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Surface Interactions in the System Rh/Al_2O_3

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Under oxidizing conditions Rh is easily dispersed on γ-Al_2O_3 up to a saturation concentration of >10% of the support area. The average oxidation state of the dispersed phase is Rh^{3+}. Excess Rh is present in the three-dimensional Rh_2O_3 particles. The interaction with the support in air is weak at <600°C and both the dispersed and three-dimensional phases are easily reduced. Multiple chemisorption of CO, NO, and H is noted on the dispersed phase. In the limit two adsorbate molecules reside on the surface Rh in very dilute samples. The multiplicity is a strong function of Rh concentration and invalidates the measurement of accessible metal area in dilute samples. H_2–O_2 titration, with proper precautions, gives more reliable results, due to a constant surface oxide stoichiometry. In heat treatment (>600°C), Rh-oxide interacts with both γ-Al_2O_3 and δ-Al_2O_3, diffusing into the subsurface region and the bulk. This process can only be partially reversed by reduction in H_2 (>550°C). Thus, the measured value of surface Rh will depend also on the prereduction procedure. Exposure of Rh/Al_2O_3 catalysts to high temperature under oxidizing conditions will cause loss of active area by both particle growth and by diffusion into the bulk of the support. In concentrated samples one can distinguish among the three Rh states: dispersed on surface, particulate, and dissolved in the support.

INTRODUCTION

Recent development of automotive three-way catalysts (*1*) where Rh is used, in small amounts, as a selective component for NO reduction required the reexamination of the interaction of Rh with the commonly used support, γ-Al_2O_3. For this particular application, the interactions taking place under oxidizing conditions and elevated temperatures (up to 800°C) are of interest. The present work was undertaken within the framework of active-component/support interaction studies carried out recently in this laboratory (*2–4*). It was noted, in the course of these investigations and also in other systems by other investigators, that in many instances both particle growth and redispersion of the active phase can occur on the surface of the support, while at higher temperatures bulk interactions take place. It has also been noted that in several systems even the precious metals do, in fact, interact with the surface of the insulator supports (*5–7*).

The Rh/Al_2O_3 system has been investigated several times, but these studies did not encompass the range of conditions of interest to us. A large study of the Rh/η-Al_2O_3 system has been made by Wanke and Dougharty (*8*) and Buyanova *et al.* (*9*). Both articles contain ample review of previous work on the system. The main conclusion reached is that, in general, simple chemisorption stoichiometries do not prevail for supported Rh catalysts. The chemisorptive behavior of Rh supported on Al_2O_3 was found to differ vastly from that of the analogous Pt system. In particular, the pretreatment history was found to have a pronounced influence on the

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chemisorptive behavior of Rh. The work presented here was aimed first at understanding the effect of the various treatments in more detail.

Another goal was to develop a reproducible procedure for the measuring of supported surface Rh in low-concentration samples. Finally, the interaction of Rh was studied not only with the high-surface area moderate temperature modification, γ-Al_2O_3, but also with the higher temperature modification, δ-Al_2O_3.

The methods described in our previous work on the Re/γ-Al_2O_3 system (*4*) were employed: conventional chemisorption of simple gases and programmed reduction. In addition, the H_2–O_2 surface titration was applied to the very dilute samples which had Rh concentrations close to those of practical interest.

EXPERIMENTAL

A. Materials. The catalysts used in this study were of both granular and monolithic form. The granular catalysts were made first by agglomerating Dispal-M γ-Al_2O_3 (Conoco Chemicals) powder by wetting, drying at 300°C, crushing and sieving. The fraction 0.5–1.0 mm in diameter was impregnated with an $Rh(NO_3)_3 \cdot 2H_2O$ solution of a desired concentration, dried at room temperature, and then rewetted and redried to achieve a uniform distribution. The samples were then calcined at 300°C in air and reduced in H_2 for 1 hr at 400°C. Subsequent treatments were performed according to need and are described in each instance.

The monolithic catalysts were made by depositing 10% by weight of Alon 30-D γ-Al_2O_3 (Cabot Corp.) on commerical monolithic cordierite substrates (American Lava or Corning). The catalysts were presintered in air for 4 hr at 600°C and for 168 hr at 1000°C. The catalysts were then impregnated with Rh-nitrate solutions and Rh was "fixed" by passing H_2S through the monolith channels. The samples were then dried, calcined for 4 hr at 500°C in air to remove the sulfur, and reduced in H_2 at 425°C for >1 hr.

The Rh content of all catalysts was determined by X-ray fluorescence. Research-grade Ar, N_2, CO, and O_2 were used without further purification. Hydrogen was purified by passing over an Engelhard Deoxo Pd catalyst and a 4-Å molecular sieve at 78°K. The nitric oxide, used in some adsorption measurements, was purified by repeated freezing–evaporation cycles, using only a portion of the middle fraction (*10*).

