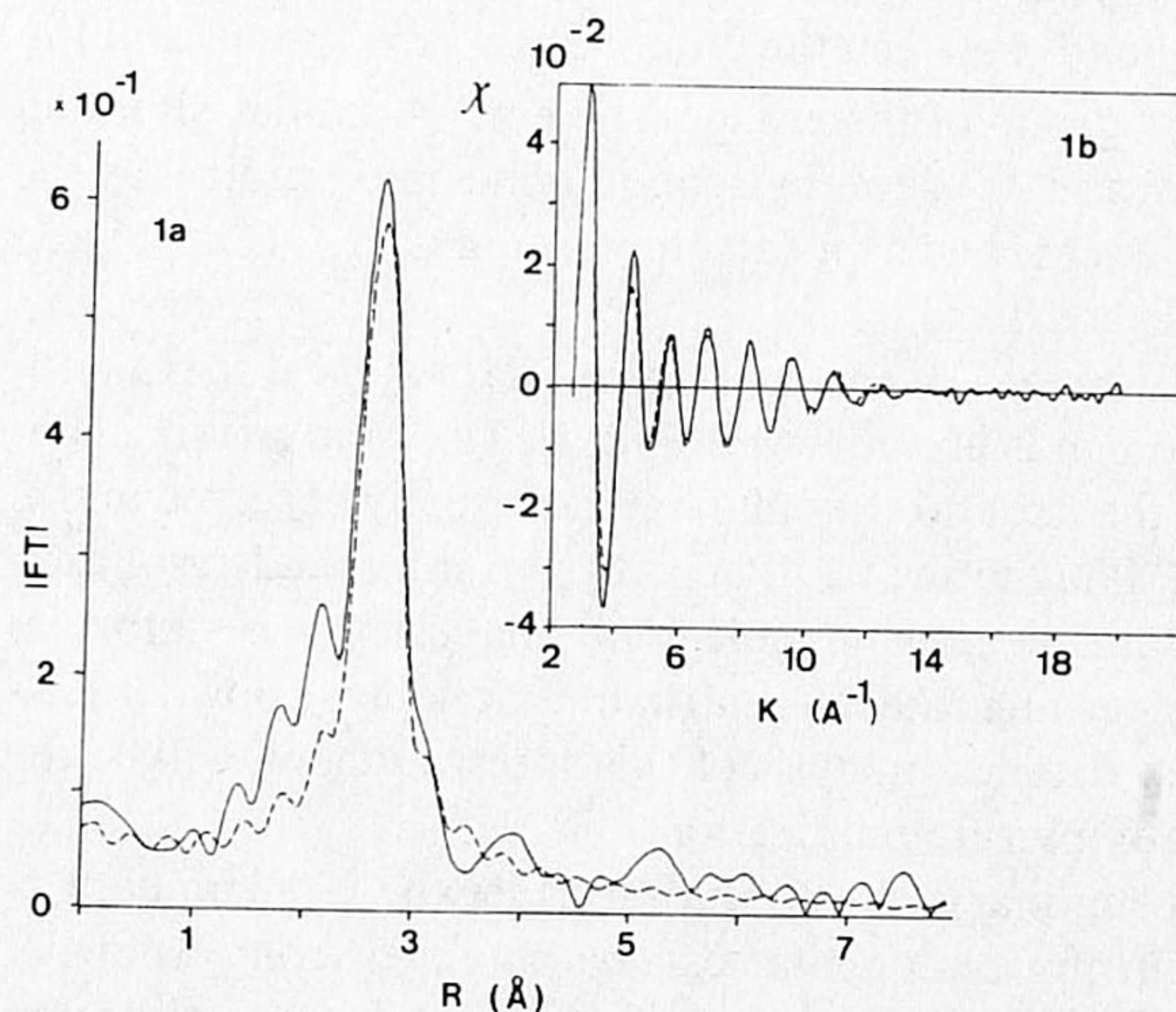


FIG. 1. (a) FT' ($3.3\text{--}12.7 \text{ \AA}^{-1}$) of original data (solid line) and calculated Rh-Rh EXAFS (dotted line); (b) EXAFS of 0.5 wt.% Rh/Al₂O₃ catalyst (solid line) and calculated Rh-Rh EXAFS (dotted line).

