Determination of Metal Particle Size of Highly Dispersed Rh, Ir, and Pt Catalysts by Hydrogen Chemisorption and EXAFS

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Hydrogen-to-metal (H/M) ratios exceeding unity for Pt and Rh and exceeding 2 for Ir were measured for highly dispersed Pt, Rh, and Ir catalysts supported on Al_2O_3 and SiO_2. Since the coordination of hydrogen to metal atoms is unknown for such highly dispersed catalysts, the metal surface area of these catalysts cannot be calculated from the hydrogen chemisorption values. Therefore EXAFS (extended X-ray absorption fine structure) measurements were performed to determine the metal particle size and thereby to calibrate hydrogen chemisorption results. The H/M ratio determined by hydrogen chemisorption is a linear function of the average metal coordination number determined by EXAFS. This linear relationship is independent of support but varies with the metal with the H/M ratio increasing in the order Pt < Rh < Ir. Several hypotheses for the high H/M values are discussed. Spillover and subsurface hydrogen are excluded as explanations and only multiple adsorption of hydrogen on metal surface atoms is shown to be capable of explaining all experimental observations. The $H/M_{surface}$ stoichiometry differs among Pt, Rh, and Ir in the order H/Pt < H/Rh < H/Ir, analogous to the order of stability of corresponding metal polyhydride complexes and of theoretical expectation. © 1987 Academic Press, Inc.

INTRODUCTION

Selective chemisorption of gaseous molecules, especially hydrogen, has been extensively used to estimate the degree of dispersion of group VIII metal catalysts (*1–27*). Chemisorption methods are of special importance for highly dispersed metal catalysts, since it is often difficult to establish the degree of dispersion by other techniques such as X-ray diffraction or electron microscopy measurements (*1*). Moreover, the chemisorption technique is relatively quick and cheap.

Hydrogen chemisorption data can be directly used to compare dispersions of a metal in different catalysts in a relative way. However, when one wants to calculate metal surface areas in an absolute way the hydrogen-to-metal stoichiometry must be known. For the most widely used platinum metal usually a H/M stoichiometry of one has been used and this assumption has been justified by calibration with XRD and TEM (*5–7*). Surface science studies fur-

thermore proved that a maximum of one hydrogen atom per metal atom could be chemisorbed on the (111) faces of fcc metal single crystals (*8*). Under the assumption that the surface of metal particles larger than, say, 2 nm consists largely of (111) faces, it is understandable that the empirical assumption of a $H/M = 1$ stoichiometry was rather successful in many studies. However, as early as 1960 data began to appear in the literature about stoichiometries exceeding one. The value of H/Pt = 1.5 − 1.65 has been measured for Pt/Al₂O₃ catalysts (*9, 10*) and H/Pt = 1.3 − 1.6 has been quoted for Pt/SiO₂ catalysts (*11, 12*), while a value of H/Pt = 2 has been observed by Rabo *et al.* for Pt deposited on a zeolite (*13*). Recently, Sato (*14*) has described a Pt/TiO₂ system made by photo-impregnation of hexachloroplatinic acid with H/Pt = 2.5, while Frennet and Wells (*15*) have reported H/Pt values around 1.2 for 6.3 wt% Pt/SiO₂. For Rh catalysts Wanke and Dougharty (*16*) have reported the adsorption of more than one hydrogen

26

atom per surface rhodium atom for Rh/ Al$_2$O$_3$ catalysts. For supported Ir catalysts even values near 3.0 have been measured. McVicker et al. (17) have found an upper limit of two adsorbed hydrogen atoms per Ir atom for Ir/Al$_2$O$_3$ systems, only using the strongly bonded hydrogen. When the total amount of adsorbed hydrogen is taken into account, they reported H/Ir values exceeding 2. Krishnamurthy et al. (18) have shown that 0.48 wt% Ir/Al$_2$O$_3$ adsorbs up to 2.72 hydrogen atoms per iridium atom, part of which is weakly bound (H/Ir = 0.28).

In literature, several explanations have been given for H/M values exceeding unity. Often a distinction has been made between reversibly and irreversibly adsorbed hydrogen, and in many cases only the irreversibly adsorbed hydrogen has been assumed to be important for the determination of the metal surface area (17–22). Several authors have ascribed the high H/M values to hydrogen spillover to the support (14, 28–30), or to an increased hydrogen-to-metal stoichiometry for metal atoms situated at the corners and edges of the small metal particles (16–18). Another explanation given for high H/M values has been the positioning of part of the hydrogen under the surface of the metal particle (31–33).

In our laboratory, Pt, Rh, and Ir catalysts supported on Al$_2$O$_3$, SiO$_2$, and TiO$_2$ have been studied in the hydrogenation of carbon monoxide to hydrocarbons and oxygenated products. We have also used hydrogen chemisorption to characterize the highly dispersed supported metal catalysts and have obtained H/M values exceeding unity for Rh and Pt catalysts (34–36) and H/M values even exceeding 2.0 for supported Ir systems (37). Because of a lack of information on the hydrogen-to-metal stoichiometry for very small metal particles, we were unable to calculate the dispersion from the chemisorption results. Therefore, we have relied on another technique to obtain information about the particle size of the highly dispersed systems: extended X-ray absorption fine structure (EXAFS). With this technique, it is possible to determine the metal coordination number of a metal atom (N) in a particle and thus to get information about the particle size (36, 38–43).