B. Apparatus. The volumetric adsorption measurements were performed in a conventional constant-volume apparatus equipped with a quartz spiral Bourdon gage (Texas Instruments).

The previously described flow system (*12*) was used (a) for the modified hydrogen–oxygen titration to measure the accessible Rh area in the monolithic catalysts and (b) for the temperature-programmed reduction of the particulate adsorbents.

RESULTS

I. Chemisorption Measurements

A. Chemisorption of H_2, CO, and NO on Rh/γ-Al_2O_3. Adsorption isotherms of H_2, CO, and NO at 25°C on a typical sample (0.92 wt% Rh) of a reduced, granular, supported catalyst are shown in Fig. 1. Similar to the presentation of Ref. (*4*), curves A and B give, respectively, the total and reversible chemisorption, while the curves marked C give the irreversible part. The measurement of the reversible adsorption followed that of the total adsorption after the same sample was outgassed at 75°C for about 1 hr. The adsorptions of CO, NO, and H_2 on alumina support were found in separate experiments to be totally reversible and are included in curves B. Only the irreversible portion of the chemisorption is used for the comparison among the various catalysts. In all cases the chemi-

sorption was carried out after the treatment described in the experimental section. Figure 2 summarizes the irreversible chemisorption of all three adsorbates on six samples in the 0.13–9.60 wt% Rh range. Table 1 gives the ratios between the reversibly chemisorbed adsorbate molecules (atoms in the case of hydrogen) and the Rh present in the samples derived from the same measurements.

It should be pointed out that, unlike supported Co (*3*) or Re (*4*), the supported Rh catalysts do not require an additional heat treatment *in vacuo* at 500°C to obtain maximum dispersion. The 300°C calcination in air used for all samples before reduction at 400°C (see Experimental) suffices to obtain maximum dispersion. In fact, calcination for 3 hr at 500°C in air before reduction has no effect on the chemisorption. Examination of Table 1 and Fig. 2 brings forth the following observations. (a) Adsorption stoichiometry is considerably lower for H atoms than for either NO or CO molecules, with that for NO slightly higher than for CO. (b) For all three adsorbents the uptake increases logarithmically with the loading of the active metal C, $q = kC^n$, as was the case with Co (*3*) and Re (*4*). (c) At a given value of Rh surface concentration this increase virtually stops. This point represents the saturation concentration of the dispersed phase. It is the same for all three adsorbates. Its value for rhodium is 2.5 μmole of Rh/m² of γ-Al_2O_3. (d) The NO/Rh, CO/Rh, and H/Rh stoichiometries from Table 1 are, in general, >1 when the Rh surface concentration is below the saturation value and <1 when this value is exceeded. This indicates multiple adsorption of all three adsorbates on the dispersed phase, or at least on a part of it. The limit of multiple adsorption observed here for Rh is ~ 2, while higher values were noted previously for well-isolated Co and Ni ions (*2*).

B. Effect of oxidation heat treatment on the surface accessibility in particulate samples of Rh/γ-Al_2O_3. It was mentioned that calcination in air above 300°C does not enhance the Rh dispersion measured by chemisorption. Indeed, as Fig. 3 shows, calcination in air below 600°C of 5-hr duration does not cause any marked decrease in NO uptake, when the reduction before the chemisorption is carried out at 400°C. Calcination at higher temperatures in air causes a sharp decrease in the uptake of NO, which reduction at 550°C can partially restore. This is direct evidence of the interaction between Rh (or rather its oxide) and the support during calcination at >600°C, which, in turn, necessitates higher reduction temperatures for reconversion to the metal. The unrecovered part of the chemisorptive capacity is either due to irreversible particle

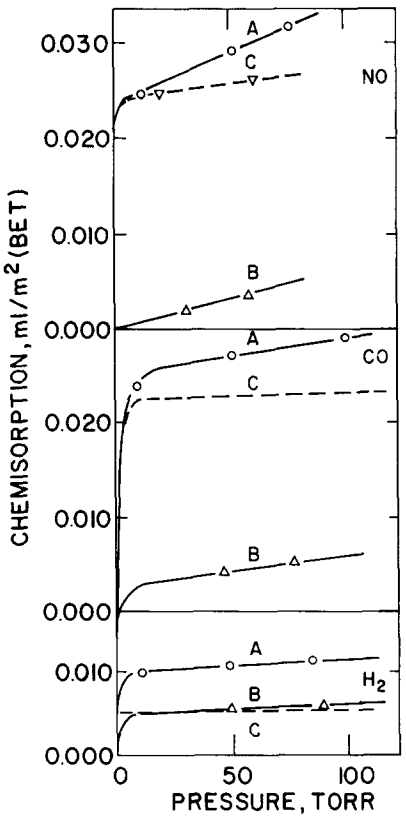

FIG. 1. Nitric oxide, carbon monoxide, and hydrogen chemisorption at 25°C on 0.92 wt% Rh/γ-Al_2O_3 catalyst. (A) Total chemisorption; (B) reversible part; (C) irreversible part.