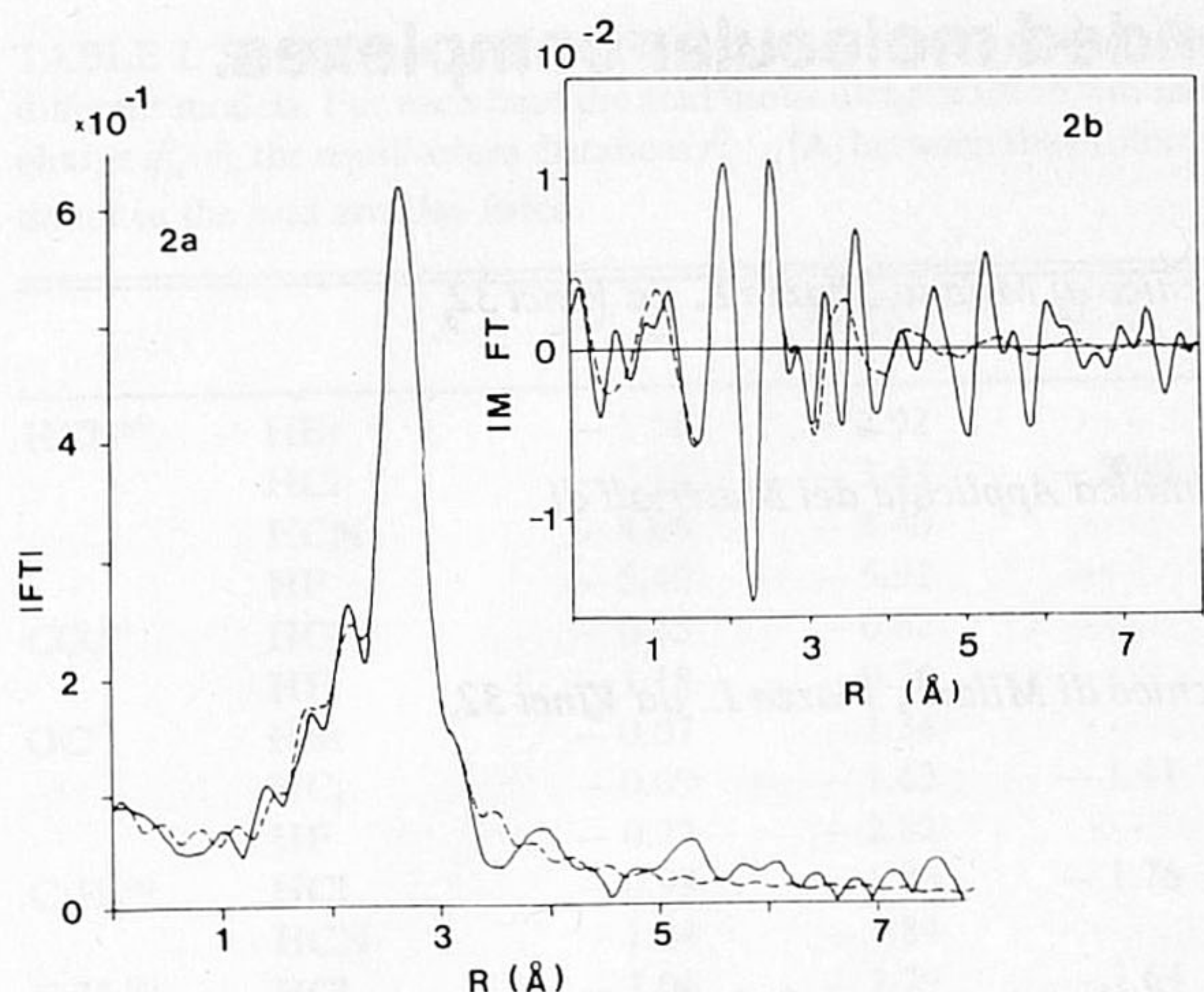


FIG. 2. (a) FT' ($3.3\text{--}12.7\text{ \AA}^{-1}$) of original data (solid line) and calculated two-shell EXAFS (Rh-Rh + Rh-O) (dotted line); (b) Imaginary part of FT ($3.3\text{--}10\text{ \AA}^{-1}$, corrected for rhodium phase shift) of the residual spectrum (solid line) and the calculated Rh-O EXAFS (dotted line).

neighbor rhodium coordination at a distance of 2.67 \AA . Figure 2(b) shows the imaginary part of a k^1 -weighted Fourier transform ($k_{\text{min}} = 3.3\text{ \AA}^{-1}$, $k_{\text{max}} = 10\text{ \AA}^{-1}$, corrected for the rhodium phase shift) of the residual EXAFS obtained by subtracting a calculated Rh-Rh EXAFS from the experimental EXAFS spectrum. The Rh-Rh parameters used for the calculated EXAFS function were obtained by adjusting the parameters until the frequency component of the Rh-Rh coordination is absent in the imaginary part of the Fourier transform of the residual EXAFS [see Fig. 2(b)]. The final parameters obtained were: $N = 5 \pm 0.5$, $R = 2.67 \pm 0.01\text{ \AA}$, $\Delta\sigma^2 = 0.0064 \pm 0.0005\text{ \AA}^2$ (relative to rhodium foil). The calculated Rh-Rh EXAFS is given in Fig. 1(b) (dotted line) and the k^1 -weighted FT' ($k_{\text{min}} = 3.3\text{ \AA}^{-1}$, $k_{\text{max}} = 12.7\text{ \AA}^{-1}$) of this function is shown in Fig. 1(a) (dotted line).

