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Pd/SiO_2

II. Effects of Pretreatment on Structure

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Experiments employing extended X-ray absorption fine structure and wide-angle X-ray diffraction, at the Cornell University High Energy Synchrotron Source, have shown that Pd catalysts of high percentage metal exposed stored in air consist primarily of crystalline PdO. Reduction of these catalysts in hydrogen results in the formation of palladium, whereas similar treatment of catalysts of low percentage metal exposed leads to palladium hydride.

INTRODUCTION

In situ X-ray diffraction studies of Pd/SiO_2 catalysts during hydrogenolysis of methylcyclopropane, and after specific pretreatments, have been reported in Part I (*1*). The compound β-$PdH_{0.7}$ forms when catalysts with percentages metal exposed (D_h) of 13.8 and 29.3% are pretreated and cooled in H_2, and exposed to either H_2 at room temperature or to a mixture of hydrogen and methylcyclopropane. A brief purge of He at room temperature decomposes the hydride to Pd but the rate of formation is faster than that of decomposition. Presumably, because of the hydride formation, the catalytic activity of these two catalysts for the hydrogenolysis of methylcyclopropane is lower when cooled from 450°C in H_2 than when cooled in He. However, the catalysts with $D_h > 29.3\%$ do not show any differences in activity for the two pretreatments. Perhaps they do not form hydride. Indeed, Boudart and Hwang (*2*) showed that the pressure required for hydride formation increases with decreasing crystallite size and Aben (*3*) has shown the total hydrogen uptake in the β-hydride phase to decrease with decreasing particle size.

In Part I (*1*), we could not confirm that the very small crystallites of $D_h > 29.3\%$ do not form hydride because we could not detect diffraction peaks with laboratory sources. However, we were able to show that less hydride formed with $D_h = 29.3\%$ than with $D_h = 13.8\%$. In this paper, we report that Pd particles having still smaller sizes than those employed in Part I definitely do not form hydride when exposed to H_2 at room temperature. We also show that after storage in air, catalysts of high D_h do not contain metallic Pd, but rather crystalline PdO.

EXPERIMENTAL PROCEDURES

The preparation and characterization of these catalysts have been presented in Ref.

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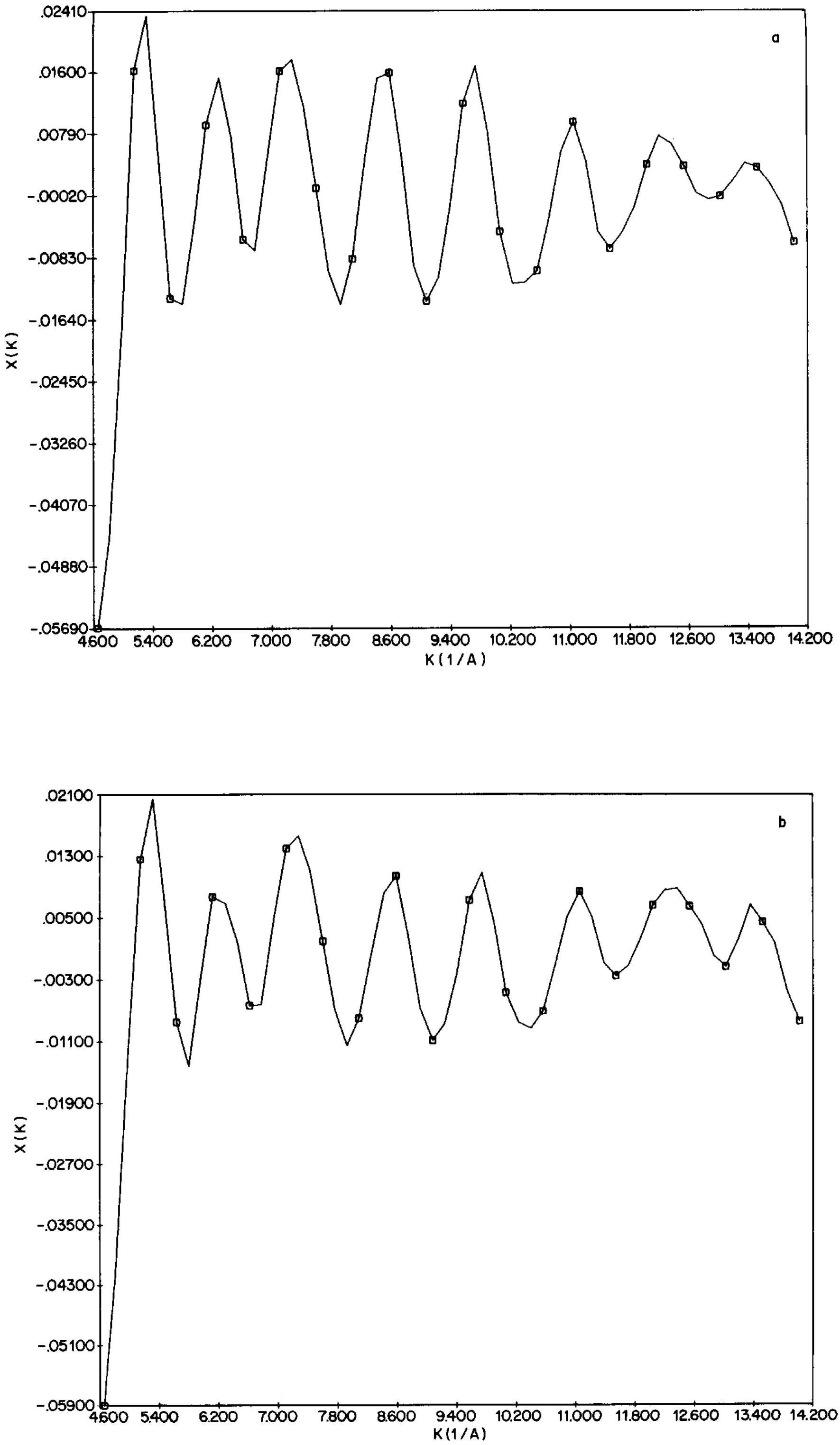

