Thermodynamic parameters of H_2 adsorption as criteria to characterize silica-supported palladium catalyst

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The thermodynamics of hydrogen adsorption on palladium catalyst supported on silica is determined by isosteric analysis of series of isochores measured by the volumetric method. The variations of this thermodynamics (ΔH, ΔS) with adsorbed amount allows the discrimination between the different hydrogen species present on such a catalyst (hydrogen strongly and weakly chemisorbed on the palladium, absorbed in the palladium particles and molecularly adsorbed on the support). Namely, the variations of only the heat of adsorption with adsorbed amount allow the determination of hydride and weakly adsorbed hydrogen species. It is shown that these amounts can even be determined from one single isochore.

Keywords: Pd catalysts, hydrogen chemisorption, thermodynamics of chemisorption

1. Introduction

Chemisorption of the reactants is an essential step in heterogeneous catalysis. Consequently, the bond strength between adsorbate and catalyst is an important parameter in surface reactions. The strength of chemisorption bonds can affect both the activation energy of a surface reaction and the surface concentration of active intermediates. Furthermore, the heat of adsorption also reflects surface properties of the adsorbent.

In this frame, chemisorption of H_2 as a probe molecule is often used (see, for example, refs. [1–3]). On the other hand, it is well known that a metal like palladium, besides its capacity to adsorb hydrogen on the metal surface, is also able to absorb it and form hydrides in two distinct solid solutions: α and β phase [1,4,5]. Moreover, Boudart and Hwang [1], and Fagherazzi et al. [6] have shown that the absorption capacity of palladium particles strongly depends on the dispersion of the catalyst since the amount of bulk palladium atoms decreases as dispersion increases.

Several methods are proposed in the literature to distinguish between *adsorbed* and *absorbed* hydrogen species for palladium-based catalysts, and thus to measure the active surface area and the dispersion of these catalysts. For example, one method is based on the difference of two isotherms performed at room temperature [1,2,4], separated by a pumping step in order to evacuate the hydrides. Another method is based on the extrapolation to zero pressure [3] of an isotherm performed at 100°C (temperature at which hydrides are decomposed). The H_2–O_2 titration proposed by Boudart and coworkers [1,4,7] is also used. Some of these methods are criticized in detail by Hubert and Frennet [8], who have recently proposed a new method based on the determination of the thermodynamics of hydrogen chemisorption and its variations with the coverage. In this work, the authors have shown that the isochore measurements, in contrast to isothermal measurements, allow the determination of variations of the isosteric heat of adsorption Q_{iso} over a large coverage range and up to the monolayer saturation. The variation of Q_{iso} with the adsorbed amount is an interesting way of determining the value of the monolayer capacity.

2. Experimental

2.1. Sample

The support used in this study is SiO_2 (Degussa Aerosil 200, 220 $m^2\ g^{-1}$). This support was compacted, ground and sieved. The 125–250 μm fraction is used for impregnation by the precursor salts. It is calcined at 673 K in flowing O_2/Ar 10% for 4 h prior to any precursor salt deposition.

Palladium precursor is $Pd(NH_3)_4(NO_3)_2$ (Johnson Matthey) in distilled water. The deposition was performed using impregnation by ion adsorption on the support. For this, a large excess (100 times the pore volume of the silica) of impregnating solution with concentration of 2.3×10^{-3} mol ℓ^{-1} is in contact with the support during 4 h under continuous stirring. Then the excess of impregnating solution is separated by filtering and the catalyst is dried in air at 393 K during one night.

The palladium weight loading is determined by plasma emission spectroscopy and corresponds to 2.5 wt% Pd/SiO_2.

Prior to any use, this catalyst is calcined in a flow of

20 cm^3 min^{-1} 10% O_2/Ar at atmospheric pressure from room temperature to 673 K with a linear increase of the temperature of 6 K min^{-1}.

The reduction is conducted in situ prior to any adsorption measurement under a flow of 20 cm^3 min^{-1} 5% H_2/Ar from 150 to 650 K at a rate of 5 K min^{-1}.

2.2. TP reduction

The TP reduction is performed for 0.5 g of the previously calcined supported precursor. The catalyst is cooled until 150 K under 20 cm^3 min^{-1} Ar flow. At this temperature, a 20 cm^3 min^{-1} 2.5% H_2/Ar flow is admitted in the reactor and a linear increase of the temperature of 6 K min^{-1} is applied up to 650 K.

2.3. Chemisorption

The chemisorption uptakes are measured in a conventional volumetric adsorption system equipped with two Baratron pressure gauges (MKS Baratron type 127A). This apparatus has already been described in detail elsewhere [8].

