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Structural investigation on the stoichiometry of β-PdH_x in Pd/SiO_2 catalysts as a function of metal dispersion

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Structural investigations of dispersed Pd/SiO_2 catalysts were carried out with XRD and SAXS techniques, supported by TPR and CO chemisorption measurements. The stoichiometry of Pd hydride, β-PdH_x, was determined by measuring the shift of Pd 111 XRD reflection in the presence of hydrogen. It was confirmed that x decreases when the metal dispersion increases. This behaviour could be quantified up to about 0.45 of Pd dispersion since the angular position of XRD peaks cannot be determined with the necessary precision at higher dispersions. TPR data, obtained up to dispersions of about 0.6, confirms such behaviour. The β-PdH_x stoichiometry versus Pd dispersion relationship substantially agrees with that found with other techniques by Boudart and Hwang.

Keywords: stoichiometry of β-Pd hydride; Pd/SiO_2 catalysts; metal dispersion; XRD; SAXS; TPR

1. Introduction

The role of metal dispersion in determining the amount of hydrogen absorbed by the fcc Pd lattice – so forming the interstitial solid solution β-PdH_x – was studied in Pd supported catalysts by many authors owing to its great importance with respect to catalytic activity (see for example refs. [1,2]). Recently, Bonivardi and Baltanas [3], as well as Sepulveda and Figoli [4], have shown, by measuring with volumetric techniques the hydrogen solubility in Pd/SiO_2, that the ratio of the hydrogen absorbed in the bulk to the total palladium decreases when dispersion (i.e. the exposed metal fraction), D, increases up to a value of about 0.55 (with D measured by chemisorption of H_2), while, for $D > 0.55$, this ratio keeps a nearly constant value of 0.3. This trend is significantly different from that established by Boudart and Hwang [5], who reported that this ratio goes to zero as $D \rightarrow 1$.

The formation of β-PdH$_x$ with the stoichiometry, x, lower than 0.72, the characteristic value for massive Pd at room temperature in H_2 at atmospheric pressure [6], was detected by Benedetti et al. [7] with in situ X-ray diffraction (XRD) investigations in Pd/charcoal catalysts exposed to a hydrogen flow. They observed this occurrence on Pd/C catalysts with average particle sizes in the range 24–44 Å, as determined by small-angle X-ray scattering (SAXS). By applying the eq. (2) reported below in section 2.5, these particle sizes correspond to Pd dispersions in the range 0.25–0.47. Moraweck et al. [8] detected by in situ XRD the formation of β-hydride phase in a Pd/SiO_2 catalyst with average particle size of 18 Å and D of 0.55, as determined by SAXS. On the other hand, Nandi et al. [9,10] could detect by XRD the formation of β-hydride in Pd/SiO_2 catalysts only up to a Pd dispersion of 0.293 and showed that more hydride formed with lower dispersion ($D = 0.138$ vs. $D = 0.293$ were compared). Therefore, it can be concluded that it was not completely clear which was the real relationship between the stoichiometry of β-PdH$_x$ and Pd dispersion.

In this paper we have undertaken a systematic structural study of nanometrically sized Pd/SiO_2 catalysts with different metal dispersion, D (as determined by both SAXS and CO chemisorption), by means of in situ XRD technique, in presence of hydrogen. We have investigated the variation of the stoichiometry of β-PdH$_x$, determined from the fcc unit cell edge enlargement, as a function of Pd dispersion. Thermal programmed reduction technique (TPR) was used in order to confirm the decrease of x as dispersion increases.

2. Experimental and methodological

2.1. CATALYST PREPARATION

The series of the SiO_2-supported Pd catalysts C1–C4 come from the same sample prepared by ionic exchange starting from an aqueous solution of $Pd(NH_3)_4Cl_2$ following the method published by Sepulveda and Figoli [4]. A silica powder with a surface area of 190 $m^2\ g^{-1}$ and pore volume of 0.9 ml g^{-1} was employed. The solid, after being dried at 110°C, was calcined in air for 4 h at 400°C (C1), 500°C (C2), 550°C (C3) and 600°C (C4), respectively, in order to achieve, by annealing, a systematically decreasing metal dispersion. These catalysts have a Pd load of 2.4 wt%, as measured by chemical analysis. We also investigated another catalyst (C5), supported on the same silica, that has instead a Pd load of 1.4 wt%. It was prepared by impregnation of the silica powder starting from an aqueous solution of H_2PdCl_4. SiO_2 was suspended in water and the H_2PdCl_4 solution was slowly added keeping the pH value of 7 by addition of aqueous NaOH. The suspension was stirred for about 30 min. Then the catalyst was filtered, washed and dried at 110°C.