FIG. 1. $\chi(k)$ vs k: Pd/SiO$_2$ catalysts with D_h: (a) 13.8%, (b) 29.3%, (c) 49.8%, (d) 65.5%, and (e) 79.1%. (Only a few of the measured points are shown.)

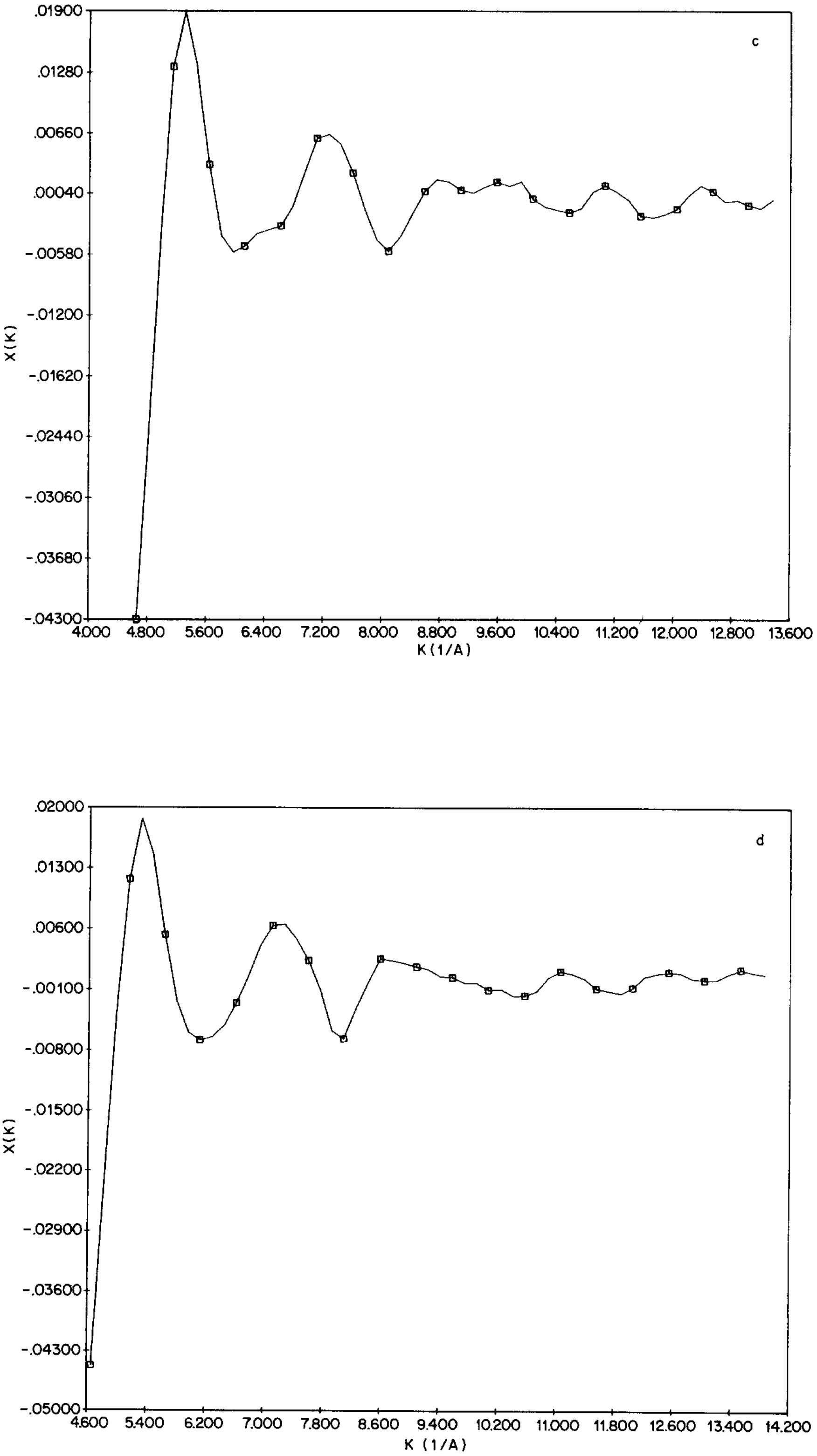

FIG. 1—*Continued.*

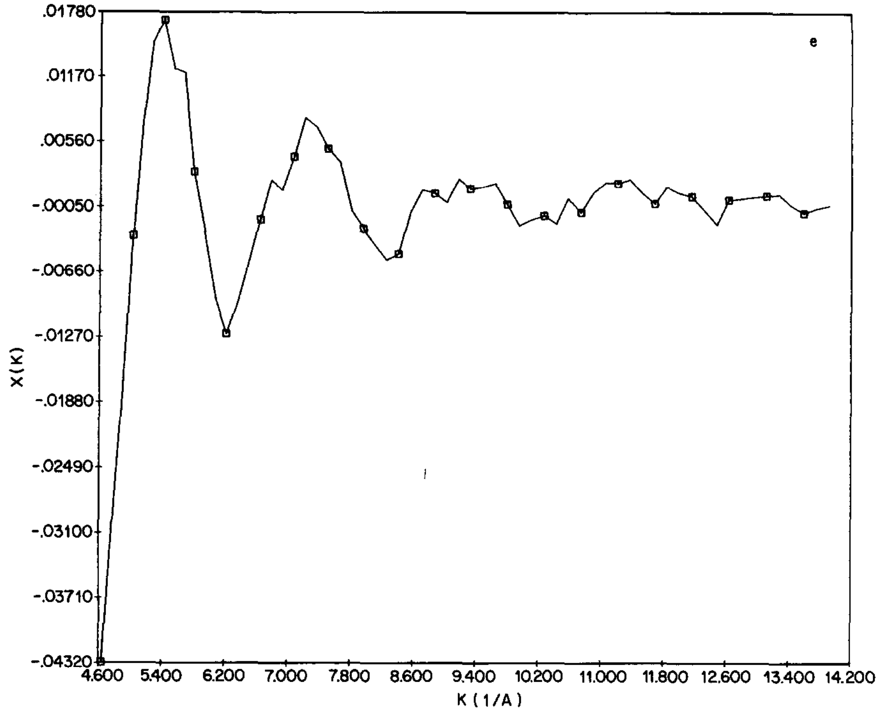

FIG. 1—*Continued.*

(*1*). Percentage metal exposed, D_h, is determined by pulsed hydrogen chemisorption. The typical loading is 2.1 wt% Pd.

The extended X-ray absorption fine structure (EXAFS) was measured above the Pd K edge at CHESS (Cornell University), employing a channel-cut Si crystal with a 220 reflection. The crystal had a weak link (a notch) to permit a slight tilt of one portion, so that the (narrower) reflections from higher harmonic wavelengths could be reduced to $\sim 10^{-2}$ of the main reflection, while reducing the latter by 50%. An 8-cm-long, flowing Ar ionization chamber was employed to detect the monochromated beam incident on the specimen (whose thickness was 2.5μ, where μ is the linear absorption coefficient of the total catalyst above the Pd edge). The transmitted beam was detected with a sealed ion chamber, 20 cm long, containing Xe at 1 atm. Our procedures for data analysis are given in Ref. (*4*).

For wide-angle X-ray scattering (WAXS), also carried out at CHESS, a thin elastically bent Si triangle was employed with a 220 reflection, to produce a wavelength of 0.945 Å (as measured with a Pt powder). Reflection from a float glass mirror was employed to reject harmonic contamination. The beam was focused to 2 mm^2 at the specimen, 3.5 m from this monochromator. The monochromator chamber was filled with He, and the path from it to the diffractometer was evacuated. Counts were taken for 10^6 monitor counts (~250 s) every 0.25° 2θ, on a standard Picker powder diffractometer, mounted vertically and equipped with a 0.1° receiving slit and a scintillation detector.

RESULTS AND DISCUSSION

The results for the WAXS will be presented first. For D_h = 49.8% (stored in air), a peak was detected at the position for a 111 reflection from metallic Pd. Despite the fact that the incident beam was 2×10^{10} cps (one order of magnitude more intense than the characteristic radiation from a Cu target on a 12-kW rotating anode X-ray generator),

