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Dispersion Measurement by the Single Introduction Method Coupled with the Back-Sorption Procedure: A Chemisorption and TPD Study of the Different Chemisorbed Hydrogen Species

I. Pt, Ru, and Rh on Alumina

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In this work a comparison is made between values of the metal surface areas of several alumina-supported Ru, Rh, and Pt catalysts obtained by hydrogen adsorption isotherms, here defined as the "Multiple Introductions" method, and those calculated by a very simple technique defined as the "Single Introduction" method. With the systematic application of the procedure designated "Back-Sorption," particularly good agreement is observed between the two techniques if dispersion is calculated on the basis of the irreversibly adsorbed hydrogen. "Back-Sorption" is a necessary practice because of the presence on the above-mentioned metals of more than one adsorbed species not to be considered for the calculation of dispersion, as shown in a more detailed manner for a Pt/Al_2O_3 catalyst using temperature-programmed desorption. Whenever the conditions for its applicability are satisfied, the Single Introduction method provides a faster and more reliable way to measure the dispersion of metal-supported catalysts than the Multiple Introductions technique.

INTRODUCTION

One of the main drawbacks in measurements of dispersion ($D_M = n_S^M/n_T^M$, where n_S^M and n_T^M are the numbers of surface metal atoms and of total metal atoms, respectively) by chemisorption is the long time needed to record the adsorption isotherm. This is usually obtained by means of the method which we will call the *Multiple Introductions* method (M.I.), consisting in exposing the solid adsorbent surface to a series of gas doses while measuring the gas uptakes at increasing equilibrium pressures. Moreover, for all the chemisorption instruments of volumetric type, usually operating under static vacuum conditions, long analysis times increase the danger of sample poisoning due to the unavoidable leakage of atmospheric gases into the system.

Among the various possible adsorbates, hydrogen is the most widely used for Group VIII transition metals, mainly because this molecule is the principal species effectively involved in many industrial catalytic reactions and also because hydrogen adsorption on all of the above-mentioned metals seems to be quite similar with respect both to the rather well-defined adsorption stoichiometry (1–3) and to the number and the properties of the principal surface species (4, 5). This allows a *consistent* measurement of D_M among different supported metals, which cannot be accomplished using CO or O_2, whose chemisorption features are strongly dependent on the nature of the substrate metal (1–3). In fact, D_M values referring to different metals can be consistently compared only if the same criterion is used to "count" the surface metal atoms; i.e., when the same "yardstick size" (6) is employed to measure n_S^M. Nevertheless, on polycrystalline surfaces and, in particular, on supported catalysts, hydrogen can adsorb in several different ways (see the discussion for supported Pt catalysts in Ref. (7a)). The population of the various surface species greatly depends on the structure of the crystallites of an individual catalyst (in particular, for Ru/NaY-zeolites, see Ref. (8)), this latter being connected with the particular details of the catalyst preparation and the kind of support used. Aiming at discriminating between the strongly chemisorbed species (H_S), irreversibly adsorbed on the metal (see the Experimental section), which are thought to have a well-defined adsorption stoichiometry by analogy with the corresponding species observed on monocrystals, and the weakly bound species (H_W), reversibly adsorbed on the metal, with variable stoichiometry and in excess of the monolayer (1, 3, 9), it is suitable to apply the so-called *Back-Sorption* procedure (B.S.), originally developed for palladium-based systems (10). Back-Sorption, which in our opinion is necessary for all Group VIII metals, requires, however, analysis

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times approximately twice as long as those needed for a single M.I. adsorption measurement. For this reason, we started to study a different method able to give an estimate of dispersion in shorter times. The latter, here defined as the *Single Introduction* method (S.I.), consists in contacting the solid with a single gas dose followed by reading a single equilibrium pressure. From the difference between initial and equilibrium pressures it is possible to calculate directly the adsorbed amount, and thus the metal dispersion. The ratio of gas to sample is such that a complete saturation of the strongly held monolayer is achieved at a suitable equilibrium pressure, on the basis of the (supposed) adsorption stoichiometry for H_S. The S.I. method is always coupled with B.S., the execution of which has been particularly optimized for a 3% Pt/Al_2O_3 catalyst by means of Temperature Programmed Desorption (TPD).

It should be noted that the study of weakly bound species on supported Group VIII metal catalysts is important not only for a correct measurement of dispersion but also for reasons concerning catalysis. In fact, the catalytic activity of the different adsorbed species not only is a function of thermodynamic quantities such as $\Delta H_a/RT_r$ (3) (where ΔH_a is the adsorption enthalpy change, expressing the energy of the chemisorption bond (11), and T_r is the reaction temperature), so that all of the surface phases are equally active at suitable different temperatures (3), but also is strongly dependent on the geometric properties of the adsorption sites (12). Following the idea that "strong" and "weak" hydrogen are coordinated on structurally different surface sites (8, 9, 13, 14), it seems plausible to expect different reactivities depending on the abundance of the various adsorbed species. As an example we recall one of the first (and few) applications of the latter concept to the study of the role of "weak" hydrogen in benzene hydrogenation on Pt/Al_2O_3 catalysts, due to Aben et al. (15).

This work is divided into two parts, the study of Pd (reported in the succeeding paper) being separated from that of Pt, Ru, and Rh on the basis of the particular characteristics of the H_2–Pd system and the known difficulties found in the measurement of palladium surface properties by means of hydrogen chemisorption.

EXPERIMENTAL

(*i*) *Materials*

All catalysts studied, listed in Table 1A, are commercial products. Their metal loading, BET (N_2) surface area, mean grain/pellet size, and chlorine content are listed in Table 1B. All of these data refer to the catalysts pretreated under the same conditions used before chemisorption. In particular, in Table 1B the reduction temperature is reported.

TABLE 1A

Catalysts Studied: Specifications

Catalyst symbol	Metal/support system	Producer	Code number
A	Pt/Al_2O_3	Engelhard	T/CH 4047 NO. 3049
B	Pt/Al_2O_3	Engelhard	T/CH 4048 NO. 3050
C	Pt/Al_2O_3	Engelhard	ESCAT 24
D	Pt/SiO_2	Johnson–Matthey	EUROPT-1
E	Rh/Al_2O_3	Janssen	20617-2
F	Rh/Al_2O_3	Fluka	CH-9470 N291642
G	Ru/Al_2O_3	Aldrich	20619-9
H	Ru/Al_2O_3	Engelhard	ESCAT 44

We chose to study catalysts with decreasing metal loadings to evaluate the sensitivity of the S.I. method. For all reduction treatments and all chemisorption experiments we used hydrogen of research grade with purity >99.995%. For instrument calibration and dead space measurement we used helium of research grade with purity >99.995%. All gases were used without further purification. For all chemisorptions preceding the thermal desorption experiments, we used hydrogen of transistor grade with purity >99.9995%, dehydrated with a Supelco High Capacity Gas Purifier to obtain adequate and reproducible vacuum levels (base pressure $= 10^{-8}$ Torr, 1 Torr = 133.3 Pa).

TABLE 1B

Catalysts Studied: Physical Characterization, Chlorine Content Analysis, and Reduction Conditions

Catalyst symbol	Metal wt (%)	N_2 BET Surface Area ($m^2 \cdot g_{cat}^{-1}$)	Mean grain size (μm)	Chlorine $10^{-2} \cdot wt\%^a$	Reduction temp. (K)
A	1	79	90	2	663
B	3	77	90	2	613
C	5	125	65	2	623
D[b]	6.3	185	375[c]	0.008	673
E	0.5	96	1/8[d]	6	663
F	5	152	60	55	663
G	0.5	85	1/8[d]	7	663
H	5	125	65	8	570

[a] These data were obtained by ion chromatography.

[b] All data reported in Ref. (27d).

[c] Arithmetic mean of the 60 wt% grain size range (27d).

[d] These data expressed in inches (1 in. = 2.54×10^4 μm), the catalyst particles being pelletized.