In this paper, the results of our hydrogen chemisorption and EXAFS measurements are compared for Pt, Rh, and Ir catalysts supported on SiO$_2$ and Al$_2$O$_3$. Several hypotheses for the observed high H/M values are discussed and it will be shown that multiple adsorption of hydrogen on metal surface atoms is the only one which can explain all experimental observations.

EXPERIMENTAL

Preparation of the catalysts. Pt, Ir, and Rh catalysts were prepared from RhCl$_3$ and IrCl$_3$ via the incipient wetness technique (34, 35, 37), from Pt(NH$_3$)$_4$(OH)$_2$ and Rh(NO$_3$)$_3$ via the ion-exchange technique (36, 44), and from IrCl$_3$ via the urea method (37). In the last method, the pH of a suspension of the support and metal ions in water is increased slowly by means of the decomposition of urea (45). The following supports were used: γ-Al$_2$O$_3$ from Ketjen (000–1.5E, surface area 200 m^2 g^{-1}, pore volume 0.60 ml g^{-1}), γ-Al$_2$O$_3$ obtained by heating boehmite (Martinswerk, GmbH, surface area 150 m^2 g^{-1}, pore volume 0.65 ml g^{-1}), and SiO$_2$ (Grace, S.D. 2-324.382, surface area 290 m^2 g^{-1}, pore volume 1.2 ml g^{-1}). The metal precursors (IrCl$_3$ · xH$_2$O, RhCl$_3$ · xH$_2$O, and Pt(NH$_3$)$_4$(OH$_2$) were supplied by Drijfhout, Amsterdam. All catalysts were dried in air at 395 K for 16 h (heating rate 2 K min^{-1}).

Hydrogen chemisorption measurements. Volumetric hydrogen chemisorption measurements were performed in a conventional glass system at 298 K. Hydrogen was purified by passing through a palladium diffusion cell. Before measuring the H$_2$ chemisorption isotherm the dried catalysts were reduced for 1 h (heating rate 5–8 K min^{-1}) and evacuated (10^{-2} Pa) for 0.5 h. The reduction temperatures, at which evacuation was also performed, are presented in Table 1. After hydrogen admission at 473 K,

TABLE 1

Hydrogen Chemisorption and EXAFS Results for
Supported Rh, Ir, and Pt Catalysts

Catalyst[a,b]	Reduction temp. (K)	H/M^c	N^d
4.2% Pt/Al$_2$O$_3$, k, A	1100	0.23	10.0
4.2% Pt/Al$_2$O$_3$, k, A	1058	0.43	10.2
4.2% Pt/Al$_2$O$_3$, k, A	573	0.77	7.6
1.06% Pt/Al$_2$O$_3$, k, A	673	1.14	5.2
2.00% Rh/Al$_2$O$_3$, b, B	673	1.2	6.6
2.4% Rh/Al$_2$O$_3$, b, A	473	1.2	6.3
1.04% Rh/Al$_2$O$_3$, k, B	773	1.65	5.8
0.47% Rh/Al$_2$O$_3$, k, B	773	1.7	5.1
0.57% Rh/Al$_2$O$_3$, b, B	573	1.98	3.8
7.0% Ir/SiO$_2$, g, B	773	0.43	11.1
1.5% Ir/SiO$_2$, g, B	773	0.83	11.0
5.3% Ir/SiO$_2$, g, C	773	1.24	8.6
1.5% Ir/SiO$_2$, g, C	773	1.70	8.6
2.4% Ir/Al$_2$O$_3$, k, B	773	1.96	7.7
1.5% Ir/Al$_2$O$_3$, k, B	773	2.40	7.3
0.8% Ir/Al$_2$O$_3$, k, B	773	2.68	6.0

[a] Support: γ-Al$_2$O$_3$ Ketjen (k), γ-Al$_2$O$_3$ boehmite (b), SiO$_2$ Grace (g).

[b] Preparation method: ion exchange (A), incipient wetness (B), urea method (C).

[c] Experimental error in H/M: ±5%.

[d] Experimental error in N: ±10%.

$P(H_2) = 93$ kPa, desorption isotherms were measured at room temperature. The total amount of chemisorbed H atoms was obtained by extrapolating the linear high pressure part (20 kPa $< P <$ 80 kPa) of the isotherm to zero pressure (2). Correction for chemisorption on the bare support was not necessary, because the extrapolated values of the desorption isotherms for the bare supports, pretreated in the same way as the catalysts, were zero within the uncertainty of the measurements.

EXAFS measurements. Catalyst samples were measured at liquid nitrogen temperature as thin self-supporting wafers in H$_2$, after *in situ* reduction. The Rh and Pt measurements were performed on beam line *I*-5 at the Stanford Synchrotron Radiation Laboratory (SSRL) at the Rh *K*-edge (23,220 eV) and Pt L_{III}-edge (11,564 eV), respectively. The data were analyzed with the use of reference compounds (38–40). In the

case of the Rh catalysts, Rh foil and Rh$_2$O$_3$ were used. For the Pt data, Pt foil and Na$_2$Pt(OH)$_6$ were used (36).

The Ir measurements were done on the Wiggler station 9.2 at the Synchrotron Radiation Source (SRS) in Daresbury, G.B. (2 GeV, 80–250 mA) at the Ir L_{III}-edge (11,215 eV). As reference compounds Pt foil and Na$_2$Pt(OH)$_6$ were used. Both theoretically (46) and experimentally (47) the choice of Pt references for the analysis of Ir data can be justified.

