Structure and size of poly-domain Pd nanoparticles supported on silica

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A polydomain internal structure was evidenced by means of High Resolution Transmission Electron Microscopy (HRTEM) in palladium nanoparticles of two 5% Pd/SiO_2 catalysts prepared by impregnation technique. Such poly-domain structure biased the line broadening analysis of the XRPD patterns, from which highly underestimated average diameters were obtained in comparison to those measured by means of Transmission Electron Microscopy (TEM).

In both the investigated catalysts, a Pd/CO average chemisorption stoichiometry close to 2 was found, in good agreement with previous results obtained for Pd/C and $Pd/\gamma\text{-}Al_2O_3$ catalysts. The consistency of this result, in cases with different particle sizes and different support materials, suggests that such average stoichiometry is of general validity for palladium, when chemisorption measurements of CO are made using pulse flow technique.

KEY WORDS: Pd catalysts supported on silica; polydomain Pd nanoparticles; X-ray powder diffraction; HRTEM; Pd/CO chemisorption stoichiometry.

1. Introduction

It has been recently remarked that catalysts represent the oldest application of nanotechnology [1]. In particular, nanoparticles are typically present in supported metal catalysts, where metal particles having a size usually in the range 1–10 nm are deposited on the external surface and/or in the porous texture of inert materials (carriers). Metal particle nanosize is a critical factor for several catalytic reactions (the so-called *structure-sensitive* or *demanding reactions*), when the surface density of the active sites depends on such particle nanosize [2]. Therefore, metal particle nanosize is a key point in catalysis by supported metals and must be known with as high an accuracy as possible. The method traditionally used by the catalytic community for measuring the metal particle size is certainly chemisorption, which requires that chemisorption stoichiometry and degree of surface coverage are known. Unfortunately, both of them are usually arbitrarily assumed (in most cases taken as 1, probably for the sake of simplicity), with consequent errors that can be as high as 100%. In fact, what is required for calculating the metal particle size from chemisorption data is the ratio between the amount of surface metal atoms and that of chemisorbed probe molecules in the chosen experimental conditions. This ratio has been called "average chemisorption stoichiometry" (S_{av}) and clearly includes the degree of surface coverage [3]. It has been previously shown [4,5] that, when the surface average metal particle nanosize has been determined by physical techniques like WAXS, SAXS or TEM, from the measurement of the chemisorbed volume V_g, the calculation, based on experimental data, of S_{av} can be done. In such a way, S_{av} has been experimentally determined for Pd/C [4] and Pd/alumina [5] catalysts, using CO as the probe molecule. In the present paper, we extend the investigation to Pd/silica catalysts.

The choice of the physical technique to be employed must be carefully done case by case, according to the characteristics of the specific catalysts. For instance, it is worth noting that the study of supported metal catalysts by SAXS technique is easy only when a good match occurs between the scattering of the support and that of the catalyst. With this fulfillment, it is possible to subtract the scattering contribution of the support and to obtain information about the metal particles. Unfortunately, this condition is not frequently met due to important interference effects between the scattering coming from the metal and that originating from the pores of the support: supported catalysts are usually three-phase systems: support–pore–metal. This occurrence can be overcome either using the pore-maskant method [6,7], which is a difficult technique and not always reliable, or using the anomalous scattering technique (ASAXS) [8,9], which requires a synchrotron source and is very time-consuming.

The 5-wt% Pd/SiO_2 catalyst discussed in this paper unfortunately shows strong interference effects, probably due to a large number of micropores and

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mesopores of the supporting silica, which has a high specific surface ($329\,m^2/g$). Due to the problems given by SAXS, for the present investigation, TEM, HRTEM and WAXS have been used, while CO was again chosen as the probe molecule for chemisorption.

2. Experimental and methodological section

The 5% Pd/SiO_2 starting catalyst (sample CS1) was prepared by incipient wetness impregnation, with a H_2PdCl_4 solution, of SiO_2 (Akzo, $329\,m^2/g$ of surface area), previously impregnated with a NaOH solution ($NaOH/Pd = 1.3\,M$) and dried at 383 K. The catalyst was then subjected to a hydrogen flux at 423 K for 1 h, followed by He purge for 2 h at the same temperature of reduction. Pd concentration of this catalyst, as measured by the atomic absorption technique, was 5.7 wt %. Another catalyst was prepared by thermally treating the sample CS1 at 773 K for 3 h, in pure H_2 and then for 1 h in N_2 (so originating the sample CS2).