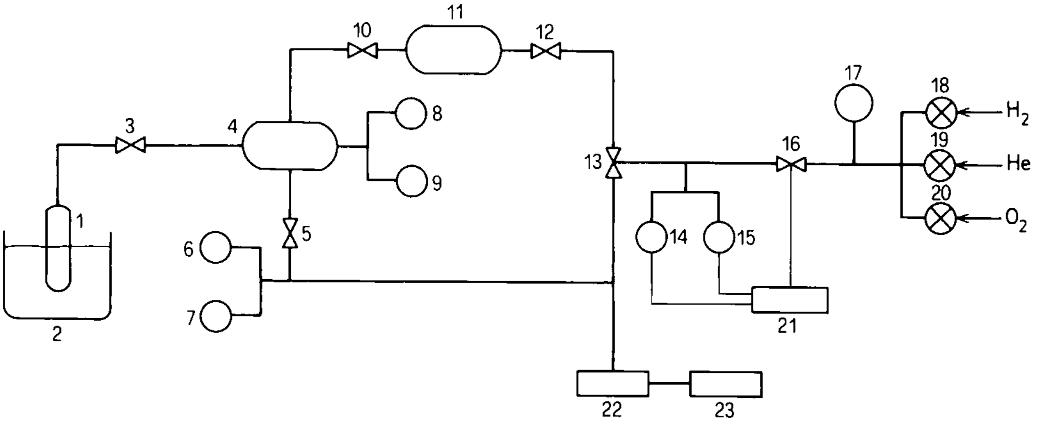

FIG. 1. Chemisorption apparatus. (1) sample holder; (2) thermal bath; (3, 5, 10, 12, 13, 16) Honeywell Lucifer high-vacuum electromagnetic valves; (4) manifold; (6) Pirani gauge; (7) Penning gauge; (8, 9, 14, 15) MKS Baratron capacitive manometers; (11) sampling chamber; (17) Bell & Howell resistive manometer; (18, 19, 20) Whitey stopcocks; (21) MKS 250/B pressure/flow controller; (22) Elettrorava 80 liter/s turbomolecular pump; (23) Edwards 5 m^3/h rotary pump.

(*ii*) *Instrumentation*

Chemisorption. The chemisorption experiments were performed in a static vacuum volumetric apparatus (base pressure = 10^{-6} Torr) with stainless steel tubing and all-metal greaseless valves. Adsorption isotherms were recorded in a completely automated way for better repeatability; in particular, gas sampling was performed by a micrometric solenoid valve driven by a pressure/flow controller MKS Baratron 250/B which allowed pressure settings to be made with a precision of ±0.01 Torr in a sampling chamber of about 20 cm^3. The pressure in the sample holder was read with two MKS Baratron capacitive heads operating in the ranges 0–100 and 0–1000 Torr with an accuracy of 0.01 and 0.1 Torr, respectively. Both the transducers were connected to a personal computer through a 16 bit analog-to-digital converter which allowed the recording of pressures with time at the speed of one reading per second. The acquisition of pressure data in real time was of great importance for reliable evaluations of the chemisorption rate at the very beginning of the gettering process. The actual amounts of gas collected were recorded with a digital printer interfaced with the capacitive heads. Figure 1 shows a simplified scheme of the instrument.

Thermal desorption. Thermal desorption analyses were performed in a high vacuum stainless steel apparatus provided with a particular system for gas introduction and equipped with a Carlo Erba Strumentazione QTMD quadrupole mass spectrometer. Figure 2 shows the scheme of the instrument. The temperature programmed heating of the samples was performed in an oven coated with a Dewar flask to obtain temperature profiles perfectly linear in time in the range 120–820K (maximum deviation between actual and set-up temperatures ±1 K). The sample cooling at the lowest temperatures was performed by an adjustable stream of nitrogen circulating in a bath of liquid nitrogen. A similar device was set up by Konvalinka and Scholten (16).

(*iii*) *Methods*

Preparation and treatment of samples. The main purpose of this work was not the determination of *absolute* values of specific surface areas, so we do not discuss all the fundamental problems to be dealt with for that end; e.g., the accurate evaluation of the stoichiometric factors (*SF* = number of surface metal atoms/number of adsorbed gas molecules, when all of the surface metal atoms are occupied), the estimate of the amount of *residual hydrogen* (H_R) present on the catalyst after the reduction/evacuation pretreatments (17), the degree of metal sintering after this latter cleaning procedure, the careful check of metal loadings by atomic absorption spectroscopy, etc. Nevertheless, in order to estimate the reproducibility of results on different portions of a given catalyst sample, we carried out the weighing of all samples after evacuation at 10^{-3} Torr at a temperature of 393 K for 1 h. This procedure enabled the elimination of nonstructural water, adsorbed on the support (Al_2O_3) and always present to the extent of about 3–5% (18). The dried catalysts were reduced (heating rate 5–10 K/min) in flowing hydrogen (60 N $cm^3 \cdot s^{-1} \cdot g_M^{-1}$, where g_M is the metal weight) at the temperatures listed in Table 1 for 3 h and then evacuated in high vacuum ($p \cong 10^{-6}$ Torr) at the reduction temperature for 16 h.

Hydrogen chemisorption. All chemisorption measurements were carried out at 305 K. At this temperature, the time needed to reach the equilibrium conditions with

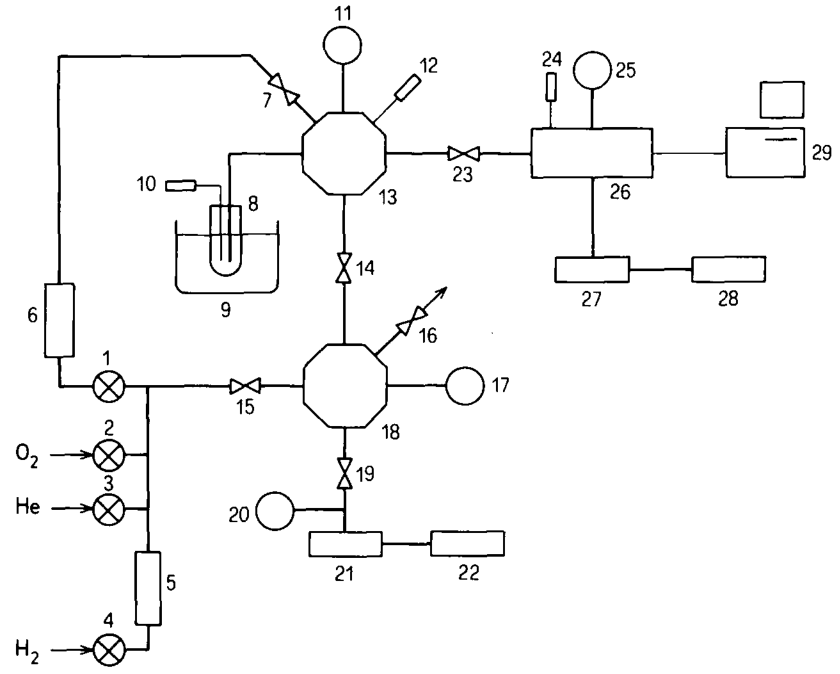

FIG. 2. Thermal desorption apparatus. (1, 2, 3, 4) Whitey stopcocks; (5) Supelco dryer; (6) flowmeter; (7) VAT 59 micrometric valve; (8) sample holder; (9) thermal bath; (10, 12, 24) thermocouples; (11) Datametrics capacitive manometer; (13) analysis chamber; (14) Nupro micrometric valve; (15, 23) Rial micrometric valve; (16) Whitey outlet valve; (17) MKS Baratron capacitive manometer; (18) sampling chamber; (19) Gambetti valve; (20) Granville-Phillips hot cathode gauge; (21, 27) Elettrorava 80 liter/s turbomolecular pumps; (22, 28) Edwards 8 m^3/h rotary pumps; (25) Penning gauge; (26) mass spectrometer; (29) personal computer.

the gas phase was found to be 30 min for samples A–F and 3 h for samples G and H. These times, determined the S.I. runs, were used before each pressure reading in M.I. isotherms.