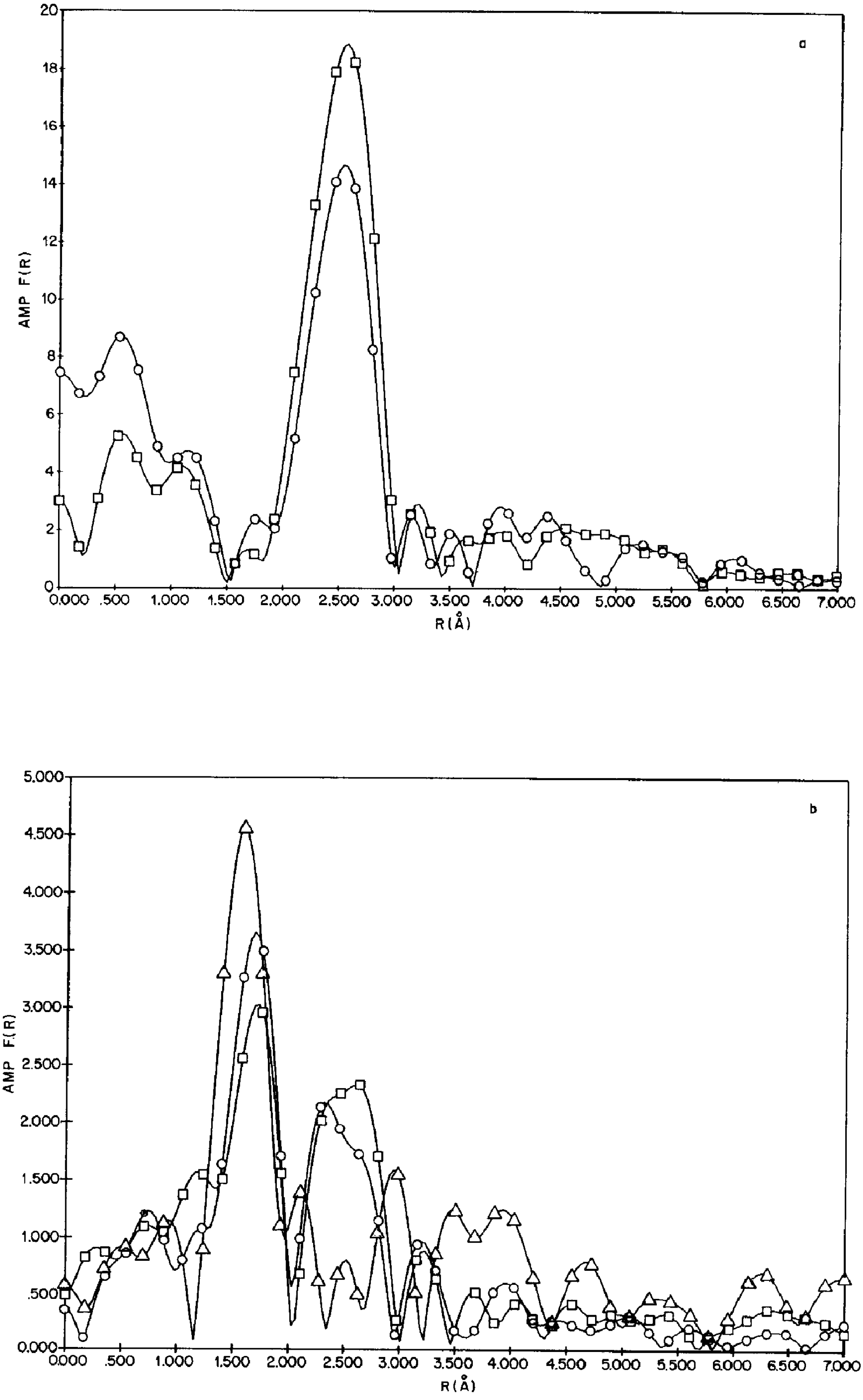

FIG. 2. Amplitude of RDF vs R. D: (a) 13.8% (□), 29.3% (○); (b) 49.8% (□), 65.5% (○) and 79.1% (△).