CO chemisorption measurements were taken at 298 K using a home-made pulse flow system. Prior to measurements, samples were subjected to a pre-treatment involving exposure to hydrogen flow for 1 h at 423 K, followed by He purge for 2 h at the same temperature.

XRPD patterns were recorded in air at 295 K, with a step size of 0.05° in a 2θ scattering angle. The intensities were collected in several runs in the preset-time mode of 10 s per run. A Philips X'Pert system was used, which was equipped with a focusing graphite monochromator on the diffracted beam and with a proportional counter having an electronic pulse–height discrimination. Moreover, a divergence slit of 0.5°, a receiving slit of 0.2 mm, an anti-scatter slit of 0.5° and a Ni-filtered CuK_α radiation (30 mA, 40 kV) were employed.

The subtraction of the X-ray scattering of the support from the XRPD patterns of the Pd/SiO_2 catalysts was carried out trying to scale the support pattern in such a way that it was possible to correctly superimpose the support pattern to that of the catalyst. The low number of Pd XRPD peaks favored this procedure.

For catalyst CS1, due to the small Pd crystallite size, only the first two Pd peaks (111 and 200) were evident. Since the 200 reflection was too weak, the line-broadening analysis was carried out by Fourier method only on the peak (111). For catalyst CS2, the angular range $25 \div 90°$ was measured, since for this sample a higher number of peaks were visible. The sample CS2 was analyzed by Warren–Averbach method using the 111 to 222 reflections [10,11].

The procedures used for calculating the surface-weighted average metal particle size from the Fourier analysis of the fitted analytical profiles were discussed in reference [5]. Furthermore, an independent approach was used to obtain the average diameter of the Pd crystallites, as performed elsewhere [5]. The second method gives the surface-weighted average diameter of a population of spherically shaped crystallites starting from the number distributions obtained using equations (2) and (3) of reference [5]. The assumption of spherically shaped particles is well justified by TEM images.

High Resolution Transmission Electron Microscopy (HRTEM) micrographs were taken with a JEM 3010 (JEOL) electron microscope operating at 300 kV. Few milligrams of the powder samples were ground in an agate mortar under high purity isopropyl alcohol: the suspension was sonicated for 5 min, in order to further disrupt possible agglomerates. A 5 μl droplet of suspension was transferred onto an amorphous holey carbon film, coating a 200 mesh copper grid (TAAB Laboratories Equipment Ltd.), and allowed to dry in a desiccator.

The surface-weighted particle size average, $\langle D\rangle_s^{\mathrm{TEM}}$ is determined starting from the number size distributions (histograms) as follows:

$$\langle D\rangle_s^{\mathrm{TEM}} = \frac{\sum_i n_i D_i^3}{\sum_i n_i D_i^2} \qquad (1)$$

where n_i is the number of particles with diameter d_i.

3. Results and discussion

Figure 1 is a typical example of TEM images of sample CS1. It can be seen that larger particles are present together with much smaller ones, outlining a very broad particle size distribution. On the contrary, images obtained for sample CS2 (see figure 2) do not show evidence of particle populations with highly different sizes.

This qualitative impression is confirmed by the particle size distributions (see histograms in figures 3 and 4) obtained by measuring the Pd particle sizes in the TEM micrographs. The CS1 histogram (figure 3) shows an almost constant size distribution in the range $1 \div 6$ nm, with a small fraction of particles with larger sizes. On the contrary, the thermally treated CS2 catalyst shows a particle-size distribution centered at about 5 nm, having the typical log-normal shape (figure 4).

Therefore, the thermal treatment causes a sintering process that induces the evolution of a fairly broad particle size distribution toward a monomodal one.

