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Interaction of Hydrogen, Oxygen, and Carbon Monoxide with Supported Rhodium

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Uptakes of hydrogen, oxygen, and carbon monoxide and the volumetric hydrogen titration of preadsorbed oxygen were investigated for a series of Rh/η-Al_2O_3 catalysts, under a variety of conditions. Behavior toward these gases was complex and differed markedly from that which has been reported for supported-platinum catalysts.

INTRODUCTION

A variety of metal catalysts is employed in the form of metal dispersed on a high-surface-area support. Since it was first demonstrated that selective gas chemisorption techniques could be used to measure the surface areas of supported-platinum catalysts, there has been a rapidly growing interest in this type of study [see reviews by Schlosser (*1*) and Muller (*2*)], as a tool for studies of catalysts and catalysis.

Platinum has been studied rather extensively by selective gas adsorption techniques, leading to the observation that platinum on silica, alumina, and silica–alumina can be prepared in extremely high dispersions and to general agreement on the interpretation of the adsorption data. Other metals have been investigated much less. While one may expect important similarities among platinum-group metals, the significance of their differences to both fundamental and practical catalysis warrants a careful investigation of the determination of the surface areas of other supported platinum-group metals.

A study of rhodium/silica catalysts has been reported by Yates and Sinfelt (*3*), in which surface-area measurements were obtained from adsorption of hydrogen or carbon monoxide. We report here a study of a series of catalysts consisting primarily of rhodium/alumina, including data on the uptakes of carbon monoxide, hydrogen, and oxygen and on volumetric titrations of preadsorbed oxygen and hydrogen (*4*).

EXPERIMENTAL METHODS

Equipment

Gas adsorption measurements were carried out in a conventional Pyrex volumetric adsorption apparatus. A mercury diffusion pump provided dynamic vacua of 10^{-6}–10^{-7} Torr. Pressures could be measured (10^{-4}–2 Torr) immediately above the catalyst sample cell with a glass-bead thermistor pressure gauge (Victory Engineering Corp., Springfield, NJ, thermistor set A-58), in addition to the usual mercury manometer. A glass pinhole leak was provided between buret and sample cell, to permit the slow, controlled introduction of gases to the catalyst samples.

Reagents

Palladium-diffused hydrogen produced by a Matheson electrolytic hydrogen generator was used throughout, both for cata-

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lyst reductions and for uptake measurements. Matheson oxygen (Extra Dry grade), carbon monoxide (CP grade), and helium (Ultra High Purity grade) were used for uptake and dead-volume determinations.

Catalyst Preparation

Catalyst supports were Davison Grade 992 η-alumina powder (—200 mesh) and Grade 926 silica gel (ground to —120 mesh). Rhodium black (98% minimum purity) and rhodium trichloride were obtained from Engelhard Industries.

Catalysts were prepared by impregnation of the supports with aqueous solutions of rhodium trichloride. An amount of solution was used such that mixing with the powdered support gave a slurry with a minimum of excess liquid. The slurry was stirred intermittently for several hours and then left partially uncovered at room temperature for 2–4 days, during which time the free water evaporated. The catalysts were then dried in air at 105°C for 20 hr and stored.

Catalyst Pretreatment

Inasmuch as it has been suggested that differences in pretreatment may account for some of the variations reported for gas adsorption by supported platinum, considerable attention was given to pretreatment procedures. Newkirk and McKee (*5*) have reported that reduction of alumina-supported rhodium trichloride begins at approximately 100°C and appears to be essentially complete at 200°C. It was found in the present study that no detectable differences in gas uptakes occurred upon treatment in hydrogen or vacuum at 500°C over periods ranging from 2 to 48 hr. Even exposure of a 5% Rh/Al_2O_3 catalyst to 750°C for eight hours in hydrogen resulted in a reduction of oxygen uptake of only approximately 5%. Evacuation after reduction was carried out at 500° and 550°C for periods of 1–25 hr. The data indicated that 1 hr of evacuation might be insufficient, but a period of 2–25 hr resulted in reproducible adsorption measurements. Hydrogen removal from supported rhodium thus appears to take place more readily than from supported platinum, since these latter results are contrary to the findings of Gruber (*6*) and of Mears and Hansford (*7*) with the latter metal. A lengthy reduction period is not necessary for the reduction of the rhodium trichloride, but it helps to stabilize the support.

Based on these observations a standard pretreatment procedure was adopted, consisting of the following steps: (1) evacuating the sample at room temperature for one-half hr, (2) heating to 150°C for 3 hr while evacuating, (3) passing hydrogen at 75 cm^3 (STP)/min over the catalyst while raising the temperature to 500°C over a period of approximately 2 hr, (4) maintaining the sample at 500°C for 10–14 hr (overnight) in flowing hydrogen, (5) evacuating at 500°C for 2 hr, and (6) cooling to adsorption temperature in vacuum over a period of one-half to one hr.

Pretreatment was carried out *in situ*. In cases where the same catalyst charge was used for more than one experiment, the complete pretreatment procedure was repeated prior to each experiment. At least five pretreatment cycles could be carried out without reducing hydrogen uptake by more than 5% for a catalyst containing 1% rhodium on alumina.

Standard Gas-Uptake Procedure

After the pretreatment procedure, gas addition to the catalyst sample was carried out either by opening a glass stopcock or by introducing the gas to the catalyst bulb through a pinhole leak at rates of 1–50 μmole/min, until the pressure over the sample rose sharply. These two methods of gas addition are referred to below as "fast addition" and "slow addition," respectively. Times for slow introduction of the gas were typically one-half to one hr. A period of one-half to one hr was then allowed for equilibration before reading volume and pressure. The shorter equilibration times were, in general, associated with the higher adsorption temperatures (200°C and above). Subsequent points at different pressures were obtained at intervals of approximately 15 min.

At the end of many runs the sample cell was quantitatively evacuated by means of a Toepler pump. Pumping was stopped when the pressure in the sample cell reached approximately 0.01, 0.1, or 0.3 Torr, depending on whether the adsorbate was oxygen, hydrogen, or carbon monoxide, respectively. The pumping time required to attain these pressures was approximately one-half hr. Sample-cell dead volumes were obtained with helium.

Catalyst Sintering

All freshly prepared catalysts showed high dispersions as indicated by adsorption uptakes, X-ray line broadening, and electron microscopy. Less well dispersed samples were prepared by sintering. Heating in hydrogen or vacuum at temperatures as high as 750°C was not effective in inducing appreciable crystallite growth. Heating in oxygen at this temperature and below was found to result in substantially reduced gas uptakes after a standard pretreatment. Sintering at 700°C for 3 hr in oxygen at atmospheric pressure reduced the hydrogen uptake by a 5% Rh/Al_2O_3 catalyst to approximately one-half its initial value, while 8 hr at 750°C for another sample of the same catalyst reduced the uptake to approximately one-sixth the initial value.

Electron Microscopy and X-Ray Diffraction

Several of the catalysts were examined with a Siemens or a JEM-7A electron microscope. Samples were prepared either by dusting the catalyst powder onto a Formvar-coated 200-mesh copper grid or by placing on such a grid a drop of ethanol in which the catalyst had been suspended by ultrasonic treatment. Micrographs were taken at magnifications of 5×10^4–3×10^5.

X-Ray line-broadening determinations were made using a General Electric Model XRD6 diffractometer employing copper $K\alpha$ radiation. Rhodium crystallite sizes were calculated from X-ray diffraction patterns using the width of the (111) and (200) rhodium peaks at half-height. Instrumental broadening was determined using a quartz reference sample, and relationships given by Klug and Alexander (*8*) were used to correct for $K\alpha$-doublet broadening and instrumental broadening.

Rhodium Black

Total surface areas of samples of rhodium black were determined by the BET technique, using krypton at −196°C as adsorbate.

