Very Active Hydrogenation Catalyst Composed of Extremely Dispersed Palladium on Vitreous Supports

By Giorgio Cocco and Giuliano Fagherazzi

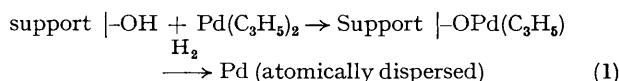(Istituto di Chimica Fisica, Calle Larga 2137 S.Marta, Venezia, Italy)

and Giovanni Carturan* and Vittorio Gottardi

(Centro di Chimica Metallorganica del C.N.R. ed Istituto di Chimica Industriale, Via Marzolo 9, Padova, Italy)

Summary The small angle X-ray scattering (SAXS) determination of the particle size distribution of Pd metal supported on vitreous materials demonstrates the extremely high degree of dispersion of the metal, which can be linearly related to the catalytic activity in hydrogenation reactions and to the physical and chemical properties of the supports.

PALLADIUM microparticles or clusters obtained upon in situ reduction of surface organometallic compounds anchored to inorganic supports are still uncharacterized with respect to their average size and the degree of dispersion. However, to account for the high catalytic activity in hydrogenation reactions of this class of catalysts a metal phase dispersed at the 'atomic level' has been invoked.[1,2] Direct evidence for this possible relationship can be provided by comparing the catalytic behaviour with the experimental structural data (obtained by small angle X-ray scattering; SAXS) here reported for the first time.

Very active hydrogenation catalysts with low Pd content were prepared by the reaction of $[Pd(C_3H_5)_2]$ with 'metalorganic glasses'[3] bearing surface –OH groups and reduction of the anchored Pd^{II} species with LiH or H_2.[2] This preparation parallels the method used by Yermakov to obtain 'atomically dispersed metals' on silica, reaction (1).[1]

$$\text{support } |\text{–OH} + Pd(C_3H_5)_2 \rightarrow \text{Support } |\text{–OPd}(C_3H_5)$$
$$\xrightarrow{\text{H}_2} Pd \text{ (atomically dispersed)} \quad (1)$$

The vitreous supports were prepared by treating a solution of Si, Al, and Na alkoxides with a stream of H_2O vapour and heating the gels obtained to 950 °C. A range of values for the OH group content can be achieved heating the gels at different temperatures in the interval 250—950 °C.

The SAXS measurements were performed under 'infinite' beam conditions with a Kratky camera aligned according to the method of Anderegg et al.[4] using Mo-K_α radiation and the calibration sample (Lupolen) method for absolute intensity determination.[5] For each catalyst sample examined, the SAXS intensities were normalized by taking into account the attenuation factor and then subtracting the corresponding intensities due to the related supports, independently measured.
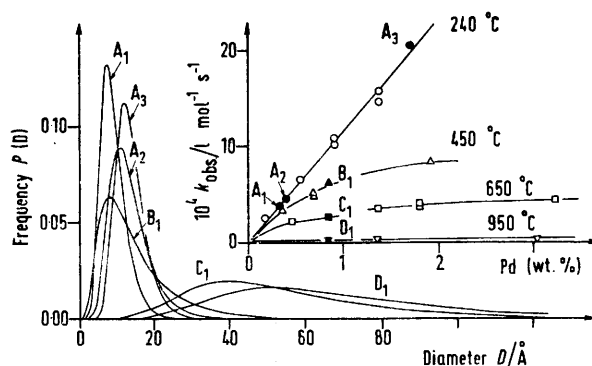

FIGURE 1. Particle size distribution curves and plot of the catalytic activity vs. % Pd.

From the Guinier diameter, D_G, and Porod diameter, D_P, determined following known methods,[6] normal-logarithmic particle size distribution curves[7] were obtained for the six Pd catalysts here studied (cf. Table and Figure 1). The other X-ray structural parameters reported in the Table are the metal and the vitreous support surface area values

<div align="center">TABLE</div>

Sample[a]	Pd[b] %	D_G/Å	D_P/Å	D_{WAXS}/Å	S_{SAXS}/m² g⁻¹	$S_{B.E.T.}$/m² g⁻¹	% of Pd exposed	OH[c]	Catalytic activity[d] /l mol⁻¹ s⁻¹
A: support obtained heating the gel up to 240 °C					522	348	—	10·3	—
A₁	0·34	20·4	12·2	—	411	—	83·3	—	3·9
A₂	0·40	31·0	18·1	—	202	—	66·1	—	4·5
A₃	1·70	21·3	15·9	—	331	—	71·9	—	20·3
B: support obtained heating the gel up to 450 °C					365	213	—	6·1	—
B₁	0·85	109	33·6	55	148	—	41·3	—	6·2
C: support obtained heating the gel up to 650 °C					11	5·4	—	1·2	—
C₁	0·85	142	85·9	—	56	—	17·9	—	2·3
D: support obtained heating the gel up to 950 °C					1	0·1	—	0·3	—
D₁	0·85	205	104	76	46	—	15·0	—	0·18

