

THE EFFECT OF GAS ENVIRONMENT ( $H_2$ ,  $O_2$ ) ON THE STRUCTURAL PROPERTIES OF SMALL IRIDIUM METAL PARTICLES SUPPORTED ON  $\gamma$ - $Al_2O_3$  AS DETERMINED BY EXAFS

D.C. KONINGSBERGER, F.B.M. DUIVENVOORDEN, B.J. KIP and D.E. SAYERS\*

*Laboratory for Inorganic Chemistry and Catalysis, Eindhoven University of Technology, P.O. Box 513, NL-5600 MB Eindhoven, The Netherlands*

*\*Department of Physics, North Carolina State University, Raleigh, NC 27695-8202, U.S.A.*

### Abstract

EXAFS measurements have been carried out on an 0.8 wt% Ir/ $\gamma$ - $Al_2O_3$  catalyst after the following treatments: 1) reduction at 773 K, 2) evacuation at 623 K, 3)  $O_2$  adsorption at 77 K, 4) subsequent heating to 100 K. The tentative results show that chemisorbed hydrogen influences the structure of the metal particles and their interaction with the support. Oxygen adsorption at 77 K (most probably physisorption) seems to produce the same kind of metal-oxygen bonds as detected for the metal-support interface, when the metal crystallites are under vacuum. Subsequent heating to 100 K resulted in the onset of oxygen chemisorption.

### 1. Introduction

Structural properties of small metal particles supported on non-interacting substrates (mylar, rare gas solids) have been extensively studied with EXAFS [1-3]. Experiments were performed under vacuum showing contractions of the nearest-neighbour distance and a decrease of the Debye temperature of the metal particle due to the softening of the phonon spectrum [4,5]. EXAFS experiments on dispersed metal catalysts (supported on stronger interacting substrates, e.g.  $\gamma$ - $Al_2O_3$ ,  $TiO_2$ ,  $SiO_2$ ) have been mostly carried out after reduction with the metallic particles covered with chemisorbed hydrogen [6-10]. Under these conditions contraction of the metal-metal coordination distance has not been observed. This can be due to the influence of the chemisorbed hydrogen or the interaction of the metallic particle with the support. Tentative EXAFS results have been reported for Pt/NaY (zeolite) [11] and Rh/ $Al_2O_3$  [12] catalysts under vacuum showing a contraction of the first neighbour coordination distance.

Chemisorbed hydrogen influences the electronic properties of the metal [13] which in turn may change the metal-support interaction. The metal-support interaction has been studied with EXAFS for Rh/ $Al_2O_3$  [8,9] and Pt/ $Al_2O_3$  [10] catalysts with the metal particles covered with chemisorbed hydrogen.

Here we present the preliminary results obtained for a highly dispersed 0.8 wt% Ir/ $\gamma$ - $Al_2O_3$  catalyst with and without chemisorbed hydrogen. Removal of chemisorbed hydrogen seems to influence the metal-support oxygen bonds. Oxygen physisorption at 77 K was carried out in order to compare the metal-oxygen bonds formed by this adsorption process with the metal-support oxygen bonds. The onset of the oxygen chemisorption process was further studied with EXAFS.

## 2. Experimental

An 0.8 wt% Ir/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst was prepared by incipient wetting the support ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, Ketjen type 000-1.5 E, surface area 200 m<sup>2</sup>g<sup>-1</sup>, pore volume 0.6 m<sup>2</sup>g<sup>-1</sup>) with an aqueous solution of IrCl<sub>3</sub>.x H<sub>2</sub>O. The catalyst was dried in air at 395 K (heating rate 2 K min<sup>-1</sup>) for 16 h followed by direct reduction in flowing H<sub>2</sub> at 773 K for 5 h (heating rate 5 K min<sup>-1</sup>). After this treatment the catalyst was passivated with O<sub>2</sub> at room temperature and stored for further use. Hydrogen chemisorption measurements resulted in H/M = 2.6, indicating highly dispersed metal particles. A further characterization of this catalyst with different physical methods has been described in [14].

