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Surface Organometallic Chemistry on Metals

I. Hydrogen and Oxygen Interaction with Silica-Supported and Alumina-Supported Rhodium

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In order to understand the reactivity of $Sn(n\text{-}C_4H_9)_4$ with supported rhodium, the chemisorption properties of silica-supported and alumina-supported rhodium toward O_2 and (or) H_2 has been investigated. It has been found that chemisorption of O_2 on rhodium is particle size dependent. At low particle size, bulk oxidation to Rh_2O_3 occurs at 300 K. At high particle size, surface oxidation to surface Rh_2O_3 occurs at 300 K and is followed by a slow bulk oxidation to Rh_2O_3. The rate of bulk oxidation can be increased considerably at 473 K. Chemisorption of H_2 on rhodium supported on silica or alumina occurs in two ways. Below 120 K, two forms of adsorbed hydrogen are present; above 260 K, only one form, an irreversibly adsorbed hydrogen, is observed. Both the results of chemisorption and those of thermodesorption suggest that below 120 K these two forms of hydrogen are present in equal amounts on the surface. For each form, the stoichiometry is close to one hydrogen atom per surface rhodium atom. Room temperature titration of the chemisorbed oxygen by hydrogen is possible according to the following equation, where y is the amount of adsorbed hydrogen (this value is pressure dependent):

$$Rh_2O_3/\text{support} + (3 + y)\ H_2 \rightarrow 3\ H_2O/\text{support} + 2\ (Rh - Hy)/\text{support}.$$

INTRODUCTION

It has been discovered in the last decade that rhodium supported on various inorganic oxides can be a very powerful catalyst for selective hydrogenation of CO and unsaturated functions as well as hydrogenolysis of hydrocarbons (*1–5*). More recently, silica-supported rhodium modified by an organostannic compound was found to exhibit a very good selectivity and a high activity in the hydrogenation of ethyl acetate into ethanol (*6*). In order to understand such a modification of catalytic properties of supported rhodium, we found it necessary to investigate the chemisorption properties of silica-supported and alumina-supported rhodium alone, before determining the modifications of these chemisorption properties due to the subsequent reaction with $Sn(n\text{-}C_4H_9)_4$, which we describe in the succeeding paper (Part II).

In every catalytic reaction carried out on supported metals, knowledge of the dispersion (fraction of surface metal atoms) is a very important parameter. Without this information no comparative catalytic studies can be made. There are two main ways for measuring metallic dispersion: the first is based on the determination of the particle size by electron microscopy, and the second on the selective adsorption of a given gas by surface metal atoms. For the first method, a hypothesis on the shape of the

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TABLE 1

Literature Data Regarding H_2 and O_2 Adsorption on Supported Rhodium

Ref.	% Rh(W)	Support	H/Rh[a]	O/Rh[a]	Temp. (K)	Size[c] (nm)	H/Rh_s[b]	O/Rh_s[b]	Remarks[d]
17	0.08	Al	0.99	1.06	300	—	1	1	a
17	0.44	Al	0.80	0.92	300	1.7	1	1	a
7	1.00	Al	1.16	—	300	1.5	1	—	b
24	2.00	Al	1.60	—	330	—	1	—	d
13	0.11	Al	1.40	—	300	—	1	1.5	e
13	1.06	Al	1.00	1.00	300	—	1	1.5	e
13	1.06	Al		1.40	473	—	1	1.5	e
13	2.09	Al	0.90	—	300	—	1	1.5	e
13	0.55	Si	0.55	—	300	—	1	1.5	e
14	5.00	Si	0.53	—	300	4.1	1	—	f
14	1.00	Si	0.94	—	300	1.2	1	—	f
14	0.30	Si	0.98	—	300	1.1	1	—	f
29	1.20	Al	1.20	—	290	—	1	—	b
29	0.92	Al	1.33	—	290	—	1	—	b
23	0.92	Al	1.33	1.50	300	2.5	1	1.5	g
23	2.95	Al	0.95	1.50	300	—	1	1.5	g

Note. Supports: Al, alumina; Si, silica.

[a] Experimental values; H or O atom/total Rh atom; see the column remarks.

[b] Assumed values; H or O atom/surface Rh atom.

[c] Particle diameter from electron microscopy, expressed in nanometers.