Isochore measurements: After in situ reduction of about 0.5 g of catalyst, the sample is outgassed for 1 h at 623 K, a temperature 50 K higher than that at which the gas is introduced to perform chemisorption measurements. The residual pressure at this temperature is lower than 10^{-5} Torr. Then a given amount of H_2 (n_t), measured in a side volume, is admitted to the reactor at 573 K. Thereafter the reactor is cooled until liquid nitrogen temperature and a linear increase of the temperature is applied from 77 up to 573 K. The measurements are conducted in a closed volume under temperature-programmed variations. Further details concerning this method have been extensively described elsewhere [8].

Isotherm measurements: The same activation sequence as mentioned above is performed. The procedure for isotherm measurement is based on successive expansions of the gas phase in known volumes at constant temperature.

3. Results

3.1. TPR

The TP reduction spectrum of the catalyst is presented in figure 1, where the partial pressures of hydrogen and water are plotted versus the temperature. One can see that the hydrogen consumption, corresponding to the reduction of the catalyst, appears at low temperature (200–300 K). For higher temperature (320 K), a peak of "production" of hydrogen is observed which is associated to the hydride phase and weakly adsorbed hydrogen evacuation. The low temperature at which the evacuation of these hydrogen species appears, as compared to that often found in the literature, is explained by the low hydrogen partial pressure in the gas phase used during the treatment. This temperature is in agreement with that observed by Zhang et al. [9]. Let us notice that the amount of hydrogen produced corresponds to 0.22 times the quantity of the palladium amount in the catalyst. The production of water appears at higher temperature than that of hydrogen consumption. This can be explained by the low temperature at which the hydrogen is consumed and by the presence of silica that retained the water at temperature lower than 250 K.

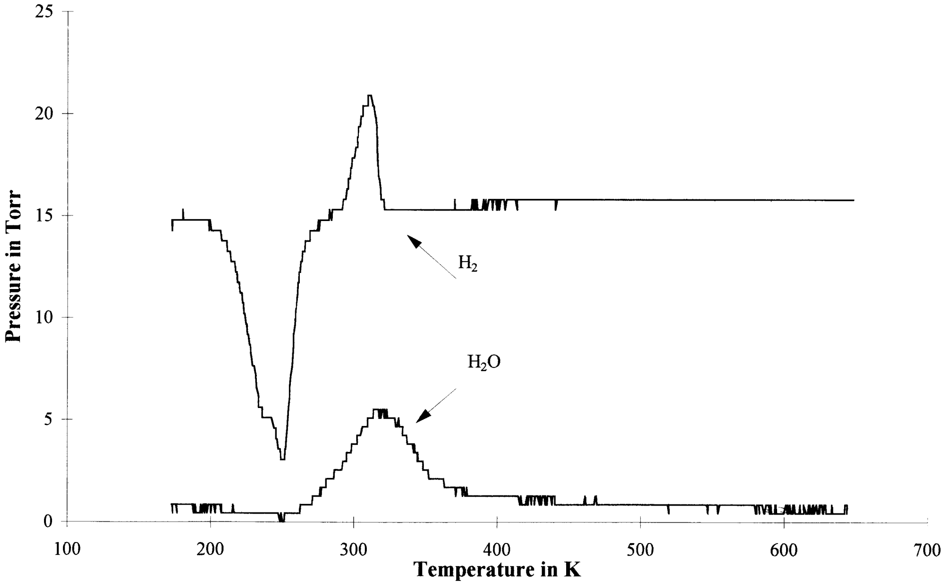

Figure 1. TPR results: hydrogen and water signals for a 2.5 wt% Pd/SiO_2 catalyst.

3.2. Isochores

Let us first emphasise the complete reversibility of hydrogen adsorption–desorption which is confirmed by the perfect superposition of the isochore in adsorption and desorption mode. The so determined values thus correspond to equilibrium values.

A typical isochore measured on Pd/SiO_2 is presented in figure 2. H_2 is introduced at 573 K. Then the reactor is cooled to $\sim$ 80 K, followed by heating to 573 K at 6 K min^{-1}. Figure 2 represents the variations of hydrogen pressure during an increase of the temperature from 77 to 573 K at a rate of 6 K min^{-1}. At low temperature ($<$ 173 K) an increase of the pressure can be observed. Then a linear relation between the temperature and the pressure seems to be reached until a temperature of 273 K. At this last temperature, a large pressure step is observed up to 323 K. The following linear increase of the pressure is maintained up to the temperature corresponding to the end of the experiment.

One can easily transform this pressure variation into the number of hydrogen atoms adsorbed for $n_t = n_g + n_a$, where n_t is the total amount of hydrogen introduced in the system, n_g is the remaining hydrogen in the gas phase after the adsorption, and n_a is the total amount of hydrogen retained by the catalyst. One must also take into account the temperature variation in a closed system, for the amount of hydrogen retained by the catalyst is calculated from a difference of two pressures (initial pressure and equilibrium pressure) in a closed system during a variation of the temperature.

