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Comparison of H_2 Adsorption, O_2 Adsorption, H_2 Titration, and O_2 Titration on Supported Palladium Catalysts

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Four different methods for Pd dispersion measurement are compared: H_2 adsorption, O_2 adsorption, H_2 titration, and O_2 titration. A correct comparison requires the knowledge of H/Pd_s and O/Pd_s stoichiometries. The H/Pd_s stoichiometry is discussed by reviewing published results, which lead us to the conclusion that $H/Pd_s = 1$. Our experimental results demonstrate that the relative O/H stoichiometry is independent of Pd concentration, type of carrier, and preparation method, $O/H = 1$; thus $O/Pd_s = 1$. If correctly performed, the four methods give the same Pd dispersion, but those based on direct adsorption have less applicability, because they require the complete removal of hydrogen used for reduction from the metal surface. A method to evaluate residual hydrogen is given.

INTRODUCTION

This paper reports on work devoted to the development of an easy-to-perform and widely applicable method for dispersion measurement of supported Pd. Here we discuss the problem of the stoichiometry factor (S) of adsorbate–metal interaction, which is the ratio of the number of atoms adsorbed on metal surface N_{ads} to the number of exposed metal atoms M_s:

$$S = N_{ads}/M_s. \quad [1]$$

During the past 30 years, the problem of stoichiometry of adsorbate–adsorbent metal interaction has been the subject of a number of papers, but until now the problem has not been fully resolved (nor has the problem of relative stoichiometries of different adsorbates on a given metal) and still receives new contributions. Excellent reviews (see, for example, (1–4)) on the topic are available.

Most works have been devoted to Pt, particularly to the H–Pt interaction, but complete agreement has not been reached even in this case. Published works on Pd are much less frequent and almost all are based on the H–Pd interaction.

In regard to H_2, a H_{irr}/Pd_s stoichiometric ratio = 1 (H_{irr} refers to irreversibly adsorbed hydrogen and Pd_s to surface Pd atoms) is generally accepted. Most authors simply use $H_{irr}/Pd_s = 1$, without any independent confirmation and regardless of the type of support, sample pretreatment conditions, adsorption temperature (298–373 K), or pressure (from 0–0.1 to 0–50 KPa). A few authors (5–8) calculated H_{irr}/Pd_s ratio by H_2 adsorption on Pd black with a known surface area. The resulting stoichiometry is not far from 1 (1.0–1.1 except for (6), which reported a value of about 1.2). In some papers H_2 adsorption results are compared to those obtained by different techniques, mainly TEM and, to a lesser degree, XRD (6, 9–17). In Fig. 1, available data of Pd particle size calculated from H_2 adsorption, assuming $H_{irr}/Pd_s = 1$, are reported in relation to corresponding TEM and XRD values. The resulting relationship ($d_{H2}/d_{TEM,XRD} = 0.96$) strongly supports the accuracy of the assumed stoichiometry. A more precise assessment of true stoichiometry by comparison methods is not possible because rough assumptions are necessary to process experimental data in order to compare them together (18). At the same time, Fig. 1 shows that a single datum and even a whole set of data can diverge significantly from the fitting straight line, pointing out the effect of experimental parameters, concerning both sample and analysis, on measured stoichiometry, as will be discussed later.

The O_{irr}/Pd_s stoichiometric ratio, not to mention the widely investigated Pt, is more open to question. Almost all authors prefer to compare O_2 adsorption data to those obtained by H_2 adsorption, assuming $H_{irr}/Pd_s = 1$. If the available results (6, 9, 10, 13, 19–23) are used to calculate O_{irr}/H_{irr} (i.e., the relative stoichiometry H_{irr}/Pd_s–O_{irr}/Pd_s), the most relevant feature is the width of range covered by obtained values (standard deviation 0.30), which makes the evaluation of stoichiometry unreliable.