The five catalysts were reduced to Pd by using a standard treatment in a flow of pure H_2 (40 cm^3 min^{-1}), at 250°C for 3 h, and successively slightly passivated for 20 min in a flow of argon containing 5% of O_2.

2.2. X-RAY DIFFRACTION

XRD patterns of the catalysts before and after exposure to hydrogen were obtained by in situ experiments carried out at room temperature by using a special sample holder where pure hydrogen was allowed to enter at 110 kPa and overflow. The holder was sealed with a thin Kapton sheet. The 2θ Bragg angle measurements were calibrated using a pure Pd reference powder, irradiated under the same experimental conditions, with a lattice parameter of 3.8898(6) Å. This reference Pd black has an average particle size of 1400 Å, as calculated from BET surface area and an average crystallite size of about 200 Å, as measured by XRD line-broadening [11]. Therefore, according to Guinier and Fournet [12], these particles are typical polydomain particles, i.e. grains formed by several crystallites. Similar crystallite sizes were measured with X-ray line-broadening by Pielaszek on some Pd blacks [13]. These large discrepancies between the crystallite size and the real particle size show that it can be wrong, as already underlined by Gallezot [14], to employ the line-broadening method for the dispersion determination of metal supported catalysts and this is the reason for which we have used the SAXS technique in order to measure the average Pd particle size.

We used a Philips vertical goniometer connected to a highly stabilized generator (Siemens Kristalloflex 805). Ni-filtered Cu Kα radiation was employed and the diffracted beam was monochromatized with a focussing graphite monochromator. A proportional counter, an entrance slit of 0.5°, a receiving slit of 0.2 mm and 0.05° step sizes in 2θ, for a collection time of 100 s per step, were used in the step-by-step scanning technique. The peak position analysis was carried out with our standard best-fit procedure [15] tailored for running on a PC. The experimental background due to the silica support was taken into account in the fitting procedure. Pseudo-Voigt (pV) functions were superimposed to this background in order to fit the crystalline peaks.

2.3. SMALL-ANGLE SCATTERING

SAXS data was collected with a Paar Kratky camera equipped with an electronic step-scanner under "quasi-infinite" primary-beam geometry. Ni-filtered Cu Kα radiation, a pulse-height discriminator and a proportional counter were used. A preset count mode was employed in order to accumulate 10^5 counts per angular abscissa in several runs. The powder samples were sealed in a brass cell having a very thin Mylar window. The intensities were corrected by subtracting the background after the absorption effect was taken into account. In order to determine the surface-weighted particle diameter distribution, $p_s(L)$, we used the Tikhonov regularization method whereby the SAXS intensities $J(h)$ were fitted in the framework of the indirect approach of Svergun, Semenyuk and Feigin [16] by means of the first-kind Fredholm equation:

$$J(h) = \int_0^{L_{\max}} K(L,h) p_n(L)\, \mathrm{d}L\,, \qquad (1)$$

where $h = 4\pi \sin(\theta)/\lambda$, with λ the radiation wave length used; L represents the particle diameter; $K(L, h)$ includes the instrumental aberration as well as the shape factor of the scattering particles here assumed spherical, as it is usual in SAXS technique for equiassic particles [14]; $p_n(L)$ is the unknown numerical distribution function of the particle diameters; $p_s(L)$ is given by $p_s(L) = L^2 p_n(L)$.

2.4. CO CHEMISORPTION

CO chemisorption measurements were performed using a pulse flow technique [17]. Prior to measurement, each sample was subjected to a thermal pretreatment which involved exposure to H_2 at 110°C for 1 h followed by He purge at the same temperature for 2 h. The samples were then cooled in a He flow to 25°C.