RESULTS

Adsorption by Supports

Since the supported metal makes up only a small fraction of the total surface area of a catalyst such as those prepared here, gas uptake by the support requires careful consideration. Adsorption isotherms for hydrogen, oxygen, and carbon monoxide on η-alumina and silica gel are shown in Figs. 1–4 for temperatures used in this study.

For hydrogen and oxygen the isotherms were linear at pressures above a few Torr, up to the maximum pressure of 600 Torr used in this study. In the case of oxygen, the isotherms extrapolate linearly to zero uptake at zero pressure. For hydrogen, linear extrapolation for temperatures of 0°C and higher gives small positive intercepts on alumina ($\simeq 0.5$ μmole/g). Adsorp-

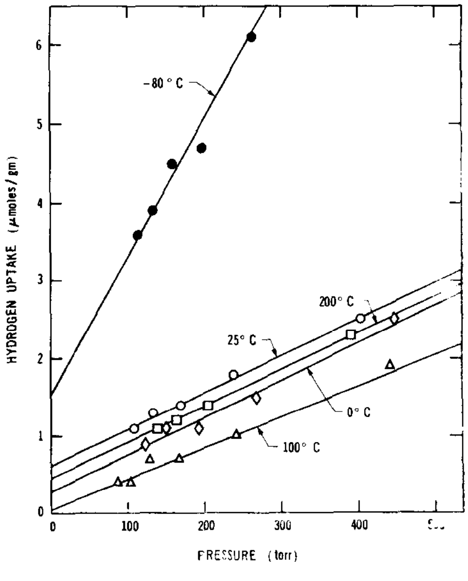

FIG. 1. Hydrogen adsorption on η-Al_2O_3.

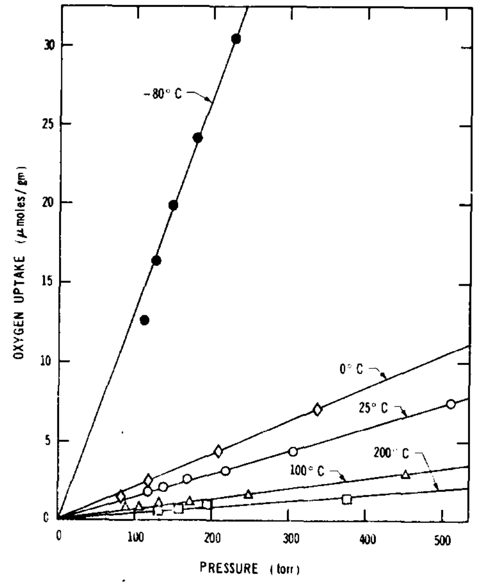

FIG. 2. Oxygen adsorption on η-Al_2O_3.

tion isotherms for samples containing supported metal were also found to be linear at pressures above about 100 Torr. Consequently, correction for uptake by the supports was made following the method of Benson and Boudart (*9*) of extrapolating the linear higher-pressure region of the isotherms to zero pressure. For hydrogen, intercepts obtained in this manner were reduced by amounts corresponding to the intercepts obtained for the support alone.

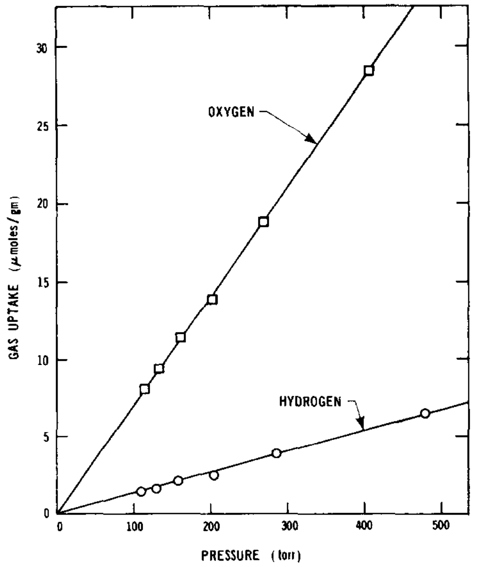

FIG. 3. Oxygen and hydrogen adsorption on silica at 25°C.

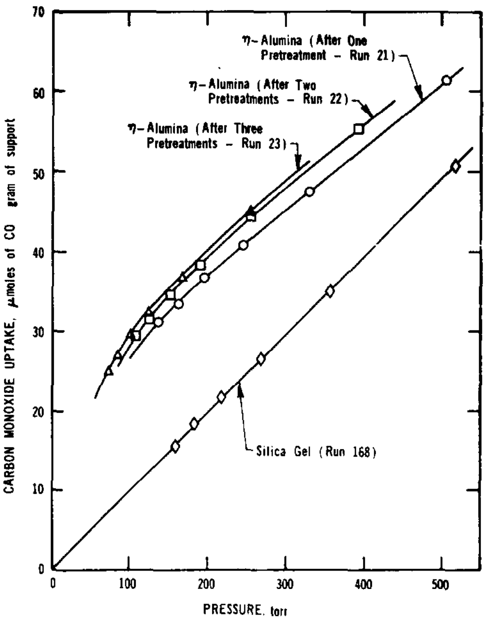

FIG. 4. Carbon monoxide adsorption on η-alumina and silica gel.

An experimentally convenient aspect of linear extrapolation to zero pressure which does not seem to have been pointed out is that the intercept is independent of the dead volume. 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. Data reported here, however, were obtained using helium dead volumes, so that the uptakes at finite pressures are actual values.

For a sample of η-alumina treated at 750°C in flowing oxygen for 8 hr, followed by the standard pretreatment, uptakes increased by approximately a factor of three for both hydrogen and oxygen. The isotherms were still linear, but the intercept values were increased to 1.8 and 2.4 μmole/g for hydrogen and oxygen, respectively. These latter correspond to a correction of only 0.01 atom of gas per rhodium atom for the 5% Rh/Al_2O_3 sample, which was the only one subjected to this sintering procedure.

To attempt to determine whether the HCl formed during the reduction of the $RhCl_3$-impregnated alumina altered the adsorption characteristics of the η-alumina, samples were treated with HCl in two different ways. A sample was impregnated with a solution of HCl at a level of 0.53 g HCl/g Al_2O_3 (equivalent to the chlorine in a 0.5% Rh/Al_2O_3 preparation), and hydrogen adsorption at 25°C was measured. The slope of the isotherm was essentially the same as for untreated alumina, and the intercept was approximately 0.2 μmole/g, slightly less than for the untreated alumina. In another experiment, hydrogen containing HCl was passed through the sample while it was being heated from 150 to 300°C (it was in this temperature interval that most HCl formation occurs in the reduction of impregnated catalysts (*5*)). The total amount of HCl introduced was approximately 200 μmoles HCl/g Al_2O_3. The oxygen and hydrogen uptakes of this sample, measured at 25°C after the standard pretreatment, were practically identical to the uptakes of the η-alumina that had not been treated with HCl. It thus appears doubtful that generation of HCl during catalyst reduction significantly affected the observations reported below.

The carbon monoxide uptake by alumina was much larger than that for hydrogen or oxygen, and the isotherm was nonlinear below about 150 Torr. For this gas, then, the net uptake by the metal was obtained by subtracting the blank for the support from the total uptake by a catalyst. The results of this procedure are discussed below.

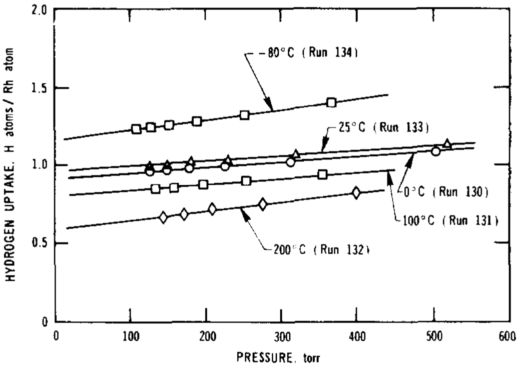

FIG. 5. Hydrogen adsorption uptakes at various temperatures for 1.06% $Rh/\eta-Al_2O_3$.