In this paper we report on the application to three different supported Pd catalysts of different methods (i.e., direct adsorption and titration) and different adsorbates (i.e., H_2 and O_2). We will show that $H_{irr}/O_{irr} = 1$ and if, on the basis of the reviewed literature, we assume $H_{irr}/Pd_s = 1$, then also $O_{irr}/Pd_s = 1$. The obtained results are independent of the method used, but the evaluation of direct adsorption measurements requires the absence or the knowledge of residual hydrogen on metal after pretreatment

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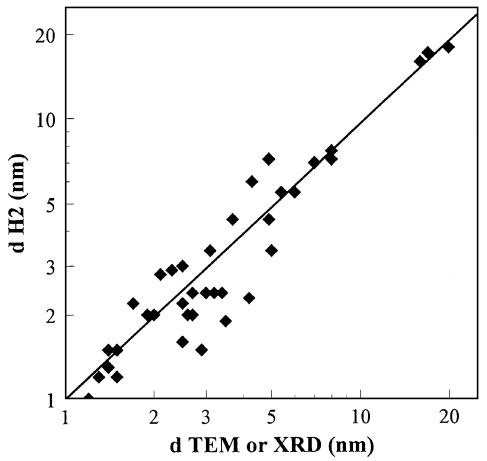

FIG. 1. Average particle size calculated from H_2 adsorption measurements assuming $H_{irr}/Pd = 1$ vs average particle size measured from TEM or XRD. Data are taken from (7–11, 15, 27, 30).

(its determination is allowed by the contemporary use of different methods).

METHODS

Sample Preparation

Pd/Al_2O_3 was prepared by impregnating γ-Al_2O_3 Alcoa CSS (surface area 122 m^2g^{-1}, pore volume 0.43 cm^3g^{-1}) with excess solution of Pd chloride and reduced by adding sodium hypophosphite. After removal of excess solution, the sample was washed with H_2O, dried in air at 390 K for 16 h, and kept in a desiccator. The residual P and Cl concentrations, as determined by XRF, were 150 and 200 ppm, respectively. The metal loading was determined by conventional ICP-AES after dissolution in *aqua regia*. A concentration of 0.57 wt% Pd was found. In the following the sample will be identified as Pd0.57/A.

Pd/SiO_2–Al_2O_3 was prepared by using as carrier silica–alumina Condea (surface area 348 m^2g^{-1}, pore volume 0.62 cm^3g^{-1}). The preparation method was the same as for Pd0.57/A, without reducing treatment. The Pd concentration was found to be 1.75 wt%. This sample will be identified as Pd1.75/SA.

Pd/SiO_2 was prepared following the sol-gel method reported by Zou and Gonzalez (24). Pd acetylacetonate and tetraethoxysilane were used as precursors. The gel was dried at 373 K for 4 h and calcined in air at 473 K for 2 h. The catalyst obtained was found to contain 1.21 wt% Pd, and it will be identified as Pd1.21/S.

Adsorption Methods

Four types of measurements were made on each sample: H_2 adsorption, O_2 adsorption, H_2 titration, and O_2 titration. Measurements were made on about 3 g of sample by a Micromeritics ASAP 2010C device equipped with a turbomolecular pump, which allowed it to attain a vacuum better than 10^{-3} Pa in the sample holder. All the treatments, including adsorption, were performed with sufficient time to reach equilibrium. In fact some steps are slow, as pointed out, for example, in (17) for the adsorption of O_2 on Pd surface. The pretreatment consisted of evacuation at 308 K for 5 min, evacuation at the pretreatment temperature T_{pre} (393 or 673 K) for 60 min, five cycles of reduction with H_2 (26 KPa) at T_{pre} for 15 min followed by evacuation at he same temperature for 15 min (the last time for 60 min), and, finally, evacuation at 308 K for 60 min. Direct adsorption measurements were made with H_2 or with O_2 at 308 K. They consisted of the determination of two isotherms in the 0.75–30 KPa range (about 60 min per point) separated by an evacuation at the same temperature for 60 min. H_2 titration measurements were made in the same way, but the adsorption was preceded by two cycles of a treatment consisting of adsorption of O_2 at 308 K and 26 KPa for 60 min followed by evacuation at the same temperature for 60 min. In the case of O_2 titration, after the last H_2 treatment, instead of the evacuation, the temperature was lowered under H_2 to 308 K, and then the sample was evacuated at 308 K for 60 min.