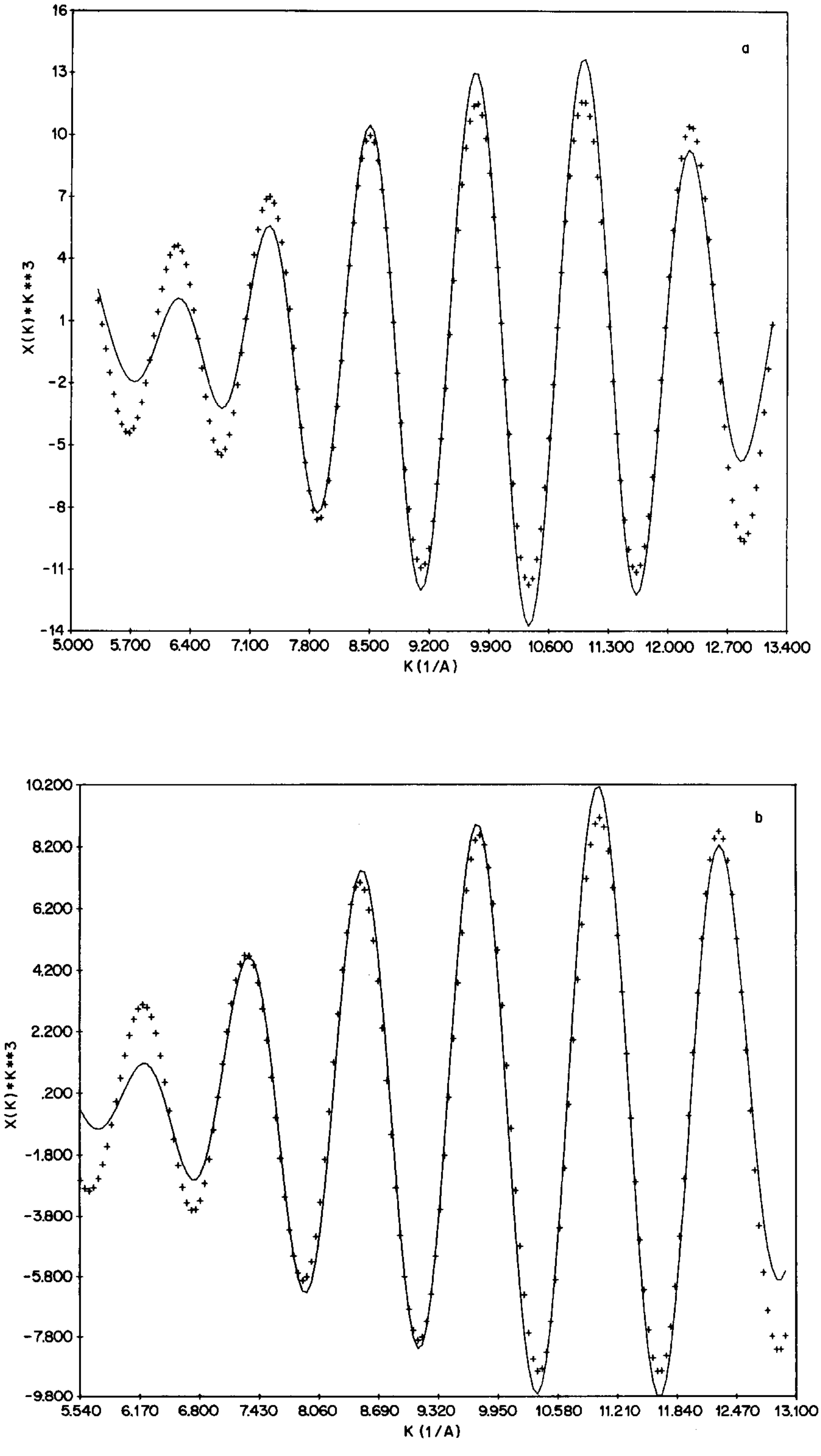

Fig. 3. The back-transformed $k^3\chi(k)$ corresponding to the main peak in the RDF (Fig. 2a), along with nonlinear least-squares fit (crosses). (a) $D_h = 13.8\%$. (b) $D_h = 49.9\%$.