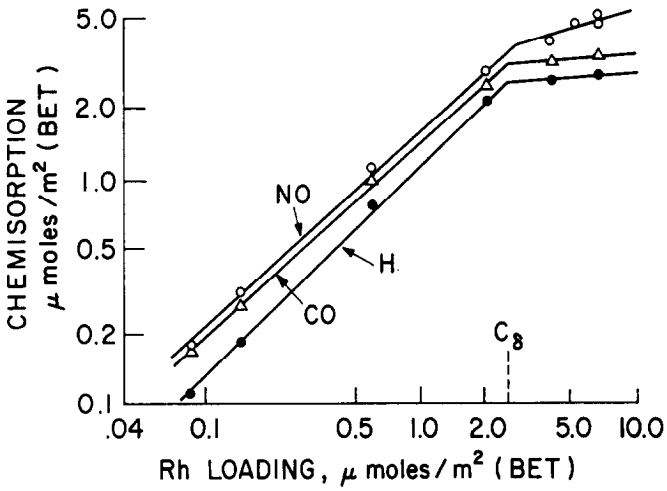

FIG. 2. Chemisorption of nitric oxide, carbon monoxide, and hydrogen at 25°C as a function of Rh loading.

growth of the Rh-containing phase and/or to an interaction which creates a dissolved phase and is not completely reversible by reduction at 550°C after the calcination in air. Further work was undertaken to distinguish between these two possible explanations.

Four of the more concentrated samples of Table 1 were heated in air at a constant temperature of 700°C for prolonged times and periodically reduced at 400°C for measurement of Rh accessibility by NO chemisorption. The results are shown in Fig. 4. The decrease in the surface accessibility with time is continuous and approaches an asymptotic value. To determine whether this decrease is associated with particle growth, the four samples of Fig. 4 were examined at the end of the runs by transmission electron microscopy at a magnification of 109,000×. Before heating at 700°C the Rh particle sizes were below the detection limit of 25 Å. The electron microscope measurements summarized in Table 2 indicate that particle growth occurs and that, within the precision of the

TABLE 1

Stoichiometry of Irreversible Chemisorption of NO, CO, and H on $Rh/\gamma\text{-}Al_2O_3$ at 25°C and 60 Torr

Rh concentration (wt%)		Surface concentration (μmole of Rh/m² BET)	NO/Rh	CO/Rh	H/Rh
Nominal	Measured by X-ray fluorescence				
0.13	n.m.[a]	0.086	2.03	1.98	1.34
0.21	n.m.	0.145	2.14	1.83	1.28
0.92	n.m.	0.63	1.60	1.49	1.33
2.95	2.79	2.20	1.30	1.11	0.95
5.34	5.51	4.40	0.85	0.68	0.57
9.80	9.12	7.20	0.61	0.51	0.36

[a] n.m., Not measured.

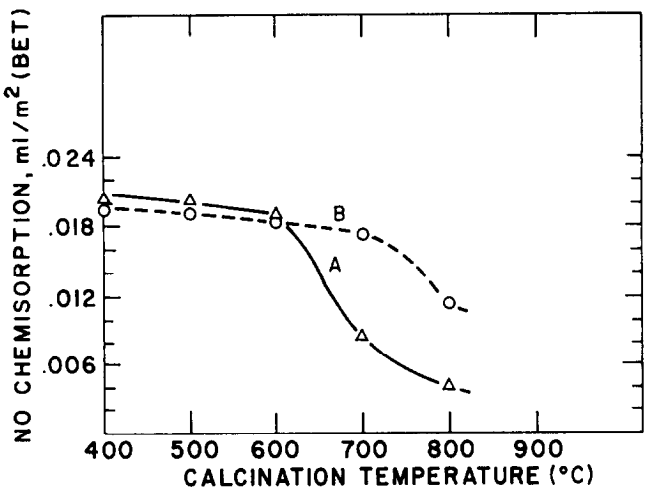

FIG. 3. Effect of the temperature of heat treatment in air on Rh surface accessibility as measured by NO chemisorption. (A) Reduced (before chemisorption) at 400°C; (B) reduced at 550°C. Sample with 0.92 wt% Rh.

method, the average size of the Rh crystallites obtained after the reduction of the calcined samples is relatively independent of the Rh concentration. The quantitative contribution to the decreased surface accessibility cannot be determined since there are no methods to measure the fraction of the Rh in the particulate phase. It will be shown below that the particle growth is not the sole or the important reason for the lowered chemisorptive capacity.