The treatments of the catalyst prior to the EXAFS experiments were performed in an EXAFS in situ cell. The sample was pressed into a self-supporting wafer with an optimum thickness to give  $\Delta\mu x \sim 1.5$ -2.0 at the iridium L<sub>III</sub>-edge. The following treatments were carried out:

1) Rereduction in flowing H<sub>2</sub> at 473 K for 1 h (producing the same reduced state as obtained after the first reduction at 773 K); 2) Evacuation at 623 K for 2 h,  $p \sim 10^{-5}$  Pa; 3) O<sub>2</sub> adsorption (10<sup>5</sup> Pa) at 77 K; 4) Heating under O<sub>2</sub> to 100 K.

EXAFS data were collected after every treatment at 77 K. The EXAFS spectra were recorded at the EXAFS station of beamline X-11A of the NSLS at Brookhaven (ring energy 2.5 GeV, ring currents 50-100 mA).

## 3. Results and Discussion

EXAFS oscillations in  $k$  space are obtained from the x-ray absorption spectrum by a cubic spline background subtraction and normalization by means of division by the height of the edge [8]. The EXAFS data for all samples are shown in Fig. 1. The imaginary part of the Fourier transforms of the EXAFS data are displayed in Fig. 2. The imaginary part contains amplitude (viz. coordination number and disorder) and phase (viz. coordination distance) information. The Fourier transforms are corrected for the metal-metal phase and backscattering amplitude, obtained from EXAFS experiments on Pt foil. The suitability of using this platinum standard for analyzing nearest and next nearest neighbours has been discussed in [15].

By comparing the experimental EXAFS data obtained after reduction (Fig. 1a) and after evacuation (Fig. 1b), it can be seen that the amplitude of the EXAFS oscillations in Fig. 1b is lower at high  $k$  values ( $k > 8 \text{ \AA}^{-1}$ ). This indicates a larger disorder for the iridium metal particles after evacuation. This also causes a lower amplitude of the corresponding Fourier transform (compare in Fig. 2a the solid line with the dotted line). A full analysis will make clear whether a decrease in coordination number (= decrease in average particle size) has also to be taken into account to explain the lower amplitude of the Fourier transform for the sample after evacuation. An increase of the Debye-Waller factor is in line with a softening of the phonon spectrum due to the removal of the chemisorbed hydrogen from the surface of the metal particles. The Ir<sup>0</sup>-Ir<sup>0</sup> first coordination shell peaks in the Fourier transform at the right distance due to the applied phase correction. It can be clearly noticed in Fig. 2a that evacuation induces a contraction of the Ir<sup>0</sup>-Ir<sup>0</sup> coordination distance.

The asymmetry at low  $r$  values ( $1.5 < r < 2.5 \text{ \AA}$ ) in the  $k^1$  weighted Fourier transforms in Fig. 2a is most probably caused by contributions of metal-support bonds analogous to the results obtained for Rh/Al<sub>2</sub>O<sub>3</sub> [8,9] and Pt/Al<sub>2</sub>O<sub>3</sub> [10] catalysts. It is obvious from Fig. 2a that the phase of the imaginary part of the Fourier transform at low  $r$  values changes after evacuation, indicating a change in coordination distance of the metal-support bonds.

Oxygen adsorption at 77 K changes the low  $k$  part of the EXAFS spectrum (compare Fig. 1b with Fig. 1c), which might be due to oxygen nearest neighbours. A clear picture can be obtained from the Fourier transforms of the corresponding EXAFS data (compare Fig. 2b the solid line with the dotted line). The asymmetrical part at low  $r$  values ( $1.5 < r < 2.5 \text{ \AA}$ ) increases in amplitude while the phase of the whole transform remains the same. From this one can directly conclude that