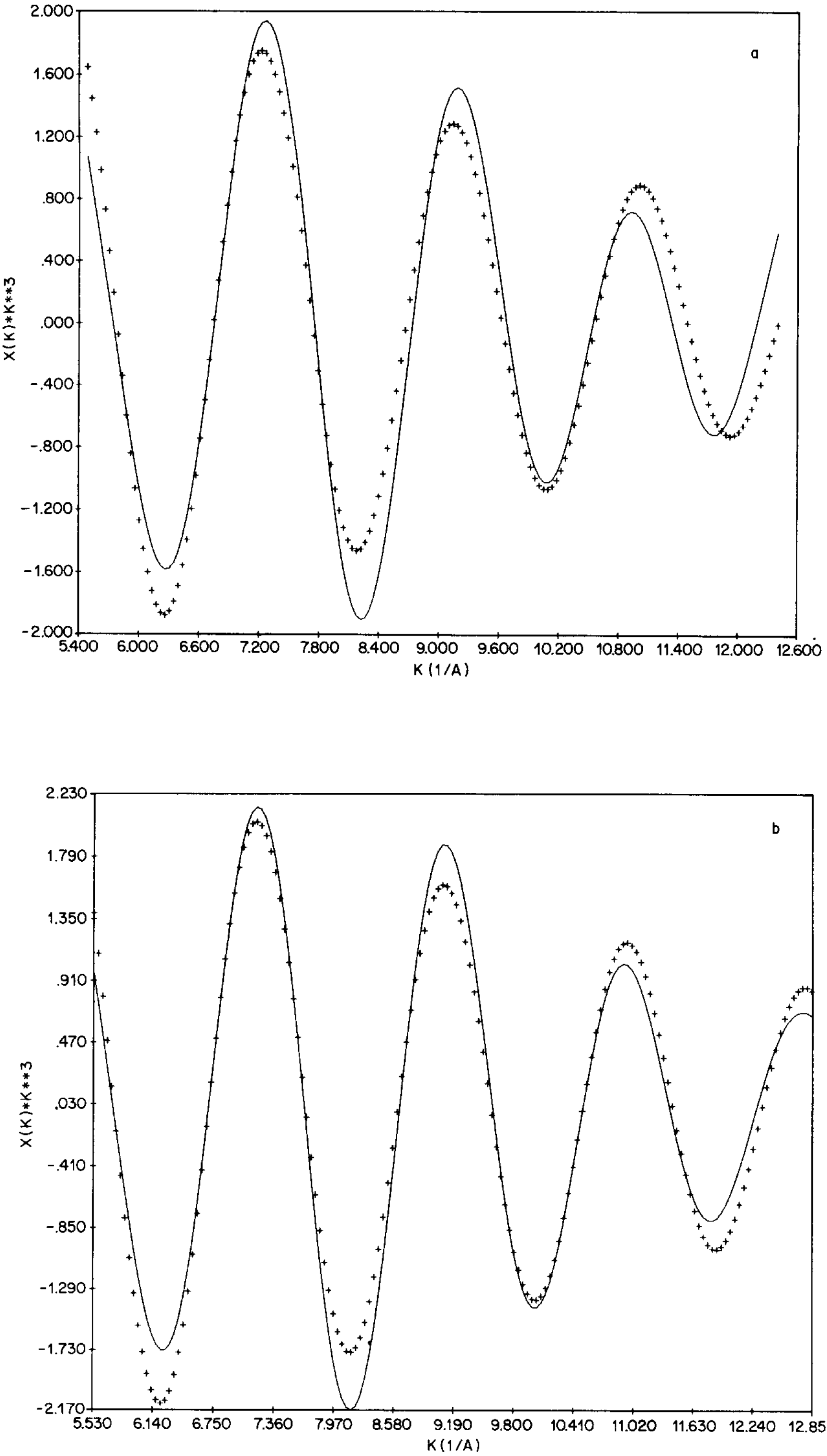

FIG. 4. The back-transformed $k^3\chi(k)$ corresponding to the main peak in the RDF (Fig. 2b) along with nonlinear least-squares fit (crosses). (a) 49.8%, (b) 65.5%, and (c) 79.1%.

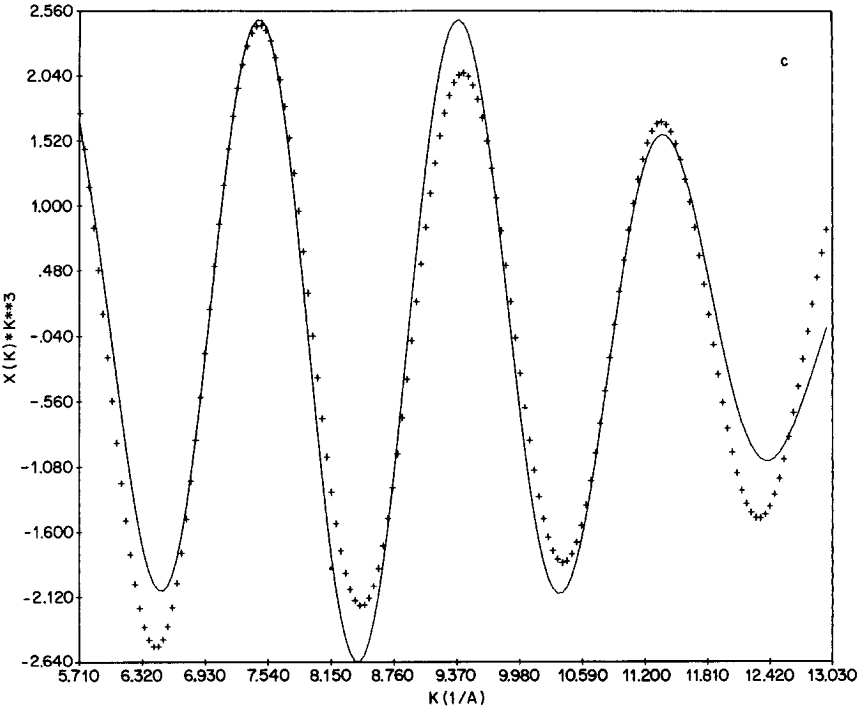

FIG. 4—*Continued.*

the peak had a count rate of 5 × 10^3 cps above the scattering from SiO_2. (The total count rate collected from Pd plus SiO_2 was typically 4 × 10^4 cps.) This relatively low intensity is due to the low metal loading and the very small particle sizes for these high dispersions. No reflections other than the first could be detected.

For stored catalyst of D_h = 65.5% there was no Pd 111 peak (the strongest peak in the pattern), but a peak 3.9° 2θ lower. The strongest peak from PdO (*5*) should occur 3.7° 2θ below the Pd 111 reflection. The position we detected strongly suggests that, for D_h = 65.5%, the catalyst is largely PdO.