Hydrogen Adsorption

Hydrogen adsorption isotherms at temperatures from −196 to 300°C were measured for various alumina-supported rhodium catalysts. Typical results are shown in Fig. 5, uncorrected for the blank. Linearly extrapolated zero-pressure uptakes, corrected for blank intercepts, are plotted as functions of temperature in Fig. 6 for several catalysts.

The room-temperature region of the hydrogen isotherms was selected for further investigation. Data are shown in Fig. 7 for the uptake of hydrogen at 25°C by a series of Rh/Al_2O_3 catalysts. These data

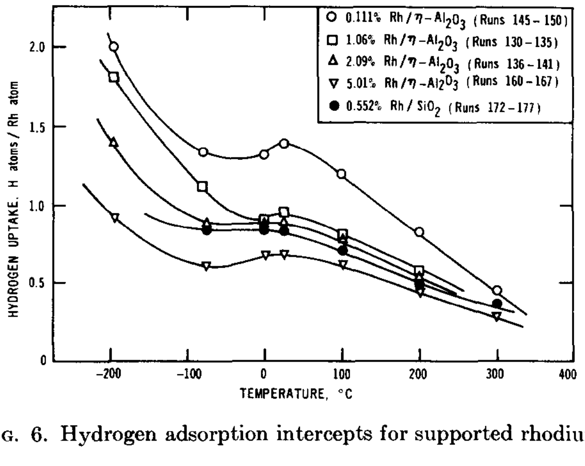

FIG. 6. Hydrogen adsorption intercepts for supported rhodium.

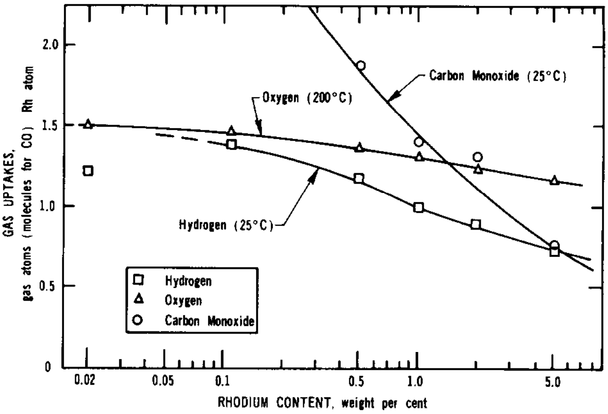

FIG. 7. Hydrogen, oxygen, and carbon monoxide uptakes for unsintered Rh/η-Al_2O_3 catalysts.

are all extrapolated zero-pressure intercepts, corrected for blanks and reported as atoms of hydrogen taken up per rhodium atom in the catalyst sample. Hydrogen uptake data for a sample of 5% Rh/Al_2O_3 which had been sintered in oxygen at 750°C for 8 hr prior to pretreatment gave a value of 0.11 H atoms/Rh atom at 25°C. Hydrogen uptake at 25°C by the 0.55% Rh/SiO_2 catalyst was 0.85 H atoms/Rh atom. Hydrogen adsorption was also measured on a sample of rhodium black at 25°C (Table 1). The difference in hydrogen adsorption for slow and fast addition of hydrogen to samples was very slight and no more than the experimental uncertainty. The hydrogen adsorption is reversible, and the measured uptakes evidently represented equilibrium or near-equilibrium values.

Oxygen Uptakes

Oxygen uptakes were measured at a variety of temperatures for samples given the standard pretreatment. In all cases the plots of oxygen uptake versus pressure were linear for pressures of 50–600 Torr. Uptakes obtained after evacuation with the Toepler pump usually were slightly higher than the linearly extrapolated zero-pressure uptakes. Slow oxygen uptakes following the initial rapid uptake were observed in the present work with supported rhodium, and the difference between the intercept uptake and the uptake after evacuation may be due wholly or in part to this slow uptake. However, even at 300°C the slow uptakes were never more than 5% of the total uptakes over the approximately 2 hr required to measure adsorption uptakes. The oxygen uptakes reported here are linearly extrapolated zero-pressure intercepts.

Figure 8 shows oxygen uptakes as functions of temperature for catalysts containing 0.1% and 1% rhodium on alumina, for both fast and slow addition for each catalyst. These are representative of the be-

TABLE 1
GAS UPTAKES BY RHODIUM BLACK

Gas	Temperature (°C)	Gas uptake (μmoles/g)	Gas uptake atoms/(surface Rh atom)	Kr BET uptake (μmoles/g)
H_2	25	11.3	1.13	8.1
O_2	−80	11.9	1.07	9.0
O_2	25	15.3	1.44	8.6
O_2	200	28	2.5	9.2
O_2	300	66	5.4	9.9

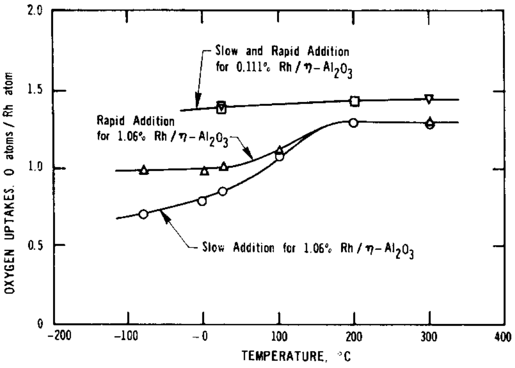

FIG. 8. Oxygen uptakes as a function of rate of addition.

havior observed for all supported catalysts toward oxygen, with the 0.1% Rh/Al_2O_3 catalyst being typical of the behavior of freshly prepared catalysts of low metal loadings and the 1% catalyst typical of those of higher metal loadings. Copious amounts of oxygen, greatly in excess of the amounts required for monolayer formation on the metal at complete dispersion, were taken up at −196°C, even at pressures below 1 Torr; consequently, the lowest temperature at which oxygen uptakes are reported is −80°C.

Oxygen uptakes at 200°C are plotted in Fig. 7 for unsintered Rh/Al_2O_3 catalysts. For the 5% Rh/Al_2O_3 sample sintered in oxygen at 750°C for 8 hr, oxygen uptakes were 0.11, 0.18, and 0.19 atoms per rhodium atom at 25, 200, and 300°C, respectively. The net uptake for a 0.55% Rh/SiO_2 catalyst was 1.19 O atoms/Rh atom, at 200°C.

After exposure to oxygen at 200°C, the catalysts in several runs were cooled to 25°C and the uptakes were again measured at this lower temperature. In all cases, it was found that the oxygen uptakes remained unchanged upon cooling, whereas uptakes measured initially at 25°C for catalysts containing 0.5% Rh and more were substantially lower than the uptakes at 200°C (see Fig. 8). The oxygen uptake by these samples evidently was an irreversible process.

A slow sintering of the rhodium black during pretreatments was observed. Table 1 gives both oxygen uptakes and BET krypton monolayer uptakes. Uptakes reported in oxygen atoms per surface rhodium atom are based on an area per krypton atom of 19.5 Å^2 and an area per surface rhodium atom of 7.9 Å^2 (arithmetic average of the site densities for the 100, 110, and 111 crystal faces).

Carbon Monoxide Adsorption

Carbon monoxide adsorption was measured at a single temperature, 25°C, for the same series of Rh/Al_2O_3 catalysts. Subtraction of the uptake by an unimpregnated alumina sample from the total CO uptake gave the results shown for two Rh/Al_2O_3 samples in Fig. 9. Straight lines of small slope are obtained for the net uptakes by the rhodium, and these data were then extrapolated linearly to zero pressure. In Fig. 7 extrapolated zero-pressure CO uptakes are shown as a function of metal loading for the Rh/Al_2O_3 catalysts. The net uptake for the 0.02% Rh/Al_2O_3 sample was 4.6 CO molecules/Rh atom in the catalyst, which it was not convenient to represent on the scale of Fig. 7.

