Catalysis Letters 6 (1990) 263–270

STACKING-FAULTS IN VERY FINE PALLADIUM PARTICLES SUPPORTED ON PUMICE

G. FAGHERAZZI, A. BENEDETTI

Dipartimento di Chimica Fisica, Università di Venezia, Calle Larga S. Marta 2137, 30123 Venice, Italy

A. MARTORANA, S. GIULIANO, D. DUCA and G. DEGANELLO

Dipartimento di Chimica Inorganica, Università di Palermo, Via Archirafi 26-28, 90123 Palermo, Italy

Received 15 March 1990; revised accepted 7 July 1990

Stacking-faults, X-ray diffraction of palladium particles, microstructure, pumice

By means of an X-ray diffraction study, carried out with best-fitting procedures, of the asymmetry and peak maximum shifts of some reflections, stacking-faults in the FCC lattice of very fine palladium particles supported on pumice were detected using the Warren-Wagner-Cohen theoretical approach.

1. Introduction

The presence of lattice disorder detectable by X-ray diffraction (line broadening, peak asymmetry and peak maximum shifts analysis) has been displayed in many structural investigations of metals and alloys in relation to cold-working processes [1–2]. On the contrary, relatively few papers have shown the presence of lattice disorder in the very fine particles of highly dispersed metal supported catalysts. As regards palladium dispersions, Nandi et al. [3] detected microstrain values $\langle \epsilon^2_{L=50\,\text{Å}} \rangle^{1/2}_{111}$ of about 0.003 at a column length $L = 50$ Å (along the [111] direction) in palladium particles supported on silica. In the same crystallographic conditions Pielaszek [4] detected relevant amounts of microstrains (about 0.007) in palladium crystallites supported on gamma-alumina. On the other hand, Benedetti et al. [5] showed that in charcoal supported palladium catalysts the principal cause of line broadening had to be attributed to crystallite smallness. Cocco et al. [6] also attributed the observed X-ray diffraction line broadening effects to palladium microcrystallinity only, in Pd catalysts supported on vitreous supports.

In the present paper a careful analysis, carried out with best-fitting techniques on the 111, 200, 220, 311, 222 X-ray reflections of two palladium dispersions supported on pumice, is reported. Palladium particles were obtained by the reaction of a pumice suspension in pentane solution of $Pd(C_3H_5)_2$ [7] at low temperature, by means of a process derived from Yermakov [8]. The anchored palladium, in the Pum-O-$Pd(C_3H_5)$ form, was then reduced at low temperature to metallic Pd with high purity H_2.

Further considerations on the synthesis of palladium catalysts supported on pumice will be reported elsewhere [9] together with a study of their activity in some hydrogenation processes.

2. Experimental

The two palladium dispersions on pumice investigated here have a metal percentage of 2.4 (wt%) (sample I) and 1.1 (wt%) (sample II), respectively. In the present paper we have studied the possible effects of lattice disorder on peak asymmetry and peak maximum shifts according to the theoretical approach by Warren [10]. A best-fitting procedure of the peak profiles has allowed us accurately to obtain the $K\alpha_1$ peak profile components on which the analysis was performed. Asymmetrical functions were employed in the fit and minimization was reached by using a Simplex modified method [11]. All programs were written in BASIC and were made to run on a PC.

The X-ray diffraction analysis was carried out with a highly stabilized Siemens generator (Kristalloflex 805) coupled with a Philips vertical diffractometer equipped with a graphite focussing monochromator on the diffracted beam and with a scintillation counter. Cu $K\alpha$ radiation and step-by-step technique were employed (steps of 0.05° as 2Θ) with collection times of 100 s per step.

3. Results and discussion

Fig. 1 shows that the 200 peaks of sample I and sample II are shifted towards lower Bragg angles as compared with the corresponding diffractogram of a pure reference Pd sample prepared by a precipitation method and having a crystallite size of about 200 Å. On the contrary, no appreciable shifts for the 111 peaks are evident. Note that the unit cell edge of pure palladium was found to be equal to 3.8898 (6) Å, in perfect agreement with the JCPDS-ASTM powder diffraction file (N. 5-0683); the angular positions of the 111, 200, 220, 311, 222, 400 peaks and the plot of Adler and Wagner [12] were used. By employing the same plot, lattice parameters a_0 of 3.899 (6) Å for sample I and of 3.897 (8) Å for sample II were obtained.