These two catalysts were then exposed to H_2 gas at 25°C for 20 min (in the cell described in Ref. (*4*)). For hydride a strong peak would occur 0.8° 2θ below the Pd 111 peak and 2.9° above the strongest peak for PdO. For D_h = 49.8% for which the diffrac-

TABLE 1

Nonlinear Least-Squares Fit to $k^3\chi(k)$, First Shell

Catalyst, D_h (%)	N_1	R_1 (Å)	σ_1^2 (10^{-3} Å^2)	λ_1 (Å)	ΔE^a (eV)
13.8	12 (fixed)	2.725 (0.005)[b]	3.9 (0.5)	4.1 (0.3)	21.4 (1.1)
29.3	11 (fixed)	2.713 (0.004)	2.9 (0.4)	3.11 (0.16)	18.9 (1.3)

[a] From the edge for metallic Pd.

[b] Numbers in parentheses are the standard deviations of the fit.

TABLE 2

Nonlinear Least-Squares Fit to $k^3\chi(k)$, First (Oxide) Peak in RDF

Catalyst, D_h (%)	N_1	R_1 (Å)	σ_1^2 (10^{-3} Å^2)	λ_1 (Å)	ΔE^a (eV)
49.8	3.8 (0.4)[b]	1.985 (0.007)	4.6 (0.8)	3.668 (fixed)	27.0 (1.3)
65.5	4.1 (0.3)	1.995 (0.004)	3.7 (0.4)	3.668 (fixed)	26.8 (1.0)
79.1	4.0 (fixed)	1.932 (0.005)	2.3 (0.5)	3.7 (0.32)	27.0 (1.3)

[a] From the edge for metallic Pd.