The representation of the number of hydrogen atoms *adsorbed* and *absorbed* on/in this palladium catalyst (figure 3) shows an interesting behavior. For values of the ratio n_a/metal atoms greater than 1, we observe an important decrease of the number of hydrogen adsorbed at a temperature of about 100 K. A small plateau seems to be reached at $n_a/\text{metal} = 1$ but at higher temperature (300 K) this ratio decreases suddenly until a value of 0.6 is reached, after which a quasi-linear decrease of the value of the ratio n_a/metal is observed.

Series of isochore measurements have been performed in different pressure ranges between liquid nitrogen temperature and 573 K. These isochores, as well as the two isotherms corresponding to the beginning and the end of the temperature range for isochores, are represented in figure 4. This figure represents the variation of the amount of hydrogen retained by the solid versus the hydrogen pressure. One can see that these isochores cover a domain of hydrogen pressure of two orders of magnitude and that they are comprised between the two isotherms over this whole range of pressure. Such a control is necessary to establish the validity of interpretations we will propose hereafter.

All the isochores are plotted in figure 5, where n_a/metal atom is represented versus the temperature. After an important decrease of the amount of adsorbed hydrogen at about 100 K down to $n_a/\text{metal atom} = 1$, all the isochores have a plateau corresponding to $n_a/\text{metal} = 1$. A step is present in all curves at $\sim$ 300 K, and is completed for the same value of $n_a/\text{metal} = 0.60$.

As the isochores are measured at adsorption–desorption or at quasi-adsorption–desorption there is a relation between n_a, P, and T. The use of the Clapeyron–Clausius equation allows the determination of the isosteric heat of hydrogen adsorption–absorption, Q_{iso}, and of ΔS and ΔG. These values are plotted versus n_a in figure 6.

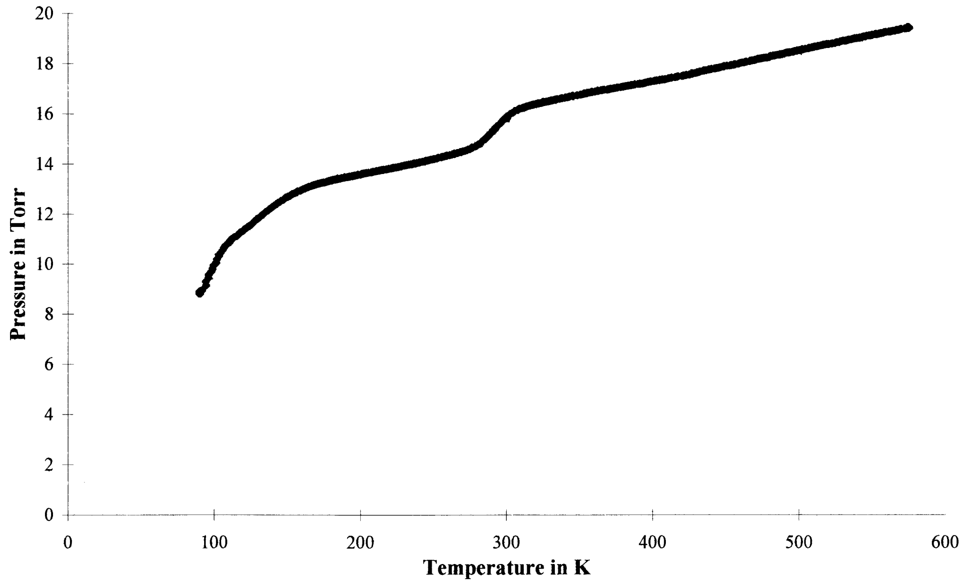

Figure 2. Typical isochore in desorption mode on 2.5 wt% Pd/SiO_2 where the variation of the pressure in the system (Torr) is plotted versus the temperature in K.