From the $N_{\text{Rh-Rh}}$, information can be obtained about the structure of the rhodium. Rhodium is neither present as isolated atoms nor as raft structures.¹² In a following paper,¹¹ it will be shown that rhodium is present in three dimensional crystallites.

Differences between the curves at lower k values in Fig. 1(b) are clearly visible and give rise to the differences between $R = 1\text{ \AA}$ and $R = 3\text{ \AA}$ in Fig. 1(a), which are assumed to be due to the support. Further data analysis of this difference signal (including backtransformation and fitting in k space) shows that this EXAFS signal is from a Rh-O coordination with $N = 1.3 \pm 0.5$, $R = 2.71 \pm 0.03\text{ \AA}$, and $\Delta\sigma^2 = 0.002 \pm 0.001\text{ \AA}^2$ (relative to Rh_2O_3). The phase shift and back-scattering amplitude for Rh-O have been obtained from EXAFS measurements on Rh_2O_3 .¹¹

The reliability of the parameters obtained from the Rh-O coordination by fitting in k space has been checked by comparing the Fourier transform of the Rh-O EXAFS function (calculated with these parameters) with the corresponding FT of the residual spectrum. This is shown as the dashed curve in Fig. 2(b), where all features between 1 and 3 Å have been reproduced. The k^1 -weighted FT' of an EXAFS function including Rh-Rh and Rh-O bonds calculated with the parameters mentioned above shows excellent agreement with the corresponding FT of the experimental data [see Fig. 2(a)]. The measured Rh-O distance of 2.71 \AA is much larger than the Rh-O distance known from Rh_2O_3 (2.05 \AA) and indicates that the rhodium crystallites are not bound to the $\gamma\text{-Al}_2\text{O}_3$ support via a Coulombic rhodium cation-oxide anion interaction but via an interaction between the rhodium metal atoms (atomic radius 1.34 \AA) and the oxygen anions (radius 1.4 \AA) of the support. This view is supported by preliminary results of other supported Rh catalysts which will be presented elsewhere.¹¹

In conclusion, by modifying the usual data analysis procedures, a more reliable separation of the Rh-Rh and Rh-support contribution to the EXAFS has been made. From the rhodium-support contribution, a Rh-O bond length of 2.71 \AA has been obtained. This shows that for this system the metal-support interaction is possibly through an ion-induced dipole ($\text{O}^{2-} \rightarrow \text{Rh}^0$) interaction of the metal particle with the support.

This work was done at SSRL which is supported by the NSF through the Division of Materials Research and NIH through the Biotechnology Resource Program in the Division of Research Resources in cooperation with the U.S. Department of Energy. One of us (DCK) would like to thank ZWO also for supplying a grant for traveling (R71-34).

¹H. Suzuki, S. Takasaki, I. Koga, A. Meno, Y. Kotera, T. Sato, and N. Tode, *Chem. Lett.* xx, 127 (1982).

²E. G. Derouane, A. J. Simoons, and J. C. Vedrine, *Chem. Phys. Lett.* **52**, 549 (1977).

³R. B. Shalvoy, B. H. Davis, and P. J. Rencroft, *Surf. Int. Anal.* **2**, 11 (1980).

⁴R. B. Gregor, F. W. Lytle, R. L. Chin, and D. M. Hercules, *J. Phys. Chem.* **85**, 1232 (1981).

⁵A. Bossi, F. Garbassi, G. Petrini, and L. Zanderighi, *J. Chem. Soc. Faraday Trans. 1* **78**, 1029 (1982).

⁶T. Huizinga and R. Prins, *J. Phys. Chem.* **87**, 173 (1983).

⁷B. Besson, B. Moraweck, A. K. Smith, J. M. Basset, R. Psaro, A. Fusi, and R. Ugo, *J. Chem. Soc. Chem. Commun.* **1980**, 569.

⁸J. C. Vis, H. F. J. van 't Blik, T. Huizinga, J. van Grondelle, and R. Prins, *J. Mol. Catal.* (to be published).

⁹D. C. Koningsberger and J. W. Cook, *Proceedings of the International Conference on EXAFS and Near Edge Structures*, Frascati, Italy, September 13-17, 1982 (Springer, New York, 1982).

¹⁰P. A. Lee and G. Beni, *Phys. Rev. B* **15**, 2862 (1977).

¹¹J. B. A. D. van Zon, D. C. Koningsberger, H. F. J. van 't Blik, and D. E. Sayers (to be published).

¹²H. F. J. van 't Blik, J. B. A. D. van Zon, T. Huizinga, J. C. Vis, D. C. Koningsberger, and R. Prins, *J. Phys. Chem.* **87**, 2264 (1983).