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Radiochemical Studies of Chemisorption and Catalysis

X.* Adsorptions of [^{14}C]Ethylene and [^{14}C]Carbon Monoxide on Rhodium–Silica and [^{14}C]Ethylene on Rhodium–Alumina

J. U. REID,† S. J. THOMSON, AND G. WEBB

Chemistry Department, The University, Glasgow G12 8QQ, Scotland

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The adsorption at room temperature of [^{14}C]ethylene on "clean" and on [^{14}C]-carbon monoxide precovered catalysts, has been studied using Rh/silica and Rh/alumina. Coverages by ethylene and carbon monoxide have been compared. The "monolayer" coverage of metal, as determined by carbon monoxide adsorption, was exceeded in ethylene adsorption on Rh/silica, where the ethylene isotherms show two regions. One steeply sloping primary region occurred at low pressure (up to $\sim 10^{-1}$ Torr), and it corresponded to a carbon monoxide monolayer on the basis of two CO molecules to one C_2H_4 molecule. The other secondary adsorption (observed up to ~ 6 Torr), of gentle slope, corresponded to coverages many times in excess of the monolayer coverage This extensive adsorption is interpreted in terms of adsorption on the support occurring via the metal. Preadsorption of carbon monoxide on Rh/silica, followed by evacuation, resulted in complete suppression of the primary ethylene adsorption, but it did not affect secondary adsorption. Hydrogen treatment of adsorbed species from [^{14}C]ethylene on Rh/silica and Rh/alumina was investigated. Some primary and some secondary material was removed at room temperature. Adsorption of [^{14}C]carbon monoxide on [^{14}C]ethylene precovered surfaces occurred to the extent of $\sim 25\%$ of the monolayer value. The results are discussed in terms of a model in which primary adsorption of ethylene occurred directly on the metal, whereas secondary adsorption involved hydrocarbon species migrating from metal to support.

INTRODUCTION

In previous studies of chemisorption and catalysis in this series we have restricted the use of the radiochemical approach to systems involving one adsorbate. In the present study we have extended these investigations to systems containing two adsorbates. In such systems it is possible, by selectively labelling one of the species with a radioactive tracer, to follow the behavior of one component in the presence of another. In this paper we describe studies in which we have exploited this technique to investigate the possible migration of hydrocarbon species between metal and support using silica- and alumina-supported rhodium catalysts.

In catalysis by supported metals, it is possible that the support may exert a chemical effect in addition to the physical role of dispersion of the metal (*1–8*). Although the interaction between the metal and the support is not well understood, it is possible that there may be an electronic effect at the metal–support interface (*6, 7*). The chemical role of the support may be extended to cover situations met with in bifunctional catalysis (*9–11*), where the widely accepted mechanism involves hydrogenation–dehydrogenation on the metal, accompanied by

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[*] Previous papers in this series: Part IX, Altham, J. A., and Webb, G., *J. Catal.* **18**, 133 (1970); Part VIII, Taylor, G. F., Thomson, S. J., and Webb, G., *J. Catal.* **12**, 150 (1968).

[†] Present Address: Edward Davies Chemical Laboratories, Aberystwyth, SY23, 1NE, U. K.

rearrangement of the olefin produced on the metal on the acidic sites on the support. The mode of transport of the olefin between metal and support is not well established. The use of mechanical mixtures (*12–14*) has indicated that gaseous diffusion of the intermediate olefin probably occurs in some systems. However, in other systems it has been suggested that surface diffusion may be involved (*15*).

In the case of hydrocarbons, there is little direct evidence of surface migration in these bifunctional systems, or in other systems, although the "spillover" of atomic hydrogen from metal to support and vice versa has been discussed by Boudart and others (*16–21*). The migration of hydrocarbon species from metal to support has been invoked to explain the observation that the extent of retention of ethylene and acetylene on silica- and alumina-supported platinum catalysts was far in excess of that which could be accounted for by adsorption only on the metal surface (*22, 23*). Further evidence for hydrocarbon migration comes from a study of the hydroisomerization of 1-butene over mercury-poisoned rhodium–silica catalysts (*24*). In these studies it was shown that, whereas the rate of hydrogenation decreased uniformly with increasing mercury coverage, the rate of isomerization was independent of the surface concentration of mercury until a metal coverage of approximately 90% had been achieved. These observations were shown to be consistent with a mechanism in which hydrogenation occurred on the metal, while migration of the hydrocarbon to the silica support was a necessary prerequisite to isomerization.