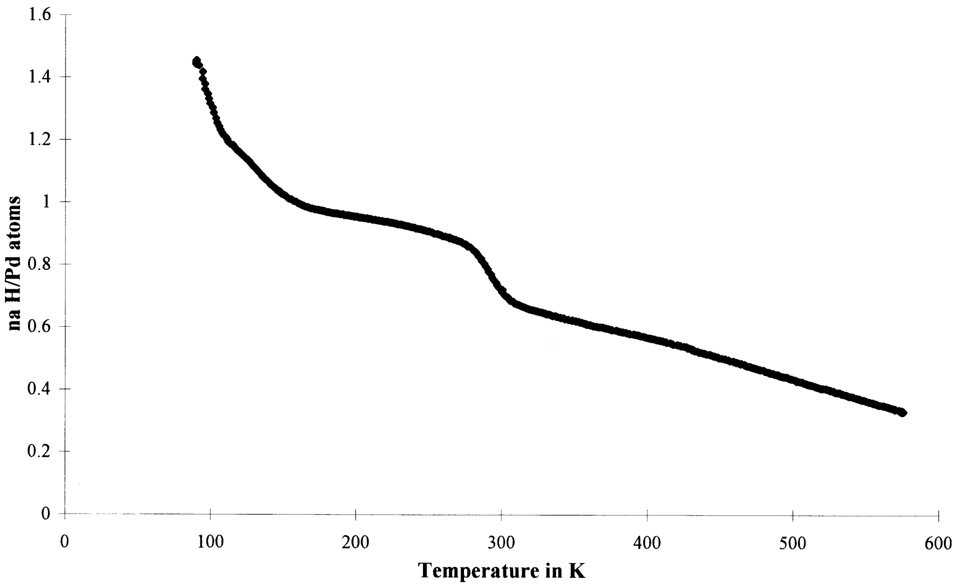

Figure 3. Typical isochore on 2.5 wt% Pd/SiO_2 with an increase rate of the temperature of 6 K min^{-1} where n_a/Pd atom is represented versus the temperature.

Figure 6 shows that the value of Q_{iso} decreases continuously from ~ 20 to 4 kcal mol^{-1} for a ratio H/metal smaller than 0.6. But for values larger than 0.6 the variation of Q_{iso} goes through a maximum corresponding to ~ 8 kcal mol^{-1} at a ratio H/metal atom of 0.8. Let us notice that these values of Q_{iso} correspond approximately to a pressure range of H_2 of 2–50 Torr and a temperature range of 250–300 K observed in the isochores. For a value of the ratio n_a/metal atom larger than 1, that of Q_{iso} decreases to ~ 3 kcal mol^{-1}.

Each value of Q_{iso} corresponds to a value of ΔS, the variation of which is represented in figure 7 versus n_a.

This diagram shows that the value of ΔS increases continuously from ~ −35 to −10 cal mol^{-1} K^{-1} for a ratio H/metal atom smaller than 0.6. For larger values of n_a/metal atom (0.8) ΔS goes through a minimum corresponding to ~ −25 cal mol^{-1} K^{-1}. For a value of the ratio n_a/metal atom larger than 1, that of ΔS increases to ~ −10 cal mol^{-1} K^{-1}.

All along the isochore, one can easily calculate the

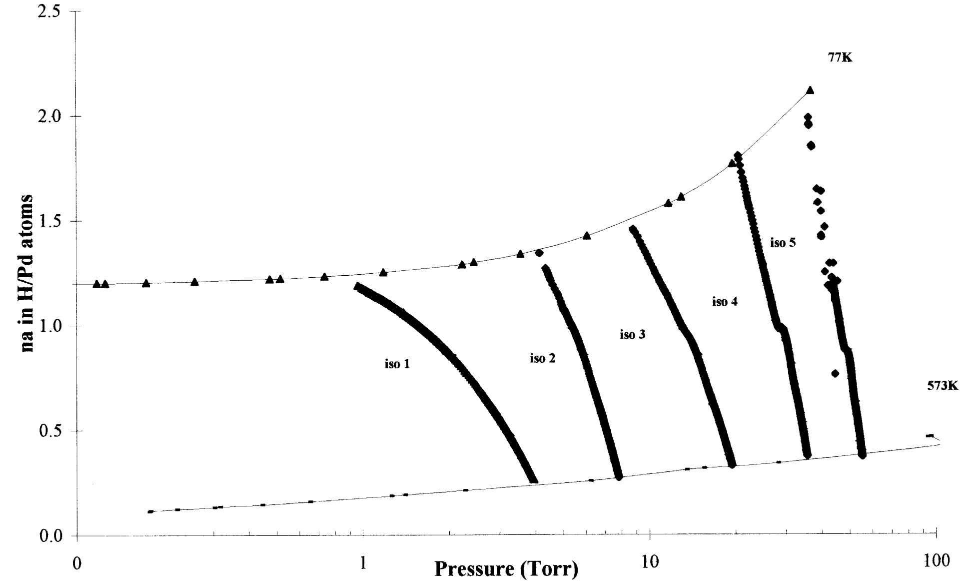

Figure 4. Isochores (iso 1–5), conducted for different amounts of hydrogen in contact with the catalyst for temperatures comprised between 573 and 77 K, and isotherms (77 K, 573 K).