Adsorbed volumes were calculated by fitting the linear portion of each isotherm with a straight line and extrapolating it to zero pressure: the first isotherm gives the total adsorbed volume, the second gives the reversibly adsorbed volume, and their difference gives the irreversibly adsorbed volume.

Starting from Eq. [1] and stoichiometry factor S, it is possible to calculate dispersion from adsorbed volume (V_{ads}) and Pd content of the sample (C_{Pd}):

$$D = M_s/M_{tot} = N_{ads}/(SM_{tot}) = KV_{ads}/(SC_{Pd}). \quad [2]$$

If V_{ads} is expressed in $cm^3\ g^{-1}$ sample and C_{Pd} in g Pd g^{-1} sample, K becomes 0.009494 for diatomic molecules; thus,

$$D = 0.009494V_{ads}/(SC_{Pd}). \quad [3]$$

RESULTS AND DISCUSSION

Pd/Al_2O_3

Measurements have been made on Pd0.57/A samples reduced at two different temperatures, 393 and 673 K, and evacuated at the reduction temperature (see Experimental).

The lowest temperature was chosen so as to assure the complete reduction of Pd eventually reoxidized after reduction by hypophosphite during the drying at 393 K and, at the same time, to avoid Pd sintering not only on the Al_2O_3-supported sample, but also on Pd supported on other carriers (for example, active carbon), in order to develop

a method having an applicability as wide as possible. The completion of Pd reduction at a temperature lower than 393 K is reported in published papers (25–27), and, as will be shown later, no further reduction was observed on our samples between 393 and 673 K. On the contrary, there is some disagreement among different published data on Pd sintering (7, 11, 24, 28–33), particularly on Pd/active carbon (28, 30–32). Nevertheless, no sintering processes up to 400 K have been proven with certainty, except for bulk Pd (7) and on very highly dispersed Pd (17). In addition, most authors report direct observations of sintering only at higher temperature (11, 17, 24, 28, 31–33). In any case, a reduction and evacuation temperature of 393 K is much lower than that required to cause metal sintering on Pd/Al_2O_3 (11, 33).

The highest temperature was chosen to allow the removal by evacuation of almost all the hydrogen present on Pd at the end of reduction. In fact, according to the literature, the amount of residual hydrogen depends on the evacuation temperature, as can easily be seen by a number of published TPD measurements (1, 4, 23, 29): a high-temperature evacuation is required to clean Pd surface from adsorbed hydrogen (28). According to (6), hydrogen is completely removed from Pd surface at 573 K, while in conformity with (5), the residual hydrogen on the Pd surface is 11% at 573 K and less than 3% at 673 K. Thus at 673 K it can be considered negligible.

In Fig. 2, isotherms obtained on samples evacuated at 393 and 673 K by H_2 adsorption (Fig. 2a), O_2 adsorption (Fig. 2b), H_2 titration (Fig. 2c), and O_2 titration (Fig. 2d) are reported. The results obtained by back extrapolation to pressure = 0 are reported in Table 1.

According to (3), the following equations can be written:

$$H_2 \text{ adsorption:} \quad Pd_sH_r + (v - r)H \rightarrow Pd_sH_v \qquad [4]$$

$$O_2 \text{ adsorption:} \quad Pd_sH_r + (z + 0.5r)O \rightarrow Pd_sO_z + 0.5rH_2O \qquad [5]$$