C. Temperature-programmed reduction. The differences in the surface accessibility of Rh/γ-Al_2O_3 samples reduced at 400 and 550°C are suggestive of the existence of at least two different states of oxidized Rh. If this is so, a temperature-programmed reduction could provide further information on the system. Figure 5 shows four temperature-programmed reduction curves for a 5.51 wt% Rh sample. All the runs were made consecutively on the same sample of the material. The calcining at progressively higher temperatures splits the low-temperature peak of hydrogen uptake into two distinct peaks. After calcining at 700°C, one observes the formation of the phase which is irreducible at 400°C, manifested by the hydrogen uptake in the 450–600°C range.

A similar programmed reduction of a more dilute sample (0.32 wt% Rh) is shown in Fig. 6. Calcination at successively higher temperatures indicates that a larger proportion of the easily reducible form has been transferred to the form requiring high-temperature reduction, than was the case in the more concentrated samples. Since in this diluted sample all the Rh is in the dispersed phase (Fig. 2), we must conclude that if this dispersed phase has not been exposed to temperatures above 600°C it is easily reduced and does not interact strongly with the support contrary to the case in the Re/γ-Al_2O_3 system (*4*). The interaction with the support which creates a dissolved phase begins only at temperatures higher than 600°C under oxidizing conditions.

The splitting of the peak in the low-temperature hydrogen uptake noted for the concentrated sample of Fig. 5 is absent for the diluted sample of Fig. 6. We attribute the splitting to the difference in reducibility between the dispersed phase and the crystallites which are both present in the concentrated sample. Successive treat-

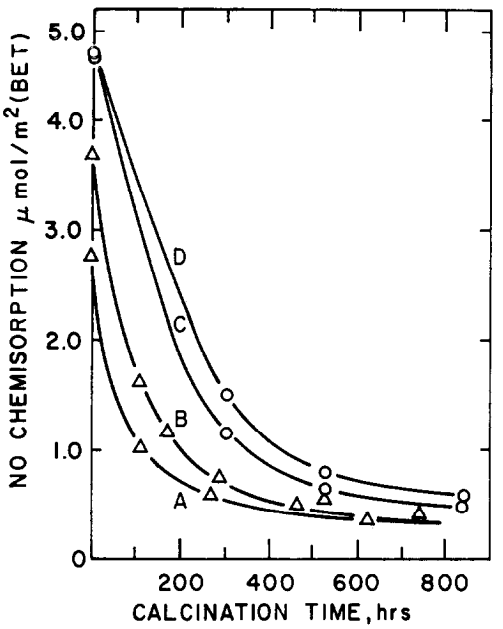

FIG. 4. Effect of long heat treatment at 700°C on Rh surface accessibility as measured by NO chemisorption. Rh wt%: (A) 2.79, (B) 5.51, (C) 9.12, (D) 12.65.

ments at high temperatures under oxidizing conditions cause crystallite growth, as noted in Table 2, and a sharper differentiation between the two phases of the Rh, the two- and three-dimensional phases, with a concomitant differentiation in their reducibility.

This interpretation was checked by the following experiment using the concentrated sample (5.51 wt% Rh). Two different pretreatments were given to the sample before calcination in air at 500°C and programmed reduction. In one case a long reduction at 700°C was applied to enhance crystallite growth, leading to the state which is difficult to disperse. In the other case, the same heat treatment was performed in nitrogen in order to augment the dispersion and minimize the presence of the three-dimensional phase. The results of the programmed reduction runs are shown in Fig. 7. The sample treated to produce a large amount of crystalline phase is reduced in the low-temperature region with the main peak at ~100°C. This hydrogen uptake is therefore taken as that associated with three-dimensional phase. The shoulder in Fig. 7, trace A, and the second peak of the doublet in Fig. 5, trace D, are therefore associated with the dispersed two-dimensional phase on the surface. The high-temperature uptake at ~550°C on all the temperature-programmed curves is associated with the product of the interaction between the rhodium and the γ-Al_2O_3 support. The extent of this interaction at high temperature can be so large after the extensive dispersion that only a fraction of the dissolved phase can be reduced during the relatively rapid scan of the programmed reduction (see Fig. 7, trace B).

The total amount of hydrogen taken up in the programmed reduction per Rh atom will depend on the pretreatment condition in a very complex fashion. It is instructive to compare the uptakes as summarized in Table 3 for the data presented in Figs. 5 and 6. Note that the weights of the samples were chosen so that the amount of Rh was nearly equal in both the dilute and concentrated samples. In the dilute supported Rh sample, where initially all the Rh is dispersed, the amount of H_2 taken up with respect to the Rh loading will monotonically decrease with the calcination temperature. This is because Rh ions which by interaction with γ-Al_2O_3 have sunk to a certain depth below the surface cannot be

TABLE 2

Average Particle Size of Rh in Samples Heated in Air for >500 hr at 700°C

Rh in sample[a] (wt%)	Average particle diameter[b] (Å)
2.79	168
5.51	132
9.12	272
11.68	219

[a] Determined by X-ray fluorescence.
[b] Determined by transmission electron microscopy.

reduced during the programmed reduction run. After the calcination at 700°C more than half of the Rh in the diluted sample is in this state. It is worth noting that the H_2/Rh uptake ratio of a sample calcined at 400°C is ~1.5, which corresponds to an average oxidation state of Rh^{3+} in the dispersed phase.