[d] Remarks:

(a) Volumetry, H_2, extrapolation to 0 mbar pressure from the pressure range 5–15 mbar.
(b) Volumetry, H_2, value measured at the equilibrium pressure of 130 mbar.
(c) Volumetry, H_2, extrapolation to 0 mbar pressure (no pressure range indicated).
(d) Pulses, H_2, H/Rh is the calculated value for the monolayer, deduced from the Langmuir hypothesis.
(e) Volumetry, H_2, extrapolation to 0 mbar pressure from the pressure range 130–650 mbar.
(f) Volumetry, H_2, horizontal part of the isotherm in the pressure range 60–130 mbar.
(g) Volumetry, H_2, irreversible fraction.

particles must be made, which can introduce discrepancies: for instance, with rhodium some authors suggest the presence of metallic rafts (*7*), while others consider spherical or cubooctahedral models for the particles (*8–9*). For the second method (CO, O_2, H_2 chemisorption), a hypothesis must be made regarding the stoichiometry of the gas adsorption.

Carbon monoxide, oygen, and hydrogen have all been used for selective adsorption. Because of the possibility of various types of bonding between CO and Rh surface atoms (linear, μ_2 bonded, μ_3 bonded) (*10–14*), this molecule does not give unambiguous results. With oxygen, the possibility of bulk oxidation (*13, 15*) constitutes an obstacle for the determination of surface rhodium atoms. There are also some problems with hydrogen. Most authors assume that the surface stoichiometry is 1 H/rhodium atom (*7, 14, 16, 17*) (Table 1). This assumption is generally supported by a comparison between the dispersions deduced from electron microscopic studies and volumetric measurements. In some cases, unsupported metal is used (*14*) and the stoichiometry is determined by the ratio between the specific area measured by the BET method and the hydrogen adsorption capacity. A detailed analysis of the published results indicates in fact that the value $H/Rh_s = 1$ is purely fortuitous (*18*). The shape of the isotherms is such that there is no valid method to extrapolate the isotherm to zero H_2 pressure at 298 K (*20*).

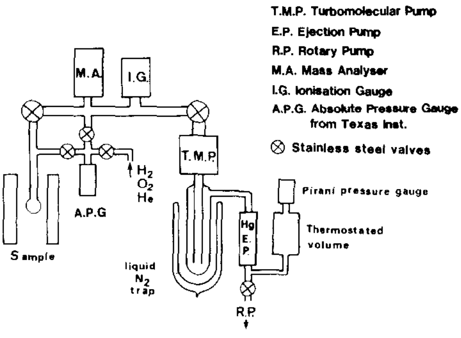

FIG. 1. Adsorption–desorption device.

Due to the complexity of the behavior of H_2 or O_2 chemisorption on supported rhodium, it therefore appeared necessary to investigate in detail the adsorption isotherm of these two gases on rhodium. Moreover, a careful study of the thermodesorption of the various types of chemisorbed hydrogen appeared necessary to have a better understanding of the rhodium–hydrogen system.

EXPERIMENTAL

1. Adsorption and Desorption Experiments

Adsorption–desorption experiments have been carried out using a UHV device. This includes a turbomolecular pump (Pfeiffer), stainless-steel valves, an ionization gauge, a mass spectrometer (V. G. Supavac), and Pyrex glass tubing (Fig. 1). The working pressure after outgassing the sample is usually lower than 10^{-7} mbar (1 mbar = 10^2 N m^{-2}). Equilibrium pressures ranging between 0.01 and 500 mbar are measured above the sample with a quartz "Bourdon" tube from Texas Instruments.

Adsorption isotherms are established step by step: the gas is admitted from a calibrated volume to the sample and the equilibrium pressure is continuously recorded. The temperature of the sample could be varied between 90 and 800 K. For adsorption measurements, the adsorbed volumes are measured with an accuracy of ±0.05 ml. This means that for a sample of 1% Rh, the adsorption isotherms are obtained with an accuracy close to 3%.

The thermal desorption curves are obtained by a slow increase in the temperature (ca. 20 K) followed by a plateau. For each step, the hydrogen desorbed from the sample is forced back into a glass reservoir by the pumping system. The rise in pressure in the reservoir measured by a conductance gauge gives the quantity of hydrogen evolved. With the mass spectrometer, it is checked that only hydrogen is present, water eventually desorbed from the sample being condensed into a liquid nitrogen trap. Each increment of temperature is maintained as long as hydrogen partial pressure is lower than 10^{-8} mbar. Consequently the thermodesorption curves are integral ones. Desorbed quantities are obtained with roughly the same precision as adsorbed quantities.