The results of the analysis of the Rh data have been published before (38–40), as well as the results for the Pt catalyst with H/M = 1.14 (36).

The metal–metal coordination parameters of the Ir and other Pt catalysts were determined as follows (48). A k^3 Fourier transform ($\Delta k = 2.7$–15 Å^{-1}) was applied to the EXAFS data. In the resulting spectrum in R-space, the peak representing the first M–M shell (but also including M–O$_{support}$ contributions) was back transformed ($\Delta R = 1.9$–3.5 Å) to k-space. In the resulting spectrum the M–O$_{support}$ contributions are only significant below $k = 8$ Å^{-1}, because a low-Z element like oxygen does not scatter very much at high k-values. Therefore, the M–M coordination parameters were determined by fitting the data between $k = 7.9$ and 13.8 Å^{-1}, in such a way that a good agreement was obtained in k- and in R-space.

RESULTS

Hydrogen chemisorption measurements. Since hydrogen chemisorption can be performed in many, slightly different ways, with often (slightly) different results, it is imperative to start with a description of our own method of measuring hydrogen chemisorption. After *in situ* reduction and evacuation we admit a certain amount of hydrogen at 473 K, as hydrogen adsorption at room temperature is a slow process. Subsequently, the sample is cooled down to 298 K under hydrogen and the amount of adsorbed hydrogen is measured ($P_{equilibrium} \simeq$ 80 kPa). Thereafter a so-called desorption

isotherm is measured at room temperature by lowering the pressure step by step ($P \simeq$ 13 kPa per step), while measuring the amount of desorbed hydrogen. The total amount of chemisorbed hydrogen is obtained by extrapolation of the linear high pressure part (20 kPa $< P <$ 80 kPa) in the isotherm to zero pressure. The H/M values obtained in this way are slightly higher than those obtained by admission at room temperature and waiting for 3 h. As an example, we obtained H/Ir values of 2.68 and 2.49 for a 0.81 wt% Ir/Al_2O_3 catalyst, after admission of H_2 at 473 K and 298 K, respectively. The H/M values obtained for our catalysts are presented in Table 1.

Other, often lower, hydrogen pressures have been used in the literature. According to Crucq *et al.*, the hydrogen adsorption isotherms of supported Pt (*49*) and Rh (*50*) catalysts are Temkin-like (showing a linear relation between log(P) and H/M over a wide pressure range) due to a strongly decreasing heat of adsorption with coverage. Therefore they recommended the measurement of a single adsorption point at $P >$ 13 kPa at room temperature, to obtain the amount of adsorbed hydrogen close to monolayer coverage. However, we always extrapolate our measurements to zero pressure. The experimental convenience of this is that the intercept is independent of the dead volume of the adsorption apparatus (*16*). Consequently, it is possible to use an arbitrarily chosen dead volume or to ignore the dead volume entirely, since the zero-pressure condition implies no residual adsorbate in the gas phase, and there is thus no necessity for the experimental determination of dead volumes.

Several authors have reported that H/M increases with decreasing temperature. For instance Boronin *et al.* (*12*) reported that for Pt catalysts H/M increased to a value of 2 as the temperature of measuring chemisorption was lowered to 77 K. Most likely different metals will have different H/M temperature dependencies and there is no a priori reason why all metals should have

the same H/M stoichiometry at a particular temperature. Furthermore, as also shown in this paper, the H/M stoichiometry is dependent on the metal particle size. For these reasons, and also to measure the H/M stoichiometries under identical conditions, we have opted to use a fixed measurement temperature for all three metals under study. For experimental reasons we have measured the desorption isotherms at 298 K. As a consequence, it should be kept in mind that the resulting calibration of the H/M values is only valid for chemisorption on Pt, Rh, and Ir at 298 K.

We have not made any distinction between reversibly and irreversibly adsorbed hydrogen, as is often done in the literature (*17–22*). All chemisorption is reversible and one can only distinguish between weakly and strongly adsorbed hydrogen. The only difference between them is the heat of adsorption, which is a function of coverage. Goodwin *et al.* (*21, 22*) have shown that hydrogen which is weakly adsorbed on supported Ru catalysts is associated with the metal, and not with the support. De Menorval and Fraissard (*51*) and Sanz and Rojo (*52*) have shown that the NMR chemical shifts of hydrogen atoms adsorbed on Pt/Al_2O_3 and Rh/TiO_2 catalysts, respectively, decrease with increasing hydrogen pressure, even at $P >$ 40 kPa. This proves that even at such pressures additional hydrogen is still adsorbed on the metal when increasing the hydrogen pressure. Subtraction of the amount of "reversibly" adsorbed hydrogen therefore does not result in a correction for the adsorption on the support, but instead to the elimination of hydrogen adsorbed weakly on the metal.