The H_2 uptake in the concentrated Rh samples behaves in exactly the opposite manner as shown in the lower part of Table 3. The Rh is present here largely in three-dimensional crystallites whose oxidation is diffusion limited through the layer of the oxide. Therefore, the oxidation of the inner part of the crystallites requires more drastic calcination conditions. If one plausibly assumes that after 700°C treatment all the reducible Rh is oxidized to the trivalent state, then about one-third of the total Rh loading must have interacted with the γ-Al_2O_3 in subsurface layers and is not reducible during the programmed reduction run. This conclusion is reached from the observed H_2/Rh ratio of 1.0 compared with the expected value of 1.5.

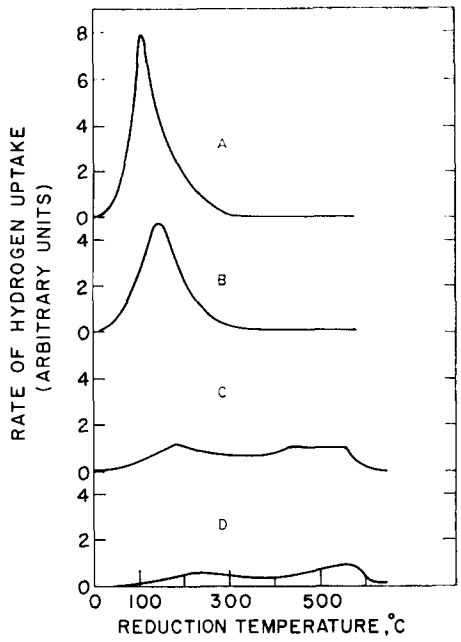

FIG. 6. Temperature-programmed reduction of 0.92 wt% Rh/γ-Al_2O_3. Calcination treatment: (A) 400°C, 2 hr; (B) 500°C, 16 hr; (C) 600°C, 16 hr; (D) 700°C, 16 hr.

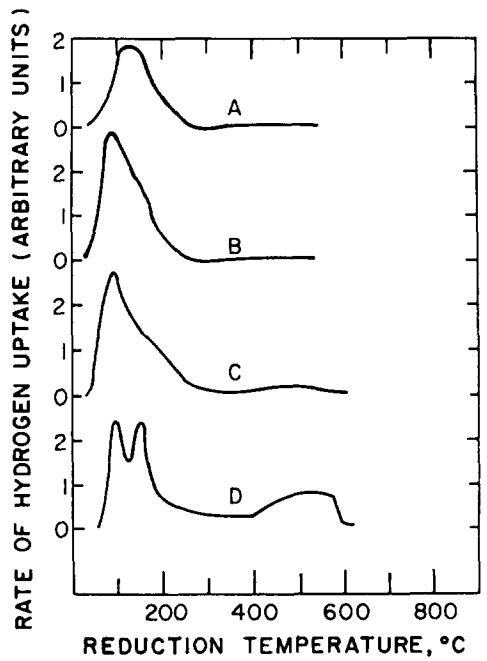

FIG. 5. Temperature-programmed reduction of Rh (5.51 wt%)/γ-Al_2O_3. Calcination treatment: (A) 400°C, 16 hr; (B) 500°C, 16 hr; (C) 600°C, 16 hr; (D) 700°C, 12 hr.

D. Sintering studies of Rh-containing practical catalysts. The monolithic catalysts described under Experimental were designed to devise a system more closely resembling those which may be employed in future automotive practice. First, the high-temperature treatment before Rh impregnation converted the γ-Al_2O_3 in the washcoat into the δ-modification with a concomitant decrease from a total BET area of 14 m^2/g of catalyst to 8 m^2/g. Second, the range of Rh concentration investigated was lower, <0.6 wt% Rh. Still, it has to be stressed that in practical applications, concentrations lower by at least another order of magnitude will probably be used. In our case the desire to maintain a suitable measurement precision prevented further lowering of the Rh concentration, and the present choice obviously represents a compromise.