For the 0.55% Rh/SiO_2 catalyst, the blank for CO adsorption by silica gel was linear with a zero-uptake intercept at zero pressure. Accordingly, direct linear extrap-

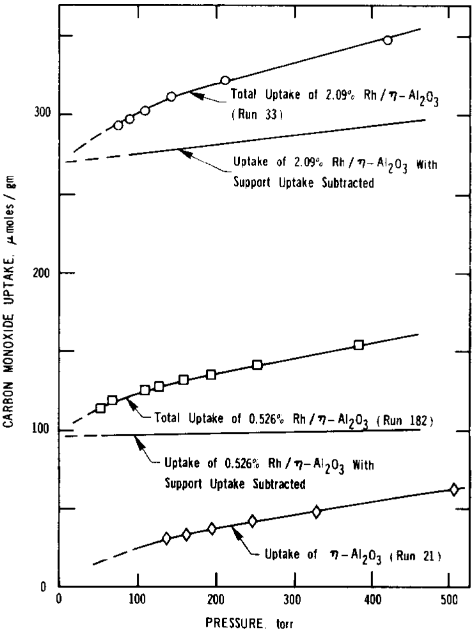

FIG. 9. Carbon monoxide adsorption at room temperature, showing correction for support uptake.

olation of the CO uptake data was used to obtain a value for net uptake by the metal of 0.87 CO molecules per rhodium atom in the catalyst.

Hydrogen–Oxygen Titration

Before it was recognized that oxygen uptakes were sensitive to temperature and rate of oxygen addition and that both hydrogen and oxygen uptakes could exceed the expected limit of one atom per rhodium atom for Rh/Al_2O_3 samples of low metal content, some experiments were carried out following the titration procedure described by Benson and Boudart (*9*). Oxygen was added to the sample (fast addition) at room temperature and pressures of 100–400 Torr. After approximately 2 hr the sample was quantitatively evacuated by means of the Toepler pump. Hydrogen was then added, and the hydrogen uptake was determined. Some results obtained with a 1% Rh/Al_2O_3 catalyst are shown in Fig. 10. The ratio of hydrogen uptake in titration to the hydrogen-adsorption uptake is close to three, and these results were for a time thought to indicate that the stoichiometry proposed by Benson and Boudart for supported platinum (*9*) carried over directly to rhodium, in the form

$$\text{Rh–O (surface)} + \tfrac{3}{2}\,H_2\ \text{(gas)} \rightarrow \text{Rh–H (surface)} + H_2O\ \text{(support)}.$$

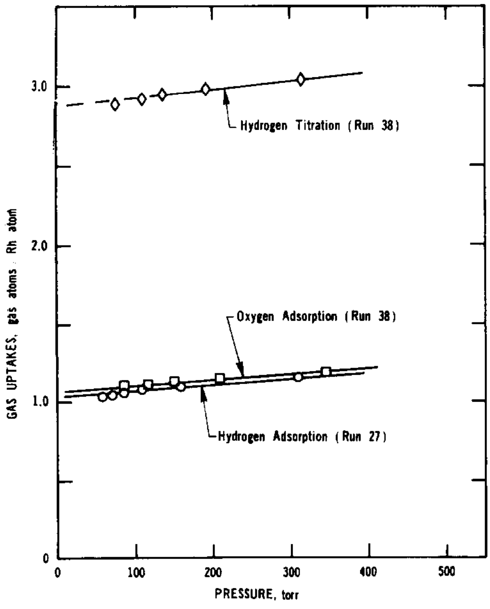

FIG. 10. Typical adsorption and titration results (1.06% $Rh/\eta\text{-}Al_2O_3$ catalyst).

However, it soon became evident that problems arose in applying this scheme. A major part of the difficulties is associated with the oxygen uptake. Because oxygen adsorption at 200°C seemed to exhibit most of the features wished of a selective adsorption process, it was decided to investigate further the hydrogen titration of this oxygen, rather than that adsorbed at room temperature.

In Table 2 data are reported for the hydrogen–oxygen titration and for direct hydrogen adsorption for various catalysts, in terms of the stoichiometric notations x, y, and z, explained by

$$\text{Rh–O}_x + [x + (y/2)]H_2 \rightarrow \text{Rh–H}_y + x\,H_2O$$

and

$$\text{Rh} + (z/2)H_2 \rightarrow \text{Rh–H}_z.$$

Note that the three stoichiometric parameters x, y, and z are referred to the total number of rhodium atoms in the samples, rather than to surface rhodium atoms. They thus do not immediately imply (except as the dispersion approaches unity) a stoichiometry for bonding at the rhodium surface. Nevertheless, this method of reporting the data serves to some extent as a means of normalizing data for different metal loadings, at comparable dispersions.

For both hydrogen adsorption and titration, the uptakes reported are the linearly extrapolated zero-pressure uptakes, while x represents the oxygen retained by the sample after Toepler-pumping. A variety of experiments, designed to determine the effects of temperatures of adsorption and titration and of rates of gas addition, are reported in Table 2.

Electron Microscopy and X-Ray Diffraction

X-Ray powder diffraction patterns for the freshly reduced unsintered catalysts showed no discernible rhodium diffraction lines, and no rhodium crystallites were visible in electron micrographs. It is be-

TABLE 2
HYDROGEN-TITRATION RESULTS

Catalyst	T_1	x	T_2	y	y'	z	Run No.	O_2 Addition	H_2 Addition
0.02% Rh/Al_2O_3	200	1.24	25	—	1.6	1.2	187	Fast	Fast
0.10% Rh/Al_2O_3	0	1.19	0	0.75	—	—	81	Fast	Fast
	25	1.24	25	0.73	—	1.22	80	Fast	Fast
	100	1.30	100	1.08	—	—	82	Fast	Fast
0.11% Rh/Al_2O_3	25	1.32	25	1.03	—	1.39	125	Slow	Fast
	200	1.47	25	0.87	—	1.39	126	Slow	Fast
0.53% Rh/Al_2O_3	200	1.35	25	—	1.15	1.21	184	Fast	Fast
1.06% Rh/Al_2O_3	−80	0.70	−80	−0.87	—	1.12	108	Slow	Fast
	−80	0.70	25	0.99	—	0.96	108	Slow	Fast (−80°C)
	0	0.96	0	0.40	—	0.91	86	Fast	Fast
	0	0.83	0	0.38	—	0.91	103	Slow	Slow
	25	0.88	25	0.78	—	0.98	84	Slow	Slow
	25	1.06	25	0.86	—	0.98	28	Fast	Fast
	100	1.10	100	0.83	—	0.81	102	Slow	Slow
	100	1.12	100	0.80	—	0.81	85	Fast	Fast
	200	1.32	25	0.77	—	0.98	107	40% slow	Fast
2.1% Rh/Al_2O_3	25	0.97	25	0.86	—	0.89	31	Fast	Fast
	200	1.24	25	0.64	0.92	0.89	143	30% slow	Fast
5.0% Rh/Al_2O_3	25	0.80	25	0.68	—	0.76	46	Fast	Fast
	25	0.83	25	0.65	—	0.70	68	Fast	Fast
	200	1.24	25	—	0.60	0.70	160	Fast	Fast
5.0% Rh/Al_2O_3	25	0.36	25	0.37	—	—	72	Fast	Fast
(sintered)	25	0.12	25	0.09	—	0.11	56	Fast	Fast
	200	0.19	25	0.10	—	0.11	128	45% slow	Fast
0.55% Rh/SiO_2	25	0.91	25	0.70	—	0.87	94	Slow	Slow
	25	1.02	25	0.82	—	0.87	95	Fast	Fast
	200	1.24	25	0.62	0.79	0.87	178	Fast	Fast

Explanation of column headings:

T_1 Temperature of oxygen uptake (°C).

x Oxygen retained by catalyst after evacuation with Toepler pump (atoms per rhodium atom in the catalyst).