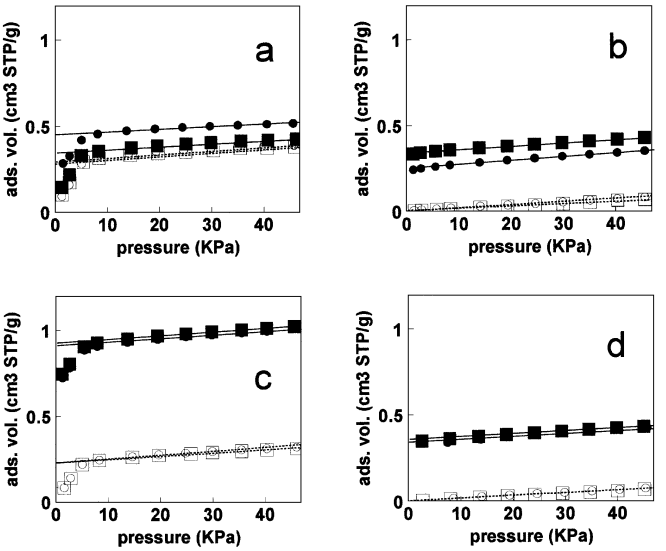

FIG. 2. Adsorption isotherms on Pd/Al_2O_3 sample after evacuation at 673 K (total adsorption (●), reversible adsorption (○)) and 393 K (total adsorption (■), reversible adsorption (□)): (a) H_2 adsorption; (b) O_2 adsorption, (c) H_2 titration; (d) O_2 titration.

$$H_2 \text{ titration:} \quad Pd_sO_z + (v + 2z)H \rightarrow Pd_sH_v + zH_2O \qquad [6]$$

$$O_2 \text{ titration:} \quad Pd_sH_v + (z + 0.5v)O \rightarrow Pd_sO_z + 0.5vH_2O, \qquad [7]$$

here

i. r is the mean number of H atoms still adsorbed on each Pd_s after the final evacuation,

ii. v is the mean number of H atoms irreversibly adsorbed on each Pd_s under analysis conditions,

iii. z is the mean number of O atoms irreversibly adsorbed on each Pd_s under analysis conditions.

Notice that the above equations are written assuming that v and z are independent of the type of measurement. The assumptions will be discussed later.

TABLE 1

Results of Adsorption and Titration Measurements on Samples Evacuated at Different Temperatures after Reduction

A	B	C	Pd0.57/A total adsorption ($cm^3\,g^{-1}$)	Pd0.57/A reversible adsorption ($cm^3\,g^{-1}$)	Pd0.57/A irreversible adsorption ($cm^3\,g^{-1}$)	Pd1.75/SA total adsorption ($cm^3\,g^{-1}$)	Pd1.75/SA reversible adsorption ($cm^3\,g^{-1}$)	Pd1.75/SA irreversible adsorption ($cm^3\,g^{-1}$)	Pd1.21/S total adsorption ($cm^3\,g^{-1}$)	Pd1.21/S reversible adsorption ($cm^3\,g^{-1}$)	Pd1.21/S irreversible adsorption ($cm^3\,g^{-1}$)
Ha	673	13-47	0.459	0.246	0.213	1.402	0.924	0.478	1.029	0.680	0.349
Oa	673	13-40	0.255	0.004	0.219	0.492	0.004	0.488	0.370	0.005	0.365
Ht	673	13-47	0.902	0.241	0.661	2.352	0.911	1.441	1.746	0.682	1.064
Ot	673	13-40	0.333	0.001	0.319	0.705	0.002	0.703	0.523	0.009	0514
Ha	393	13-47	0.269	0.236	0.033	1.050	0.909	0.141	0.939	0.787	0.152
Oa	393	13-40	0.346	0.002	0.322	0.625	0.001	0.624	0.451	0.000	0.451
Ht	393	13-47	0.924	0.241	0.683	2.331	0.905	1.426	1.808	0.735	1.073
Ot	393	13-40	0.346	0.001	0.336	0.712	0.000	0.712	0.506	0.002	0.504

Note. The values of adsorbed volume were obtained by back extrapolation to pressure = 0. A, type of measurement; B, reduction and evacuation temperature (K); C, pressure range used for calculations (KPa).

By defining Ha as the experimentally determined number of hydrogen atoms consumed in reaction [4] per Pd atom; Oa, Ht, and Ot as the corresponding number of atoms consumed in Eqs. [5], [6], and [7], respectively; and D as the metal dispersion, the following system can be written:

$$\mathrm{Ha} = D(v - r) \quad [8]$$

$$\mathrm{Oa} = D(z + 0.5r) \quad [9]$$

$$\mathrm{Ht} = D(v + 2z) \quad [10]$$

$$\mathrm{Ot} = D(z + 0.5v). \quad [11]$$

The system contains four unknowns (D, r, v, z). Unfortunately, as can be easily verified, only two equations are independent and D is a multiplying factor of all equations.