Back-sorption. The Back-Sorption technique, in practice, consists in the execution of the sequence

$$\text{adsorption}(T_a) \rightarrow \text{pumping}(T_a, t_{bs}, p_{bs}) \rightarrow \text{adsorption}(T_a), \quad [1]$$

where p_{bs} is the pressure just over the sample during B.S. (to be maintained with a suitable pumping speed, v_p) and T_a is the adsorption temperature, usually (but not necessarily) coincident with the temperature used for the intermediate sample evacuation. For a given p_{bs} (i.e., v_p) value, the amount of desorbing hydrogen (n^{H}_{REV}) depends solely on the duration of pumping (t_{bs}). For reasons discussed in the next section, the desorption of reversibly chemisorbed hydrogen was carried out by pumping all of the catalysts for t_{bs} = 30 min at a pressure $p_{bs} \cong 10^{-6}$ Torr.

Thermal desorption. The typical experimental sequence of a thermal desorption experiment is schematized in Fig. 3. *Weighing, reduction,* and *outgassing* of the samples were performed as previously described. Hydrogen chemisorptions preceding the TPD experiments were made on 0.2 to 0.3 g of catalyst by the S.I. method: weakly bound species could be studied by sampling as much gas as was needed to produce an equilibrium pressure (p_{eq} in Fig. 3) comprised in the range defined by the plateau of the adsorption isotherm (see Figs. 4a and 4c). This ensured that the strong chemisorption was complete and the weakly chemisorbed phase was present on the surface. When it was desired to observe all of the surface species,

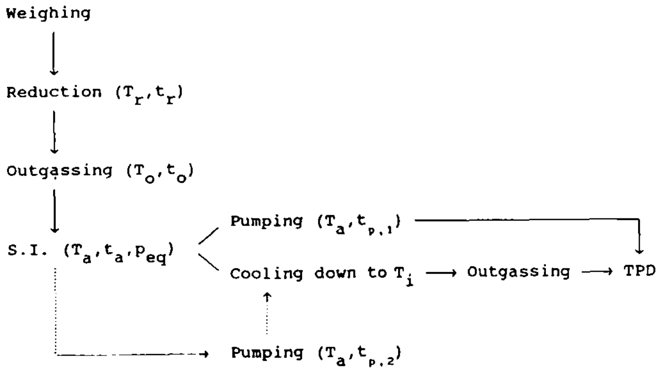

FIG. 3. Experimental sequence preceding a TPD measurement. T = temperature; t = time; r = reduction, o = outgassing, a = adsorption, p = pumping. T_i = initial temperature (i.e., TPD can be started either at the adsorption temperature, T_a, or at T_i). $t_{p,1}$ and $t_{p,2}$ are generally different (see text). p_{eq} is the hydrogen equilibrium pressure.

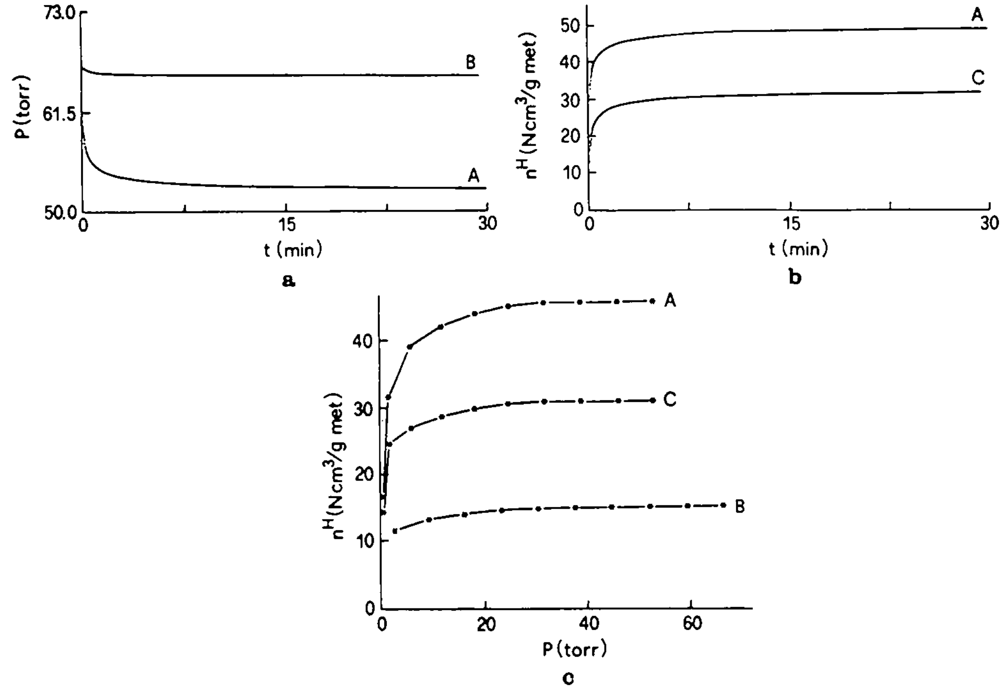

FIG. 4. Typical S.I. curves ((a) pressure vs time and (b) adsorbed amount vs time) compared with M.I. curves ((c) adsorbed amount vs equilibrium pressure) for catalyst F at 305 K. Labels A and B refer to adsorption on clean catalyst (which gives n^H_T) and to back-sorption after the intermediate pumping (which gives n^H_{REV}), respectively, Labels C specify n^H_{IRR} curves.

including the very loosely bound ones, we increased the residence time of the adatoms (19) by cooling the sample to a suitably low temperature (e.g. $T_i \cong$ 120 K in Fig. 3). Otherwise, the gas phase and the low-energy surface species were eliminated by pumping the reactor at $p \cong 10^{-3}$ Torr for short times ($t_{p,2} \cong$ 1 min). Longer pumping times ($t_{p,1} \cong$ 1 h) allowed weak hydrogen to desorb, too, as shown in the following. All the thermodesorption profiles reported in this work were obtained using a heating rate of 5 K/min to increase peak resolution (20a). Readsorption was thus made negligible by using a high pumping speed (mean lifetime of a molecule in the chamber $\tau = v_p/V \cong$ 0.6 s, where v_p is the pumping speed and V is the chamber volume) (21, 22). Furthermore, intraparticle diffusion was verified not to be limiting using very finely powdered catalysts (mean particle diameter ≅400 mesh) (21, 22).

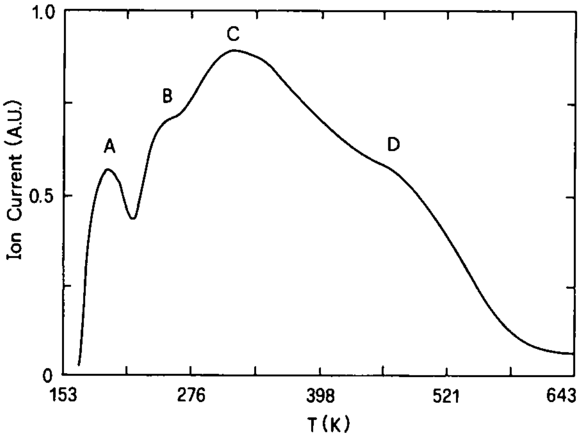

FIG. 5. Thermal desorption of H_2 from catalyst B after adsorption at 305 K. Initial pressure was 15.5 Torr and final equilibrium pressure was 13.5 Torr. Peaks A and B come from mobile hydrogen while peaks C and D are related to weakly and strongly chemisorbed hydrogen, respectively.

RESULTS AND DISCUSSION

Thermal Desorption

In Fig. 5 a TPD profile obtained after the adsorption on catalyst B of an amount of hydrogen exceeding the monolayer volume is shown. Cooling the sample to 120 K made it possible to stabilize two very loosely bound species that give rise to peaks A and B, with maxima at the temperatures, T_M, of 195 K and 252 K, respectively. The broad peak C, with T_M = 315 K, is attributed to weakly chemisorbed hydrogen while peak D, with T_M = 465 K, is assigned to strongly chemisorbed hydrogen.

All the different TPD analyses were performed up to about 643 K, no H_2 desorption from pure Pt black samples having been detected in the temperature range 643–873 K.