T_2 Temperature at which hydrogen titration was carried out and hydrogen uptake measured (°C).

y Hydrogen titration uptake in excess of that required for conversion of oxygen to water (atoms per rhodium atom in the catalyst).

y' Hydrogen titration uptake in excess of that required for conversion of oxygen to water, measured at T_2 after a brief heating to 100°C (atoms per rhodium atom in the catalyst).

z Hydrogen adsorption uptake (atoms per rhodium atom in the catalyst).

lieved that, with the techniques employed in this investigation, rhodium particles with dimensions of 40 Å and larger could have been detected, since in a separate study of supported palladium, 40 Å crystallites were readily detected.

Rhodium particles were easily detected by either method for the sintered samples. For the 5% Rh/Al_2O_3 sample which had been sintered in oxygen for 8 hr, the mean particle diameter obtained from line broadening was 530 Å. Electron micrographs for this sample showed rhodium particles ranging in size from 200 to 800 Å, with a number-average particle size of 350 Å and a surface-average size of 495 Å. Some indication of particles with sizes less than 40 Å was obtained from micrographs of this sample, but the images in the micrographs could not be attributed to rhodium particles with any certainty.

DISCUSSION

If surface areas of a supported metal are to be measured by selective adsorption methods, several requirements must be met.

(a) A suitable pretreatment procedure must be established which does not in itself affect the metal surface area significantly and which leaves the surface in a state which does not offer any interference with the subsequent adsorption processes. (b) An adsorbate must be chosen which exhibits a well defined superficial stoichiometry with the exposed metal. (c) This stoichiometry, along with suitable conditions under which it is displayed, must be determined from experiment. (d) A procedure for correcting for adsorbate uptake by the support must be developed.

A number of different adsorbates and quite an assortment of conditions for the determination of surface areas of Group VIII metals have been proposed (*1*, *2*). Virtually all the procedures described in the literature are based on simple stoichiometric ratios of adsorbate atoms to surface metal atoms which are presumed to apply to all catalysts in a given investigation. The results obtained here imply that the situation is rather more complex with the catalysts investigated in this study and that a very careful examination is required to set limits to the accuracy and reliability of selective chemisorption methods.

Hydrogen Adsorption

Hydrogen has been the gas most frequently chosen for the determination of supported-metal surface areas. However, except among the earlier studies (primarily with platinum), where it was felt necessary to justify fully the selective-chemisorption technique, the type of data represented by Fig. 6 has not often been reported.

Under conditions corresponding to a definite stoichiometry, one would expect to find uptakes rather insensitive to experimental conditions. Insensitivity to pressure is exhibited by the data obtained here, in the relatively small slopes of the adsorption isotherms (e.g., Fig. 5) even without correction for uptake by the support. While it was impossible to distinguish uptake by the support from uptake by the metal, the qualitative agreement between the slopes of the isotherms for the supported catalysts and for the support itself suggests that the adsorption on the metal is almost constant over the range of 100–500 Torr. At the same time it is evident that except for the catalysts of low metal surface area the results are not substantially affected by the blank-correction procedure used here, the support uptake being only a small fraction of the uptake by supported catalysts (e.g., 0.01 H atom/Rh atom for the 1% catalyst).

Less freedom is justified in the choice of adsorption temperature. Figure 6 shows that at temperatures of 100°C and above, hydrogen adsorption decreases continuously with increasing temperature, which tentatively can be ascribed to the effect of temperature on the equilibrium of an exothermic adsorption. At a temperature of −196°C, on the other hand, at the pressures employed large uptakes are observed which obviously cannot correspond to a superficial reaction with the rhodium. Evidently under these conditions the correction fails, inasmuch as the corrected uptake at −196°C is of the same order of magnitude as the uptake by the support alone. This underscores the need for adsorption conditions under which the support uptake is expected to be small, as well as where a simple correction procedure such as linear extrapolation seems reasonable.

Over the temperature range of approximately −80°C to room temperature, the hydrogen adsorption shows a definite plateau. A temperature of 25°C was selected out of this range as suitable for attempting to characterize the extent of dispersion of supported rhodium.

Yates and Sinfelt (*3*) report values for the rhodium surface areas of a series of Rh/SiO_2 catalysts, calculated from hydrogen adsorption at room temperature and 100 Torr and based on a stoichiometry of one hydrogen atom adsorbed per surface rhodium atom. In no case did the ratio of hydrogen atoms to total rhodium atoms exceed unity. Wilson and Hall (*10*) recently reinvestigated several cases of H/Pt ratios reported to be greater than unity and concluded the evidence to be doubtful for such ratios for supported platinum. A striking feature of the results shown in Fig. 7 is that for four of the six catalysts H/Rh ratios greater than unity are observed—substantially and reliably greater for the 0.1% and 0.5% Rh/Al_2O_3 catalysts. For these last two the blank correction, which has already been applied in Fig. 7, amounts to only approximately 0.12 and 0.02 hydrogen atoms per metal atom.

Finally, one may note that the data describe a smooth curve and that even the datum for the 0.02% Rh/Al_2O_3 sample, for which the blank correction is 0.6 hydrogen atoms per rhodium atom and experimental uncertainty is substantial (±0.3 hydrogen atoms per rhodium atom), lies close to an asymptotic extrapolation of that curve. Experimental uncertainties in this study are estimated to be approximately ±0.1 H atom/Rh atom for the 0.1% Rh/Al_2O_3 sample and ±0.02 H atom/Rh atom or less for samples with greater amounts of metal. Experimental precision was somewhat better than these values, by approximately a factor of two. There thus appears to be no demonstrable basis for rejecting these unexpected results as artifacts. Indeed, Pliskin and Eischens (*11*) inferred from their IR spectra of hydrogen adsorbed on silica-supported platinum two types of adsorbed hydrogen atoms such that H/Pt ratios greater than unity could be understood; and Bond (*12*) has argued that hydrogen-to-metal ratios greater than unity can occur at nonplanar sites on small metal crystallites. The findings of the present investigation are consistent with Bond's prediction that smaller crystallites would yield greater H/Rh ratios than larger crystallites, if we make the reasonable inference that decreasing metal loadings are associated with decreasing crystallite sizes. On the other hand, particularly since the report of Sinfelt and Lucchesi (*13*), there has been a growing concern that hydrogen adsorption onto an alumina support can be induced by a supported metal. For the purposes of surface-area determination it is immaterial whether variations of metal–adsorbate stoichiometry are real or apparent; insofar as the ratio of gas uptakes to exposed metal atoms is not constant, the accuracy and reliability of the method must suffer.

Finally, for a stoichiometry of one hydrogen atom per surface rhodium atom the specific surface area of 1.07 m^2/g calculated from hydrogen adsorption at 25°C on rhodium black (Table 1) is in rather good agreement with the specific surface area of 0.95 m^2/g calculated from the BET krypton monolayer uptake. Yates and Sinfelt (*3*) reported similar agreement with BET argon uptakes, for this stoichiometry. The stoichiometry of adsorption on a metal black would be expected to present a limit to which supported metals approach at large crystallite sizes. Lanyon and Trapnell (*14*) and Ponec, Knor, and Cerny (*15*) reported values near one hydrogen atom adsorbed per surface rhodium atom for evaporated films, although both of these groups made their measurements at low temperature and low pressures.

Oxygen Uptake

While preliminary data suggested the adequacy of an interpretation of one oxygen atom taken up in adsorption at room temperature per surface rhodium atom, in close agreement with the amount of hydrogen taken up in adsorption and interpreted in the same way, further experimentation revealed important discrepancies showing a systematic variation with metal loading.

The difference between the results of fast and slow oxygen addition for the 1% Rh/Al_2O_3 catalyst, shown in Fig. 8, is believed to be due to heating of the rhodium particles to transient temperatures appreciably in excess of the ambient temperature. Cusumano and Low (*16*) have recently measured surface-temperature transients of supported nickel during oxygen uptake, reporting transient temperature rises exceeding 200°C. It appears to be necessary to invoke *local* heating here, rather than quasiadiabatic heating of the samples as a whole, since the maximum adiabatic *uniform* temperature rise for the sample is expected to be less than 20°C for the 1% Rh/Al_2O_3 catalyst (based on complete oxidation of all rhodium to Rh_2O_3).