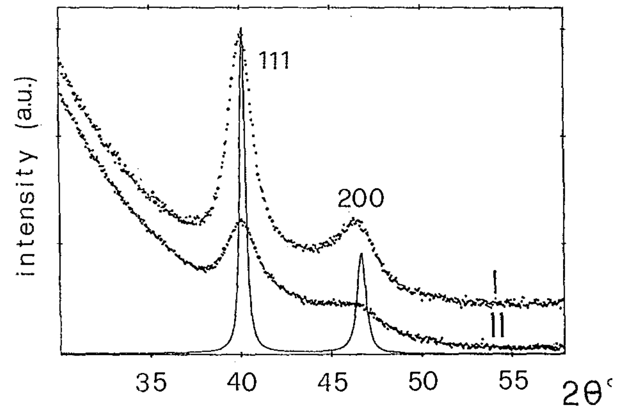

Fig. 1. Comparison among the 111 and 200 peak profiles of catalyst I (2.4 wt% of Pd), of catalyst II (1.1 wt% of Pd) and of a reference sample of pure Pd continuous line). A shift of the 200 peak maximum for the catalysts, towards a lower Bragg angle, clearly appears for both samples.

Fig. 2a shows a portion of the diffractogram of sample I on which the relevant portion of the diffractogram of pumice has been matched. Owing to its low surface area (5 m^2/g) and absence of micropores we observed that the experimental background due to the amorphous support could be subtracted in a consistent way in the fitting procedure. From fig. 2b, where the background has been suitably scaled and then subtracted, the 200 peak clearly appears asymmetrical.

Both the $K\alpha_1$ and $K\alpha_2$ components of each peak profile were best-fitted with asymmetrical functions built up with a two "half" pseudo-Voigt functions, one defined for $2\Theta \geq \Theta^{\circ}_{\mathrm{PPM}}$ and the other for $2\Theta \leq 2\Theta^{\circ}_{\mathrm{PPM}}$, where $2\Theta_{\mathrm{PPM}}$ is the peak maximum position. In each pair of "half" pseudo-Voigt functions all parameters are in common with the exception of the half width at half maximum. The two $K\alpha_1$ and $K\alpha_2$ contributions of each peak investigated are bound together by the usual crystallographic constraints. For the definition of a pseudo-Voigt function and its use in fitting procedures of X-ray diffraction peak profile analysis see for example ref. [13].

Owing to the great broadness of the peaks of both samples I and II the asymmetry due to instrumental factors can be ignored and therefore the observed asymmetry can be entirely ascribed to stacking-faults since directional strains are very unlikely in samples not subjected to mechanical treatments. With this type of analysis and starting from the results of the fitting it was possible to determine the difference $\Delta 2\Theta^{\circ}(hkl) = 2\Theta^{\circ}_{\mathrm{PCG}}(hkl) - 2\Theta^{\circ}_{\mathrm{PPM}}(hkl)$ between the baricentre $2\Theta^{\circ}_{\mathrm{PCG}}$ and the peak maximum position for the $K\alpha_1$ component. By applying to the 111–200 pair of peaks the formula reported by Cohen and Wagner [14]:

$$\Delta 2\Theta^{\circ}(111) - \Delta 2\Theta^{\circ}(200) = (11 \tan \Theta^{\circ}_{111} + 14.6 \tan \Theta^{\circ}_{200})(\beta + 4.5\alpha''),$$

where β are twin or growth stacking-fault probabilities and α'' are double (extrinsic) deformation stacking-fault probabilities, it was possible to calculate for