2.5. TEMPERATURE-PROGRAMMED REDUCTION

TPR measurements were performed in a standard apparatus previously described [17]. In order to detect peaks due to the β-PdH$_x$ decomposition, the reduced and then passivated catalysts (samples of 0.1 g) were heated at a linear rate of 15°C min^{-1} from 25 to 200°C with a 5% H_2–Ar mixture flowing at 40 cm^3 min^{-1}.

2.6. Pd DISPERSION DETERMINATION

Some comments about the Pd dispersion calculation starting from the average particle size $\langle L \rangle$ can be useful at this point. Several authors (see, for instance, refs. [3,4,10,18]) employed the following simple equation valid for a population of spheroidal or equiassic particles:

$$D = 11.2/\langle L \rangle\,, \qquad (2)$$

where $\langle L \rangle$ is expressed in Å and the constant is determined on the basis of an assumed spherical particle shape and the number of surface palladium atoms per polycrystalline surface unit area [19]. It is worth noting that Bonivardi and Baltanas [3], as well as Sepulveda and Figoli [4], showed a close agreement in several Pd/SiO$_2$ catalysts of 15–30 Å particle size between the $\langle L \rangle$ value, as obtained from eq. (2), where D was determined by H$_2$ chemisorption methods, and the mean particle diameter as directly obtained by TEM. Furthermore, Fagherazzi et al. have recently shown [18] a very good agreement between SAXS and TEM particle distributions on a Pd catalyst of 49 Å particle size, supported on pumice, so confirming the validity of a spherical particle shape model for the SAXS data treatment.

3. Results and discussion

No PdO XRD peak was detected in the catalysts reduced at 250°C. TPR experiments performed on the unreduced catalyst showed that complete reduction of precursors to Pd occurs below 250°C for all our samples, in agreement with the results reported for Pd catalysts prepared by the same procedure on silica supports [2,4]. Table 1 reports the edge, a_0, of the fcc Pd unit cell of catalysts C2, C3, C4 and C5 (C1 could not be measured as discussed below) as well as the edge a_0 of the relevant β-PdH$_x$. The corresponding parameters of the reference sample are also reported. While for this sample the 111, 200, 220, 311, 222 and 400 peak maxima and the plot of Adler and Wagner [20] could be used, for the catalysts, only the most intense 111 peak maximum of palladium could be analysed since the other reflections were too weak and diffuse. For this reason the a_0 values determined for the catalysts were less accurate. On the contrary, for the Δa_0 difference between the β-hydride lattice edge and the Pd lattice edge, as determined on the same catalyst placed in the same holder before and after the hydrogen exposure, the systematic errors cancel. The ratio $\Delta a_0/\Delta a_0^*$, where Δa_0^* was found by us to be equal to 0.1475 Å for the Pd reference sample, is also reported in table 1. This ratio, multi-

Table 1
Lattice parameters of Pd and β-PdH$_x$ (with relevant errors), and stoichiometry, x, of β-PdH$_x$ (with relevant error), as derived by XRD assuming the stoichiometry of 0.72 for massive Pd hydride

Sample	a_0 (Å)		$\Delta a_0/(\Delta a_0^*)$ [a]	Stoichiometry x
	Pd	β-PdH$_x$		
reference	3.8898(6)	4.0373(6)	1.00	0.72
C2	3.929(5)	3.998(5)	0.47(6)	0.34(4)
C3	3.913(5)	4.009(5)	0.65(6)	0.47(4)
C4	3.912(5)	4.014(5)	0.69(6)	0.50(4)
C5	3.917(5)	4.012(5)	0.64(6)	0.46(4)

[a] $\Delta a_0^* = [a_0(\beta\text{-PdH}_x) - a_0(\text{Pd})]_{\text{ref}} = 0.1475$ Å; $\Delta a_0 = a_0(\beta\text{-PdH}_x) - a_0(\text{Pd})$.

plied by 0.72, gives the stoichiometry, x, in our catalysts when the well known linear Vegard law [21] is applied to the homogeneous Pd–PdH solid solution.

As examples, the 111 and 200 XRD peaks, due to Pd or to β-PdH$_x$, obtained by subtracting the background scattering of the support material, are shown in the lower parts of figs. 1 and 2 for catalysts C2 and C4. Catalyst C1 was too dispersed to give a reliable XRD difference pattern, but hydrogen exposure caused an immediate and significant change of the relevant XRD pattern (see fig. 3) in accordance with the TPR results discussed below.