As a consequence, direct determination of all parameters is not possible. Nevertheless, under particular conditions, the system, or more exactly each couple of independent equations, allows the determination of important parameters, namely z/v, r/v, and D. However, also if the system is redundant, the contemporary use of all equations allows a cross checking of the reliability of the results and of the assumptions made, as shown in the next.

Reliability of Measurements

Taking the work of O'Rear *et al.* (3) as a starting point, it is possible to define two parameters R_H (named R_t in the quoted paper) and R_O:

$$R_\mathrm{H} = \mathrm{Ht}/(\mathrm{Ha} + 2\mathrm{Oa}) \quad [12]$$

$$R_\mathrm{O} = \mathrm{Ot}/(0.5\mathrm{Ha} + \mathrm{Oa}). \quad [13]$$

On the basis of Eqs. [8] and [11],

$$R_\mathrm{H} = R_\mathrm{O} = 1. \quad [14]$$

Checking the validity of Eq. [14] is a very good way to test both the validity of the above assumptions (i.e., v and z independent of type of measurement) and the correctness of the experimental procedure.

The values calculated from our data at both 673 and 393 K are within 2% of unity, as shown in Table 2. This shows that v and z are really independent of type of measurement also in the case of Pd and allows most errors to be excluded from measurement, thus confirming that the data obtained are suitable for calculations.

Further proof of the reliability of results can be obtained by taking into account data on reversible adsorption. These values should depend almost solely on adsorbate molecule and on measurement conditions. Then all reversible H_2 uptakes must have the same value, as should the corresponding values obtained with O_2. As shown in Table 1, the maximum difference among H_2 reversible adsorption data is 0.010 cm^3g^{-1} (4.2% of average value), and that among O_2 based data is 0.003 cm^3g^{-1} (negligible).

Evaluation of z/v

As pointed out above, evacuation at 673 K ensures that residual hydrogen is negligible; thus assuming $r = 0$ it is possible to calculate z/v by a suitable combination of equations [8]–[11]. The results on sample evacuated at 673 K (Table 3) show that z/v is within 3% of unity, which is within the experimental error of the method. In the following, concerning Pd0.57/A sample we will assume that $z/v = 1$.

The fact that the hydrogen/oxygen stoichiometric ratio is close to unity strongly supports the existence of a simple and well-defined adsorption stoichiometry for both gases on Pd. However, it must be taken into account that the resulting relationship $z/v = 1$ is valid only under experimental conditions used to perform our measurements. Nothing can be inferred for different conditions. For example, as pointed out by a few authors (5, 22, 34, 35), irreversible adsorption of both H_2 and O_2 changes with adsorption temperature.

Evaluation of r/v

If $z/v = 1$, Eqs. [8]–[11] allow the calculation of residual hydrogen fraction r/v. After evacuation at 673 K, different combinations of equations, and thus different combinations of adsorption methods, give residual hydrogen values between 0 and 6% (average 2%), which is in good agreement with (5).

In the same way, evaluation of data obtained after evacuation at 393 K is possible. Also in this case, calculation with different equations and data gives nearly the same result: residual hydrogen = 83–87% (average 85%). This

TABLE 2

Calculation of R_H and R_O on Samples Evacuated at Different Temperatures after Reduction

Type of measurement	Evacuation temperature (K)	Equations	Pd0.57/A	Pd1.75/SA	Pd1.21/S
H_2 ads., O_2 ads., H_2 titr.	673	$R_\mathrm{H} = \mathrm{Ht}/(\mathrm{Ha} + 2\mathrm{Oa})$	1.01	0.99	0.99
H_2 ads., O_2 ads., O_2 titr.	673	$R_\mathrm{O} = \mathrm{Ot}/(0.5\mathrm{Ha} + \mathrm{Oa})$	0.98	0.97	0.95
H_2 ads., O_2 ads., H_2 titr.	393	$R_\mathrm{H} = \mathrm{Ht}/(\mathrm{Ha} + 2\mathrm{Oa})$	1.01	1.03	1.02
H_2 ads., O_2 ads., O_2 titr.	393	$R_\mathrm{O} = \mathrm{Ot}/(0.5\mathrm{Ha} + \mathrm{Oa})$	0.99	1.03	0.96