The observed behavior is probably due to the particle growth mechanism via migration and coalescence (see, for example, the case reported in detail by Sushumna and Ruckenstein [12] for the sintering of Pt/alumina catalysts). The present sample behaves in the opposite way with respect to some cases reported in literature [13–15], where particles evolved from mono-modal size distribution toward a bimodal one. In that case, this

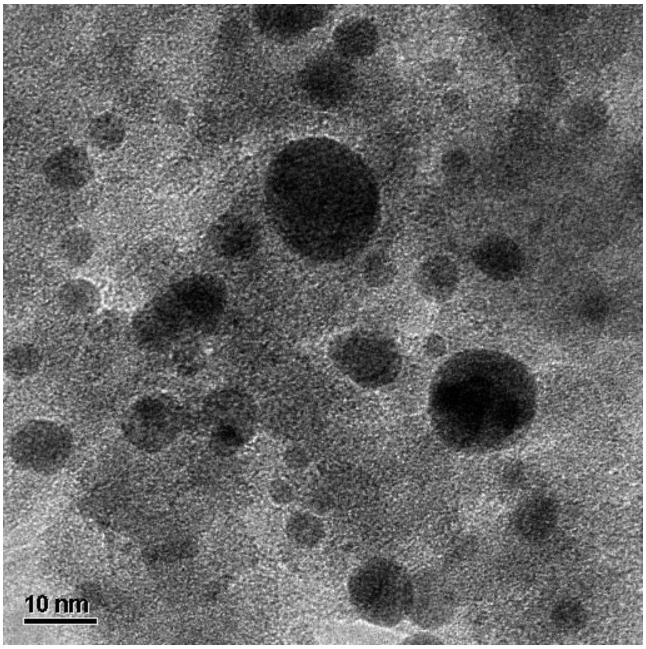

Figure 1. TEM image of CS1 catalyst.

phenomenon was ascribed to the Ostwald ripening mechanism as the predominant cause of crystal growth.

As a matter of fact, the shape of the mono-modal particle size distribution shown by the histogram of our sintered CS2 catalyst (figure 4) is very asymmetric, with a long tail toward larger particle sizes. This is in agreement with the classical results by Granquist and Buhrman [16] for a growth mechanism via migration and progressive coalescence of the smallest particles into the largest ones.

The surface-weighted average particle sizes, $\langle D \rangle_s^{\mathrm{TEM}}$, have been calculated using equation (1) (see table 1) from the particle size distributions of figures 3 and 4. This type of average can yield much larger values than the arithmetic one [17], especially when a long tail of large particles is present, as in the case of the CS2 sintered sample.

It is important to note that, among the different possible ways to calculate averages, the surface-weighted average is the most meaningful in the field of heterogeneous catalysis since the studied phenomena depend on the particle surface. For instance, this type of average is required when comparing chemisorption results with those obtained by Transmission Electron

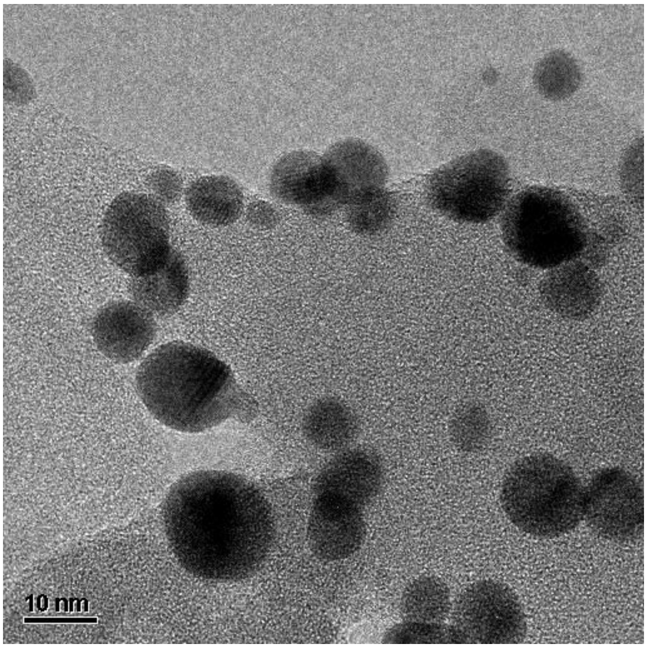

Figure 2. TEM image of CS2 catalyst.