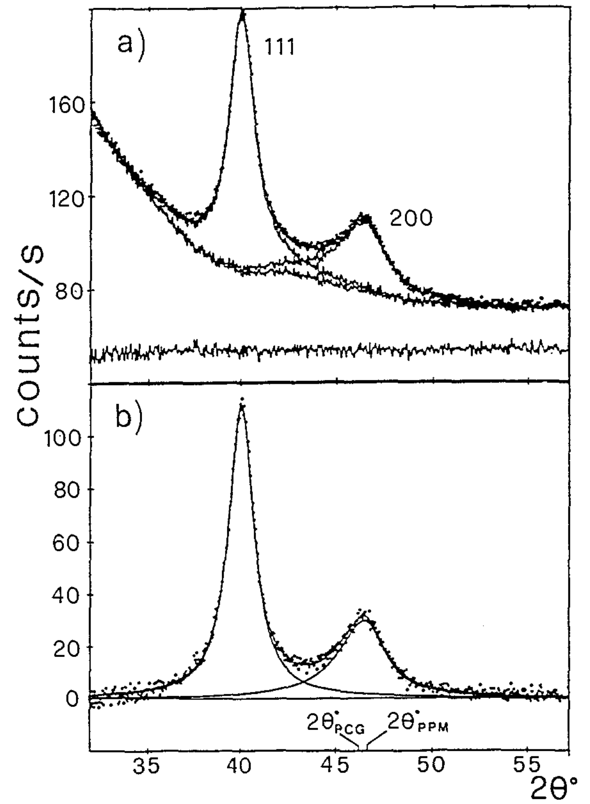

Fig. 2. 111 and 200 peak profiles of catalyst I (2.4 wt% of Pd). The continuous curves represent the sums of the matched (suitably scaled) experimental background with the optimized analytical functions. The asymmetry of the 200 peak can be estimated (see section b of the figure), from the difference between the baricentre $2\Theta_{\mathrm{PCG}}$ position and the peak maximum $2\theta_{\mathrm{PPM}}$ position ($\Delta 2\Theta°(200) = -0.55°$). Note that in b) the background was subtracted.

$\beta + 4.5\alpha''$ values of 0.05 and 0.03 for sample I and sample II, respectively.

From the peak shifts analysis (see Wagner in ref. [15]) we were able to compute two further parameters connected to lattice disorder: the deformation stacking-fault probability α and the residual strain $\langle \epsilon_L \rangle$. These two parameters were obtained using the following equation [15]:

$$(\Delta a/a)_{hkl} = (\Delta a/a)_{\mathrm{ref}} + \langle \epsilon_L \rangle + G(hkl)\alpha,$$

where $(\Delta a/a)_{hkl} = (a_{hkl} - a_{hkl}^{\mathrm{ref}})/a_0$, $(\Delta a/a)_{\mathrm{ref}} = (a_0 - a_0^{\mathrm{ref}})/a_0$ with

a_{hkl}^{ref} = lattice parameter of reference sample calculated from the peak maximum position of the hkl reflection

a_{hkl} = lattice parameter calculated from $2\Theta_{\mathrm{PPM}}^{\circ}$ of the hkl reflection of the supported palladium

a_0 = extrapolated or true lattice parameter of the supported palladium

a_0^{ref} = extrapolated lattice parameter of reference sample.

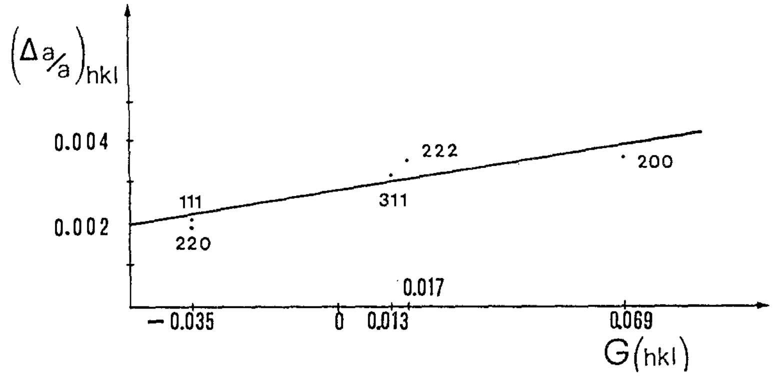

Fig. 3. Plot of $(\Delta a/a)_{hkl}$ vs. $G(hkl)$ for catalyst I. From the slope the α stacking-fault probabilities are determined. The intercept at zero gives $(\Delta a/a)_{\text{ref}}+\langle\epsilon_L\rangle$ which in this case is $\approx(\Delta a/a)_{\text{ref}}$.

In order to determine α and $\langle\epsilon_L\rangle$ we have plotted $(\Delta a/a)_{hkl}$ vs. the parameter $G(hkl)$ that depends on the hkl reflection (see table 7.1 of ref. [15] where the values of $G(hkl)$ are recorded).

From this type of plot a rather low value of α was determined, equal to 0.015, for catalyst I (see fig. 3), while no residual strain was found. Similar qualitative results were obtained for catalyst II, but the much less intense reflections of this palladium dispersion with respect to sample I did not permit a precise enough peak shift analysis to be performed.

Table 1 records all the parameters deduced on catalyst I and catalyst II from the present X-ray diffraction study.

4. Conclusions

From all these results we can conclude that in very fine palladium particles supported on pumice stacking-faults could be detected, mainly in the form of growth faults.