Using Eq. [2] for the rate of desorption,

$$r_{\mathrm{d}} = -(d\theta/dt) = k_{\mathrm{d}} \cdot \theta^2 \cdot \exp[-E_{\mathrm{d}}(\theta)/RT], \qquad [2]$$

where θ is the coverage, a very rough estimate of E_{d} for peaks A and B can be made by means of both a semiempirical correlation due to Knor (11), Eq. [3], and an equation given by Smutek (20b) for the case of a homogeneous surface with no readsorption, Eq. [4]; $E_{\mathrm{O}}(x_{\mathrm{M}}) = \exp(x_{\mathrm{M}})/x_{\mathrm{M}}$, $x_{\mathrm{M}} = E_{\mathrm{d}}/(RT_{\mathrm{M}})$, a_{M}, and θ_{M} are the heating rate and the coverage at the peak maximum, respectively, and n is the desorption order:

$$E_{\mathrm{d}}(\mathrm{kJ/mol}) \cong 0.23\, T_{\mathrm{M}}(\mathrm{K}) \qquad [3]$$

$$(1/n) \cdot \theta_{\mathrm{M}}^{(n-1)} = (k_{\mathrm{d}} \cdot T_{\mathrm{M}} \cdot a_{\mathrm{M}}^{-1}) \cdot E_{\mathrm{O}}(x_{\mathrm{M}}). \qquad [4]$$

A straightforward calculation with Eq. [3] gives $E_{\mathrm{d}}(\mathrm{A}) \cong$ 10.7 kcal/mol (1 Kcal = 4.184 kJ) and $E_{\mathrm{d}}(\mathrm{B}) \cong$ 13.8 kcal/mol while with Eq. [4], assuming $k_{\mathrm{d}} = 10^{13}$ s^{-1} (a very common assumption; see Ref. (20a) and references cited therein), $n = 2$ and $a_{\mathrm{M}} = 5$ K/min, we obtain $E_{\mathrm{d}}(\mathrm{A}) \cong$ 13.7 kcal/mol and $E_{\mathrm{d}}(\mathrm{B}) \cong$ 17.9 kcal/mol. Despite their large approximation (due to the very simplified forms of Eqs. [3] and [4]), these values demonstrate that peaks A and B cannot be produced by desorption of molecules physisorbed on the metal crystallites, as also expected from more qualitative considerations (23). Moreover, from a deeper study on the nature of these species (24), it results that these kinds of hydrogen ($\mathrm{H_M}$) are adsorbed on the metal surface as nonlocalized atoms, free to diffuse over the first chemisorbed layer. For these reasons, they should not be considered in the calculation of D_{M}.

The assignment of peak C to desorption of $\mathrm{H_W}$ is consistent with the disappearance of this feature when the gas phase is eliminated by pumping catalyst B in high vacuum and also with the agreement of the ratio of the peak areas, i.e. $A_{\mathrm{W}}/(A_{\mathrm{W}} + A_{\mathrm{S}})$, giving the relative amount of gas desorbed (20a), with the B.S. results. The values of 17.3 kcal/mol and 22.5 kcal/mol for $E_{\mathrm{d}}(\mathrm{C})$ are readily calculated, using $k_{\mathrm{d}} = 10^{13}\mathrm{s}^{-1}$, $n = 2$, and $a_{\mathrm{M}} = 5$ K/min, with Eqs. [3] and [4], respectively. The highest calculated E_{d} value is of the expected magnitude for a surface species which is reversible at $T \cong 300$ K (25a).

Peak D is very similar to others obtained on both monocrystalline platinum (for example on Pt(111), Ref. (26), where $T_{\mathrm{M}}(\mathrm{H_S}) = 470$ K) and supported platinum (in particular, peak C in curve 2 of Fig. 5, Ref. (27a)). This peak could be obtained alone, without peaks A–C, either by pumping the catalyst in vacuum, as shown in Fig. 6, or by adsorbing a suitable amount of hydrogen, as shown in Fig. 7. The isolation of this peak allowed the application of the method proposed by Tokoro *et al.* (28) to calculate both k_{d} and E_{d}, for the case of heterogeneous surface with nonlinear variation of the desorption energy and constant frequency factor with the coverage. The values of 1–5 · 10^{13} s^{-1} for k_{d} and of 22–36 kcal/mole for E_{d}, when θ varies from 1 to 0, were obtained, in good agreement with others already reported in the literature (5, 29–33). In Fig. 8 a typical profile $E_{\mathrm{d}} = E_{\mathrm{d}}(\theta)$, calculated with the model of Tokoro *et al.*, is shown.

The effect of pumping on the populations of surface species was studied for increasing t_{bs}, as shown in Fig. 6. As Yang and Goodwin correctly point out (in a study of weakly bound hydrogen species on Y-zeolite-supported Ru (34)), all the adsorbed species can be desorbed at a given temperature in a sufficiently long time but, in practice, the rate of desorption becomes negligible after about 14 h, when no further variation of the TPD peak area can be observed (Fig. 6b).

Back-sorption

For the calculation of D_{M}, knowledge of $n_{\mathrm{S}}^{\mathrm{M}}$ and $n_{\mathrm{T}}^{\mathrm{M}}$ is needed. $n_{\mathrm{T}}^{\mathrm{M}} = W_{\mathrm{C}} \cdot f_{\mathrm{M}}$, where W_{C} is the weight of the catalyst sample and f_{M} is the metal fraction, is correctly evaluated provided that both W_{C} and f_{M} are measured following the same pretreatment procedure (i.e., drying at the same temperature, for the same time, in flowing nitrogen or under vacuum, etc.). $n_{\mathrm{S}}^{\mathrm{M}}$ is usually obtained from the relation $n_{\mathrm{S}}^{\mathrm{M}} = SF_{\mathrm{m}} \cdot V_{\mathrm{m}}$, where the subscript "m" refers to monolayer quantities. The main problem when dealing with dispersion measurements is the definition of the *monolayer uptake*, V_{m}, the amount of adsorbed hydrogen needed to "count" all the *surface metal atoms*. The notion of surface metal atom is in turn connected with the less ambiguous notion of atom *coordination number*, Z (12, 35). In fact, if Z_{b} is the coordination number of an atom in the crystallite bulk (e.g., $Z_{\mathrm{b}} = 12$ for f.c.c. metals), a surface atom can be formally defined as an atom which (i) has $Z < Z_{\mathrm{b}}$ and (ii) is accessible to the given probe molecule (condition (i) is fulfilled also by *bulk* atoms located near defects in the *bulk* of the crystal lattice; this is the reason why also condition (ii) is needed to unambiguously define a surface metal atom). Two definitions for V_{m} are commonly found in the literature, (i) $V_{\mathrm{m}} = n_{\mathrm{T}}^{\mathrm{H}}(T, P)$ and (ii) $V_{\mathrm{m}} = n_{\mathrm{IRR}}^{\mathrm{H}}(T, P, \{\mathrm{B.S.}\})$, where $n_{\mathrm{T}}^{\mathrm{H}}$ is the total hydrogen uptake at the temperature and pressure of adsorption and $n_{\mathrm{IRR}}^{\mathrm{H}}$ is the irreversible hydrogen uptake, defined by giving also the B.S. conditions ({B.S.}) used to eliminate the reversibly adsorbed fraction, $n_{\mathrm{REV}}^{\mathrm{H}}$. The main purpose of the B.S. procedure is thus the elimination from the catalyst surface of all species not belonging to definition (ii) of the adsorbed monolayer. The choice between total and irreversible uptakes depends on the availability of the corresponding stoichiometric factors, SF_{T} and SF_{IRR}, respectively, which should be accurately known for *absolute* D_{M} evaluations, and quite independent of the particular preparation of any specific catalyst for *relative* D_{M} measurements. In other words, this latter