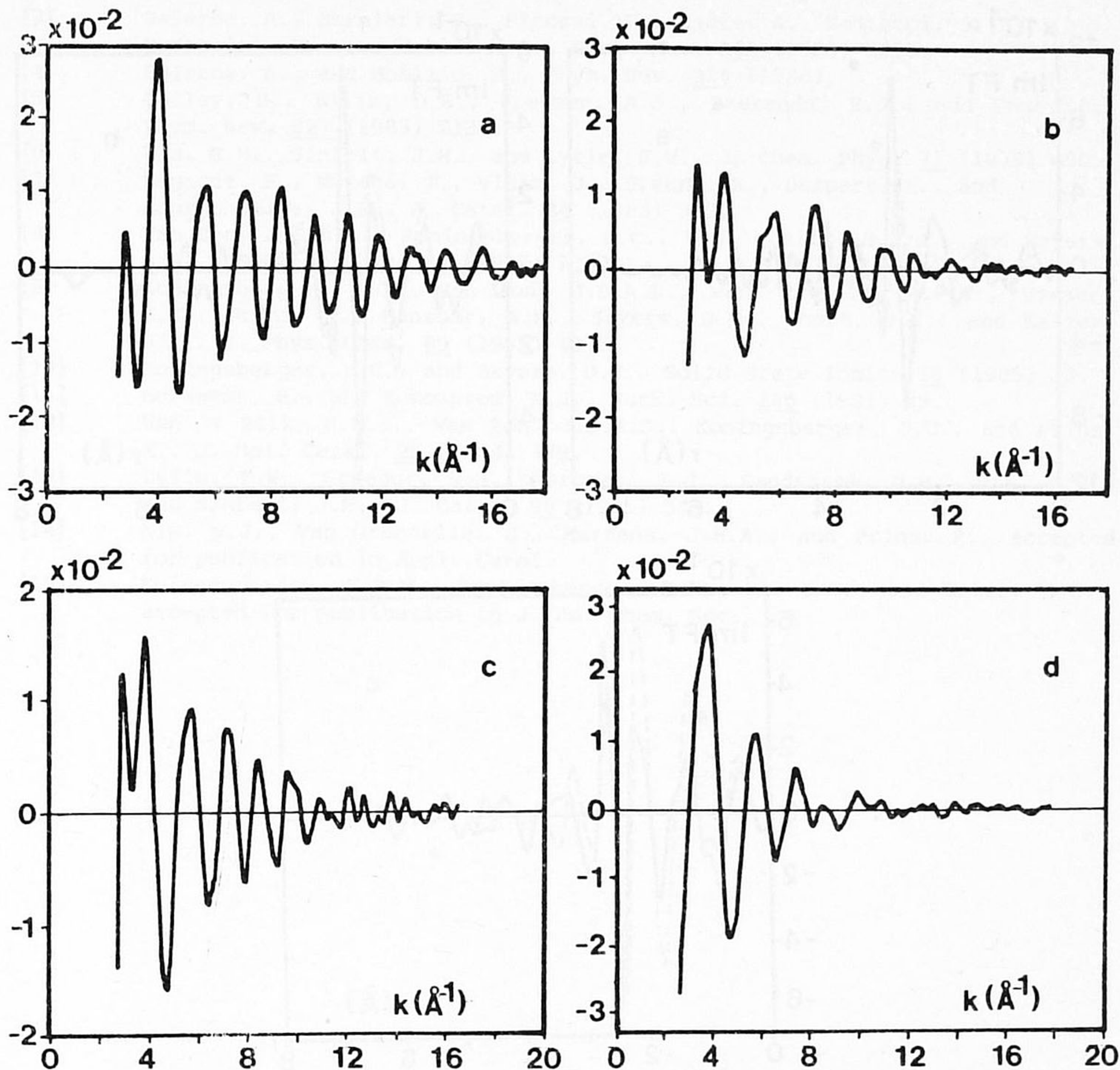


Figure 1. EXAFS data for the 0.8 wt% Ir/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst: a) reduction at 773 K, b) evacuation at 623 K, c) O<sub>2</sub> adsorption at 77 K, d) subsequent heating to 100 K.

the oxygen adsorption process at 77 K leads to oxygen neighbours at the surface of the iridium metal particles with the same type of metal-oxygen bonds as present in the metal-support interface after evacuation.