Table 2 records the average surface-weighted particle diameters $\langle L\rangle_s$ and the dispersions D_x calculated with the SAXS regularization method. Fig. 4 shows the SAXS intensities fitted with the regularization procedure. The excellent agreement between experimental and calculated intensities is evident. Through this fitting procedure SAXS particle size distributions, $p_s(L)$, could be simultaneously obtained. Fig. 5 shows the $p_s(L)$ vs. L plots for the series of C1–C4 catalysts which were prepared starting from the same fresh catalyst. In the last column of table 2 the dispersions, D_{CO}, measured by CO chemisorption and calculated on the basis of a

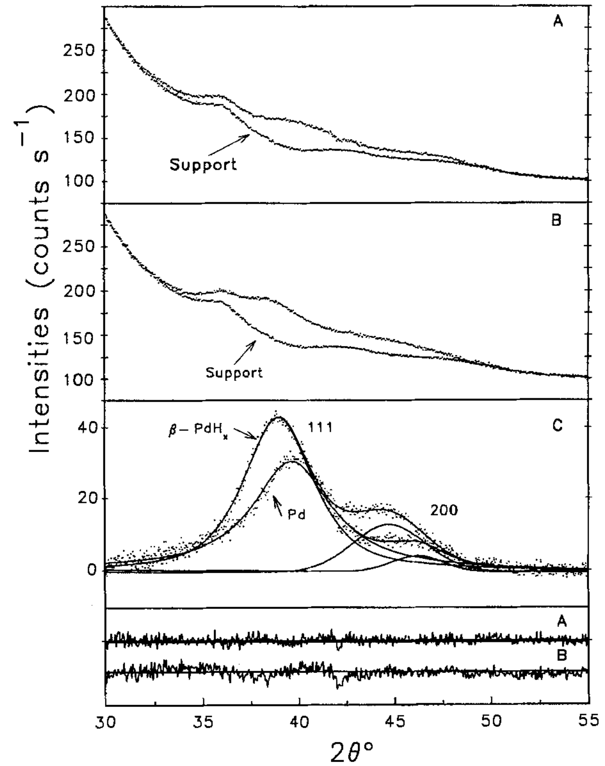

Fig. 1. X-ray patterns of catalyst C2 (upper pattern in A) and of the same catalyst when exposed to hydrogen at room temperature (upper pattern in B). In part C the 111 and 200 peaks due to Pd and β-PdH$_x$ are shown. The residuals (differences between the observed and fitted intensities) are reported at the bottom of the figure.

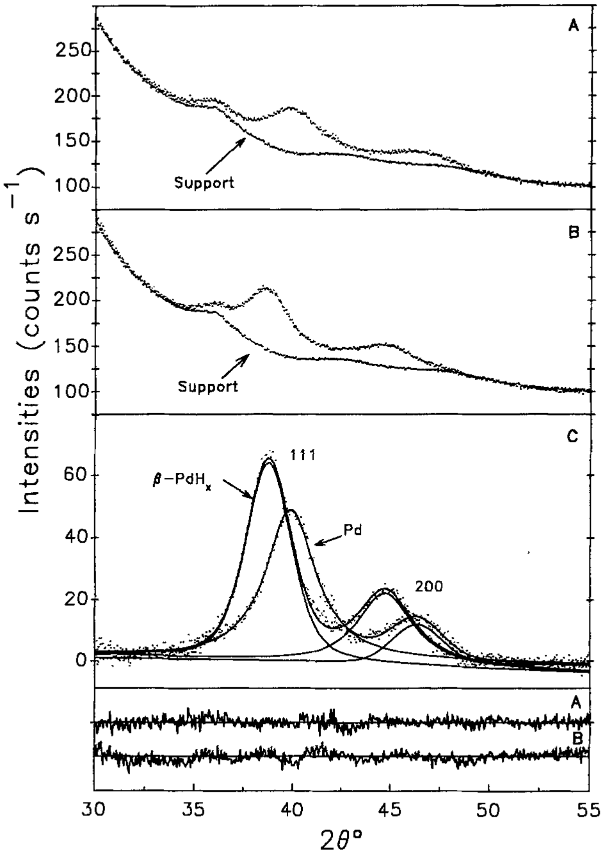

Fig. 2. As in fig. 1 for the catalyst C4.