[b] Numbers in parentheses are the standard deviations of the fit.

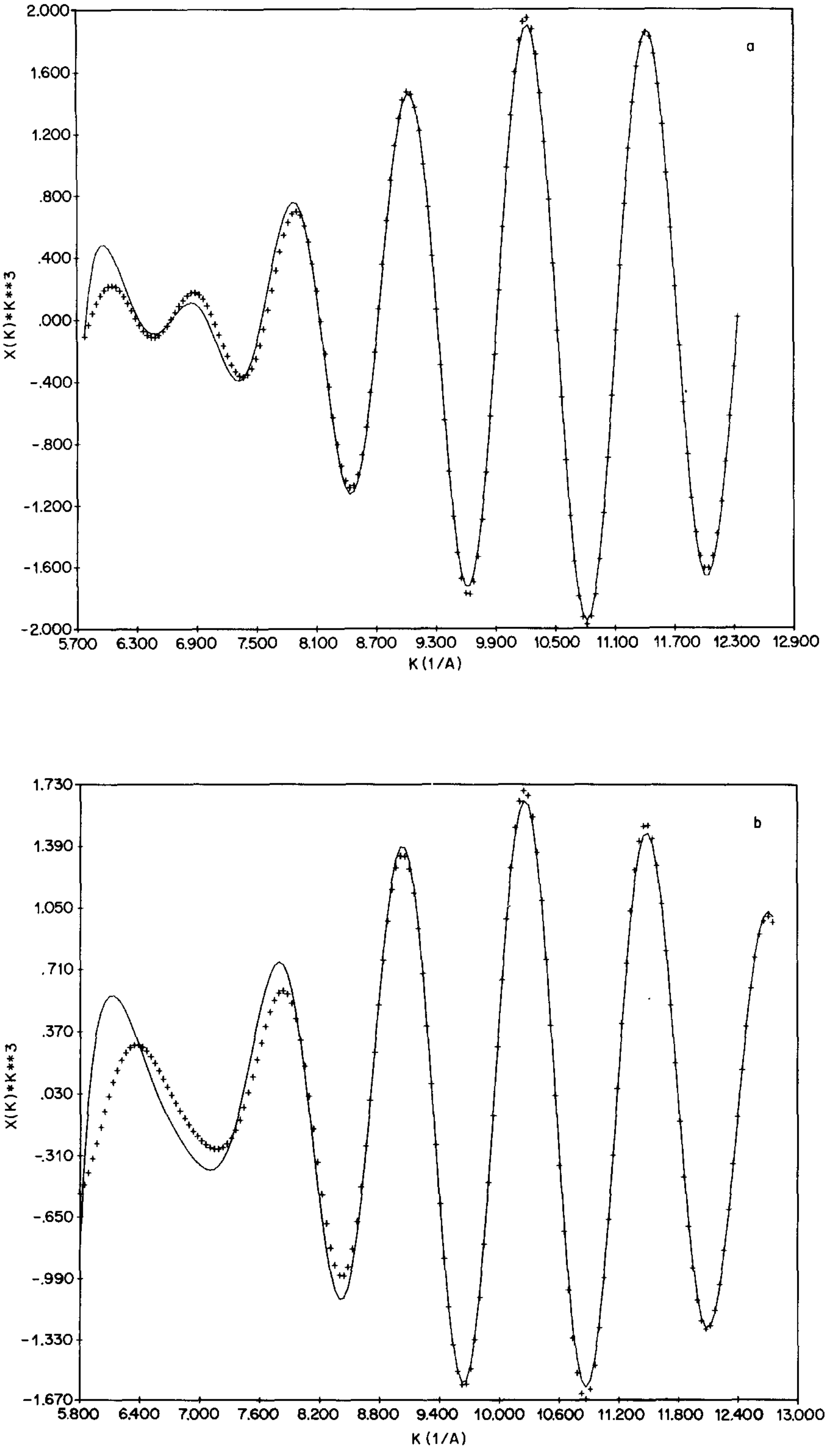

FIG. 5. The back-transformed $k^3\chi(k)$ corresponding to the merged peak in the RDF (Fig. 2b), along with nonlinear least-squares fit (crosses). (a) 49.8% and (b) 65.5%.

TABLE 3

Nonlinear Least-Squares Fit to $k^3\chi(k)$, Merged Peak (Fig. 2b)[a]

Catalyst, D_h (%)	R_2	σ_2^2 (10^{-3} Å^2)	N_2	ΔE[b] (eV)	R_3 (Å)	σ_3^2 (10^{-3} Å^2)	N_3	ΔE[b] (eV)
49.8	2.795	2.0	0.8	11.4	3.130	6.0	2.4	22.9
	(0.014)[c]	(1.5)	(0.3)	(2.1)	(0.016)	(2.0)	(0.8)	(2.1)
65.5	2.784	4.5	1.5	11.4	3.125	6.0	1.5	25.2
	(0.005)	(1.9)	(0.6)	(2.9)	(0.035)	(3.8)	(1.6)	(5.0)

[a] λ fixed at 3.9 Å.

[b] From the edge for metallic Pd.