The conclusions drawn from the results mentioned above are further supported by the following results. Heating the sample under O<sub>2</sub> to 100 K gives rise to a significant change in the EXAFS spectrum. The spectrum (Fig. 1d) is now dominated by oxygen as backscatterer with a different (shorter) coordination distance. This can be seen clearly in Fig. 2c. The amplitude of the low  $r$  part (due to oxygen) of the Fourier transform largely increases accompanied by a change in phase (different metal-oxygen distance). The metal-metal part of the Fourier transform ( $2.5 < r < 3$  Å) decreases in amplitude showing the onset of the oxidation of the metal particles.

In conclusion, the results presented here definitely show the influence of chemisorbed hydrogen on the structural properties of small metal particles. Chemisorbed hydrogen also influences the metal-support interaction. Oxygen physisorption at 77 K produces the same type of metal-oxygen bonds as present in the metal-support interface of naked oxide-supported metallic particles. A complete analysis of the EXAFS data is in progress and will be published elsewhere.

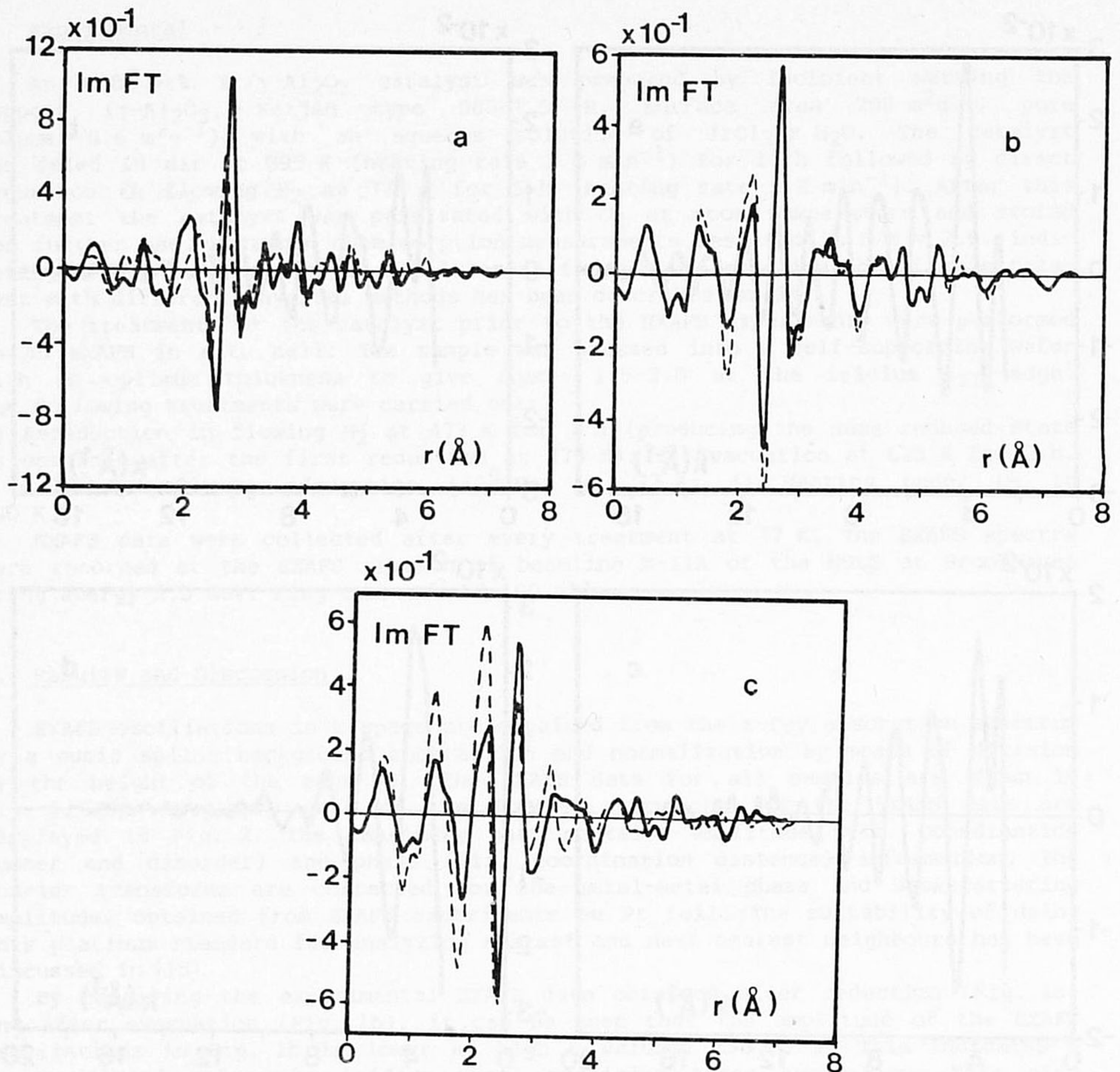


Figure 2. Imaginary parts of the Fourier transforms ( $k^1$ ,  $\Delta k = 3-12 \text{ \AA}^{-1}$ , phase and amplitude corr.) of the EXAFS data obtained after different treatments. a) Solid line: reduction at 773 K, Dotted line: evacuation at 623 K; b) Solid line: evacuation at 623 K, Dotted line:  $\text{O}_2$  adsorption at 77 K; c) Solid line:  $\text{O}_2$  adsorption at 77 K, Dotted line: subsequent heating to 100 K.

#### Acknowledgment

One of us (DES) likes to acknowledge grant DE-A505-80ER10742 provided by the Department of Energy for the development of beamline X-11A (NSLS).