Variation of the slow gas-addition rate revealed that rates were readily achieved below which no further diminution of oxygen uptake was observed. The data reported for slow gas addition are thus regarded as appropriate to the reported adsorption temperature, uninfluenced by self-heating to the extent that this can be controlled by limiting the rate of access of gas to the sample.

With the reduced oxygen uptakes on slow gas addition at room temperature for the 1% Rh/Al_2O_3 sample, the agreement between oxygen and hydrogen uptakes exhibited in Fig. 10 disappears. Considering further the oxygen uptake for slow addition to the 1% Rh/Al_2O_3 catalyst, one sees that the uptakes over the temperature range from —80 to 100°C increase continuously and substantially with increasing temperature. The temperature-insensitivity one wishes of uptake measurements thus is lacking. Similar behavior was observed for the 5% Rh/Al_2O_3 sample sintered in oxygen for 8 hr at 750°C.

The data for fast and slow addition of oxygen to the 0.1% Rh/Al_2O_3 sample show no effect of addition rate on oxygen uptake. The insensitivity to rate of addition could be explained by a lower transient temperature rise due to the lower metal content (*16*). However, a second very important difference is evident. While the uptake by the 1% catalyst increases by more than 50% between room temperature and 300°C, the uptake by the 0.1% catalyst increases by only a very small amount. Temperature insensitivity is thus exhibited by the 0.1% catalyst over the entire range, while only for temperatures of approximately 200°C and higher does the 1% catalyst appear to reach a saturation uptake independent of temperature over a substantial range.

It is thus only in the temperature range of 200–300°C that the data obtained in this study exhibit qualitatively similar behavior. For this reason, it is the oxygen uptakes at 200°C which are presented in Fig. 7.

Such a high temperature raises the possibility that the uptakes measured may represent the formation of a bulk oxide, rather than of a surface species. Indeed, uptakes of approximately 1.5 oxygen atoms per rhodium atom immediately suggest the formation of the species Rh_2O_3. Inspection of the uptakes in Fig. 7 and that reported for the sintered 5% catalyst, nevertheless, reveals that such an oxidation cannot be complete, since uptakes by the samples of higher metal loading are substantially less than would correspond to the complete formation of Rh_2O_3. In fact, for the sintered 5% catalyst the net uptake is only 0.18 atom/Rh atom and is only approximately 50% greater than the room-temperature hydrogen adsorption on the same sample.

In this last regard, it is worthy of note that for samples containing more than 1% rhodium, including the sintered sample, oxygen uptakes at 200°C and room-temperature hydrogen uptakes are all in the ratio of 1.5 ± 0.1. Unless fortuitously both hydrogen and oxygen are involved in processes in the bulk of rhodium crystallites in almost precisely proportional amounts over this range, the data lead one to infer that both uptakes likely represent predominantly surface phenomena.

The data obtained for oxygen uptake by the rhodium black, however, indicate a need for some modification of this conclusion. Contrary to the results obtained for the supported catalysts, the rhodium black shows no evidence of a saturation of adsorption sites in the 200–300°C range. Instead, the uptake continues to increase with increasing temperature, amounting to more than two oxygen atoms per surface rhodium atom at 200°C and more than five at 300°C. As was remarked earlier, one would expect considerable similarity in behavior between the black and the larger metal crystallites in a sample such as the sintered 5% Rh/Al_2O_3. Yet no appreciable increase in oxygen uptake was detected for this latter between 200 and 300°C. On the other hand, while oxidation below the surface layer of the black seems to take place at 300°C, even at this temperature the uptake exceeds that for the formation of a *surface* species of nominal stoichiometry $RhO_{1.5}$ by less than a factor of four. At 200°C, this factor is reduced to less than two. The continuous decrease of oxygen uptake down to —80°C suggests that the ratio of 1.44 oxygen atoms taken up per surface rhodium atom at 25°C is fortuitous, rather than indicative of $RhO_{1.5}$ at that temperature.

The behavior of oxygen with rhodium noted here probably has some analogues in the behavior of the platinum–oxygen system. Wilson and Hall (*10*) concluded that oxygen uptakes by supported platinum fail to provide any direct measure of platinum surface area, under the conditions of their study. Weller and Montagna (*17*), absorbing O_2 on Pt/Al_2O_3 at 475 and 525°C after a 550°C reduction, found O/Pt ratios as high as 3.7, part of which they attribute to reduction and reoxidation of the alumina support. In the present study with rhodium at lower temperatures than these, however, O/Rh ratios never exceeded that for the oxide Rh_2O_3, and there is no need to invoke such an explanation.

Hydrogen–Oxygen Titration

The several advantages of a hydrogen–oxygen titration scheme for the measurement of metal surface areas have been pointed out by Benson and Boudart (*9*). That a hydrogen–oxygen titration over rhodium would prove feasible was suggested by work of Ponec, Knor, and Cerny (*15*) with evaporated rhodium films. The stoichiometry of hydrogen titration of oxygen-exposed catalysts will at best be heir to all of the variabilities of the stoichiometries of the individual hydrogen and oxygen uptakes. This was amply verified in the present study. Nevertheless, several interesting questions arise to which answers were sought from experiment. Will gaseous hydrogen react completely with the oxygen taken up by the catalysts, some of which may involve oxidation below the rhodium surface layer? Does water formed interfere with subsequent hydrogen adsorption?

In practice, it is difficult to separate these questions, since in our experiments it was not possible to distinguish between hydrogen which reacted with oxygen to form water and hydrogen which was adsorbed. From Table 2, the negative value calculated for y for the 1% Rh/Al_2O_3 catalyst in Run 108 indicates that the hydrogen uptake at −80°C was less than that required for complete conversion of sorbed oxygen to water. Thus, while some of the hydrogen uptake may represent adsorbed hydrogen, reaction with oxygen at this temperature obviously was not complete. Upon heating to 25°C the hydrogen uptake increased, and the value calculated for y became positive and equal to z within experimental error. This increase is in contrast to the findings for platinum black of Vannice *et al.* (*18*) in their hydrogen-titration measurements at −80°C and room temperature. Ponec *et al.* (*15*) report that no molecular hydrogen is taken up at 78°K by rhodium films completely covered by oxygen.

At all temperatures of 0°C and higher, however, for all catalysts the calculated values of y are greater than zero, indicating more than adequate hydrogen uptakes for water formation from all residual oxygen. The data for the 1% Rh/Al_2O_3 catalyst for identical oxygen-uptake and titration temperatures show a small increase in the ratio y/z with increasing temperature, over the range 0–100°C, but the increase amounts to only 10–15% of the total hydrogen titration uptake. Whether the deficiencies of y from z at temperatures below 100°C imply reduced hydrogen adsorption or incomplete reaction with oxygen could not be determined. However, at 100°C the deficit has disappeared and y and z are in agreement, within experimental uncertainty.

As to whether oxygen adsorbed at 200°C behaves in titration similarly to oxygen adsorbed at room temperature, one can compare the results of Runs 84 and 107 for the 1% catalyst, Runs 31 and 143 for the 2% catalyst, Runs 56 and 128 for the sintered 5% catalyst, and Runs 95 and 178 for the 0.5% Rh/SiO_2 catalyst. For the first and third of these pairs, the agreement between values of y for oxygen adsorption at 200 and 25°C, followed by titration at 25°, is very close. For the other two pairs, agreement is somewhat less satisfactory, although the discrepancy is only 8% of the total hydrogen uptake for both cases. Thus, while some doubt may remain that oxygen taken up at the two temperatures behaves equivalently toward hydrogen titration at 25°C, any differences following this procedure are relatively small in effect on total hydrogen uptakes. The differences may result from small differences in details of procedure, combined with differences among the samples. For example, 30–40% of the oxygen was added slowly in Runs 107 and 143, but the importance of thermal effects could differ between the two different catalysts. Approximately half the oxygen was added slowly in Run 128, while the oxygen was added fast in Run 178. However, no definite trend is evident from these few experiments. More importantly, the discrepancies could be removed by permitting hydrogen to contact the catalyst at 100°C for a brief period.