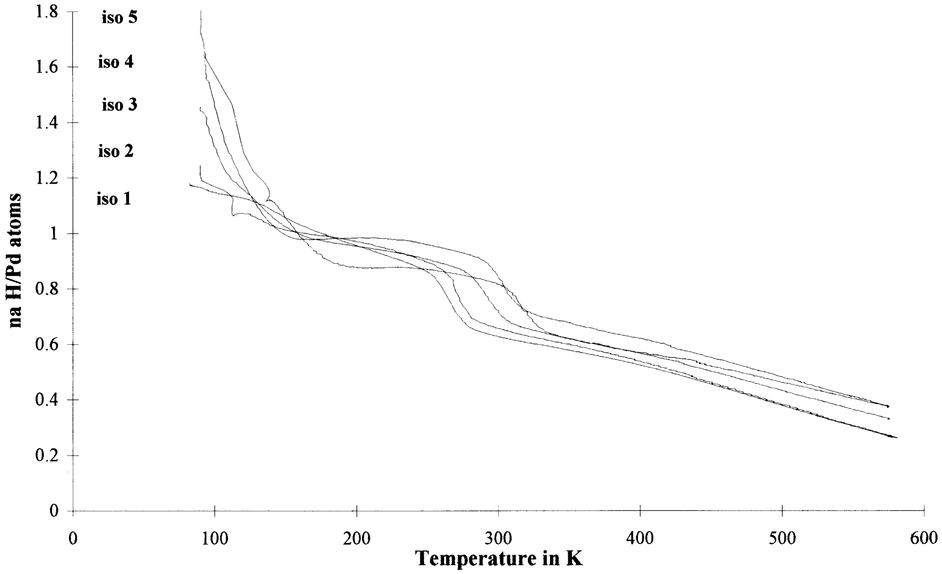

Figure 5. Same isochores as on figure 4 plotted as a function of T.

value of ΔG at each point since $\Delta G = RT \ln P$. These values of ΔG are represented as a function of n_a/metal atom on figure 8.

Figure 8 shows the variation of the different ΔG curves corresponding to each isochore versus the amount of hydrogen retained by the solid. Let us notice that ΔG must increase with the coverage for such experiments. Indeed, one can observe that ΔG continuously increases from small values of n_a/metal atom to values of that ratio larger than one. At the middle of the ΔG curves, a small plateau between n_a/metal atom values of 0.65 and 0.90 is observed. For values larger than 0.9, ΔG increases again and reaches the same equilibrium value (-1000 cal mol^{-1}) for each isochore at a value of n_a/metal atom $= 1.2$.

Boudart's titration has been performed on our catalyst according to the procedure presented in the literature [1,4] and gives a value of the dispersion close to 55%. In order to calculate the size of the particles from the dispersion, several authors [6,10,11] employ the following simple equation valid for a population of spheroidal or equiassic palladium particles:

$$D = 11.2/L,$$

where L is expressed in angstrom. Using this equation, an average particle size close to 20 Å is calculated.

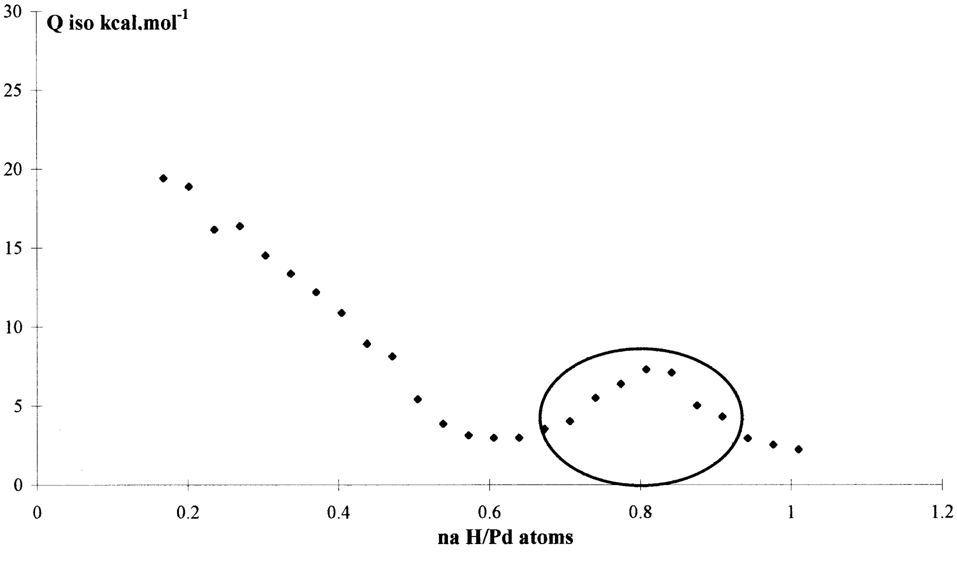

Figure 6. Variation of the isosteric heat of hydrogen adsorption versus H/Pd atoms (surf. + bulk).