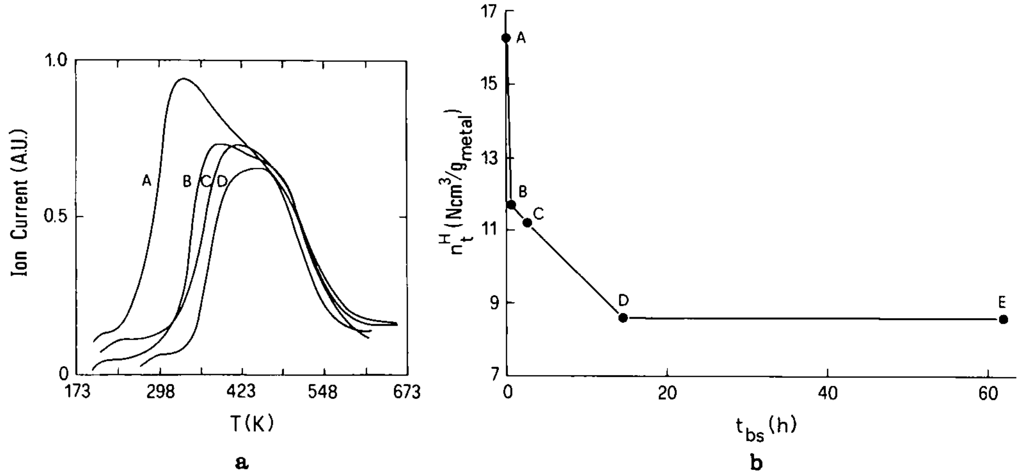

FIG. 6. (a) Thermal desorption of H_2 from catalyst B after adsorption at 305 K and successive evacuation of the sample at 10^{-6} Torr for $t_{p,1}$ = 3 min, A, 30 min, B, 60 min, C, and 14 h 30 min, D. (b) Irreversibly adsorbed hydrogen vs t_{bs} as obtained from Fig. 6(a). Initial pressure was 15.5 Torr and final equilibrium pressure was 13.5 Torr in all three cases.

condition guarantees the *consistency* of measurements among different catalysts (this should at least hold when all of the catalysts have a mean crystallite diameter higher than the critical value of 1 nm (2)).

At present, it seems that at least two kinds of chemisorbed hydrogen are nearly always found on supported Group VIII transition metals, namely H_W and H_S (4, 8, 36–39). These species, identified in the present context by means of the corresponding thermodesorption peaks, differ both in the surface bond energy and in the geometry of the adsorption site on which they are located (see, for example, Ref. (7a)). Hydrogen strongly chemisorbed on polycrystalline surfaces, H_S, has the same properties of the corresponding species found on metal monocrystals, for which both structural and energetic information are available (11, 25b), while weakly chemisorbed hydrogen, H_W, is often found only on heterogeneous systems and, despite its variable adsorption stoichiometry, SF_W, it seems to be held on the metal surface "in excess of the monolayer" (3). For these and other reasons discussed later, we feel that definition (ii) for V_m is the correct one so that D_M measurements by (at least hydrogen) chemisorption should be done by the B.S. procedure. In correlating the many mentioned surface species, the following mass balances are useful,

$$n_T^H = n_{REV}^H + n_{IRR}^H \qquad [5]$$

$$n_{REV}^H = n_M^H + n_W^H + n_{SS}^H + n_H^H + n_D^H + n_F^H + n_{REV,m}^H \qquad [6]$$

$$n_{IRR}^H = n_S^H + n_R^H + n_{SP}^H \qquad [7]$$

$$V_m = n_S^H + n_R^H + n_{REV,m}^H, \qquad [8]$$

where $n_S^H, n_M^H, n_{SS}^H, n_H^H, n_D^H, n_F^H, n_{SP}^H$ and n_R^H are, respectively, strongly chemisorbed, mobile (as observed on Rh/SiO_2 catalysts (40)), subsurface (7b), hydridic (7c), bulk dissolved (41), physisorbed, spilled over (7d), and residual (17) hydrogen uptakes. $n_{REV,m}^H$ is a fraction of adsorbed hydrogen which is reversible under the conditions of B.S. but has to be considered as a less strongly bound H_S species so that it should be included in the computation of the monolayer.

None of the metals studied in this work form solutions with either hydrogen nor hydrides in appreciable amounts (i.e., $n_D^H \cong 0$ and $n_H^H \cong 0$, respectively (41)). We also verified that the supports do not adsorb hydrogen in measurable amounts, so that $n_F^H \cong 0$. It is important to check for the presence of H_{SS} because this species is thought to

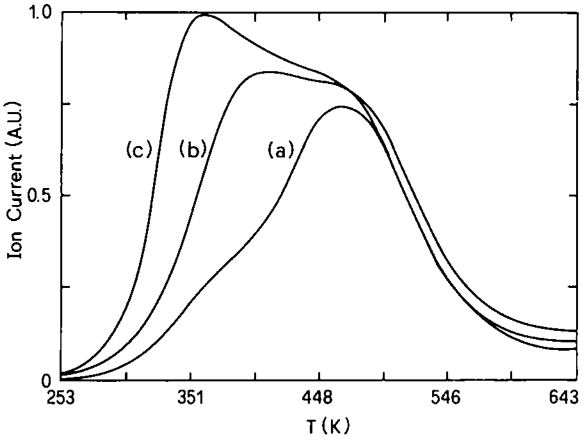

FIG. 7. Thermal desorption of H_2 from catalyst B after adsorption at 305 K of 7 N cm^3/g$_{metal}$ (a), 8 N cm^3/g$_{metal}$ (b), and 11.3 N cm^3/g$_{metal}$ (c). Final equilibrium pressure was lower than 10^{-3} Torr in all three cases.

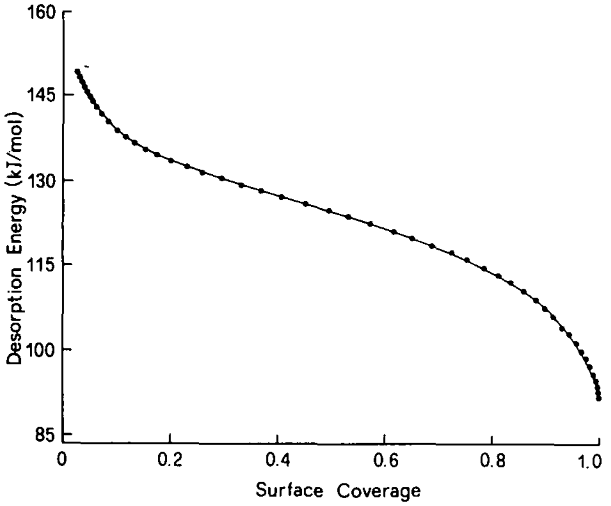

FIG. 8. Variation of desorption activation energy, E_d, with surface coverage calculated for strongly bound hydrogen on catalyst B (peak D in Fig. 5) with the model of Tokoro *et al.* (28). Circles mark the values of E_d calculated by solving the set of linear equations (2) in Ref. (28), while the continuous line is the analytical desorption energy distribution function obtained by least-squares fitting of the same E_d values with the coverage power-series expansion (3) in Ref. (28).

desorb by coupling with hydrogen atoms chemisorbed at the surface (as shown in the case of Pd in Refs. (16, 42)) and, in particular, with H_S. By this mechanism, a part of the surface metal atoms will incorrectly be neglected, being no longer "counted" by H_S. Whether it is possible for metals other than Pd and Ni to form subsurface hydrogen is an open question (7b) but, in any case, at the adsorption temperatures used in this work the population of the subsurface layer should be quite negligible (7e) so that $n^H_{SS} \cong 0$. Further, $n^H_{SP} \cong 0$ because all of the metals are supported on "nonreducible" oxides which certainly do not cause strong metal–support interactions (SMSI) at temperatures of adsorption around 300 K (7f). From Eq. [7] we can thus state that $n^H_{IRR} \cong n^H_S + n^H_R$ and, since the pretreatment conditions are such that $n^H_R \ll n^H_S$ (43), $n^H_{IRR} \cong n^H_S$. Unfortunately, it is not possible to separate the terms n^H_W and $n^H_{REV,m}$ through chemisorption experiments (e.g., one cannot determine a transition pressure) but, from the deconvolution of the TPD peaks, one can however state that $n^H_{REV,m} \ll n^H_W$ (see Fig. 9). From Eq. [8] it finally results that $V_m \cong n^H_S \cong n^H_{IRR}$.