TABLE 3

Calculation of z/v Ratio of Different Samples by Using Different Equations and Assuming $r = 0$

Type of measurement	Evacuation temperature (K)	Equations	z/v		
			Pd0.57/A	Pd1.75/SA	Pd1.21/S
H_2 ads. + O_2 ads.	673	$z/v = Oa/Ha$	1.03	1.02	1.04
H_2 ads. + O_2 titr.	673	$z/v = 0.5(2Ot/Ha - 1)$	0.99	0.97	0.97
H_2 titr. + O_2 ads.	673	$z/v = 0.5/(Ht/2Oa - 1)$	0.98	1.05	1.08
Average			1.00	1.01	1.03

Note. The resulting average value is 1.013 ± 0.015.

means that evacuation at 393 K leaves most hydrogen on Pd surface: thus it is not suitable for direct adsorption measurements. If evacuation at low temperature is required to avoid Pd sintering or other sample damaging, only titration methods can be performed.

Calculation of D

Calculation of dispersion D by Eqs. [3] and [8]–[11] requires the knowledge of at least one stoichiometric factor. Here we assume, as already discussed, that $H_{irr}/Pd_s = 1$ ($v = 1$) and we have shown that under our conditions $O_{irr}/H_{irr} = 1$ ($z/v = 1$), and thus also $O_{irr}/Pd_s = 1$ ($z = 1$). The fact that the hydrogen/oxygen stoichiometric ratio is close to unity strongly supports the existence of a simple and well-defined adsorption stoichiometry for both gases on Pd. If calculation of D is made by direct adsorption data also r must be known. In our evaluation we used the two average obtained values: $r/v = 0.02$ (673 K) and $r/v = 0.85$ (393 K).

The knowledge of all three parameters allows the calculation of D from different measurements. On the samples pretreated at 393, D varies from 37.3 to 37.9% (average 37.5%), while on the samples pretreated at 673, D varies from 35.4 to 36.7% (average 36.0%).

It can be noticed that, at a given evacuation temperature, all measurements give results which are close to one another (standard deviation < 1%). This means that, at least under adopted experimental conditions, all methods are suitable for Pd dispersion measurements.

Dispersion seems to be independent of pretreatment (reduction and evacuation) temperature. This means that no sintering occurs between 393 and 673 K on Pd/Al_2O_3 or, more precisely, a possible sintering at 673 affects metal dispersion less than 4% of value measured at 393 K.

Pd/SiO_2–Al_2O_3

The Pd1.75/SA sample differs from the previously described Pd0.75/A sample by carrier, preparation method, and Pd content. Notwithstanding that, the results draw a very similar picture.

The reliability of measurements is assured by R_H and R_O values within 3% of unity (Table 2) and by the constancy of reversible H_2 uptakes (maximum difference 2% of the average value: see Table 1). The O_2 reversible adsorption is negligible also on this sample. The z/v ratio, i.e., the O_{irr}/H_{irr} stoichiometric ratio, is again close to unity: the average value is 1.01 (Table 3).

The residual hydrogen (expressed as r/v ratio) is absent after evacuation at 673 K, while about 67% of the total hydrogen remains adsorbed if the evacuation is made at 393 K. This value differs from the value of 85% found for the Pd0.57/A sample. We have not gone deeper into this question; we only notice that the Pd dispersions of the two samples are not the same, suggesting the possibility of a relationship between capability of Pd to retain adsorbed hydrogen and different fractions of exposed faces or different ratio of plane, edge, and corner Pd atoms.

The obtained values confirm that all adsorption and desorption methods give the same metal dispersion: after evacuation at 673 K the average value is 26.0% with standard deviation of 0.4, and after evacuation at 393 K the average value is 25.0% with standard deviation of 1.2. Moreover, no sintering occurs between 393 and 673 K: difference in average values obtained at the two temperatures can be considered to be within the experimental error.

On the whole, the four tested adsorption and titration methods give the same results as those obtained for the Pd0.57/A sample, namely a O_{irr}/H_{irr} stoichiometric ratio close to unity.

Pd/SiO_2

The data obtained for the Pd1.21/S sample further support the results given by the two previously discussed samples.