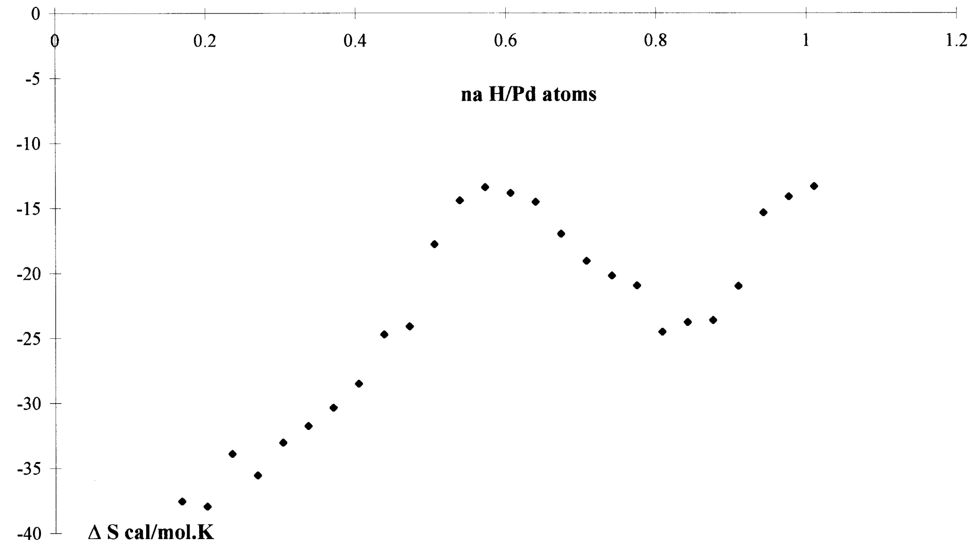

Figure 7. Variation of ΔS of hydrogen adsorption versus H/Pd atoms (surf. + bulk).

4. Discussion

Hubert and Frennet [8] have shown that the isochore method applied to the chemisorption of hydrogen as a probe molecule is a powerful tool to provide, through the isosteric heat of adsorption as a function of the coverage, the value of the active surface area and thus the dispersion of a supported metal.

The use of temperature-programmed variation makes it easy to cover a temperature range from 77 up to 673 K. This allows one to cover a range of θ of about 80% in one experiment and to obtain results in the monolayer content range.

It was concluded in that work that the variation of Q_{iso} with n_a could allow one to differentiate the adsorbed amount characteristic of the monolayer coverage on the metal surface from molecularly adsorbed hydrogen on the support. One has to expect on a supported palladium catalyst, besides these two types of hydrogen species present on a supported platinum catalyst, the presence of bulk hydride atoms (α and β phase), strongly adsorbed hydrogen atoms and weakly adsorbed hydrogen atoms, the latter allowing rapid exchange between the hydride and gas phase [12,13].

Our results show that the analysis of series of isochores measured on the Pd/SiO_2 supported catalyst allows the discrimination among these different hydrogen species retained by such a catalyst.

Indeed, one can observe in figure 6 that for values of the n_a/metal atom ratio greater than 1, the isosteric heat of adsorption remains constant at a value of $Q_{\text{iso}} \approx 3$ kcal mol^{-1}. The value of the entropy change (-10 cal mol^{-1} K^{-1}, figure 7) remains also constant and the value of ΔG is quite small (-1 kcal mol^{-1}, figure 8).

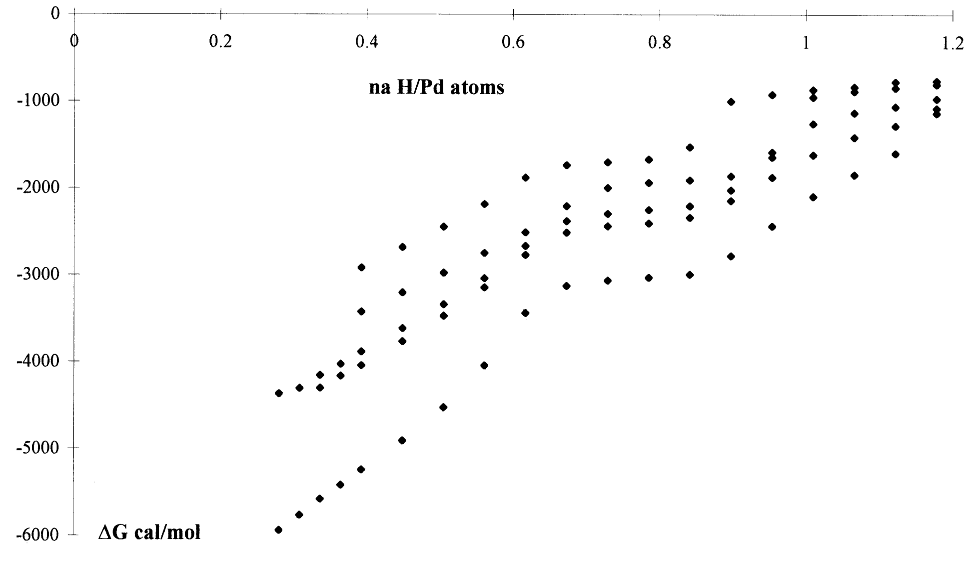

Figure 8. Variation of ΔG of hydrogen adsorption versus H/Pd atom (surf. + bulk).