Moreover, we feel that the amount of weakly adsorbed hydrogen is difficult to determine objectively, as it depends on the apparatus, pump, and evacuation time used (*49*). To obtain an idea of the amount of hydrogen which is relatively weakly bound to the metal under our conditions, measurements were done for the 0.81 wt% Ir/Al_2O_3 catalyst. After 20 min of pumping, 23% of
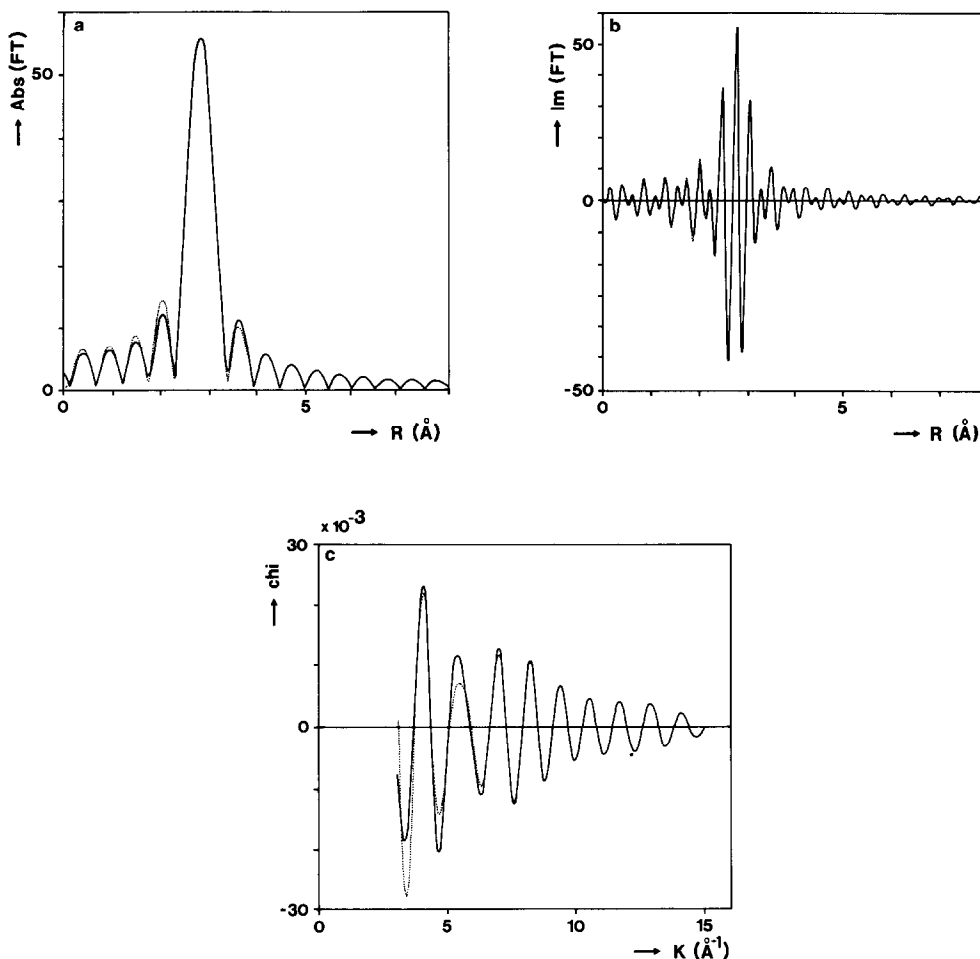
FIG. 1. Fit obtained in the EXAFS analysis of 4.2 wt% Pt/Al_2O_3, $H/Pt = 0.77$; (—) experiment, ($\cdots$) fit. (a) Amplitude of the Fourier transform of the EXAFS obtained by a k^3 Fourier transform between k = 7.9 and 13.8 $Å^{-1}$; (b) imaginary part of the Fourier transform; (c) fit in k-space. The Pt–Pt spectrum has been calculated on the basis of the fit for $7.9 < k < 13.8$ $Å^{-1}$, with $N = 7.6$, $R = 2.75$ Å, and $\Delta\sigma^2 = 0.0035$ $Å^2$.

the original amount of adsorbed hydrogen could be readsorbed (H/Ir_{strong}) = 2.07, H/Ir_{weak} = 0.61). It is obvious that even if only the strongly bonded hydrogen was considered, our H/M values would still exceed unity in many cases.

EXAFS measurements. In order to obtain the metal particle sizes of our highly dispersed catalysts, we used the EXAFS technique. Details about the data analysis used with some of the measurements have been reported earlier (*36, 38–40*), or will be reported (*47, 48*). The quality of the fit ob-

tained for the first metal–metal shell in the EXAFS data was always good. As an example the fits in R-space and in k-space are shown in Fig. 1 for the 4.2 wt% Pt/Al_2O_3 sample with a H/M value of 0.77. The fit has been obtained between $k = 7.9$ (below this limit Pt–O contributions are present and 13.8 $Å^{-1}$ (signal-to-noise ratio is too low above this limit). In k-space a clear deviation is observed for $k < 7$ $Å^{-1}$ between the Pt–Pt spectrum calculated on the basis of the fit parameters, and the experimental spectrum. This deviation is caused by Pt–O

contributions which cannot be neglected in this region (48).

The average numbers of metal atoms N obtained from the EXAFS analysis are presented in Table 1 and Fig. 2. As can be seen in Table 1, two supports and a variety of preparation methods have been used. However, if any of these parameters has an effect on the hydrogen-to-metal stoichiometry, it can only be a minor one since the metal–metal coordination number versus H/M relationship can be described by a single straight line for each metal. Rather unexpectedly there is a large difference between the three metals. This difference is very marked and experimentally significant above $H/M = 1$, but still exists at lower H/M values. For a given particle size (equal metal–metal coordination number) the H/M values increase in the sequence H/Pt < H/Rh < H/Ir.