The increasingly good agreement between y and z which was noted earlier as the titration temperature was increased suggested that it might be possible to improve the agreement between these two for room-temperature titrations by a brief heating of the sample to a temperature around 100°C, while hydrogen contacted the sample. This was done in several runs, usually by heating the sample bulb to 100°C for one-half hr following hydrogen admission, followed by cooling to room temperature where the uptake measurements were completed. The data for y' and z for Run 184 for the 0.5% Rh/Al_2O_3 catalyst, Run 143 for the 2% catalyst, Run 160 for the 5% catalyst, and Run 178 for the 0.5% Rh/SiO_2 catalyst show that good agreement is obtained by this method. Furthermore, the two cases in which oxygen was taken up at 200°C for which y was noted above to be lower than z (Runs 143 and 178) have higher uptakes after heating, for final values of y' which agree with z within experimental uncertainty.

As with oxygen uptakes, an effect of self-heating was observed for hydrogen-titration experiments in which the hydrogen was introduced rapidly. Hydrogen was introduced slowly in Runs 84, 94, and 102, from Table 2, with addition times ranging from 30 to 60 min. Comparing Run 84 with 28 and Run 94 with 95, one sees that fast hydrogen addition resulted in greater hydrogen uptakes, as one would expect from a momentary temperature rise. At the higher titration temperature of 100°C in Runs 102 and 85 no such effect was observed, which would be expected if, as was inferred above, a temperature of 100°C were adequate to cause the hydrogen–oxygen reaction and displacement of the water to go to completion. Additional experiments were performed in which samples heated to 100°C during the titration were reheated to the higher temperature of 150°C. No change in hydrogen uptake was observed upon cooling to 25°C; a temperature of 100°C evidently was sufficient.

With regard to the state of sorbed oxygen and its reactivity with hydrogen, an experiment was carried out in which hydrogen was introduced at 25°C to the sintered 5% Rh/Al_2O_3 sample (8 hr in oxygen at 750°C) *before* its reduction and pretreatment. This sample was probably extensively oxidized. Hydrogen uptake was only 15 μmole/g, compared with an uptake of 84 μmole/g for the titration of oxygen which had been sorbed at 25°C after the standard pretreatment (Run 56). The more severe oxidation apparently suppresses the reaction of hydrogen with even superficial oxygen at 25°C.

Finally, a series of experiments was carried out in which oxygen addition followed by evacuation was alternated with hydrogen titration through seven oxygen–hydrogen cycles at 25°C, without intermediate heating during evacuations. In this way, it was possible to form substantial amounts of water *in situ* at the rhodium crystallites. Giordano and Moretti (*19*) have recently made a preliminary report of experiments in which water was added back to outgassed samples of Pt/Al_2O_3 by addition to a carrier gas passing over the samples, but it is difficult to know in this sort of experiment to what extent water has access to the metal itself. In our experiments the hydrogen-titration uptakes decreased continuously from cycle to cycle, except that fast hydrogen addition resulted in some increase over a previous slow hydrogen addition. The hydrogen uptake in the seventh titration (fast hydrogen addition) was only approximately 70% of that for the first cycle. This decrease was not due to a change in rhodium dispersion, as was shown by imposing the standard pretreatment procedure on the catalyst sample and subsequently obtaining practically the same hydrogen titration uptake as in the first cycle (137 μmole/g, as compared with 143 μmole/g originally). The cumulative effect of the formation of water *in situ* on the rhodium suggests that the decreasing uptakes result from interference with hydrogen adsorption by the water formed. This seems more likely than the accumulation of an unreactive oxygen species. This interference is contrary to the inference of Vannice *et al.* (*18*) from their volumetric data for the hydrogen titration of oxygen adsorbed on platinum black. Nevertheless, whether or not a close parallel exists with platinum, it is evident from our results that special steps must be taken for our Rh/Al_2O_3 catalysts to bring the results of direct hydrogen adsorption and of net hydrogen adsorption in titration at room temperature into agreement. A brief warming to 100°C accomplished this.

Carbon Monoxide Uptake

The success of the Rh/Al_2O_3 blank-correction procedure used here in yielding linear, almost horizontal curves for the net uptake as a function of CO pressure lends some support to this procedure. An alternative method of removing the weakly held CO and measuring the amount of CO retained by the catalyst would be to evacuate the sample quantitatively with the Toepler pump. This method too presumably would eliminate the need for adsorption measurements on the support and is closely related to the method employed by Yates and Sinfelt (*3*). This second procedure was carried out for several of our catalysts, as well as for samples of the alumina support alone. The results are given in Table 3. The alumina was found to retain 6.9 μmoles of CO per gram of alumina at room temperature after Toepler pumping. For catalysts containing sufficient metal that this amount of uptake by the support is unimportant, excellent agreement was obtained between net uptakes obtained by subtraction of the blank isotherm from the isotherms for the supported catalysts followed by linear extrapolation and the values of CO retention after evacuation with the Toepler pump.

For the 0.10% Rh/Al_2O_3 catalyst, however, the correction for this 6.9 μmoles/g of uptake by the alumina is significant, and good agreement with the original procedure is obtained only after subtraction of this quantity. Thus, for catalysts for

TABLE 3

CARBON MONOXIDE UPTAKES ON SUPPORTED RHODIUM, CORRECTED FOR SUPPORT UPTAKE

Catalyst	Uptake, μmole/(g of catalyst)		
	Corrected by subtraction of blank, followed by linear extrapolation	Retained after evacuation with Toepler pump	
		Uncorrected	Corrected by subtraction of retention by blank after Toepler-pump evacuation
η-Al_2O_3	0	6.9	0
0.02% Rh/Al_2O_3	9.0	—	—
0.10% Rh/Al_2O_3	17.5	24.6	17.7
1.06% Rh/Al_2O_3	142	150	143
2.1% Rh/Al_2O_3	270	267	260
2.1% Rh/Al_2O_3	248[a]	243	236[a]
5.0% Rh/Al_2O_3	383	394	387
0.55% Rh/SiO_2	47	—	—
0.55% Rh/SiO_2	45[b]	—	—

[a] Measured after several pretreatments.

[b] Pretreatment of Yates and Sinfelt (*3*) used for this experiment.

which corrections of this magnitude are important *neither* of the two procedures proposing to eliminate support–uptake measurements would be satisfactory. The two methods employed for our data are essentially independent, one employing the uptake data for pressures above 100 Torr and the other the uptakes after evacuation to less than 1 Torr. The excellent agreement between the two affords further support to the values reported.

Yates and Sinfelt (*3*) report for Rh/SiO_2 catalysts H/Rh and CO/Rh ratios which under their conditions agree rather closely. Such agreement is observed in the present study with Rh/Al_2O_3 only for the sample containing 5% metal. Yates and Sinfelt report only a single catalyst, 0.1% Rh/SiO_2, for which the CO/Rh ratio exceeds 1.01 (CO/Rh = 1.4), but they tend to discount the reliability of this one datum.

Assuming that the net CO/Rh ratios extracted from the data of the present study are not falsified by some factor not evident (*e.g.*, massive failure of the blank-correction procedure), one is led to conclude that the adsorption stoichiometry of carbon monoxide on the Rh/Al_2O_3 samples is not simple and invariant. Carbon monoxide adsorption on supported platinum has been found to be a function of the support (*20*, *21*), as well as of the platinum dispersion (*6*). Much less work has been done with rhodium, but the rhodium–carbon monoxide system appears to be perhaps even more complex than the platinum–carbon monoxide system. From IR studies with supported rhodium (*22*) the occurrence of $Rh(CO)_2$, RhCO, and Rh_2CO surface species was inferred; and rhodium is known (*23*) to form carbonyls $[Rh(CO)_3]_n$, $Rh_2(CO)_8$, and $[Rh_4(CO)_{11}]_n$. Formation of surface species with high CO/Rh ratios should be restricted to rhodium atoms with a low coordination number, such as edge and corner sites, since steric hindrance would be expected to prevent their formation on rhodium atoms located in the interior of crystal faces. Thus, the observation here of increasing CO/Rh ratios with decreasing metal loading is consistent with the expectation of decreasing particle size.