In the present study, the amount of ethylene adsorbed on supported rhodium catalysts was observed directly. An attempt was made to differentiate between the hydrocarbon adsorbed on the metal, and that adsorbed on the support, by a technique involving comparison of carbon monoxide and ethylene adsorption, and poisoning of the metal by adsorption of carbon monoxide. In this way it was planned to investigate the migration of adsorbed ethylene between metal and support.

EXPERIMENTAL

Apparatus and Experimental Procedure

The apparatus consisted of a conventional high-vacuum system to which was connected a reaction vessel (Fig. 1), which was an improved version of that used by Cormack, Thomson, and Webb (*25*) in "direct monitoring" studies of ethylene adsorption on a variety of alumina-supported metal catalysts. With the catalyst boat situated beneath the Geiger–Muller tubes (G–M1 and 2), the amount of ^{14}C-labelled adsorbate could be found by subtraction of the gas-phase count rate recorded on G–M2 from the (gas + surface) count rate recorded on G–M1. The surface count rates so determined were used as relative count rates. Since it was not possible to reproduce exactly the distribution of the catalyst beneath the G–M counter,

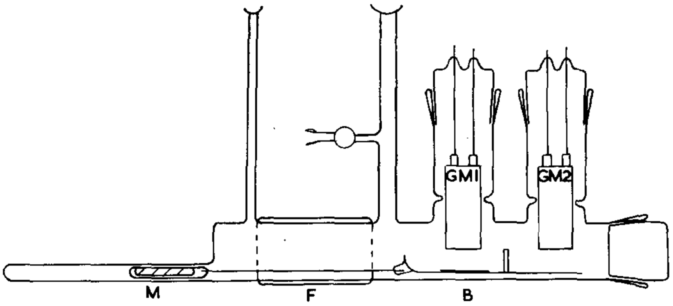

FIG. 1. Reaction vessel. G-M1 monitors catalyst plus gas phase: G-M2 monitors gas phase only. The catalyst boat B could be moved by the magnet M into the furnace area F.

surface count rates were comparable only where the same catalyst sample was used. It was, however, possible to use the same sample for several experiments, since the standardized procedure for cleaning the catalyst was shown to remove all but a small amount (<5%) of the radioactive adsorbates used: results were corrected for this count rate. It was also shown that the positioning of the boat beneath the counters could be carried out in a reproducible manner.

Before each adsorption experiment, the catalyst sample was cleaned of adsorbate by being heated to 350°C, in the furnace region of the reaction vessel, for 12 hr in a stream of hydrogen. The catalyst was then evacuated for 6 hr at 350°C to remove adsorbed hydrogen, and finally cooled to ambient temperature *in vacuo* over a period of 45 min.

Following the cleaning procedure, the catalyst boat was repositioned under the counters. Small amounts of ^{14}C-labelled gas were admitted to the reaction vessel and the count rates on G–M1 and G–M2 were recorded for each aliquot of gas. The surface coverage at ambient temperature was built up in this manner and an adsorption isotherm for the gas derived.

The count rates (counts min^{-1}) below were usually derived from one-minute counts. The error on a count rate of 3000 count min^{-1} is ca. 1.8% while on a count rate of 9000 count min^{-1}, the error is less than 1.1%.

The Mullard MX 168 G–M tubes were correlated, one with another, by a series of different counts using a small amount of radioactive gas in the reaction vessel and the empty catalyst boat in the counting position. Thus a correlation factor was derived whereby the gas-phase count rates recorded on G–M2 could be converted to an expected gas-phase count rate for G–M1 before subtractions were carried out. A gas-phase count rate of ca. 500 counts min^{-1} corresponded to a pressure of radioactive gas of 7.5×10^{-2} Torr. Gas count rates were found to be nearly proportional to gas pressure in the pressure range used in this work.

Materials

^{14}C-labelled ethylene and [^{14}C]carbon monoxide (Radiochemical Centre, Amersham) were diluted in a calibrated system before use to a specific activity of 0.1 mCi/m*M* with the appropriate nonradioactive gas. Counts per minute for a given pressure were then established by counting the gas-phase radioactivity using G–M2.