The main problem to contend with in the application of the Back-Sorption procedure is the determination of the temperature, T_{bs}, and the duration, t_{bs} of the evacuation step that follows the first chemisorption on the bare surface of a catalyst. Since the aim of B.S. is the elimination from the catalyst surface of the species "in excess of the monolayer," identified with the weakly chemisorbed hydrogen species, the evacuation temperature should be close to that of the TPD peak maximum of H_W, $T_{M,W}$. In the case of the H_2–Pt/Al_2O_3 system, $T_{M,W} \cong 300$ K. Since this temperature is nearly equal to the adsorption temperature, $T_a = 305$ K, we chose to work at $T_{bs} = T_a$.

The determination of t_{bs} is indeed the essential problem. In fact, as shown in Figs. 6a–b, the amount of hydrogen held on the surface of catalyst B markedly decreased with increasing t_{bs} and attained a constant value only after ca. 14 h. The irreversibly adsorbed hydrogen uptake, n^H_{IRR}, which must be used to calculate D_M through the relation $n^M_S = SF_m \cdot n^H_{IRR}$, is thus strongly dependent on the duration of the pumping step. As long as a simple *comparison* among D_M values is needed (obtained either by means of S.I. and M.I. methods on the same catalyst sample or with the same method on different catalysts), one can merely choose a suitable *reference* pumping time. This time could be the one that leaves on the catalyst surface only those hydrogen species which desorb as a single TPD peak in the H_S region, without any shoulder attributable to H_W. In the case of catalyst B, this happened after 1 h pumping, giving curve C in Fig. 6a.

To use the B.S. procedure for an *absolute* measurement of D_M, a more precise definition of t_{bs} is needed. The most direct way to obtain the minimum time required to desorb all of the hydrogen "in excess of the monolayer," say $\bar{t}_{bs}$, is to make a suitable instrument/catalyst *calibration.* By performing a series of B.S. cycles at increasing t_{bs} on a catalyst with known dispersion, say $\bar{D}_M$, it should be possible to specify a time $\bar{t}_{bs}$ such that $\bar{D}_M = n^M_S/n^M_T = SF_m \cdot n^H_{IRR}(\bar{t}_{bs})/n^M_T$.

Although we were not primarily interested in the absolute determination of D_M but rather in the comparison between S.I. and M.I. methods, the B.S. estimate of the absolute dispersions of the platinum catalysts was made by previous calibration against the 6.3% Pt/SiO_2 standard

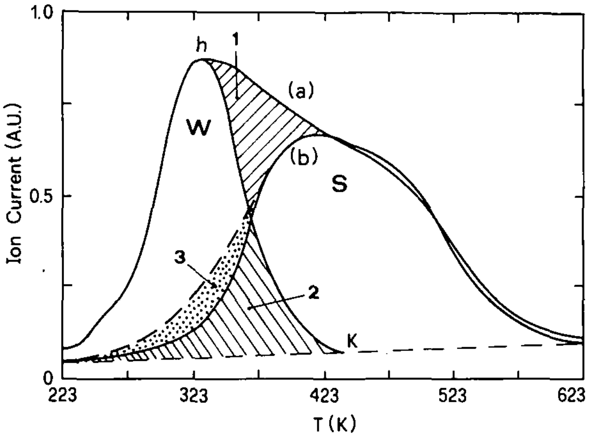

FIG. 9. Nature of the term $n^H_{REV,m}$ in hydrogen mass balances [6] and [8] (the experimental conditions are reported in Fig. 6: curves (a) and (b) correspond to curves A and C in Fig. 6a, respectively). Given the right side *hk* of peak W (weakly adsorbed hydrogen), a sharpening of peak S (strongly adsorbed hydrogen (due to pumping in high vacuum may render unequal the areas 1 and 2 and may give rise to the area 3 proportional to $n^H_{REV,m}$.

TABLE 2

Comparison of Total Hydrogen Uptakes (n_T^H), Monolayer Volumes (V_m), Metal Dispersions (D_M), and Metal Surface Areas (MSA) as Obtained by the Multiple Introduction (M.I.) and Single Introduction (S.I.) Methods Coupled with the Back-Sorption (B.S.) Procedure

Catalyst	Wt% metal	M. I. method		S. I. method		Relative difference (%)[c]	
		First adsorption[a]	After outgassing[b]	First adsorption[a]	After outgassing[b]	First adsorption	After outgassing
A	1	28.52	17.51	29.79	17.88	4.5	2.1
		0.49	0.30	0.52	0.31		
		136.4	83.7	142.5	85.5		
B	3	18.16	11.69	18.90	11.90	4.0	1.8
		0.32	0.20	0.33	0.21		
		86.9	55.9	90.4	56.9		
C	5	15.91	9.52	17.91	9.72	12.6	2.1
		0.28	0.17	0.31	0.17		
		76.1	45.5	85.7	46.5		
D	6.3	59.8	38.6	60.8	39.2	1.7	1.5
		1.04	0.67	1.06	0.68		
		286.0	184.6	290.6	187.6		
E	0.5	44.17	29.16	52.50	29.82	18.8	2.3
		0.40	0.27	0.48	0.27		
		180.4	119.1	214.5	121.8		
F	5	45.08	31.30	49.51	32.25	9.8	3.0
		0.41	0.29	0.45	0.30		
		184.1	127.8	202.2	131.7		
G	0.5	26.64	18.89	31.45	20.50	18.0	8.5
		0.24	0.17	0.28	0.18		
		129.31	91.7	152.6	99.5		
H	5	34.37	23.86	33.81	3.15	−1.6	−3.0
		0.31	0.21	0.30	0.21		
		166.8	115.8	164.1	112.3		

Note. n_T^H is obtained from the first adsorption, and $v_m = n_{IRR}^H$ is obtained after outgassing. Catalyst designations as in Table 1.

[a] Upper numbers for each catalyst denote n_T^H (in N cm^3/g$_M$), middle numbers denote D_M, and lower numbers denote MSA (in m^2/g$_M$).

[b] Upper numbers for each catalyst denote $V_m \equiv n_{IRR}^H$ (in N cm^3/g$_M$), middle numbers denote D_M, and lower numbers denote MSA (in m/g$_M$).

[c] Relative difference (%) = $100 \cdot (V_{m,SI} - V_{m,MI})/V_{m,MI}$.

catalyst EUROPT-1 (27b). Following the same pertreatments indicated as "procedure 1" in Ref. (27a), S.I. and M.I. chemisorptions at 305 K were performed on EUROPT-1 first using t_{bs} = 30 min. The two M.I. isotherms, obtained through B.S., turned out to be parallel above $p^* \cong 50$ Torr and almost horizontal above 90 Torr. The M.I. results reported in Table 2 refer to hydrogen uptakes at 90 Torr to allow a comparison with the total S.I. hydrogen uptake obtained at the same pressure. The dispersion of EUROPT-1 evaluated from the S.I. measurement (t_{bs} = 30 min), assuming $SF_{IRR} \equiv SF_m = 2$, was 0.68. This value is quite close to that of 0.65 reported by Frennet and Wells (27a), who used the same stoichiometric coefficient. Due to the good agreement between S.I. and M.I. results (see Table 2) for t_{bs} = 30 min, further B.S. experiments at longer t_{bs} were carried out using only the S.I. method. As for catalyst B, $n_{IRR}^H(t_{bs}) = n_T^H - n_{REV}^H(t_{bs})$ continuously decreased with increasing t_{bs}; in particular, we found that $D_M = SF_m \cdot n_{IRR}^H(t_{bs} = 1\text{ h})/n_T^M \cong 0.60$, a value coincident with the one obtained by Geus and Wells by means of electron microscopy (27c). As the H_2–Pt/Al_2O_3 system is quite similar to the H_2–Pt/SiO_2 system, it can be concluded that for both catalysts the duration of the intermediate pumping in the B.S. procedure, carried out at 305 K and 10^{-6} Torr, should be between 30 min and 1 h, this latter time being probably better.