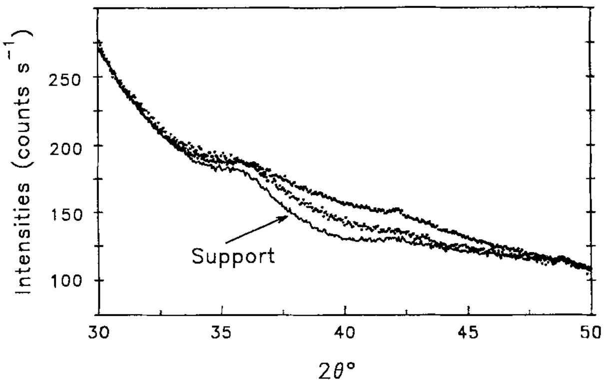

Fig. 3. X-ray patterns of C1. The upper pattern was obtained when the catalyst was exposed to hydrogen at room temperature. The intermediate pattern corresponds to the catalyst before exposure to hydrogen.

Table 2
Average Pd particle size obtained by SAXS and corresponding dispersion values D_x (with the relevant error interval). The dispersions obtained by chemisorption, D_{CO}, are also shown

Sample	$\langle L\rangle_s$ (Å)	D_x [a]	D_{CO} [b]
C1	20(4)	0.56 (0.47–0.70)	0.80
C2	26(5)	0.43 (0.36–0.53)	0.45
C3	38(8)	0.29_5 (0.24–0.37)	0.29
C4	40(8)	0.28 (0.23–0.36)	0.28
C5	38(8)	0.29_5 (0.24–0.37)	0.27

[a] D_x is given by the equation: $D_x = 11.2/\langle L\rangle_s$.

[b] These values were calculated with the value of 2 for the ratio between Pd atoms and CO adsorbed molecules (bridge form).

chemisorption stoichiometry Pd/CO = 2, are reported. A very good agreement was obtained between the two series of dispersion values determined by SAXS and by CO chemisorption, except for the most dispersed catalyst C1 for which a stoichiometry of about 1.3 is required for the agreement with the corresponding SAXS value. As a matter of fact, it is known (see ref. [2]) that for very small Pd particle sizes most of the CO molecules are adsorbed in the linear form (Pd/CO = 1). Therefore, the SAXS D_x value is to be considered more reliable.

In fig. 6 the stoichiometry values reported in table 1 are plotted as a function of D_x with the relevant errors. It can be seen that the only use of structural techniques has shown a substantially linear decrease of hydrogen content in the β-palladium hydride when dispersion increases, so confirming the results of Boudart and Hwang [5]. Unfortunately, it was not possible to establish the trend of stoichiome-

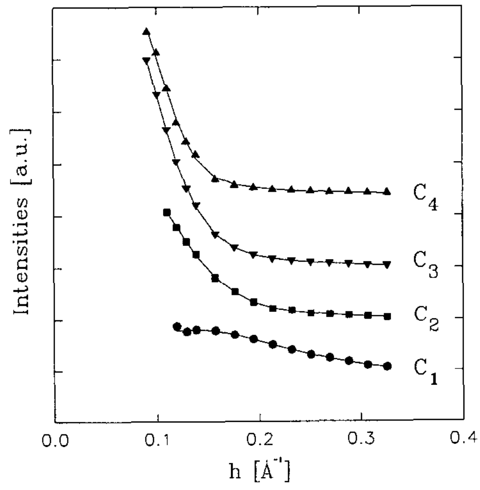

Fig. 4. SAXS data fitted with the regularization method for the catalyst series C1–C4. The continuous line represents the calculated intensities.