Table 1
Pumice supported palladium microstructural features

Catalyst (Pd wt%)	Unit cell parameter (Å)	Stacking-fault probabilities		Apparent crystallite crystallite size (Å)	Microstrain $\langle\epsilon^2_{L=20\,\text{Å}}\rangle^{1/2}_{111}$
		$\beta+4.5\alpha''$	α		
I (2.4)	3.899 (6)	0.05 (1)	0.015 (6)	42 (4) [a]	0.0027 (7)
II (1.1)	3.897 (8)	0.03 (1)	n.d.	25 (3) [b]	n.d.

[a] Volume-weighted apparent crystallite size and r.m.s. microstrain obtained by the Warren-Averbach analysis from the line broadening of the 111–222 pair of reflections.

[b] Volume-weighted apparent crystallite size obtained by a single peak Fourier analysis.

Since none of the structural studies reported in literature on Pd dispersions (see introduction) discussed a possible presence of faults, it seems reasonable to think that the presence of this type of disorder can depend on the used support material (pumice in the present case) as well as on the chemical preparation.

It is worth noticing that the amount of microstrain measured on catalyst I (containing 2.4 wt% of Pd) is very similar to the one detected by Nandi et al. [3] on Pd catalysts supported on silica.

A line-broadening investigation carried out on the 111, 200, 220, 311 and 222 peaks of the present palladium dispersions has confirmed the presence of faulting. In the present letter these results cannot be adequately reported and discussed; they will be published elsewhere [9].

Also a mathematical model, which will be reported in another paper [16], developed in order to explain a possible presence of stacking-faults on the Pd catalysts here investigated, has confirmed the present conclusions.

Acknowledgements

We thank CNR (Progetto strategico: Metodologie Chimiche per la Protezione e Salvaguardia dell'Ambiente and Progetto finalizzato Materiali speciali) and Ministero dell'Università e Ricerca Scientifica (MURST 40%) for financial support.

Pumex S.p.A. for supplying pumice and for a grant to S. Giuliano is acknowledged.

Thanks are due to Mr. L. Bertoldo for technical assistance in the experimental X-ray diffraction work.

References

[1] H.P. Klug and L.E. Alexander, *X-ray Diffraction Procedures* (J. Wiley & Sons, New York, 1974).

[2] D.E. Mikkola and J.B. Cohen, in: *Local Atomic Arrangements Studied by X-ray Diffraction*, eds. J.B. Cohen and J.E. Hilliard (Gordon & Breach, Sci. Publ., New York, 1966).

[3] R.K. Nandi, R. Pitchai, S.S. Wong, J.B. Cohen, R.L. Burwell, Jr. and J.B. Butt, J. Catalysis 70 (1981) 298.

[4] J. Pielaszek, Catal. Lett. 1 (1988) 117.

[5] A. Benedetti, G. Cocco, S. Enzo, G. Piccaluga and L. Schiffini, J. Chim. Phys. 78 (1981) 961.

[6] G. Cocco, L. Schiffini, G. Strukul and G. Carturan, J. Catal. 65 (1980) 348.

[7] P.W. Jolly, Angew. Chem. 24 (1985) 283.

[8] Yu.I. Yermakov, Catal. Rev. 13 (1976) 77.

[9] G. Deganello, D. Duca, S. Giuliano, A. Martorana, G. Fagherazzi, A. Benedetti and G. Spoto, J. Catal., submitted.

[10] B.E. Warren, *X-ray Diffraction* (Addison-Wesley Publ. Co., Reading, Ma, 1969).

[11] J.A. Nelder and R. Mead, Comput. J. 7 (1965) 308.

[12] R.P.I. Adler and C.N.J. Wagner, J. Appl. Phys. 33 (1962) 3451.
[13] S. Enzo, G. Fagherazzi, A. Benedetti and S. Polizzi, J. Appl. Cryst. 21 (1988) 536.
[14] J.B. Cohen and C.N.J. Wagner, J. Appl. Phys. 33 (1962) 2073.
[15] C.N.J. Wagner, in *Local Atomic Arrangements Studied by X-ray Diffraction*, eds. J.B. Cohen and J.H. Hilliard (Gordon & Breach, Sci. Publ., New York, 1966).
[16] A. Martorana, A. Benedetti, G. Deganello, D. Duca, G. Fagherazzi and S. Giuliano, J. Appl. Crystallogr., to be submitted.