Cylinder hydrogen (B.O.C. Ltd.) was used for catalyst reduction without further purification. For all other purposes, the hydrogen was purified by diffusion through a palladium thimble. Ethylene (B.O.C. Ltd.) was degassed before use and carbon monoxide (B.O.C. Ltd.) was used without further purification.

Catalysts

Catalysts were prepared by adding an aqueous solution of $RhCl_3 \cdot 3H_2O$ to an aqueous suspension of the support, followed by evaporation to dryness. The supported salt was finally dried in an air oven at 150°C overnight, followed by reduction at 200°C in a stream of hydrogen for 24 hr.

Catalysts prepared in this manner consisted of 5% and 15% w/w Rh/silica ("Aerosil," Degussa Ltd.) and 5% w/w Rh/alumina (Peter Spence Type "A") or 5% w/w $Rh/\gamma\text{-}Al_2O_3$ (Degussa Ltd.).

For use, a sample of catalyst (ca. 0.1 g) was slurried with distilled water and spread thinly and evenly on to the catalyst boat. Drying at 200°C in air for 24 hr followed. After insertion into the reactor, the catalyst was cleaned as described earlier, before carrying out the adsorption experiments.

Samples of alumina and silica used for comparison purposes were treated in exactly the same manner as that used for the supported rhodium catalysts.

RESULTS

All adsorptions reported are for ambient temperature, ~18°C.

Carbon Monoxide Adsorption

A typical [^{14}C]carbon monoxide adsorption isotherm on 5% Rh/silica is shown

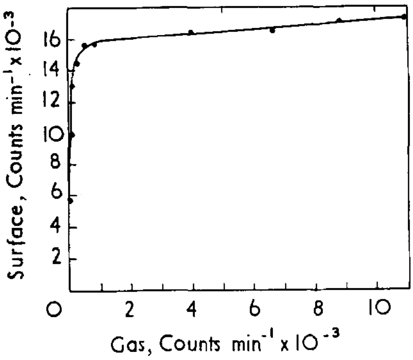

FIG. 2. ^{14}CO adsorption on 5% Rh/SiO$_2$.

in Fig. 2. Extrapolation of the isotherm plateau to zero gas-count rate gave the "monolayer count," a measure of the amount of surface metal present. The effect of evacuation of the reaction vessel for 1 hr after such an adsorption was small. In ten experiments the mean amount removed was 9.5 ± 1.5%.

A carbon monoxide adsorption and "monolayer count" were measured immediately before or immediately after any experiment in which a [^{14}C]ethylene adsorption isotherm was determined. Thus it was possible to compare the amount of [^{14}C]ethylene and [^{14}C]carbon monoxide taken up by the same catalyst sample, only the catalyst cleaning procedure having intervened.

Ethylene Adsorption

Typical adsorption isotherms for ethylene on 5% Rh/silica are shown in Fig. 3. Comparison of Figs. 2 and 3 shows clearly that ethylene and carbon monoxide adsorption on these catalysts displayed quite different characteristics. The adsorption of ethylene continued with increase in gas pressure; no plateau region was observed. A steep "primary" gradient was followed by a more shallow "secondary" gradient. The secondary gradients varied between 0.5 and 1.5, although 1.0 was a typical value for 5% Rh/silica catalyst. Although gas pressures of between 6 and 8 Torr were sometimes attained, no diminution in secondary gradient was observed, and the amount of adsorbate involved in this type of adsorption was often many times greater than that involved in the primary adsorption.

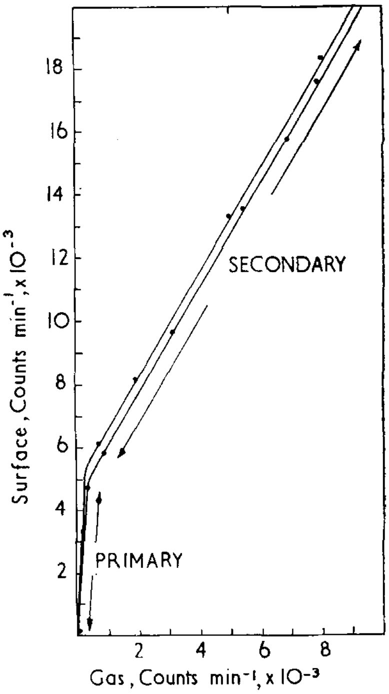

FIG. 3. $^{14}C_2H_4$ adsorption on 5% Rh/SiO$_2$. Two adsorptions are shown on the same catalyst.