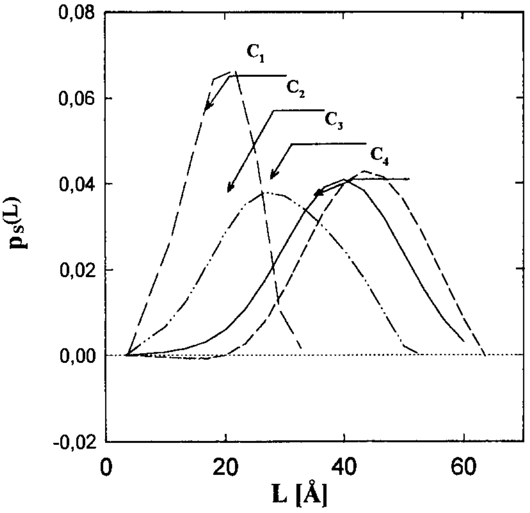

Fig. 5. Pd particle size distributions for the catalyst series C1–C4 obtained with the SAXS technique.

try at dispersions higher than about 0.45, since XRD technique fails for too weak and diffuse peaks.

This trend was qualitatively confirmed by TPR, in agreement with our previous results [22]. The TPR profiles of the Pd/SiO$_2$ catalysts have shown a negative

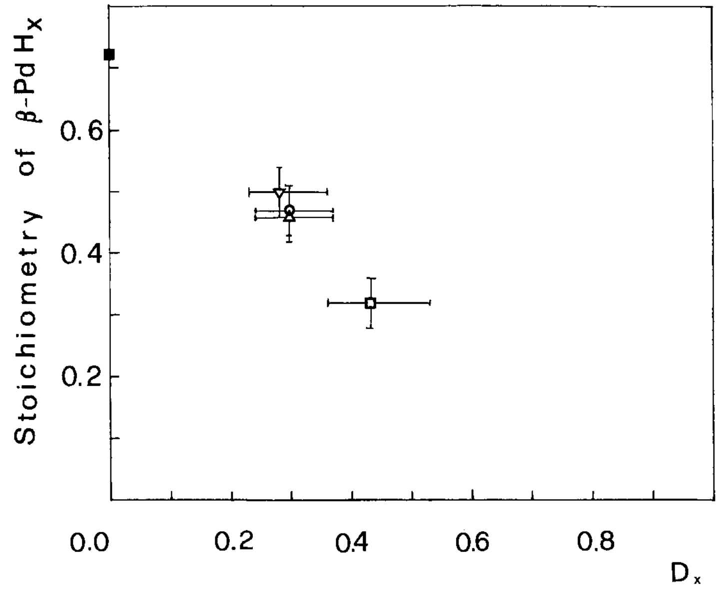

Fig. 6. Plot of the stoichiometry, x, of β-PdH$_x$ as a function of dispersion, D_x, as determined by SAXS. Symbols: (□) C2, (○) C3, (▽) C4, (△) C5.

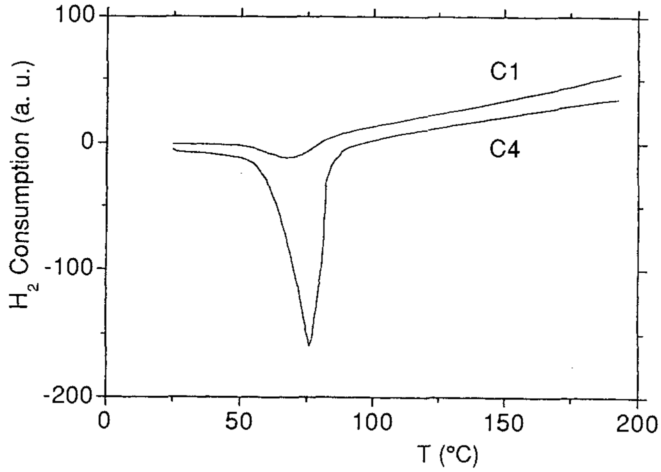

Fig. 7. TPR peaks of C1 ($D_x = 0.56$) and C4 ($D_x = 0.28$) showing the different amounts of decomposed β-PdH$_x$.

peak centered in the range 67–76°C, due to a hydrogen evolution from β-hydride decomposition [23,17]. Fig. 7 shows the two limiting cases investigated here, i.e. the TPR peaks of the most dispersed catalyst (C1) and the least dispersed catalyst (C4). In this case the technique is used as TPD. The very negative small TPR peak at 70°C for sample C1, having D_x around 0.6 agrees qualitatively well with the trend reported by Boudart and Hwang [5].

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