The results are reliable: the values of R_H are close to unity and those of R_O, though a bit low, are still acceptable (Table 2). However, the z/v value is a bit further from unity than values obtained for other samples (Table 3: 1.03 instead of 1.00 and 1.01). In our opinion the difference is not high enough to call into question the previous conclusions.

The adsorbed hydrogen shows the usual behavior as regards the evacuation: all the hydrogen is removed at 673 K, while most of it (58%) remains on the sample after

evacuation at 393 K. The Pd1.21/S shows the lower retention capacity of hydrogen among the investigated samples, though not far from values obtained on Pd1.75/SA sample, having a similar metal dispersion.

Also in this sample, Pd dispersion does not change with pretreatment temperature: the difference between the average values obtained at 673 (minimum 26.9%, maximum 28.5%, average 27.8%) and 393 K (minimum 26.4%, maximum 28.4%, average 27.6%) cannot be considered meaningful. Finally, the results further confirm that all the adsorption and titration methods give the same results of metal dispersion.

CONCLUSIONS

Let us summarize the results presented in this paper, devoted to the direct comparison of the results of four different methods: H_2 adsorption, O_2 adsorption, H_2 titration, and O_2 titration. The contemporary use of these methods allows:

i. the determination of relative stoichiometry H_{irr}/Pd_s–O_{irr}/Pd_s ($H_{irr}/O_{irr} = 1$); since (according to the reviewed literature) $H_{irr}/Pd_s = 1$, also $O_{irr}/Pd_s = 1$;

ii. the determination of hydrogen still present on metal surface after evacuation, which requires high temperature to be completely removed;

iii. the checking of reliability of the methods (by R_H and R_O);

iv. the comparison of dispersion values, obtained by different methods, that result independent of the method, at least under our experimental conditions.

It is evident that the contemporary use of four different methods is limited to the development stage of a new application or when controls on used methods are needed. Usually one method is enough to measure metal dispersion. The choice depends on the problem being studied.

Direct H_2 adsorption has been preferred by most authors for almost all metal dispersion measurements because of its simplicity, of the better knowledge of adsorbate/metal stoichiometry, and of the availability of a number of data suitable for comparison in the literature. H_2 adsorption is the most often used technique also in the case of Pd, notwithstanding that measures have been generally performed under particular conditions (high temperature and/or low pressure) to avoid H_2 absorption in bulk Pd (2, 4, 5, 7–9, 13–16, 19–23). In this paper, as well as in (23), it has been shown that the fulfilment of this condition is not strictly required and, as a result, the method is easy to perform.

Direct O_2 adsorption has been used less frequently, mainly because of the uncertainty of oxygen/metal stoichiometry (6, 9, 10, 13, 20–22). Our results point out that O_{irr}/Pd_s is close to unity, at least under used experimental conditions, and thus the method can be used as well as H_2 adsorption. An advantage of O_2 compared to H_2 is the lower sensitivity of its irreversible uptake to adsorption temperature (22). In addition, the reversible O_2 adsorption is negligible (see Table 1 and Ref. (22)), at least on oxide supports; this makes the method potentially more precise than that based on H_2 adsorption.

The assessment of oxygen/Pd_s stoichiometry makes methods based on the titration of preadsorbed molecules, not often used until now (10, 11, 19–21, 23), suitable for dispersion measurement. Differences between H_2 titration and O_2 titration are similar to those discussed with regard to correspondent direct adsorption methods.

Titration methods, even if a little more complicated than those based on direct adsorption, have a wider applicability (1, 4). For example, they must be adopted whenever:

i. low evacuation temperature has to be used to preserve metal from sintering, and thus adsorbed hydrogen cannot be completely removed from metal surface;

ii. low adsorption values are foreseen owing to low metal dispersion or content; as regards direct adsorptions, the amount of gas consumed in O_2 titration is 1.5 times higher, and in H_2 titration it is 3 times higher.

Obviously the choice must always be related to characteristics of the sample under study.

The approach discussed in the paper has a wide applicability. It is not limited to Pd as metal and to inorganic oxides as carrier, as we have found, by investigating other supported metal samples such as Pd/C, Pt/Al_2O_3, Pt/SiO_2, Pt/C, and so on (36).

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