The small value of ΔS can be interpreted in terms of a small loss of the degree of freedom due to the adsorption [15,16]. It is shown in the literature [8,14] that hydrogen molecularly adsorbs on silica with a value of $Q_{iso} \approx 3$ kcal mol^{-1}. This allows us to consider that in figure 6 the value of Q_{iso} for n_a/Pd atom ratios larger than 1 is characteristic of adsorption on the SiO_2.

The presence of this type of hydrogen could only be put in evidence owing to the opportunity given by the use of temperature-programmed variations allowing one to conduct measurements in the 77 to 150 K temperature range.

For values of adsorbed amounts n_a/metal atom around 0.8, values of Q_{iso} are at first sight surprisingly going through a maximum. Anyway in the range of the ratio n_a/metal atom extending from 0.65 to 0.95 the value of ΔG (figure 6) as a function of n_a/metal atom along an experimental isochore curve needs to exhibit a monotonic variation. In fact, this is the case as presented in figure 8 and is due to the compensating values of ΔS with n_a/metal (figure 7) exhibiting a symmetrical variation to that of Q_{iso} with n_a/metal. Moreover, let us notice that these values of ΔS look very consistent with the four proposed criteria in the works of Boudart et al. and Vannice et al. [15,16].

The calculated values of Q_{iso} around the maximum at n_a/metal atom = 0.8 are about 8 kcal mol^{-1}. The literature provides a value for the heat of formation of palladium hydrides close to 8 kcal mol^{-1}. Nevertheless, it must be taken into account that for small palladium particles it is very difficult to distinguish and separate bulk hydride from weak chemisorption as they are both rapid and reversible processes [12,13,17]. Moreover, the end of the shoulder in the isochore curves corresponds to a temperature of ~ 350 K, temperature at which the hydrides are decomposed for low hydrogen pressures [1,4,9,12,13]. Figure 5 shows that, in reality, all the isochores performed on this catalyst have the same shape and that the lower the hydrogen pressure, the lower the temperature of complete hydride decomposition is. This is characterized in this figure by a shift of the isochores, performed at low hydrogen pressure, to the left.

This diagram also reveals that all the isochores include a shoulder for the same value of the ratio n_a/metal atom (0.95–0.65) which corresponds to the width of the shoulder in the Q_{iso} diagram (figure 6) and the ΔS diagram (figure 7). Let us also notice that along this shoulder, the value of ΔG remains constant and begins to decrease for lower value of the ratio n_a/metal atom.

Moreover, Boudart's titration reveals a dispersion of our catalyst close to 55%. As mentioned in the literature [2,6,9], such a dispersed catalyst seems to be able to absorb ~ 0.3 H/Pd$_{tot}$ atom. Regarding to the width of the shoulder in the isochores (figures 2, 3 and 5), we can see that it corresponds approximately for each one to 0.3 H/Pd$_{tot}$ atom. Furthermore, the widths of the shoulders in the Q_{iso} and the ΔS diagrams are also of the same order.

All these results allow us to consider that these shoulders are qualitatively and quantitatively related to the hydride decomposition added to the weakly adsorbed hydrogen species.

One can see in figure 6 that a minimum in the Q_{iso} curve appears for a value of the ratio n_a/metal atoms = 0.6, which corresponds to a maximum in the ΔS curve (figure 7) and to an inflection point in the slope of the curve representing ΔG (figure 8) as a function of n_a/Pd$_{tot}$. This is to be compared with the isochore curves (figures 2, 3 and 5) which show that this value of the ratio n_a/Pd$_{tot}$ corresponds exactly to the end of the hydride decomposition and weakly adsorbed hydrogen elimination. Let us recall that Boudart's titration has given a value of the dispersion of 55%. The comparison between these two values, in addition to the fact that the minimum in the Q_{iso} curve appears when hydride are completely decomposed, suggests *one associate the value of the ratio n_a/Pd$_{tot}$ at the minimum in the Q_{iso} curve and at the maximum of the ΔS curve to the monolayer content*.

The part of the Q_{iso} curve, at values of the ratio n_a/Pd$_{tot}$ < 0.6, shows a continuous increase of the heat of hydrogen adsorption to which corresponds a continuous decrease of the value of ΔS (figure 7). That amount of hydrogen retained by the solid corresponds to the linear part in the isochore curves (figures 2, 3 and 5) for temperatures higher than 350 K. This behavior corresponds to the so-called variation of the isosteric heat of *adsorption* with coverage for neither hydride nor hydrogen molecularly adsorbed on the support remains at this temperature and for low hydrogen pressures.