Electron Microscopy and X-Ray Diffraction

It is very desirable to compare the results of selective chemisorption measurements with physical measurements of the metal crystallite size. Unfortunately, in the present studies the catalyst preparation technique apparently was quite successful in obtaining high dispersions of the rhodium, to the extent that neither electron microscopy or X-ray diffraction examinations detected the existence of rhodium crystallites in unsintered catalysts. Qualitatively, however, this is in agreement with the conclusions drawn from the chemisorption measurements that metal dispersions approaching unity were achieved.

Only for the sintered 5% Rh/Al_2O_3 catalysts was it possible to determine a particle size from electron microscopy and X-ray data. Values of 495 and 530 Å, respectively, are to be compared with a value of 90 Å calculated from hydrogen chemisorption measurements (assuming one hydrogen atom adsorbed per surface rhodium atom, an average area per surface rhodium atom of 7.9 Å, and spherical particles). Agreement among these results is not more than qualitative. Kral (*21*) reports a similar disagreement between X-ray and adsorption results for supported platinum, which he attributed to the inability of X-ray measurements to detect small metal particles. The results are thus consistent with a particle-size distribution which is broad and possibly even multimodal. Even a small fraction of the total rhodium (of the order of 10%) in the sintered samples being present as small particles undetected by the physical methods could explain the observed discrepancy.

CONCLUSIONS

For catalysts of the type prepared for this investigation, it appears that carbon monoxide adsorption at 25°C is not suitable for metal surface-area measurements. Values for H/Rh_{total} approaching 1.5 for catalysts containing small amounts of rhodium are not consistent with the value of $H/Rh_{surface}$ inferred from experiments with rhodium black. The evidence is strong that bonding of more than one hydrogen atom per surface rhodium atom occurs for Rh/Al_2O_3 catalysts.

Oxidation beyond the surface layer, as observed with rhodium black at higher temperatures, renders both oxygen adsorption and hydrogen–oxygen titration unsuitable for surface-area determination, if one may infer that similar behavior is exhibited by the supported metal. The data on effects of rate of admission on oxygen sorption stress the need for proper control of experimental conditions, particularly in dealing with strong and frequently irreversible adsorptions favored for surface-area determinations.

The sorption and titration data are undoubtedly amenable to several consistent or partial explanations. A consistent view capable of encompassing all the data can be constructed, based on the wide discrepancy between chemisorption and electron-microscope particle sizes for the sintered sample. Oxidation of large crystallites can be expected to be similar to that of the metal black, for which oxidation apparently proceeds at 200°C to the equivalent of only two to three atomic layers in several hours. If in all the unsintered samples there exists a distribution of particle sizes, with the smallest exhibiting dispersions near unity and a high reactivity toward oxidation almost completely to Rh_2O_3, while somewhat larger metal particles react only incompletely with oxygen, one can understand the differences in temperature dependence of oxygen uptake with metal loading. At the same time, if the sintered sample contains a large fraction of its rhodium atoms but only a small fraction of its metal surface area in the form of large metal crystallites, while a small fraction of the rhodium atoms (*e.g.*, $\simeq 10\%$) but a large fraction of the metal surface area ($\simeq 85\%$) occur as small particles of approximately unit dispersion and high reactivity toward oxygen, the O/H ratios of 1.5 can be understood if one assumes that hydrogen adsorbs approximately to a H/Rh_{surface} ratio of unity in the samples. The percentages given are consistent with a bimodal distribution consisting of particles of unit dispersion combined with particles of approximately 500 Å diam as indicated by electron microscopy, taken together with the measured gas uptakes.

In samples for which the dispersion is high, or for which particles of high dispersion make up the greater part of the *surface*, oxygen uptakes then might provide a useful means of estimating surface areas. That is, particles of high dispersion and reactivity would take up approximately 1.5 oxygen atoms per rhodium atom, while large particles consuming an uncertain number of oxygen atoms (but presumably of the order of one to several) per surface rhodium atom would contribute so little to the total uptake as to have little effect on the precision of the measurement.

In this view, then, hydrogen adsorption, interpreted in terms of a single hydrogen atom adsorbed per surface rhodium atom, would provide the norm of behavior for samples whose dispersions do not reach levels at which substantial amounts of excess hydrogen are sorbed, while in the region where the latter is a problem the oxygen uptake data, tending smoothly to the limit of $O/Rh = 1.5$, would provide a means of extrapolation to the limit of unit dispersion.

The complexity of the experimental observations reported here does not lend itself particularly well to convenient summary or simple and unequivocal analysis. It is quite clear, however, that the data for hydrogen, oxygen, and carbon monoxide uptakes by these Rh/Al_2O_3 catalysts are not amenable to interpretations in terms of simple and unique surface stoichiometries. One thus is well advised to use caution in inferring metal surface areas from gas uptake measurements and, especially, to beware of attributing to comparisons by means of relative uptakes an undeserved precision.

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REFERENCES

1. SCHLOSSER, E. G., *Chem. Ing. Tech.* **7**, 409 (1967).
2. MULLER, J., *Rev. Pure Appl. Chem.* **19**, 151 (1969).
3. YATES, D. J. C., AND SINFELT, J. H., *J. Catal.* **8**, 348 (1967).
4. WANKE, S. E., Ph.D. thesis, University of California, Davis, 1969.
5. NEWKIRK, A. E., AND MCKEE, D. W., *J. Catal.* **11**, 370 (1968).
6. GRUBER, H. L., *J. Phys. Chem.* **66**, 48 (1962).
7. MEARS, D. E., AND HANSFORD, R. C., *J. Catal.* **9**, 125 (1967).
8. KLUG, H. P., AND ALEXANDER, L. E., "X-Ray Diffraction Procedures," Chapter 9. Wiley & Sons, New York, 1954.
9. BENSON, J. E., AND BOUDART, M., *J. Catal.* **4**, 704 (1965).
10. WILSON, G. R., AND HALL, W. KEITH, *J. Catal.* **17**, 190 (1970).
11. PLISKIN, W. A., AND EISCHENS, R. P., *Z. Phys. Chem. (Frankfurt am Main)* **24**, 11 (1960).
12. BOND, G. C., Preprint No. 67, Int. Congr. Catal., 4th, Moscow, June 1969.
13. SINFELT, J. H., AND LUCCHESI, P. J., *J. Amer. Chem. Soc.* **85**, 3365 (1963).
14. LANYON, M. A. H., AND TRAPNELL, B. M. W., *Proc. Roy. Soc., Ser. A* **227**, 387 (1955).
15. PONEC, V., KNOR, Z., AND CERNY, S., *Collect. Czech. Chem. Commun.* **30**, 208 (1965).
16. CUSUMANO, J. A., AND LOW, M. J. D., *J. Catal.* **17**, 98 (1970).
17. WELLER, S. W., AND MONTAGNA, A. A., *J. Catal.* **20**, 394 (1971).
18. VANNICE, M. A., BENSON, J. E., AND BOUDART, M., *J. Catal.* **16**, 348 (1970).
19. GIORDANO, N., AND MORETTI, E., *J. Catal.* **18**, 228 (1970).
20. EISCHENS, R. P., AND PLISKIN, W. A., *Advan. Catal. Relat. Subj.* **10**, 1 (1958).
21. KRAL, H., *Z. Phys. Chem. (Frankfurt am Main)* **48**, 129 (1966).
22. GUERRA, C. R., AND SCHULMAN, J. H., *Surface Sci.* **7**, 229 (1967).
23. COTTON, F. A., AND WILKINSON, G., "Advanced Inorganic Chemistry," p. 612. Interscience Publishers, New York, 1962.