2. Determination of Particle Size

The particle sizes have been measured by direct transmission electron microscopy (JEOL). For each histogram, approximately 200 particles have been measured.

3. Materials

Ultrahigh-purity "Air Liquide" gases (adsorbates or reactants) have been dried by passage through a zeolite column.

Two types of catalysts have been prepared, namely Rh/Al_2O_3 and Rh/SiO_2. On alumina(cubic, 250 m^2 g^{-1}), rhodium is impregnated from a rhodium trichloride solution. Impregnation is obtained by competition with chloride ions presumably according to the equation

$$[RhCl_6]^{3-} + 3(\equiv Al\text{-}OH) \rightarrow [\equiv Al]_3^+[RhCl_6]^{3-} + 3OH^-$$

It has been found by X-ray analysis that the rhodium dispersion on the alumina surface is homogeneous (*21*). Two samples Rh/Al_2O_3 **A** and Rh/Al_2O_3 **B** with, respectively, 0.88 and 0.27 wt.% Rh have been prepared in this way. On silica (Aerosil, Degussa, 300 m^2 g^{-1}), the rhodium is deposited by exchange of the acidic sites of the support by $RhCl(NH_3)_5^{2+}$, with ammonium as competitor ions:

$$\equiv Si{-}OH + NH_4OH \rightarrow \equiv Si{-}O{-}NH_4 + H_2O$$

$$[RhCl(NH_3)_5]^{2+}, \quad 2Cl^- + 2\equiv Si{-}O{-}NH_4 \rightarrow 2[\equiv Si{-}O{-}]^-[RhCl(NH_3)_5]^{2+} + 2NH_4Cl.$$

In both cases, after 24 h of contact between the solution and the solid, the solid is filtered and air dried at 383 K. It is then calcined at 673 K in flowing dry air and reduced at the same temperature in flowing hydrogen. The amount of rhodium thus deposited is respectively 0.88 and 0.27 wt% for Rh/Al_2O_3 **A** and **B**, and 1.0 and 1.3 wt% for Rh/SiO_2 **A** and **B**.

In order to achieve a low dispersion of the rhodium, one sample of silica-supported catalyst Rh/SiO_2 **A** has been sintered under vacuum at 873 K for 10 h to give Rh/SiO_2 **C**.

When the sample is treated under dry hydrogen at high temperatures, strong metal–support interaction (SMSI) (*22*) can minimize greatly the adsorption capacity of the so-called metallic phase. This phenomenon depends on the nature of the support and can be minimized with inert supports such as alumina and silica if the thermal treatment under H_2 is carried out below 673 K (*23*). We therefore limited this study to catalysts treated under conditions where no SMSI occurs.

RESULTS

1. Determination of the Dispersion by Electron Microscopy (E.M.)

For reduced Rh/Al_2O_3 **A** and **B** no particles are detected by CTEM; their size must therefore be below 0.8 nm which is the limit below which our microscope does not detect particles. However, the presence of rhodium is detected by X-ray analysis (*21*).

For Rh/SiO_2, particles are detected by CTEM. The particle size distributions for two typical samples **A** and **C** are shown in Fig. 2. In both cases the particles are homogeneous in diameter with a maximum at 1 nm for the Rh/SiO_2 **A** and 2 nm for the Rh/SiO_2 **C**. No rhodium was detected by X-ray analysis (STEM) outside the observed particles. This suggests that in contrast to alumina, silica-based catalysts do not contain ultradispersed particles with a size below 0.8 nm.

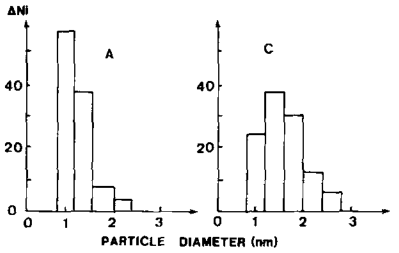

FIG. 2. Particle size distribution deduced from electron microscopy. Left, Rh/SiO_2 **A**; right, Rh/SiO_2 **C**.

2. Hydrogen and Oxygen Adsorption

Before each adsorption measurement, the samples are treated under hydrogen for 2 h at 573 K and then evacuated at 673 K until the equilibrium pressure is below 10^{-8} mbar. At this temperature, strong metal–support interaction does not occur and the metal is completely reduced (*23*).