Similar comparable studies have been made by Leon y Leon et al. [17], in which isobare formalisms have been treated. This interesting work shows that using this formalism, derived from isotherm measurements, it is possible to distinguish between "reversible" and "irreversible" hydrogen species. Nevertheless, these results have to be taken with care since figure 3 of their work presents the increase of the amount of "reversible" hydrogen species with increasing temperature. We cannot accept a scientific analysis related to the concept of distinguishing "reversible" and "irreversible" based on the difference between two isotherms. Indeed, it has been extensively shown that the amount of hydrogen evacuated after the first isotherm measurement strongly depends on the evacuating system used [8,18]. As shown in these papers, evacuation of hydrogen is controlled by the transport in the gas phase and thus conducted at quasi-equilibrium of adsorption–desorption. The amount of hydrogen evacuated (reversible) is thus a function of the ratio of the pumping speed at the catalyst level and the total amount of adsorbed hydrogen (size of catalyst sample). Considering our experience and the work of these authors, the only curve representing the total hydrogen includes valuable information. Yet, it is in good agreement with the one presented in figure 3 of our article. Finally, let us stress the fact that in their work, the authors needed to perform series of isotherms to be able to calculate the corresponding isobars. Everyone knows the time needed to measure isotherms added to the fact that it is very difficult to use a thermostatic bath in the temperature range lower than room temperature. We believe that the isochore measurements are a useful tool for such studies.

As a conclusion, the isosteric analysis of only a few isochore adsorption measurements of hydrogen conducted on Pd/SiO_2 catalyst, using temperature-programmed variations between 77 and 623 K, provides values of the thermodynamic potentials (Q_{iso} and ΔS) characteristic of that adsorption and their variations with the adsorbed amount.

The values of these thermodynamic potentials and the shape of their variations allow to differentiate qualitatively and quantitatively the different hydrogen species present in/on the catalyst:

– molecularly adsorbed hydrogen on the support,

– absorbed hydrogen species (hydrides) associated with the eventual weakly chemisorbed hydrogen,

– strongly chemisorbed hydrogen species at the metal surface.

Furthermore, the association of shoulders in the isochore curves with the variations of the thermodynamic potentials with n_a/metal atom show that the amounts of these different species of hydrogen on the catalyst can be evaluated from one single isochore and thus allow the determination of the dispersion of the catalyst.

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References

[1] M. Boudart and H.S. Hwang, J. Catal. 39 (1975) 44.
[2] Pen Chou and M.A. Vannice, J. Catal. 104 (1987) 1.
[3] W. Juszczyk and Z. Karpinski, J. Catal. 117 (1989) 519.
[4] J.E. Benson, H.S. Hwang and M.Boudart, J. Catal 30 (1973) 146.
[5] A.L. Cabrera, E. Morales-Leal, J. Hasen and I.K. Schuller, Catal. Lett. 30 (1995) 11.
[6] G. Fagherazzi, A. Benedetti, S. Polizzi, A. Di Mario, F. Pinna, M. Signoretto and N. Pernicone, Catal. Lett. 32 (1995) 293.
[7] R.F. Hicks and A.T. Bell, J. Catal. 90 (1984) 205.
[8] C. Hubert and A. Frennet, Catal. Today 17 (1993) 469.
[9] Z. Zhang, L. Xu and W.M.H. Sachtler, J. Catal. 131 (1991) 502.
[10] A.L. Bonivardi and M.A. Baltnanas, J. Catal. 138 (1992) 500.
[11] P. Nadi, P. Georgopoulos, J.B. Cohen, J.B. Butt and R. Bruwell, J. Catal. 77 (1982) 421.
[12] T.-C. Sheng and I.D. Gay, J. Catal. 77 (1982) 53.
[13] A.A. Chen, A.J. Benesi and M.A. Vannice, J. Catal. 119 (1989) 14.
[14] M.-N. Zauen, A. Crucq, L. Degols, G. Lienard, A. Frennet, N. Mikhalenko and P. Grange, Catal. Today 5 (1989) 237.
[15] M. Boudart, D.E. Mears and M.A. Vannice, Ind. Chim. Belge 32 (1967) 281.
[16] M.A. Vannice, S.H. Hyun, B. Kalpakci and W.C. Liauh, J. Catal. 56 (1979) 358.
[17] C.A. Leon y Leon and M.A. Vannice, Appl. Catal. 69 (1991) 269.
[18] A. Crucq, L. Degols, G. Lienard and A. Frennet, Acta Chim. Acad. Sci. Hung. 111 (1982) 547.