Model calculations. To investigate if the high H/M values can be explained by adsorption at the surface metal atoms, model calculations were performed. A computer program was made to determine the area available for chemisorption around a supported small metal particle. In the spirit of Wynblatt and Gjostein (53) the shape of the

metal particle was calculated as a function of the relative magnitude of the metal–metal and metal–support interaction energy by minimizing the total energy. We assumed the support to consist of a flat (111) layer of oxygen anions, the size of which was taken equal to that of the metal atoms. The metal atoms were assumed to be fcc packed, and thus to fit epitaxially on the support surface. The shape of a metal particle with $n + 1$ atoms was obtained from that of the particle with n atoms by putting the extra metal atom at the position of minimum energy. Such calculations were carried out over a whole range of α-values, with α being the ratio of the metal atom–oxygen anion interaction $E(M-O^{2-})$ and the metal atom–metal atom interaction $E(M-M)$.

To obtain an estimate of the number of hydrogen atoms that can be placed around such a metal particle, we assumed that the hydrogen atoms will occupy the free fcc positions around the metal particle and that only one hydrogen atom per vacant fcc position is allowed. Although diffraction results for metal hydride complexes point to a hydrogen atom radius which is much smaller than that of the Pt, Rh, or Ir atoms (54), these same results also point out that H–H distances smaller than M–M distances are rarely observed. Similarly, in line with results obtained in surface science (8), our model predicts that the maximum number of hydrogen atoms which can adsorb on the (111) surface of an fcc metal single crystal is equal to the number of metal atoms in that surface. Our assumptions therefore seem reasonable. They lead to a lower bound for the number of hydrogen atoms that geometrically can be put around a supported metal cluster.

Table 2 summarizes the results of the calculations for two situations. One in which the interaction between metal and oxygen is half that of the metal–metal interaction, $E(M-O^{2-})/E(M-M) = \alpha = 0.5$, which results in spherical particles, and one in which $\alpha = 2$, resulting in raft-like particles.
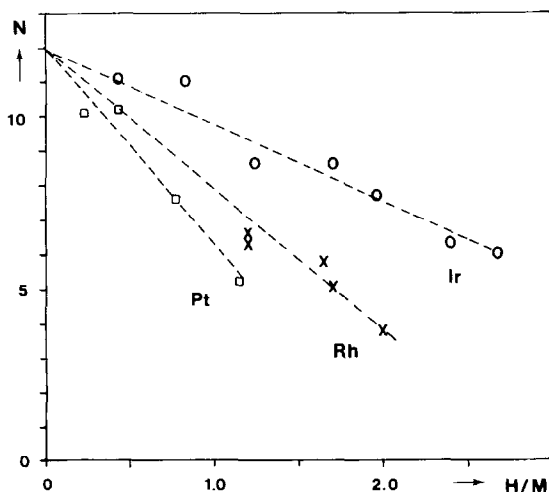

FIG. 2. Metal–metal coordination number N from EXAFS versus H/M from chemisorption, for Pt (□), Rh (×), and Ir (○).

TABLE 2

Results of the Computer Calculations on Small Metal Particles

α^a:			0.5					2.0		
Number of atoms per particle:	4	10	30	100	800	4	10	30	100	800
Empty positions[b] with: Metal neighbors										
1	9	15	16	19	36	11	13	14	14	39
2	9	8	21	35	81	6	10	21	41	85
3	0	5	10	33	125	1	4	10	23	129
4	0	2	4	15	113	0	1	6	21	92
5	0	0	2	2	15	0	1	0	0	18
Dispersion	1.0	1.0	0.80	0.62	0.36	1.0	1.0	0.80	0.60	0.35
H/M^c	4.5	3.0	1.8	1.0	0.46	4.5	2.9	1.7	1.0	0.45
H/M^d	2.3	1.5	1.2	0.85	0.42	1.8	1.6	1.2	0.85	0.41
N^e	3.0	4.8	6.8	8.5	10.2	2.5	4.2	6.5	8.3	10.2
D^f	2.1	3.3	4.4	7.0	12.9	2.8	3.7	5.1	7.4	14.0

[a] $\alpha = E(M-O^{2-})/E(M-M)$.

[b] Vacant fcc positions around the metal particle which have at least one metal neighbor, and which can be occupied by H atoms.

[c] Assuming that all vacant fcc positions around the particle are filled by hydrogen.

[d] Assuming that only vacant positions with more than one metal neighbor are filled by hydrogen.

[e] Metal–metal coordination number.

[f] Diameter of the particle expressed in metal atom diameters.

Dispersions (defined as the fraction exposed metal atoms), metal–metal coordination numbers, diameters of the particles (expressed in metal atom diameters), and H/M values are presented as a function of the number of atoms per particle. The H/M values were calculated on the basis of two assumptions. Very high H/M values (up to 4.5) were obtained if hydrogen was allowed to occupy all vacant fcc positions, even those where the hydrogen atom is bonded to only one metal atom. If only vacant positions were considered, where the hydrogen atom is bonded to at least two metal atoms, still a H/M value of 2.3 could be obtained. In Fig. 3 we have plotted the two series of H/M values as a function of the total number of atoms in a metal particle, using $\alpha = 0.5$. In the same figure also the corresponding coordination number N, to be compared with the EXAFS results, and the dispersion are presented.