S.I. and M.I. Chemisorption

The effectiveness of the reduction conditions, similar to others reported in the literature (36, 44–49), was tested by verifying the absence (sensitivity better than 0.5%) of the peaks of the respective oxidized metals in the X-ray photoelectron spectra of the catalysts. For this purpose we used a Surface Science Instruments M-Probe ESCA spectrometer, described elsewhere (50). The outgassing step following the reduction did not completely remove the adsorbed hydrogen, as verified by the presence of mass 1 and mass 3 signals in the thermodesorption spectrum of deuterium adsorbed on the platinum catalysts at the end of this treatment (24). In each case, all M.I. measurements followed the S.I. ones after the samples were outgassed under the same conditions used for the evacuation following the reduction, so that the surfaces of the catalysts were left (at least) at the same reference state prior to the two kinds of measurement. The possible sintering of the samples, due to this intermediate outgassing step, was checked for by performing, in series, S.I.–M.I.–S.I. analyses. The values of specific surface areas obtained from the two S.I. runs differed by no more than 3%, a value corresponding to the reproducibility of measurements on different portions of the same catalyst sample.

In Fig. 4 we show (a) the pressure vs time and (b) the adsorbed amount vs time graphs relative to a typical S.I. measurement on catalyst F and (c) a M.I. adsorption isotherm on the same sample. For some metal/support systems, the adsorption isotherms on both the clean catalyst and on the catalyst after the intermediate pumping present a final horizontal section in the region of higher pressures (say, higher than p^*, see Fig. 10b) where, besides the absence of physical processes, spillover included, the strong chemisorption is completed and the weak chemisorption is pressure-independent. In this case, it is possible to contact the solid with one gas dose such that the equilibrium state ($dp/dt \cong 0$) is reached at $p_1 > p^*$ (Fig. 10a). After the elimination of the reversible species, as explained in the previous paragraph, and a second gas introduction, the system equilibrates at $p_2 > p^*$. The total amount of gas adsorbed after the first introduction is obtainable as $n_T^H = \alpha \cdot \Delta p_1 = \alpha \cdot (p_0 - p_1)$ and the uptake following evacuation as $n_{REV}^H = \alpha = \Delta p_2 = \alpha \cdot (p_0 - p_2)$, where α is a calibration constant (N cm^3/Torr) and p_0 is the initial pressure at time $t = 0$, also obtained by calibration. Since the corresponding M.I. final sections are parallel and horizontal, the amount of hydrogen irreversibly bound, $n_{IRR}^H = n_T^H(p_1) - n_{REV}^H(p_2)$, although calculated on the basis of different equilibrium pressures, is very close to that obtainable by subtraction of the adsorbed volumes on the M.I. curves in correspondence of any pressure $p > p^*$. If the final regions of the isotherms are parallel but not horizontal, the B.S. procedure is still applicable but the n_{IRR}^H values obtained from S.I. will be lower than those calculated from M.I. (Fig. 10c).

In Table 2 we compare the values of monolayer volumes ($V_m \cong n_{IRR}^H$, N cm^3/g$_M$), metal dispersions (D_M), and metal surface areas (*MSA*, m^2/g$_M$) obtained by extrapolation to zero pressure of the linear (and usually almost horizontal) portion of the M.I. isotherms with those drawn from the observed pressure gradients, $\Delta p = p(t_0) - p(t_{eq})$, of the corresponding S.I. analyses. Metal surface areas were calculated with the equation $MSA = 2 \cdot K \cdot V_m \cdot SF_m \cdot \sigma$, where the factor of 2 accounts for dissociative chemisorption, $K \cong 0.2687$ (m^2 · N cm^{-3} · Å^{-2}) is a group of constants, $SF_m = n_S^M/V_m$ is the stoichiometric factor (*assumed* to be equal to 2 for all the metals studied), and σ is the average area occupied by one surface metal atom (Å^2/atom). The values of σ used for Ru, Pt, and Rh are 9.03, 8.9, and 7.6 Å^2/atom (2), respectively.

Under the pressures generally used in our adsorption experiments (up to 13 Torr for catalysts A–D and up to 40 Torr for catalysts E–H, depending on the value of p*; see Fig. 10), the fraction of the total gas uptake that could be removed by simple pumping at the adsorption temperature, both in S.I. and in M.I. measurements, was always between 35% and 45%. Comparing columns (3) and (5) with columns (4) and (6) in Table 2, it can be noted that the agreement between S.I. and M.I. methods on the n_{IRR}^H values is markedly better than that on the n_T^H values, with an average deviation of about 3% (column 8) and 10% (column 7), respectively. Catalyst H is the only exception to this trend, the equilibration time used for the S.I. probably being too short. These data can be explained by making some assumptions on the nature of weakly chemisorbed hydrogen.

Since the H_M species is absent from the metal surface at the adsorption temperature of 300 K (we verified that H_M adsorption takes place during the decrease in temperature to 120 K by measuring a decrease of gas pressure markedly higher than the amount calculated with the equation of state, corrected for the nonideality of the gas), the difference $n_{REV}^H = n_T^H - n_{IRR}^H$ can be entirely attributed to H_W species. As the adsorption temperature and the range of pressures used are the same in S.I. and M.I. experiments, it seems that the population of the weakly bound species depends on the way in which the adsorbate comes into contact with the solid. The desorption energies calculated for H_S, i.e., the energies of the H_S surface chemical bond (11, 25c), are consistent with the values expected for hydrogen adsorption on 3- and 4-fold symmetry surface sites. The great majority of surface atoms that can give rise to "ensembles" with such symmetry are those located on the flat portions of the crystallite surface (35), i.e., atoms having a high coordination number, *Z*. However, we can imagine that, on a very irregular surface, C_{3v} and C_{4v} sites can be composed of both high-*Z* (HZ) and low-*Z* (LZ) metal atoms. A simple representation of a 4-fold site made by LZ and HZ atoms is shown in Fig. 11. The observed characteristics of weakly bound hydrogen (e.g., reversibility, E_d, etc.) seem to indicate, for this species, adsorption sites with $C_{\infty v}$ and C_{2v} symmetry, i.e., on-top and bridged chemisorption (13, 25b). We suggest that H_W could be mainly adsorbed on LZ atoms belonging to high-symmetry sites which are also involved in bonding with H_S. We call such atoms LZ_S atoms. The ability of LZ_S atoms to bind both H_W and H_S should be ascribed to their partially unsaturated coordination shell

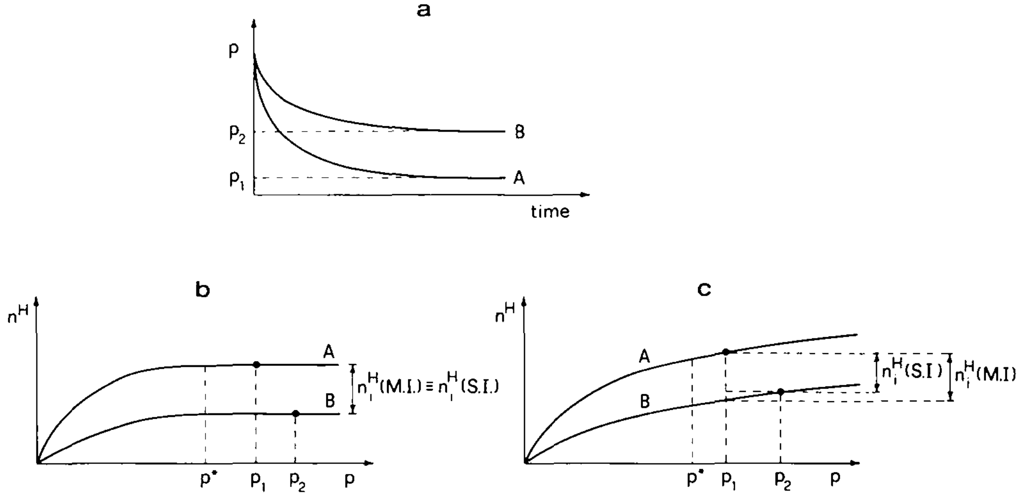

FIG. 10. Conditions for the applicability of the S.I. method. S.I. measurements (a) on clean catalyst, A, and after intermediate pumping, B, give two different equilibrium pressures. Nevertheless, if the final sections of the M.I. isotherms (b) are parallel and horizontal beyond some pressure p^*, the two techniques give the same results. If the M.I. isotherms (c) are parallel but not horizontal beyond p^*, the S.I. method estimates the monolayer uptake with some error.