Two experiments were carried out using the 15% Rh/silica catalyst. Primary adsorption was approximately two to five times that observed with a typical 5% Rh/silica catalyst, although with both catalysts secondary gradients of 1.1 to 1.2 were observed. Differences in adsorption can be ascribed to metal areas not being strictly proportional to loading of metal and to differences in counting geometries.

Ethylene adsorption on 5% Rh/alumina displayed similar characteristics to those observed with 5% Rh/silica, although the secondary gradients were somewhat greater, approaching a value of 2.0. The results obtained with the various catalysts are summarized in Table 1. This table shows the surface count rates at the change-over point from primary to secondary gradients and the evacuation data. In all cases, evacuation of the catalyst for 1 hr had little effect upon the surface count rate. The fall in count rate can be ascribed to removal of ethylene directly adsorbed

TABLE 1

ETHYLENE ADSORPTION ON Rh/Al_2O_3 AND Rh/SiO_2 AT 17°C

Catalyst	Counts min^{-1} at turning point	Secondary gradient	Effect of 1 hr evacuation counts min^{-1}	
			Before	After
5% Rh/SiO_2	3250	1.2	17755	17264
	3000	1.4	24345	22340
	3500	1.1	14268	14363
	6500	0.6	12575	11383
	5250	0.9	13001	11035
15% Rh/SiO_2	15000	1.1	24475	23260
	14000	1.2	29537	28640
5% Rh/Al_2O_3	2500	1.7	27402	25100
	2000	2.0	11088	9000
	1500	1.8	14950	12490

on the support. We would draw attention to the difference in gradients for secondary adsorption on supported catalysts and on the supports themselves. It was also found that, over periods up to 17 hr, the extents of both primary and secondary adsorptions were independent of the time of contact of the catalyst with gas-phase ethylene (see Table 2).

Ethylene Adsorption on Silica and Alumina

Ethylene adsorptions on amounts of silica or alumina (Peter Spence Type 'A') equal to those used in the rhodium catalysts, and treated in an identical manner, followed approximately linear isotherms with gradients of 0.17 (silica) and 0.75 (alumina). Evacuation for 1 hr removed 62% of the adsorbed ethylene from silica and 47.5% from alumina.

TABLE 2

EXAMINATION OF CONSTANCY OF ETHYLENE ADSORPTION ON 5% Rh/SiO_2

	Time (h)	Counts min^{-1} from surface	Counts min^{-1} from gas
Primary adsorption	0	3932	871
	1	4078	851
Secondary adsorption after further $[^{14}C]C_2H_4$ admitted	0	8583	4958
	1	8572	4889
	2	8498	5303
	17.5	8301	5195

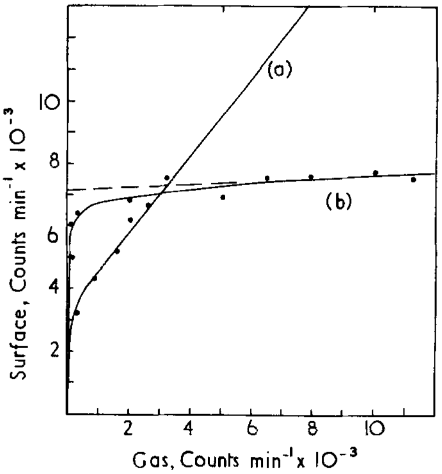

FIG. 4. (a) $^{14}C_2H_4$ adsorption and (b) comparative ^{14}CO adsorption on the same sample of 5% Rh/SiO_2.

Comparative Adsorption of Ethylene and Carbon Monoxide

Figure 4 shows a comparison of the adsorption of carbon monoxide and ethylene on the same sample of 5% Rh/silica catalyst. The results from a series of comparative adsorptions are shown in Table 3. The number of ethylene molecules involved in primary adsorption was approximately equal to one half the number of carbon monoxide molecules in the monolayer.