After reduction under hydrogen (200 mbar, 473 K), desorption under vacuum at 673 K, and adsorption under ca. 100 mbar at 300 K, the quantity of adsorbed hydrogen for each sample is shown in Table 2 (experiment 1). If the sample is then heated to 673 K under hydrogen in a closed volume for 1 h and cooled to 300 K, the quantity of adsorbed hydrogen does not change Table 2, experiment 3). This result confirms that the samples are stable in size and composition; it also indicates that the reduction is achieved already at 473 K and that no spillover adsorption could be involved, as this phenomenon would be an activated mechanism and then would increase when the temperature rises.

Typical hydrogen adsorption isotherms

TABLE 2

H_2–O_2 Interaction with Supported Rhodium

Samples	Experiment number[a]								
	1 H/Rh	2 H/Rh	3 H/Rh	4 H/Rh	5 O/Rh	6 H/Rh	7 H/Rh	8 O/Rh	Part. diam.[b] E.M. (nm)
Rh/SiO_2 **A**	1.11	1.30	1.12		1.45	3.90	1.10	1.40	1.5
Rh/SiO_2 **B**	1.10	1.30	1.10	1.20	1.30	3.90	1.10	1.40	1.5
Rh/SiO_2 **C**	0.65	0.80	0.66	0.68	1.40	3.45	0.65	1.45	2.0
Rh/Al_2O_3 **A**	1.50	1.85	1.52	1.20	1.43	4.52	1.50	1.50	1.0
Rh/Al_2O_3 **B**	1.40	—	1.45	—	1.50	4.40	—	1.50	1.0

[a] Experiment number:

(1) Hydrogen adsorption for an equilibrium pressure of 100 mbar at 300 K.

(2) Hydrogen adsorption for an equilibrium pressure of 100 mbar at 170 K.

(3) Hydrogen adsorption after heating under 100 mbar of hydrogen at 673 K for 2 h, measured at 300 K.

(4) Oxygen adsorption extrapolated at zero time.

(5) Oxygen adsorption after heating under 100 mbar of oxygen at 473 K for 2 h, measured at 300 K.

(6) Hydrogen consumption under 100 mbar of hydrogen at 473 K for 2 h, measured at 300 K, after experiment 5.

(7) Hydrogen desorption (under vacuum at 673 K) after experiment 6.

(8) Oxygen reduced, deduced from [(H/Rh expt. 6) − (H/Rh expt. 7)]/2.

[b] Part. diam. E.M. (nm), average particle diameter from electron microscopy.

in the range 0–500 mbar are represented in Fig. 3. No measurable adsorption occurs on the two supports alone. With rhodium on silica or alumina, adsorption isotherms at 300 K exhibit a pseudo-level above 100 mbar, but there is no real plateau. At lower temperatures (below 173 K), the adsorption isotherms have roughly the same shape but with higher values for H/*M*. The results obtained are summarized in Table 2.

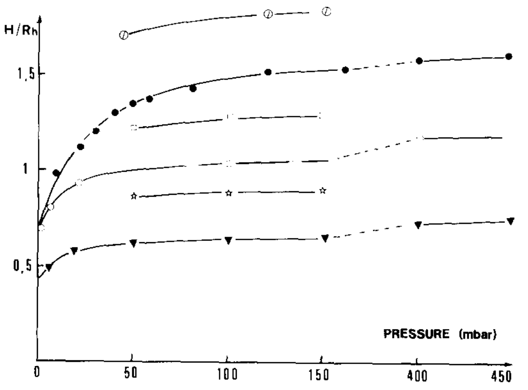

FIG. 3. Hydrogen adsorption isotherms. Rh/SiO_2 **A**, 300 K (○); 173 K (□). Rh/SiO_2 **C**, 300 K (▼); 173 K (☆). Rh/Al_2O_3 **A**, 300 K (∅); 173 K (●).