[c] Numbers in parentheses are standard deviations of the fit.

tion peak after storage in air was due to metallic Pd there was no change of the peak position (to within 0.2° 2θ). However, after flushing with He, which should have removed any hydride, the peak position was unchanged, nor did it change after reexposure to air. It appears that this catalyst remains as metallic Pd for all these treatments.

For $D_h = 65.5\%$, the introduction of hydrogen gas led to an increase in 2θ of the peak by 3°, which is within 0.1 of the shift expected on converting PdO to Pd $H_{0.7}$ or Pd. However, when the catalyst was swept with He, which should reduce any hydride, the peak did not shift. After exposure to air, the peaks shifted to lower 2θ by 2.5°. These results are consistent with the reduction of oxide to metal by hydrogen, and reoxidation on exposure to air.

Fourier analysis of the peak shape after storage in air (assuming no strains, as these were low-angle peaks), following the procedures in Ref. (*1*), yielded crystallite sizes of 26 and 16 Å for D_h = 49.8 and 65.5%, respectively. These sizes may be converted to values of percentage exposed from WAXS, D_x, of 43 and 70%, in good agreement with D_h.

The EXAFS oscillations above the Pd K absorption edge, $\chi(k)$, vs the photoelectron wave vector, k, are shown in Figs. 1a–e for catalysts with D_h = 13.8–79.1%, after storage in air. The catalysts with D_h = 49.8% or greater exhibit rapidly decaying oscillations, characteristic of oxides. Now:

$$\chi(k) = \sum_j [N_j F_j(k)/kR_j^2] \exp(-2k^2\sigma^2) \exp(-2R_j/\lambda) \sin[2kR_j + \Phi_j(k)]. \quad (1)$$

Here $F_j(k)$ is the backscattering amplitude of the atom at j and N_j is the number of neighbors at a distance R_j; σ_j^2 is the relative mean-square atomic displacement, λ is the electron mean-free path for inelastic collisions, and Φ_j is the phase shift introduced by the absorbing and backscattering atoms. The radial distribution functions (RDF) derived from the Fourier transform of $\chi(k)$ are shown in Fig. 2a for D + 13.8 and 29.3% and in Fig. 2b for D_h = 49.8, 65.5, and 79.1%. (As is usual with such plots, the positions of peaks are shifted from the true values due to the phase shifts, $\Phi_j(k)$, associated with the backscattering process.) The results of nonlinear least-squares analysis of the back-transformed $\chi(k)$ for the first shell, to obtain the interatomic distance R_j, relative amplitude of vibration, σ_j, electron mean-free path, λ, and shift of the edge, ΔE, from that for bulk Pd, are given in Table 1, for D_h = 13.8 and 29.3%. The theoretical values from Ref. (*6*) for $\Phi_j(k)$ and $F_j(k)$ are employed in this fit. Also presented are the standard deviations of these parameters. The results of the analysis are shown in Figs. 3a and b. The nearest-neighbor distance is (within the usual EXAFS experimental error of 0.02 Å) that of the Pd–Pd distance in bulk Pd, 2.75 Å. This is in agreement with Part I in which no change in the lattice parameter of these catalysts was detected in WAXS for Pd/SiO$_2$ of D_h = 13.8 and 29.3%.

The RDFs of the more highly dispersed catalysts, Fig. 2b, are quite different from those for the low dispersions, Fig. 2a. The strongest peak is at a distance ~0.5 Å lower in Fig. 2b than in Fig. 2a. Furthermore, the height of this peak *increases* with percentage exposed, in contrast to the low dispersions (for which the decrease is due to decreasing coordination as D_h increases). For PdO, around each absorbing Pd atom there are four oxygen ions at 2.01 Å, and four Pd ions at 3.03 Å (*5*). Assuming this is the correct structure for these catalysts, the least-squares fit to the back-transformed $k^3\chi(k)$ for the region of the first shell is shown in Figs. 4a–c, for D_h = 49.8, 65.5, and 79.1%. The parameters are given in Table 2. These results suggest that for these high dispersions, the catalysts do indeed contain considerable amounts of PdO. Also, the PdO distance is reduced at the highest dispersion. However, for D_h = 49.8 and 65.5% there is a broad double peak in the RDF at 2.5 Å (Fig. 2b). The analyses of the back-transforms of these regions for these two catalysts are shown in Figs. 5a and b, and in Table 3. There are two distances, 2.75 Å, corresponding to Pd–Pd pairs in bulk Pd, and 3.03 Å, corresponding to Pd–Pd pairs in PdO. Evidently, in these catalysts, some of the particles are not completely converted to PdO. Note, however, that the metallic Pd–Pd distance is greater in this highly dispersed form than in coarser catalysts (compare Tables 1, 3).

CONCLUSIONS

1. For Pd catalysts stored in air, the amount of PdO, as compared to Pd, increases with percentage exposed. At a value of percentage exposed of 79.1% a stored catalyst is nearly completely oxidized.
2. Catalysts with percentage metal exposed equal to or greater than 49.8% do not form hydride at P_{H_2} = 1 atm.
3. To properly characterize highly dispersed catalysts examination by both EXAFS and WAXS is recommended.

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