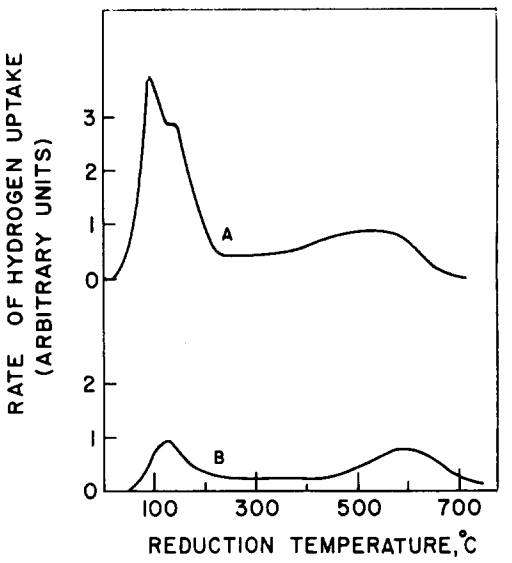

FIG. 7. Temperature-programmed reduction of Rh (5.51 wt%)/γ-Al_2O_3. (A) After 18 hr in H_2 at 700°C and 2 hr in air at 500°C; (B) after 18 hr in N_2 at 700°C and 2 hr in air at 500°C.

Because of the changing adsorption multiplicity (*8*, *9*) in the adsorption of simple molecules on dilute supported Rh samples (see also Table 1 above), a method of hydrogen–oxygen titration was developed for a reliable determination of the Rh surface. This is possible, since oxygen adsorption underlying the titration appears to be relatively constant.

First it was necessary to establish a reproducible technique for the titration, since at room temperature erratic values are obtained and the titration reaction on the surface, contrary to the wide experience with Pt (*11*), appears to be rate limited. The titration reaction, in general, is represented by the equation

$$Me_{(s)}O_n + (n + x/2)\cdot H_2 \rightarrow Me_{(s)}H_x + nH_2O. \quad (1)$$

In the case of Rh, as indicated above, the value of x depends on the concentration and also on the temperature, while the value of n is almost constant and equal to $\frac{3}{2}$. Thus the surface Rh is oxidized by exposure to oxygen at room temperature to the trivalent Rh^{3+} state which is stable to at least 300°C. This is shown in Fig. 8 where the adsorption of oxygen on supported Rh reaches the same constant value at 25 and 300°C and is also practically irreversible. The ratio of this uptake of O atoms with respect to the total amount of Rh for the diluted sample (0.92 wt% Rh/γ-Al_2O_3) was ~1.5 at both temperatures.

To establish a temperature range in which the amount of hydrogen consumed in the titration is constant, a well-characterized Rh sample was subjected to the titration procedure in the 20–430°C range and the results are given in Table 4. There is a wide interval between 106 and 268°C where the titration results are constant and the titration reaction is fast. In this region, the value of x in Eq. (1) is constant and is assumed to be unity. At room temperature the titration is incomplete, while at temperatures above 270° the value of x can sharply drop off. At even higher temperatures the value of n can also, conceivably, decrease.

From the values in Table 4 the temperature of 115°C was chosen for the titration procedure. The sample was always prereduced and exposed to air at room temperature before the titration.

The important finding with the deliberately presintered monolithic catalysts is that, when exposed to prolonged calcination in air, they showed a behavior very similar to that of the granular Rh/γ-Al_2O_3 samples. Figure 9 shows that calcination at 600°C decreases somewhat the titratable area. The surface accessibility decreases much more sharply when the calcination temperature is in excess of 700°C.

To assess whether the loss of metal surface area, as measured by titration, is due to the same interactions with the support as observed for the Rh/γ-Al_2O_3 samples the following experiment was performed. A sample with 0.066 wt% Rh was heated in air at 700°C and the titration values

TABLE 3

Specific Uptake of Hydrogen in the Temperature-Programmed Reduction of Rh/γ-Al_2O_3

Sample	Oxidation pretreatment		H_2 uptake[a] (μmole)	H_2/Rh
	Temperature (°C)	Time (hr)		
0.92 wt% Rh; total Rh: 61.6 μmole	400	2	95.8	1.6
	500	16	86.7	1.4
	600	16	67.6	1.1
	700	16	40.4	0.7
5.51 wt% Rh; total Rh: 67.7 μmole	400	16	22.5	0.3
	500	16	34.0	0.5
	600	16	42.6	0.6
	700	12	66.2	1.0

[a] In reduction, molecular hydrogen is considered.

were measured in the usual manner, i.e., after reduction at 425°C. In another specimen the titration values were measured twice: once exactly in the same manner and then after an additional reduction for 16 hr at 560°C. These results are shown in Fig. 10. For both samples where the titration was carried out after reduction at 425°C, a common curve can be drawn. The additional reduction at 560°C produces a series of titration points lying on a curve representing a higher surface accessibility of Rh. Both curves originate at the same point, indicating that before calcination the different reduction temperature does not influence the titration value.