With oxygen, it is impossible to have an adsorption isotherm since for a given pressure, the O/Rh value increases slowly with time. Nevertheless, an extrapolated value to zero time can be determined (Fig. 4 and Table 2, experiment 4). If the samples are heated under oxygen (100 mbar) at 473 K for 1 h and then cooled to 300 K, the resulting value obtained is constant with time (Fig. 4 and Table 2, experiment 5). For the three catalysts this value is close to 1.5

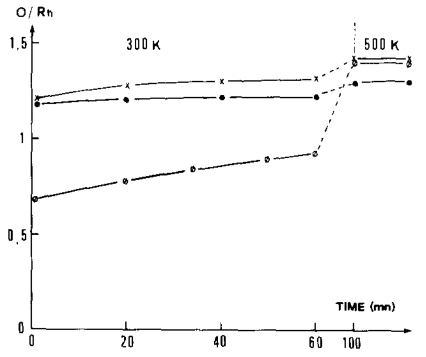

FIG. 4. Oxygen adsorption at 300 and 500 K: Rh/SiO_2 **A** (x), Rh/SiO_2 **C** (∅), Rh/Al_2O_3 **A** (●).

O/Rh total, which corresponds to the formation of bulk Rh_2O_3.

3. Hydrogen–Oxygen Interaction

If hydrogen is admitted to oxygen-covered rhodium, at a given pressure $P(H_2)$, a reaction occurs. This reaction of water formation and H_2 adsorption depends on both the temperature and the amount of O_2 adsorbed. At room temperature, reduction could be incomplete if the sample is fully oxidized; in contrast at 473 K reduction is fast and complete regardless of the oxidized sample. The determination of the stoichiometry of the reaction at 473 K between adsorbed oxygen and gaseous hydrogen is carried out on partially or fully oxidized samples (Rh_2O_3). After reduction at 473 K under 200 mbar of H_2, the sample is cooled to 300 K. The amount of H_2 consumed by the reduction (Table 2, experiment 6) and desorbed subsequently (Table 2, experiment 7) is determined. By subtraction of the H/Rh values for experiments 6 and 7 (Table 2), the amount of oxygen atoms reduced by hydrogen can be deduced (experiment 8). Comparison of H/Rh values in experiment 7 with H/Rh values in experiment 1 shows an excellent agreement for the number of H atoms chemisorbed. Comparison of O/Rh values in experiment 8 with O/Rh values in experiment 5 also gives an excellent agreement for the number of O atoms chemisorbed. The following reaction stoichiometry can be therefore deduced from the results,

$$RhO_x/\text{support} + (x + y/2)H_2 \rightarrow RhH_y + xH_2O/\text{support},$$

where x is the quantity of O atoms fixed by the sample and y the quantity of H atoms adsorbed on the catalyst at the equilibrium pressure $P(H_2)$, (Fig. 3).

4. Hydrogen Thermodesorption

For the three representative samples Rh/Al_2O_3 **A** and Rh/SiO_2 **B** and **C**, the thermodesorption curves in the temperature range (100–600 K) are shown in Figs. 5 and 6. On alumina or silica alone, no desorption of hydrogen occurs.

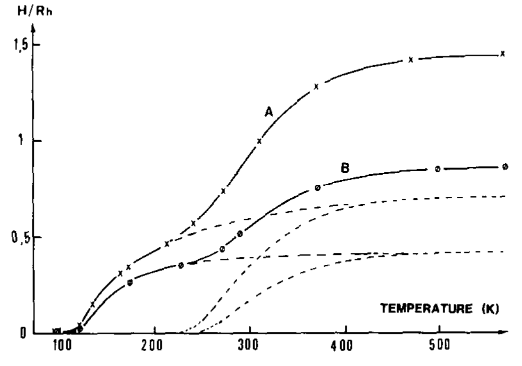

FIG. 5. Hydrogen thermodesorption from Rh/SiO_2 **A** and **B**. Dotted lines are the extrapolated curves.

In all cases, the total amount of hydrogen desorbed is very close to the value of hydrogen adsorbed at 173 K under an equilibrium pressure of 200 mbar (Fig. 3 and Table 2). Clearly, the hydrogen desorbs in two steps, the first (B_1) beginning at 110 K and the second (B_2) at ca. 250 K. By extrapolating the low-temperature part of the curves, we are able to identify two species A_1 and A_2 of adsorbed hydrogen. The quantity corresponding to each species can be determined (Figs. 5 and 6). For each sample, the ratio A_1/A_2 is roughly equal to 1, regardless of the total amount of adsorbed hydrogen.