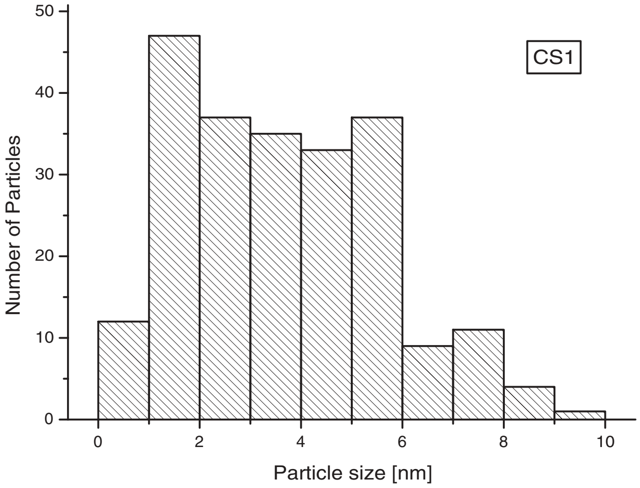

Figure 3. Size distribution TEM histogram of CS1 catalyst.

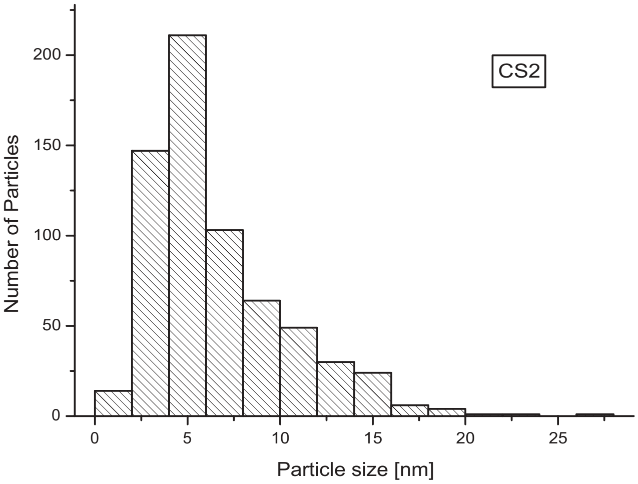

Figure 4. Size distribution TEM histogram of CS2 catalyst.

Microscopy (TEM) and X-ray Diffraction (XRD) methods [5].

The internal structure of the metal particles was revealed by HRTEM. Figures 5 and 6 show, as typical examples, HRTEM images for the two catalysts. The poly-domain (or multiple twinned) particle internal structure of palladium is clearly evidenced in these micrographs. It is worth noting that a systematic HRTEM analysis showed this polydomain nature as characteristic of the Pd particles investigated by us in both the catalysts examined here. On this basis, the LB-XRPD analysis is strongly biased since, in the case of poly-domain particles, the average crystallite size (i.e. the mono-domain average size) will be much smaller than the true average particle size. The surface-weighted average crystallite diameters of samples CS1 and CS2 obtained by XRPD are reported in table 1. It can be seen that these values are much smaller than the corresponding quantities determined by TEM. This result is an unquestionable proof that, when poly-domain particles are investigated, the LB-XRPD technique fails. As a practical consequence, supported metal catalysts should always be checked by HRTEM before applying LB-XRPD analysis for the measurements of metal particle size.

The spheroidal shapes of the Pd particles observed by TEM are probably favored by the poly-domain structure of these particles. This random growth along all space directions, starting from the initial mono-domain crystalline nuclei, causes sufficiently smooth external spheroidal shapes. On the contrary, when mono-domain Pd particles are observed by HRTEM, as in the case of the highly dispersed Pd/γ-Al_2O_3 catalysts [5], sharp edges due to planar faceted (111) and (100) surfaces are clearly displayed by the nanosized particles, which show the typical *fcc* cube-octahedral geometry.

It is not clear why the present preparation of Pd catalysts supported on silica gave rise to poly-domain particles. Probably, the growth conditions were too fast or too much perturbed to allow the formation of ordered single crystals. The nature of the support could favor the obtainment of one of the two possible internal particle structures (mono- or poly-domain like).