With the aid of these calculations, the metal–metal coordination numbers deter-

mined by EXAFS were used to calculate dispersions. These dispersions versus the measured H/M values are shown in Fig. 4. It is clear from this figure that the $H/M_{surface}$
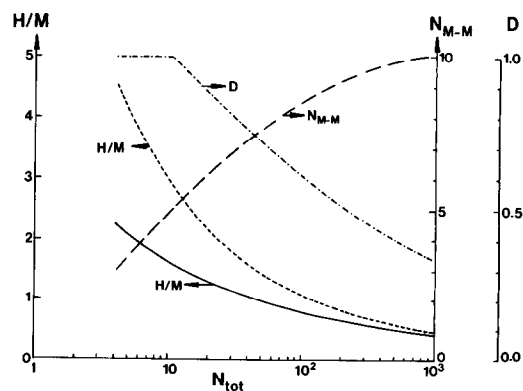

FIG. 3. Results of model calculations for $\alpha = 0.5$. Calculated H/M, assuming that all free positions around the metal particle are filled with hydrogen (---), or that only the free positions with at least two metal neighbors are filled (—), vs total number of metal atoms in one particle N_{tot}, and calculated dispersion D (—·—·) and metal–metal coordination number N_{M-M} (—·—) versus N_{tot}.
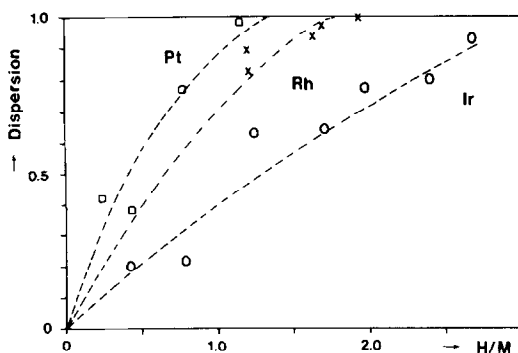
FIG. 4. Dispersion ($M_{\text{surface}}/M_{\text{total}}$) obtained on the basis of model calculations ($\alpha = 0.5$) for Pt ($\square$), Rh ($\times$), and Ir ($\bigcirc$), versus H/M.

stoichiometry cannot be taken as equal to one, and varies among the group VIII metals studied.

DISCUSSION

First, we want to exclude several trivial effects which could explain the high H/M values:

—Unreduced M^{n+} was not present, as can be concluded from TPR experiments (34–37). Within the experimental error (5%), all metal was reduced to M^0.

—Contamination of the catalysts with carbon did not occur. Elemental analysis (using Perkin–Elmer Element Analyzer Model 240) showed that no carbon residues existed initially on the catalysts. Carbon residues could be produced by grease or oil vapors during the evacuation. However, TPD experiments, which are absolutely free of grease and oil vapor, resulted in similarly high H/M values (37).

—Partial reoxidation during outgassing at high temperature, mentioned by Martin et al. for Fe (55) and Ni (56), can be excluded, because oxygen consumption during oxidation at 773 K after reduction and evacuation at 773 K was measured to be O/Ir $= 1.96$ for 1.5 wt% Ir/Al$_2$O$_3$. IrO$_2$ is the most stable oxide of iridium, so these results prove that Ir was in the zero valent state after reduction and evacuation.

In the literature several explanations have been proposed for high H/M values. A common explanation is that in fact not all hydrogen is adsorbed by the small particles but that part of the hydrogen is adsorbed by the support through hydrogen spillover from the metal particles. Kramer and Andre (28) have reported the spillover of atomic hydrogen (formed by dissociation of H$_2$ on the platinum) on alumina and calculated a maximum surface capacity of their alumina for atomic hydrogen of 2×10^{16} atoms m^{-2}. Cavanagh and Yates (29) have studied hydrogen spillover on alumina by exchange of D$_2$ with OH-groups and have shown that near 300 K, the rate of the exchange process is high in the presence of Rh particles on Al$_2$O$_3$. However, this experiment does not constitute proof for hydrogen spillover because the occurrence of exchange of hydrogen on the metal with hydrogen of the OH-groups on the support is a necessary but not sufficient condition for spillover to take place. Hydrogen spillover has also been reported on SiO$_2$, especially by Teichner and co-workers (30).

We do not believe that spillover can explain our results. In the first place, it is not expected that the extent of spillover will differ greatly among the group VIII metals, and thus it cannot explain the observed differences between Pt, Rh, and Ir. Besides, it is often said that spillover depends on the type of support used. In the case of Ir we have used two supports, SiO$_2$ and Al$_2$O$_3$, and the H/Ir versus N values were found to lie on a straight line, independent of the support. Moreover, the reported number of sites on Al$_2$O$_3$, available for hydrogen spillover (2×10^{16} H-atoms m^{-2} (28)), can only account for a fraction of the hydrogen chemisorbed by our catalysts. We cannot imagine any trap for hydrogen on alumina or silica (what can be reduced?) besides defects or impurities. The adsorbed amounts of hydrogen are far too high to be compatible with the concentration of impurities or defects.

Thus, we come to the conclusion that the main reason for the observed large H/M

values must be an adsorption stoichiometry larger than one. There are two ways to achieve such a high adsorption stoichiometry: (A) adsorption beneath the metal surface, or (B) multiple adsorption on (parts of) the metal surface. Both explanations have been proposed in the literature (*31–33, 16–18*). In fact the difference is not that great, subsurface hydrogen can be considered as being bound to subsurface metal atoms, or alternatively as being bound to surface atoms. In the latter case the metal surface atom is multiply coordinated by hydrogen.