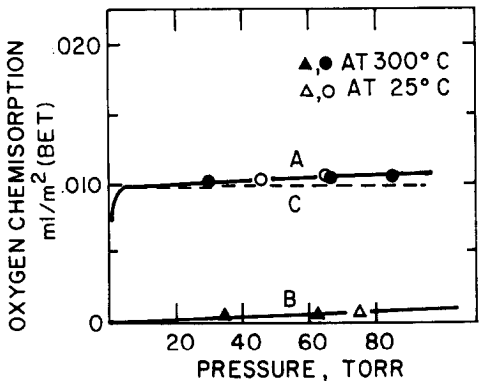

FIG. 8. Oxygen chemisorption at 25 and 300°C on 0.92 wt% Rh/γ-Al_2O_3 (notation as in Fig. 1).

Hence, the behavior of Rh/δ-Al_2O_3 is exactly analogous to that of Rh/γ-Al_2O_3. It is plausible to assume here also that there are two processes that diminish the surface accessibility: interaction between Rh oxide and the support and particle growth. The parallelism of the two curves in Fig. 10 suggests that the amount of recoverable dispersed phase reaches a constant value, as could, perhaps, be expected. Were the time and temperature of the additional reduction different, the separation between the two curves in Fig. 10 might differ as well. In fact, it was established by preliminary experiments that the

TABLE 4

Hydrogen Uptake in Titration as a Function of Temperature[a]

Temperature (°C)	H_2 uptake (μmole/g)
20	4.22 ± 0.25
106	6.63 ± 0.10
127	6.83 ± 0.02
205	6.63 ± 0.16
268	6.40 ± 0.30
335	4.91 ± 0.08
428	4.15 ± 0.16

[a] For 0.20% Rh on 10% δ-Al_2O_3 (American Lava Honeycomb).

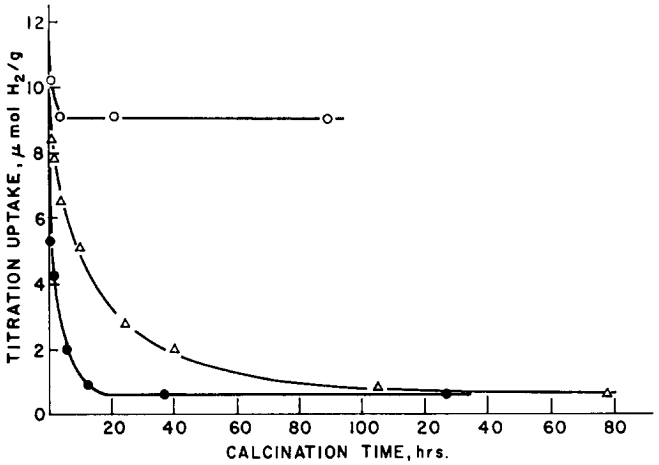

FIG. 9. Hydrogen–oxygen titration of a monolithic catalyst (0.16% Rh/δ-Al_2O_3 washcoat), after calcination in air: (○) 600°C; (△) 700°C; (●) 800°C.

recoverable surface accessibility during reduction at 550–560°C is time dependent.

DISCUSSION

The following remarks are intended to summarize the observations of this paper and to explain where possible the differences with the previous work on this subject, mainly that in Refs. (*6*, *8*, *9*). It will become apparent that the contradictions within the literature can be reconciled to a large degree.

First, under mildly oxidizing conditions, trivalent Rh ions disperse easily over the surface of γ-Al_2O_3 with a relatively weak interaction with it. This is seen by the rather minor difference in the reduction conditions required for the dispersed monolayer phase and the nondispersed particulate phase. This observation is in agreement with the conclusion of Newkirk and

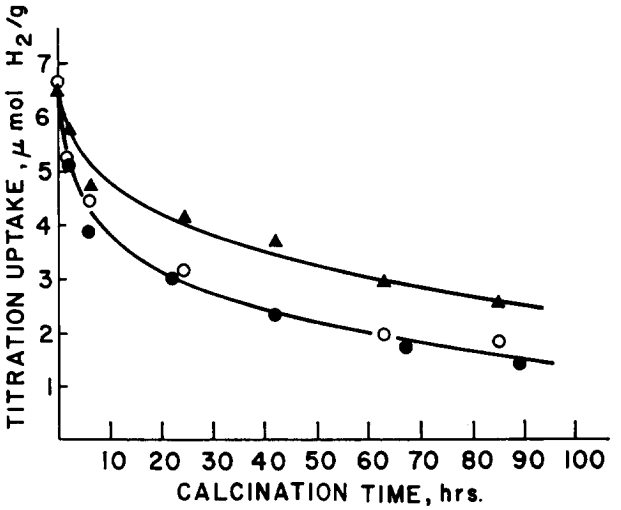

FIG. 10. Hydrogen–oxygen titration of a monolithic catalyst (0.066% Rh/δ-Al_2O_3 washcoat) after calcination in air at 700°C: (○, ●) Prereduction at 425°C; (▲) additional prereduction at 560°C.