(25b), i.e., to some residual "dangling bonds" available for chemisorption. This will explain the "excess" nature (1, 2) of Hw (and of other adsorbates which give rise to "weak" species, such as CO, NH_3, etc.) and also the values listed in Table 2. In fact, due to the higher density of free valences and to the higher statistical probability of LZ atoms with respect to HZs (i.e., the probability for a H_2 molecule to impact on isolated atoms of atoms with only one neighbor instead of on atoms surrounded by more than one neighbor), we expect a chemisorption rate on LZ atoms higher than that on HZ atoms. (Note: The above-mentioned statement that the statistical probability of LZ atoms is higher than that of HZs strictly holds only for sufficiently large D_M values (35), such as those measured in this work). Indeed, as can be seen in Fig. 12, representing S.I. chemisorption on the 5% Rh/Al_2O_3 catalyst, the rate of pressure lowering (i.e., the apparent chemisorption rate at constant volume, $r_a = dn^H/dt \approx dp/dt$) during the adsorption that follows the intermediate

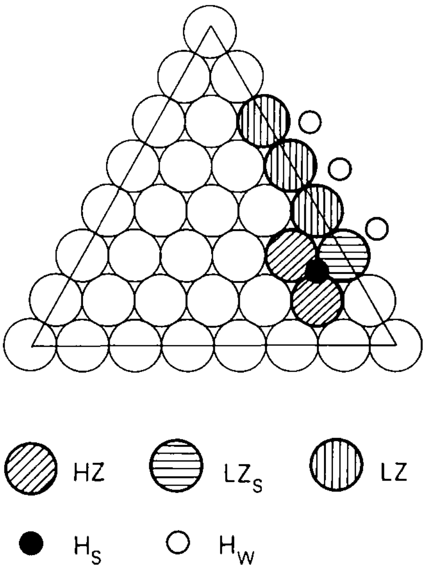

FIG. 11. Suggested role of low- and high-coordination-number surface atoms in hydrogen chemisorption on the face-centered cubic octahedron model of a metal crystallite (35): a high-symmetry surface site, on which H_S chemisorption takes place, can be formed also by LZ atoms, available for further H_W chemisorption (LZ atoms involved in H_S chemisorption are called LZ_S atoms in the text).

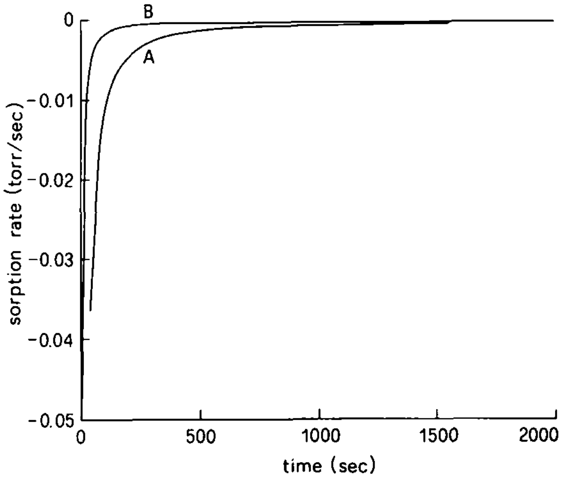

FIG. 12. Apparent hydrogen chemisorption rates on catalyst F at 305 K after adsorption at the same temperature on the clean catalyst (A) and after the intermediate pumping (B).

pumping (i.e., on the catalyst with all strong sites saturated, curve B in Fig. 12) is always higher than that measured during the chemisorption on the clean surface (curve A). For this reason, in this latter case, when all the gas sampled is contacted with the solid, LZ_S atoms are occupied first by H_W under "kinetic control" while all remaining HZ atoms belonging to H_S sites are occupied later under "thermodynamic control." On the other hand, in M.I. experiments the catalyst surface is contacted stepwise by the gas to be adsorbed. During the first gas introduction both LZ_S and HZ atoms will be occupied to some extent. The gas to be adsorbed in the second and the successive doses finds a surface on which LZ_S atoms are partially saturated through H_S bonding, so that further adsorption of H_W is inhibited.

It has to be noted that, if this interpretation of the nature of H_W turns out to be correct, the B.S. procedure should cause the elimination of *all* the hydrogen bound to LZ atoms, including those "isolated" surface atoms (not belonging to any ensemble), certainly present at least on very highly dispersed catalysts, that should be considered in the evaluation of n_S^M, and thus of D_M.

Furthermore, with reference to Fig. 7, it can be seen that the weakly bound hydrogen peak appears only after the *completion* of the strongly held monolayer, in apparent contradiction to the simultaneous occupation of "strong" and "weak" sites expected from the above-mentioned considerations on the chemisorption rates. However, the peak sequence in Fig. 7 can be explained by taking into account the surface mobility of weakly bound species during the temperature ramp of a TPD experiment. In fact, if the metal surface has both "weak" and "strong" sites partially saturated, e.g., as after the first gas introduction in a M.I. measurement, the temperature rise is certainly able to cause the desorption of H_W and its subsequent readsorption on the high-symmetry sites still available (20a), so that all hydrogen appears to desorb as H_S.

It is possible to draw an analogy between the relation that exists between the S.I. and M.I. methods and the one existing between the one-point and the classical BET methods. Just as in this latter case it is essential to perform a complete physisorption isotherm to estimate the magnitude of the "C parameter" of the BET equation, which can legitimate or not the use of the one-point method (51), so the applicability of the S.I. method must be verified by means of a complete M.I. chemisorption isotherm (coupled with the B.S. procedure) to determine the pressure p^* above which the final sections are parallel and, depending on the support, horizontal. This check being performed, the S.I. method can be very useful, especially when one needs to carry out many dispersion measurements on similar catalysts (e.g., catalysts made with the same support material or with the same preparation procedure). Examples of applications could be the quality control of a series of catalysts, directed by the manufacturer to the optimization of a particular preparation procedure, and also the periodic measurement of the degree of sintering of a working catalyst.

CONCLUSIONS

The existence of weakly chemisorbed hydrogen cannot be ignored in the calculation of the dispersion of supported metal catalysts. In our opinion, a standard procedure for the measurement of this important property should determine at least three quantities: the total gas uptake, n_T^H, the irreversibly adsorbed amount, n_{IRR}^H, and the reversibly adsorbed amount, n_{REV}^H. Under the given interpretation of the nature of weakly chemisorbed hydrogen, the accurate measurement of n_W^H and n_S^H could be useful in estimating the relative amounts of LZ and HZ, surface atoms which are known to play different roles in surface-sensitive and surface-insensitive reactions (12).

The S.I. method, despite its simplicity, provides estimates of the catalyst dispersion in good agreement with those obtainable from a complete M.I. adsorption isotherm. The accord between the two methods is particularly good when only to the irreversibly adsorbed hydrogen is considered. For measurements carried out at or above the ambient temperature we could not detect any adsorption by the supports, so that it is possible to operate in pressure ranges such that the weak chemisorption equilibrium is pressure-independent; i.e., all adsorption isotherms have almost horizontal final sections. When these sections are parallel but not horizontal, the S.I. provides only an approximate estimate of dispersion.

The standard Pt/SiO_2 catalyst EUROPT-1 (27b) was used as a reference to assess the correctness of our S.I. method.

The noteworthy advantages of the S.I. method over the M.I. method are (i) analysis times reduced by an order of magnitude, (ii) greater control of the surface cleanliness, and (iii) no cumulative errors (both random and systematic) due to multiple pressure readings. Consequently, we conclude that, at least for routine comparative measurements, the S.I. technique coupled with the B.S. procedure can be a valuable alternative to the classical adsorption isotherms.

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