Subsurface hydrogen has already been observed for, e.g., Pt(111), Ni(111), and Pd(111) by surface characterization techniques like XPS (*32*). Also, Yates *et al.* (*33*) have invoked subsurface hydrogen to explain the delayed desorption of H_2 from a H_2/D_2 covered Ru(0001) surface, while Konvalinka and Scholten (*31*) have explained the TPD results of Pd/C with subsurface hydrogen. Because the hydrogen solubility in the bulk of Pt, Rh, and Ir is rather low (*57*) the hydrogen can only be located just below the surface. Wells (*58*) has given an explanation for the different hydrogen absorption characteristics of the group VIII metals. He has related the degree of internal perfection of a metal particle to the amount of subsurface hydrogen (as determined by butadiene titration and deuterium exchange) and stated that the degree of perfection is determined by the height of the reduction temperature, relative to the Hüttig temperature. The Hüttig temperature is taken as one-third of the melting temperature, that is, the temperature at which surface mobility becomes possible. For Pt this Hüttig temperature is 682 K, for Rh 746 K, and for Ir 894 K. Especially in the case of Ir, the Hüttig temperature is not reached during reduction, and thus the existence of internal defects is expected. These defects might accommodate subsurface hydrogen atoms.

While for large particles it is difficult to attribute the differences in H/M for Ir, Rh,

and Pt to multiple adsorption or subsurface adsorption exclusively, it is much easier to make a choice for the small metal particles. In the small metal particles almost all metal atoms occupy a surface position, and the number of subsurface atoms is not sufficient to accommodate a large number of extra hydrogen atoms. Besides, subsurface hydrogen can never explain a hydrogen-to-metal stoichiometry above one, because subsurface adsorption sites need subsurface metal atoms in order to exist.

Therefore, we conclude that multiple adsorption on exposed metal atoms must be the main reason for the high H/M values observed by ourselves and others. For very small particles almost all metal atoms will have an edge or corner position, independent of the type of metal and thus we are left with the conclusion that certainly in the case of very small particles, high H/M values must be explained by high $H/M_{surface}$ stoichiometries.

Multiple hydrogen adsorption has mostly been considered for edge and corner metal atoms, and a H/M stoichiometry of 2 has been assumed (*16–18*). The results of our model calculations demonstrate that from a geometrical point of view high H/M values are acceptable, even those for the highly dispersed Ir catalysts with $H/M > 2.0$. Easing up our assumptions (no fcc structure for the smallest metal particles and more than one hydrogen atom filling an fcc vacancy at the surface of the metal particle), only results in still higher hydrogen-to-metal ratios. The calculations show that high H/M values can indeed be caused by multiple adsorption at the corners and edges of the metal particle. The extremely high H/M values found for the Ir catalysts lead to two possibilities on the basis of these calculations. Either a relatively large proportion of the metal surface atoms occupies a corner or edge position (irregular particle shape), or the H/M stoichiometry for corner and edge iridium atoms is relatively high. The first possibility is unlikely since in the EXAFS analysis no higher Debye–Waller fac-

tor has been found for the iridium systems (48), while a metal particle with many edges and corners is expected to have a high degree of disorder and thus a high Debye–Waller factor.

Although the model calculations indicate that there is room enough around the metal particles to accommodate a large number of hydrogen atoms, they do in fact not constitute proof that all these hydrogen atoms are really bonded strong enough to stay adsorbed at room temperature at a pressure of tens of kPa. Recently Christmann et al. (59) performed studies of hydrogen adsorption on the Ni(110) and Rh(110) surfaces and found that at higher hydrogen pressure the Ni, respectively Rh atoms in the exposed rows all adsorb 1.5, respectively 2 hydrogen atoms. This proves that for Ni a stoichiometry of H/Ni = 1.5 and for Rh a stoichiometry of 2.0 is at least possible.

The calculations do not make clear either why there is such a difference in H/M values for Pt, Rh, and Ir catalysts with the same dispersion, as shown in Fig. 4. The explanation for these questions must come from electronic arguments. The most simple explanation, differences in heats of adsorption for hydrogen on Pt, Rh, or Ir, does not seem to be valid, because these heats do not differ markedly (60). But the reported spread in the heats of adsorption is large and no real comparison for similar metal crystal surfaces at the same hydrogen coverage has been published yet. Theoretically one would indeed expect platinum to adsorb the least number of H atoms, because Pt has one (antibonding) electron more than Rh and Ir. The fact that Ir has a higher hydrogen adsorption capacity than Rh can be related to the larger size of 5d orbitals, which gives better overlap and stronger bonding.

But the difference in H/M values between Pt, Rh, and Ir can also be explained by taking a closer look at the analogy between the hydrogen-covered small metal particles (d < 15 Å) and transition–metal polyhydride complexes. This can be justi-

fied by the fact that these very small particles are not truly metallic, because they consist of too few atoms. Thus, by using ^{1}H NMR, Sanz and Rojo (52) have observed the similarity between the chemical shifts of chemisorbed hydrogen on Rh/TiO$_2$ at hydrogen pressures above 40 kPa, and of diamagnetic nonmetallic hydride coordination compounds of the transition–metal elements.

In the case of Pt, hydride complexes with H/Pt > 2 are rarely mentioned in the literature (54). Recently Minot et al. (61) performed extended Hückel calculations on the hydrogenation of small Pt$_n$ (n = 2–13) clusters and they reported stable complexes with rather high numbers of bonded hydrogen atoms and dihydrogen molecules. Thus for Pt$_4$ and Pt$_6$ clusters the maximum amount of hydrogen which could be bonded corresponded to the Pt$_4$H$_{16}$(H$_2$)$_2$ and Pt$_6$H$_{12}$(H$_2$)$_4$ complexes, respectively. These calculations indicated that in all cases the hydrogen atoms (hydride ions) were stronger bonded than the dihydrogen molecules and that the dissociation of the dihydrogen molecules in the complexes with maximum number of hydrogen and dihydrogen would lead to an increase, rather than a decrease in total energy.