Using the $\langle D\rangle_s^{\mathrm{TEM}}$ values reported in table 1, it was possible to determine an average Pd/CO chemisorption stoichiometry, S_{av}, by means of the following equation:

$$S_{\mathrm{av}} = \frac{1}{V_g \langle D\rangle_s^{\mathrm{TEM}}} \frac{k V_m C_m}{N_A \rho_m} \tag{2}$$

where V_g is the volume of gas chemisorbed per gram of metal, V_m is the molar volume, C_m is the surface density of metal atoms, N_A is Avogadro's number, ρ_m is the Pd density (g/cm^3) and k is a factor depending on the metal particle shape and the extent of surface contact with the support. According to Anderson [18], C_m is equal to 1.27×10^{15}atoms/cm^2 for Pd in the case of "spheroidal" particles with crystallite surface areas "ideally" composed of equal amounts of (111), (100) and (110) planes. For a cubic shape, when one face is in contact with the support, $k = 5$, whereas for an ideal spherical shape, for which no contact surface exist, $k = 6$. Evidently, high roughness of the support can favor the occurrence of different contact areas between the Pd particles and the support itself, along different orientations in the space. Also, a particle entrapped within a pore can offer a larger contact surface area. Indeed, a value of $k = 5$ can be reasonably assumed as the most likely value also for spheroidal particles, and this value was used in the present work, as well as in our previous papers [4,5].

From equation (2), it can be seen that the average chemisorption stoichiometry S_{av} is easily determined from two experimental quantities: the chemisorbed volume V_g and the surface-weighted average metal particle size (in this case from TEM data).

The values of S_{av} obtained in this way and reported in the last column of table 1 for sample CS1 and CS2, are both close to 2. Such a value was previously found, within an error of ±10%, for all the nanostructured Pd catalysts

Table 1
Comparison between the surface-weighted average crystallite or particle sizes obtained by LB-XRPD and by TEM, respectively, for Pd/SiO$_2$ catalysts. Average Pd/CO chemisorption stoichiometries, as derived from $\langle D\rangle_s^{\mathrm{TEM}}$

Sample	Average crystallite size from LB-XRPD techniques		Average particle size from TEM Histograms $\langle D\rangle_s^{\mathrm{TEM}}$ (nm)	Pd/CO average stoichiometry S_{av}
	Fourier tangent method[a] $3/2\langle d\rangle_s$ (nm)	Diameter distributions[b] $\langle D\rangle_s^{\mathrm{diam}}$ (nm)		
CS1	2.9	2.5	5.6	1.8
CS2	6.3	5.7	11.1	1.9

[a] This method gives directly, from the Fourier transforms of the corrected XRPD peak profiles, the $\langle d\rangle_s$ quantities, which represent surface-weighted average dimensions of chords within spherically shaped crystallites. By multiplying $\langle d\rangle_s$ by 3/2, a surface-weighted average crystallite diameter is obtained [5].

[b] This method gives the surface-weighted average diameter of a population of spherically shaped crystallites starting from the number distributions obtained using equations (2) and (3) of reference [5].

investigated by us, which were supported on different materials, such as γ-Al$_2$O$_3$ and active carbon [4,5].

Surface-weighted average metal particle diameters equal to or larger than about 5 nm, as obtained by TEM histograms, can be considered rather reliable, that is, not too biased by the presence of very small, barely visible, particles. As an indirect check of this statement, it was recently verified by us [5] that in a calcined (and then reduced) Pd/γ-Al$_2$O$_3$ catalyst, having mono-domain particles, the LB-XRPD particle sizes and the corresponding values found by TEM were remarkably close to one another.

A similar consistency of data (between SAXS and TEM techniques in that case) was obtained by some of us also in the case of a Pd/pumice catalyst with a surface-weighted Pd average particle size of about 5 nm [19]. In the case of the samples discussed here, in particular for CS1, a small portion of the smallest-size Pd particles might have escaped the TEM counting, and this can explain the S_{av} value lower than 2 of CS1. In fact, in the determination of particle size distribution by TEM, the basic assumption is that all the sizes are observed with the same probability, but when the sizes are very small, the contrast in the images is poor and the particles can be interpreted as a background fluctuation of the intensity.