McKee (*13*) when referring to the reduction of the trivalent Rh ions present as chlorides on the alumina surface.

The limiting surface saturation concentration of the dispersed Rh^{3+} phase is quite close to that of Re^{4+}, 2.5 μmole/m^2 of γ-Al_2O_3 (vs 2.0 for Re^{4+}) although the interaction, judging from the resistance to reduction, is much weaker. All the excess Rh is going into the three-dimensional crystallites of the particulate phase.

Chemisorption of simple gases is inadequate for the assessment of dispersion of Rh in dilute samples because of the multiple chemisorption observed both here and in Ref. (*8*). This multiple chemisorption is a rather strong function of surface Rh concentration at the dilute end of the concentration range. Indeed, multiple chemisorption has been noted by Yang and Garland (*14*) and by Arai and Tominaga (*15*) by ir methods in the same system. Our own ir spectra on diluted Rh samples show the antisymmetric (2100 cm^{-1}) and symmetric (2030 cm^{-1}) motions of a doublet of CO molecules adsorbed on a single Rh site, very similar to those reported by Yang and Garland. In fact, after adsorption only these bands are seen, supporting the limiting $CO/Rh_{(s)}$ ratio of 2. Multiple chemisorption of NO in dilute supported base metals has been reported before (*2*, *3*). On the other hand, chemisorption methods for the measurement of the available metal area are absolutely adequate in several systems for samples containing several percent of active components and will probably give acceptable results in the Rh/γ-Al_2O_3 system as well. It is worth recalling that Buyanova *et al.* (*9*) have noted that a dilute sample of supported Rh takes up twice the amount of CO per Rh site than do the metallic Rh black powders. They have attributed it to linear and bridged CO bonding in the respective cases. From our work, it appears that multiple CO chemisorption in the diluted sample could be responsible for a large part of this difference.

Oxygen chemisorption, or more precisely surface oxidation, stoichiometry is a separate case and has been studied by the aforementioned groups of workers (*6*, *8*, *9*). Depending on the temperature, the value of $O/Rh_{(s)}$ in diluted samples has attained values up to $\sim$1.5 in the work of Wanke and Dougherty (*8*). The difference between the stoichiometry observed at 25 and 200°C was small. This observation is in essential agreement with the stoichiometry observed here.

On the other hand, Buyanova *et al.* (*9*) and Sverdlova *et al.* (*6*) claim that the surface oxidation stoichiometry is $\sim$1.0, although at least one sample in Ref. (*9*) attained the value of 1.5. It is interesting to note that the authors of Ref. (*6*) postulate that the stable oxidation state of Rh is +3, but come to the conclusion that it is not attained on the surface when re-exposed to oxygen after prereduction. It is not easy to trace the exact reason for the low value of the $O/Rh_{(s)}$ stoichiometry in the cited work, but it is most likely associated with the dynamic chromatographic pulse method in which any trace of an oxidizing impurity in the carrier gas will tend to underestimate the oxygen adsorption stoichiometry.

All the literature data indicate, nevertheless, that the surface oxidation stoichiometry is relatively constant as a function of dispersion and therefore the hydrogen–oxygen titration which is based on it is a suitable technique for the measurement of Rh dispersion in dilute samples. Wanke and Dougherty (*8*) carried out a lengthy series of such measurements. The only difference proposed in this work is to carry out the titration procedure in the temperature range (110–250°C) where the titration reaction goes to completion. On the other hand, the exposure to oxygen before the titration should not be made above room temperature since this may lead to

the oxidation of subsurface layers in the three-dimensional phase, if present, which when reduced during the subsequent titration will give exaggerated values of surface Rh.

Finally, the present data are in essential agreement with Sverdlova *et al.* (*6*) on the interaction of Rh-oxide with the support which renders the Rh irreducible by hydrogen below 500°C. In our samples of γ-Al_2O_3 this interaction under oxidizing conditions begins at ~600°C, while in the cited reference it apparently took place as low as 400°C. Even higher temperature forms of alumina, such as δ-Al_2O_3, interact with the Rh oxide. It will be of interest to explore whether the high-temperature, relatively inert, modification, α-Al_2O_3, can also interact in this fashion.

This work indicates that there are practical limits for the use of Rh catalysts with respect to temperature and atmosphere. If such limits are exceeded the disappearance of the Rh from the surface will make it inaccessible for the catalytic reactions. The presence of other constituents in the catalyst, such as other noble metals which could alloy with the Rh or metal oxides which may interact with γ-Al_2O_3 can be expected to modify profoundly the interactions of Rh with the support. These more complex systems will be the subject of a further inquiry.

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