While these theoretical results already suggest that dihydrogen molecules are much weaker bonded to a metal atom than hydrogen atoms, experimental results in the field of organometallics have presented convincing proof for this. Thus Kubas et al. (62) were the first to demonstrate that transition–metal complexes containing a coordinated dihydrogen molecule, bonded side-on in the η^2 mode, could be prepared. But the H$_2$ in their M(CO)$_3$(PR$_3$)$_2$(H$_2$) complexes (M = Mo, W and R = cyclohexyl, i-propyl) is extremely labile. Other authors have in the past years followed up on Kubas' work and have prepared other complexes in which one or two dihydrogen molecules are coordinated to a transition metal atom (63–68). In all cases the dihydrogen molecules are readily lost from these complexes and

only a few complexes were isolable in crystalline form. For that reason we have assumed that also in our case, with small metal particles on a support at room temperature under a pressure of a few tens of kPa, the bonding of dihydrogen molecules to the metal particles is very weak and that the experimentally observed H/M values have to be explained in terms of hydrogen atoms (hydride ions) bonded to metal particles only.

Besides direct quantum mechanical calculations such as the ones published by Minot *et al.* (*61*), also rules based on (semiempirical) theory might shed a light on the number of hydrogen atoms which can be bonded to a particular metal cluster. Based on a topological approach and coupled with chemical intuition backed up by semiempirical MO calculations, Wade (*69*), Mingos (*70*), Lauher (*71*), and Teo (*72*) developed rules to explain the existence of boron hydrides and metal carbonyl clusters. These rules have been very successful and can even explain the existence of high nuclearity clusters. Applying these rules to our metal particles, the binding of many hydrogen atoms to small metal clusters, with a resultant H/M stoichiometry above 1, is no surprise. Stoichiometries above 2 for Pt and above 3 for Rh and Ir are easily explained, if it is assumed that every H atom donates one electron. As examples we quote the existence of the $Pt_{38}(CO)_{44}H_{12}^{2-}$ and $Rh_{13}(CO)_{24}H^{4-}$ clusters, in which each CO molecule donates two electrons and each H atom one electron. According to the rules of Mingos, Lauher, or Teo this means that complexes like $Pt_{38}H_{100}^{2-}$ and $Rh_{13}H_{49}^{4-}$ might be stable, resulting in stoichiometries of $H/Pt = 2.6$ and $H/Rh = 3.8$, respectively.

Independent of the size of the metal cluster, all rules predict that all things being equal the H/M stoichiometry for a Pt atom should be smaller by one than for Rh and Ir particles, and that Rh and Ir should have equal stoichiometry. In essence the reason for that is the same as for mononuclear complexes, for which the 18-electron rule

holds for octahedral and trigonal bipyramidal symmetry and the 16-electron rule for square planar symmetry. Since Rh and Ir atoms have one valence electron less than Pt atoms, they can coordinate one one-electron donating ligand more than Pt can. Therefore Pt is expected to have the lowest H/M value, and indeed it has. When Rh and Ir atoms or ions have the same valency, they have an equal number of valence electrons and therefore they are expected to coordinate an equal number of ligands. A difference between Rh and Ir is that Ir can reach a higher valency than Rh, Ir^{4+} ions are more stable than Rh^{4+} ions. As the M–H band can formally be described as M^{+}–H^{-}, we expect higher polyhydrides for Ir. Indeed many higher Ir polyhydrides are known, with H/Ir even as high as 6, while Rh polyhydrides are more rare, and are only known up to $H/Rh = 5$ (*54*). This tendency is very clear in complexes of Ir and Rh that have the same ligands besides hydride ions. Thus Garlaschelli *et al.* (*73*) prepared $H_5Ir[P(i-Pr)_3]_2$ (i-Pr = isopropyl) from $HIrCl_2[P(i-Pr)_3]_2$, while the analogous procedure for Rh yielded only $H_2RhCl[P(i-Pr)_3]_2$. So the H/M stoichiometries in polyhydride complexes increase in the order Pt < Rh < Ir.

CONCLUSIONS

We conclude that the very high H/M values for the group VIII metals Pt, Rh, and Ir are due to multiple adsorption of hydrogen on metal surface atoms. Differences in H/M values are due to different valencies of the three metals and are completely in line with the observed order of stability of corresponding metal polyhydride complexes. We do not want to fully exclude hydrogen spillover or subsurface hydrogen as explanation, but we think that they give only minor contributions to the high H/M values observed.

The results of this study clearly show that hydrogen chemisorption measurements cannot be used directly to determine particle sizes of highly dispersed metals,

because of the uncertainty in the hydrogen-to-surface metal stoichiometry. Of course, for a particular metal the hydrogen chemisorption results can always be used to compare metal particle sizes in a qualitative way. But by means of the EXAFS technique a calibration can be made, and by using this calibration H/M values can be quantitatively related to the percentage of exposed metal atoms as shown in Fig. 4. At the moment, in this calibration we still have to rely on assumptions with regard to the metal particle shape. Thus in this work we relied on our model calculations to determine dispersion from metal coordination number. When in the future better EXAFS information becomes available, including second- and third-neighbor shells, then the calibration can really be made model independent.

ACKNOWLEDGMENTS

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