4. Conclusions

Two differently nanostructured 5% Pd/SiO$_2$ catalysts were investigated. In the Pd/SiO$_2$ catalyst subjected to the lowest temperature treatment (423 K), a fairly broad particle size distribution was observed, whereas the same

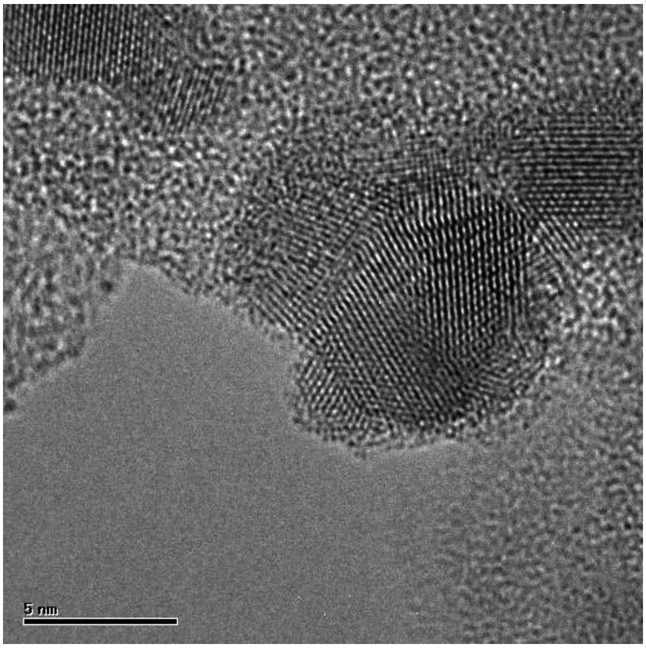

Figure 5. Poly-domain-like internal structure of a Pd particle of CS1 catalyst.

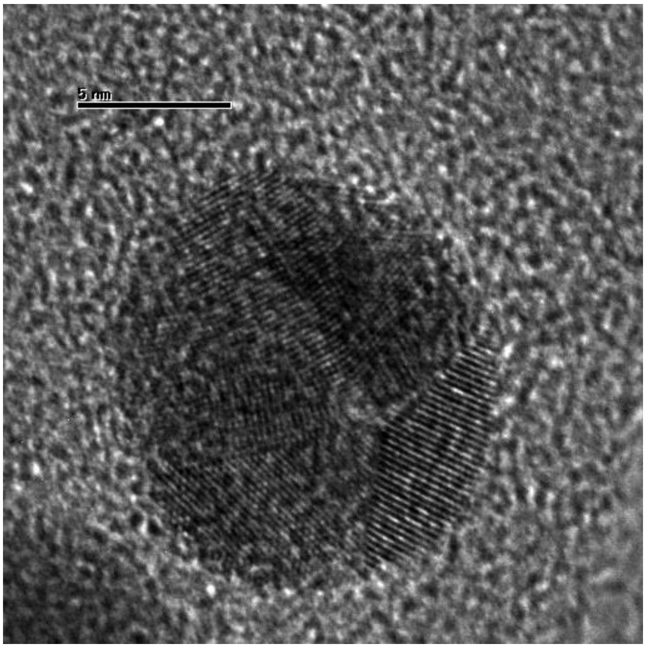

Figure 6. Poly-domain-like internal structure of a Pd particle of CS2 catalyst.

sample showed a log-normal particle size distribution after a thermal treatment at 773 K.

In both the catalysts, poly-domain metal particles, whose internal structure was observed by HRTEM, cause significant biased effects on the line broadening of the XRPD patterns. This bias yielded strongly underestimated average diameters with respect to the corresponding values measured by means of TEM histograms. Therefore, only TEM data were used to determine the Pd/CO average chemisorption stoichiometry, S_{av}, which resulted to be close to 2.

This value is in good agreement with the values found for other Pd-supported catalysts like Pd/C [4] and Pd/γ-Al_2O_3 [5], suggesting the general validity of such a result, which proves to be independent of the metal dispersion and the support material. Therefore, the use of this stoichiometry ($S_{av} = 2$) allows the obtainment of the Pd surface average particle diameter from a simple measurement of V_g by the pulse flow technique. Moreover, other important connected quantities, such as Pd dispersion or Pd surface area, can be calculated by simple equations like those shown by some of us for Cu catalysts [3].

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