#### References

- [1] Apai, G., Hamilton, J.F., Stohr, J., and Thompson, A., Phys. Rev. Lett. **43** (1979) 165.
- [2] Montano, P.A., Shenoy, G.K., Morrison, T.I. and Schulze, W., in 'EXAFS and Near Edge Structure III', Eds. K.O. Hodgson, B. Hedman, and J.E. Penner-Hahn (Springer-Verlag, Berlin, 1984) p. 231.

- [3] Balerna, A., Bernieri, E., Picozzi, P., Reale, A., Santucci, S., Burattini, E., and Mobilio, S., Phys. Rev. B31 (1985) 5058.
- [4] Balerna, A., and Mobilio, S., Phys. Rev. B34 (1986).
- [5] Delley, B., Ellis, D.E., Freeman, A.J., Baerends, E.J., and Post, D., Phys. Rev. B27 (1983) 2132.
- [6] Via, G.H., Sinfelt, J.H., and Lytle, F.W., J. Chem. Phys. 71 (1979) 690.
- [7] Lagarde, P., Murata, T., Vlaic, G., Freund, E., Dexpert, H., and Bournonville, J.P., J. Catal. 84 (1983) 333.
- [8] Van Zon, J.B.A.D., Koningsberger, D.C., Van 't Blik, H.F.J., and Sayers, D.E., J. Chem. Phys. 82 (1985) 5742.
- [9] Koningsberger, D.C., Van Zon, J.B.A.D., Van 't Blik, H.F.J., Visser, G.J., Prins, R., Mansour, A.N., Sayers, D.E., Short, D.R., and Katzer, J.R., J. Phys. Chem. 89 (1985) 4075.
- [10] Koningsberger, D.C., and Sayers, D.E., Solid State Ionics 16 (1985) 23.
- [11] Moraweck, B., and Renouprez, A.J., Surf. Sci. 106 (1981) 35.
- [12] Van 't Blik, H.F.J., Van Zon, J.B.A.D., Koningsberger, D.C., and Prins, R., J. Mol. Catal. 25 (1984) 379.
- [13] Lytle, F.W., Greigor, R.B., Marques, E.C., Sandstrom, D.R., Via, G.H., and Sinfelt, J.H., J. Catal. 95 (1985) 546.
- [14] Kip, B.J., Van Grondelle, J., Martens, J.H.A., and Prins, R., accepted for publication in Appl. Catal.
- [15] Duivenvoorden, F.B.M., Koningsberger, D.C., Uh, Y.S., and Gates, B.C., accepted for publication in J. Am. Chem. Soc.