[a] Final glass composition: SiO_2 78·1 %, Al_2O_3 13·9 %, Na_2O 7·4 %. [b] From elemental analysis. [c] Number of OH groups per g of support expressed in ml of H_2 evolved in 1 h from the reaction: support–OH + LiH → support–OLi + H_2. [d] Rate constants for the hydrogenation of hex-1-ene (0·24M) in tetrahydrofuran at 25 °C and P(H_2) = 760 ± 12 mmHg with 0·5 g of catalyst (cf. ref. 2).

determined from SAXS absolute intensities and Kratky's method.[8] Moreover, only for two samples, the average particle size, D_{WAXS}, was determined by X-ray line broadening analysis at wide angle using Scherrer's formula,[9] after both instrumental and doublet broadening effects had been eliminated. The Table also reports: (i) the percentage of Pd exposed and calculated as the ratio between the number of atoms present in a mono-layer at the surface of the Pd microparticles and the number of atoms present in the total spherically averaged volume of the particles; (ii) the B.E.T. surface area of the vitreous supports; (iii) a parameter related to the number of OH groups per g of support; and (iv) the catalytic activity.

Figure 1 shows the catalytic activity plotted against the Pd content for the six samples studied here and also for others previously reported.[2] In the case of samples of type A, the catalytic activity is a linear function of the Pd percentage and the average Pd cluster sizes, D_P, are in the range 12·8—18·1 Å, while the metal surface areas are in the range 202—411 m²g⁻¹. For the other samples the catalytic activity is no longer a linear function of the Pd content and this deviation from linearity becomes more and more marked on going from samples B to C and D.[2] Moreover, at constant Pd content (0·85%) the catalytic activity decreases linearly as a function of the cluster or particle size (cf. Figure 2) and this parallels the dramatic decrease in
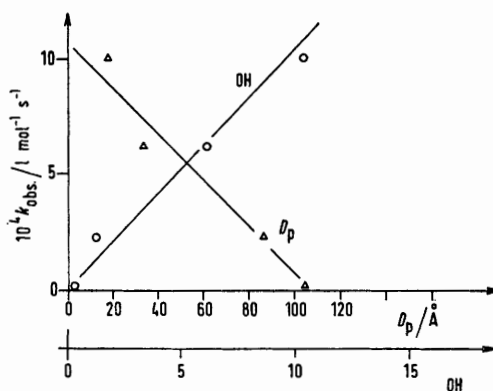

FIGURE 2. Plots of the catalytic activity vs. particles size and number of OH groups on the support's surface (cf. footnote c of Table).

surface OH groups on the support observed on increasing the temperature to which the support was heated. This demonstrates the direct relationship between the number of OH groups on the surface of the support, the catalytic activity, and the degree of dispersion of the metal.

[1] Yu. I. Yermakov, Catalysis Rev., 1976, 13, 77.

[2] G. Carturan and V. Gottardi, J. Mol. Catalysis, 1978, 4, 349.

[3] B. E. Yoldas, J. Materials Sci., 1977, 12, 1203; H. Dislish, Angew. Chem. Internat. Edn., 1971, 10, 363; G. Carturan, V. Gottardi, and M. Graziani, J. Noncryst. Solids, 1978, 29, 41; G.. J. McCarthy and R. Roy, J. Amer. Ceram. Soc., 1971, 54, 639.

[4] J. W. Anderegg, P. G. Mardon, and R. W. Hendricks, 'An Alignment Procedure for the Kratky Small Angle X-ray Camera,' Report ORNL-4476, Oak Ridge National Laboratory, Tennessee, 1970.

[5] L. B. Shaffer and R. W. Hendricks, J. Appl. Crystallography, 1974, 7, 159.

[6] A. Guinier and G. Fournet, 'Small Angle Scattering of X-rays,' Wiley, New York, 1955, 126.

[7] G. Fagherazzi, G. Cocco, L. Schiffini, S. Enzo, A. Benedetti, R. Passerini, and G. R. Tauszik, Chimica e Industria, in the press.

[8] O. Kratky, 'Proceedings of the Interdisciplinary Conference on Electromagnetic Scattering,' Pergamon, Oxford, 1963, p. 459.

[9] H. P. Klug and L. E. Alexander, 'X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials,' Wiley, New York, 1974, p. 637.