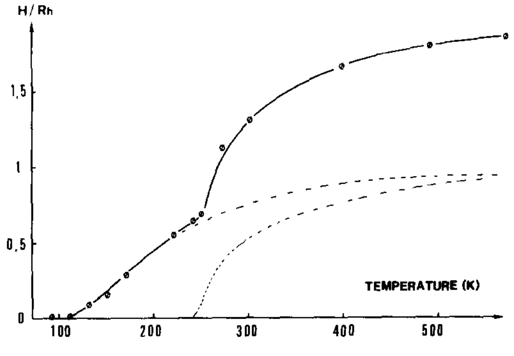

FIG. 6. Hydrogen thermodesorption from Rh/Al_2O_3 **A**. Dotted lines are the extrapolated curves.

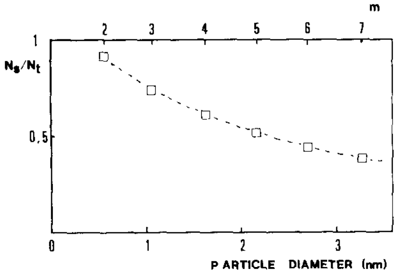

FIG. 7. Dispersion (N_S/N_t) versus particle diameter assuming a cubooctahedral shape (m is the number of layers).

DISCUSSION

The purpose of our work was to determine the stoichiometry of adsorption of H_2 or O_2 with surface and (or eventually) bulk rhodium supported on silica or alumina, in order to understand the possible modification due to the reaction of organometallic compounds with rhodium surfaces (*6*).

Particle Size Distribution

On alumina, no metallic particles are detected by electron microscopy. In that case the size of the rhodium particles must be lower than 0.8 nm, according to the resolution limit of the electron microscope used. The shape of the particles could not be determined. Yates *et al.* (*7*), by IR spectroscopy and ultrahigh-resolution microscopy, suggest the presence of ultradispersed rhodium rafts on alumina. Whatever the shape of the particles, rhodium would be fully dispersed on the surface.

On silica, particle sizes ranging between 1 and 1.5 nm, with a maximum close to 1 nm, are detected on Rh/SiO_2 **A** and **B**. With Rh/SiO_2 **C**, the particle size ranges between 1.5 and 3 nm. From electron microscopic studies, no metallic rafts seem to be detected. By high-resolution weak-beam electron microscopy, Yacaman *et al.* (*8*) have shown that on silica, rhodium particles (1–2.5 nm) have an icosahedral or decahedral structure and that the smallest ones have a non-fcc icosahedral structure. For example, the 1-nm particles contain 50 rhodium atoms each, with only ca. 3 bulk atoms. From the calculations of van Hardeveld and Hartog (*27*) relating to ideal cubooctahedral particles, it is possible to correlate the dispersion with the particle diameter (Fig. 7). Assuming such a geometry for our samples, we can deduce a dispersion of 80% for Rh/SiO_2 **A** and **B** and 50% for Rh/SiO_2 **C**.

Behavior of H_2 on Metallic Rhodium

Chemisorption of hydrogen on rhodium was already investigated by numerous authors (see Table 1 and Fig. 8). Some people observe a stoichiometry of one hydrogen atom per surface rhodium, while others find higher values (Table 1). Consequently the possibility of having more than one H atom adsorbed per Rh atom should not be excluded.

In the determination of a true surface stoichiometry, the main difficulty arises from the definition of standard conditions of adsorption (pressure, temperature, method). Figure 8 indicates, on the same graph, the results obtained by several authors. Although the results, for each support, are not drastically different, the authors claim different stoichiometries. For instance, Fuentes and Figueras (*17*) extrapolate the isotherm to zero pressure at 300 K and claim the stoichiometric value of 1

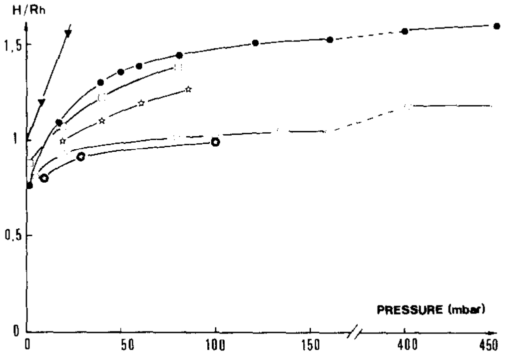

FIG. 8. Hydrogen adsorption isotherms on supported rhodium. Comparison between data from various studies. ▼, From Ref. (*17*); □, from Ref. (*22*); ⊙, from Ref. (*14*); ☆, from Ref. (*27*); ●, this work; ○, this work.

H/Rh_s while others, taking the adsorption value at 300 K, 100 mbar, suppose a value higher than unity. Moreover, there is no real fundamental basis to make a distinction between "reversible" and "irreversible" adsorption of H_2, since this reversibility is temperature dependent. At 80 K, we find that all the hydrogen is "irreversibly" adsorbed.

First, we should recall here that we never heat the sample at a temperature higher than 673 K under hydrogen, so that SMSI does not occur (*22, 23*). Moreover, no "irreversible" H_2 adsorption occurs on silica or alumina support even at 80 K; the chemisorbed quantity being proportional to the metallic surface, physisorption must not be involved in the thermodesorption curves. Second, it has been found that after reduction under hydrogen at 473 K, the chemisorption and thermodesorption experiments are reproducible many times.

On both supports, thermodesorption curves from 90 to 673 K show clearly two steps of hydrogen desorption. The first one begins at 120 K and is practically achieved at ca. 270 K with a maximum of the differential curve close to 140 K. The second begins at 240 K and finishes above 573 K with a maximum between 260 and 320 K. These results are in perfect agreement with the work of Yates *et al.* (*25*) who obtain two thermodesorption peaks for hydrogen adsorbed on Rh(111), the main one at 270 K and a second one at 120 K. Similar results were previously obtained by Mimeault and Hansen (*26*) on polycrystalline Rh (150 and 290 K). It is interesting to note that these results are obtained on unsupported samples; consequently the low-temperature desorption species could not be attributed to adsorption on the support.

Our results indicate clearly the following:

(a) at saturation, the global stoichiometry of hydrogen chemisorption is higher than unity and probably close to 2H/(surface Rh atoms);

(b) two chemisorbed hydrogen species, A_1 and A_2, are detected on rhodium, roughly in equal quantities.

These results are in agreement with those already obtained by two of us on Pt (*9*). In fact, rather than two types of adsorbed hydrogen, one may reasonably assume that there are roughly two types of *situation*, B_1 and B_2.

At high coverage and low temperature, the two types of chemisorbed hydrogen are simultaneously present so that desorption of H_2 from B_1 situation is an easy process. At half-coverage (i.e., at a temperature close to 260 K) situation B_2 would be the main state for adsorbed hydrogen and desorption would require a higher activation energy to have the two hydrogens in close proximity. In this model, in agreement with the process of microscopic reversibility, H_2 should be dissociated on a single rhodium atom to give at low coverage the situation B_2 and at higher coverage, the situation B_1.

One may now speculate on the B_1 and B_2 situations. There are many possible interpretations. The most obvious would be to assume that in the B_1 situation, H would be present in both a linear and a multibonded type. In the B_2 situation, after elimination of one-half of a monolayer, the remaining hydrogen would be only multibonded.

A more sophisticated situation could be eventually proposed from what is known about the "state" of hydrogen in molecular clusters such as $(Rh_{13}(CO)_{24}H_{5-n})^{n-1}$ with $n = 2$ or 3. In these clusters, it has been proved by ^1H NMR (*28*) that the two hydrogens are present in both tetrahedral and octahedral cavities of the hexagonal close-packed cluster. We have no proof to suggest that this situation is relevant to the surface situation but at least this "interstitial" hydrogen on the rhodium surface constitutes a hypothesis which cannot be ruled out for the B_2 situation.

Oxygen Adsorption and Subsequent Reaction with Hydrogen

As shown in Fig. 4, no stable value of oxygen adsorption at 298 K can be obtained. Progressive bulk oxidation seem to be involved as already suggested by Wanke and Dougharty (*13*) even at 300 K. Stable values corresponding to the formation of Rh_2O_3 are obtained by heating the sample at 473 K. It is possible that this process begins by a fast surface oxidation followed by a slow bulk oxidation. This surface reaction can be easily deduced from the data of Fig. 2 where at zero time, the O/Rh surface value corresponds to the stoichiometry $Rh(surface)_2O_3$. It is only after heating at 473 K that bulk Rh_2O_3 is obtained.

Our findings for reduction of Rh samples agree well with the results published by Yates *et al.* (*11*) and confirm that reduction of oxidized rhodium particles on Al_2O_3 and SiO_2 is total at 473 K under hydrogen.

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