TABLE 3

COMPARATIVE $^{14}C_2H_4$ AND ^{14}CO ADSORPTION ON SAME SAMPLES OF CATALYST, 5% Rh/SiO_2

Sample number	Counts min^{-1} at turning point for $^{14}C_2H_4$ adsorption	Counts min^{-1} at ^{14}CO monolayer	Ratio
1	3600	6900	1:1.9
2	6500	14800	1:2.3
3	3800	8300	1:2.2
4	2500	4700	1:1.9
5	2500	6000	1:2.4
6	3000	6200	1:2.1
7	4500	9800	1:2.2
8	5200	10000	1:1.9

Effect of Pre-Adsorption of CO on Ethylene Adsorption on 5% Rh/Silica

Catalyst samples were exposed to a few Torr of nonradioactive carbon monoxide for a few minutes and the reaction vessel was evacuated for 1 hr. [^{14}C]ethylene was then admitted in small aliquots to the catalyst vessel and the adsorption isotherm determined. Comparison was then made with the ethylene adsorption isotherms obtained in the absence of carbon monoxide using the same catalyst sample. Typical results are shown in Fig. 5. When carbon monoxide was pre-adsorbed on the catalyst, no primary adsorption of ethylene was observed and the gradient of the adsorption isotherm was the same as that for secondary ethylene adsorption on the unpoisoned catalyst. In the experiment shown in Fig. 6, [^{14}C]ethylene adsorption on a "clean" catalyst was stopped at point A and the catalyst evacuated. Carbon monoxide to a pressure of a few Torr was then admitted, followed by further evacuation. [^{14}C]ethylene adsorption was recommenced at point B. Some adsorbed ethylene was removed by displacement and evacuation; thus point B is lower than point A. However, no change in gradient was observed, and the secondary adsorption was equal to that observed in the adsorption on the CO-prepoisoned catalyst [curve (b)].

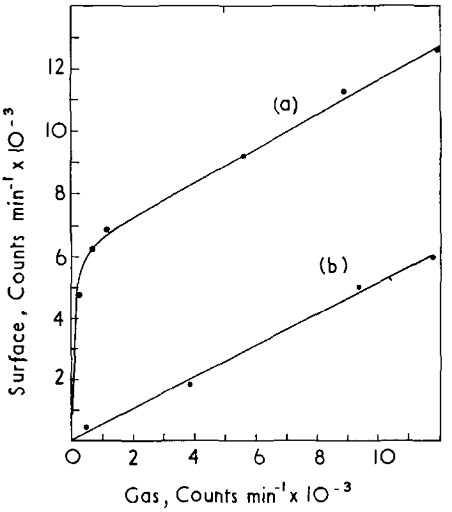

FIG. 5. Effect of preadsorption of CO on $^{14}C_2H_4$ adsorption on 5% Rh/SiO$_2$. (a) $^{14}C_2H_4$ on clean catalyst. (b) $^{14}C_2H_4$ on CO-precovered catalyst.

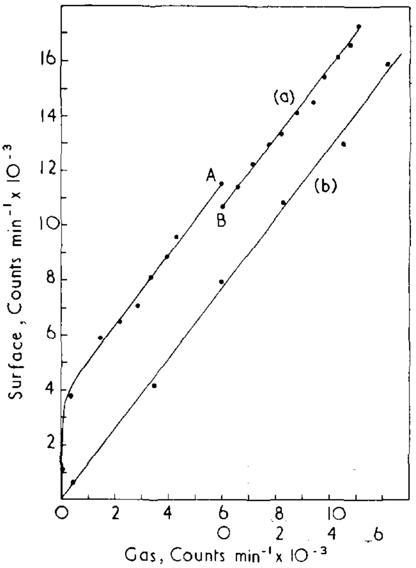

FIG. 6. (a) $^{14}C_2H_4$ adsorption on 5% Rh/SiO$_2$. Adsorption was stopped at A, the system evacuated, exposed to CO, evacuated, and $^{14}C_2H_4$ adsorption recommenced at B. (b) $^{14}C_2H_4$ adsorption on a CO precovered catalyst. Same catalyst used in (a) and (b).

To measure the amount of adsorbed carbon monoxide displaced on the admission of gas phase ethylene, [^{14}C]carbon monoxide was admitted to a clean catalyst; the catalyst was evacuated for 1 hr, nonradioactive ethylene was then admitted to the catalyst and the change in surface count rate after 1 hr was recorded. The results are shown in Table 4 together with the results obtained when nonradioactive carbon monoxide was admitted to a [^{14}C]ethylene precovered surface. Figure 7 shows a comparison between the adsorption of [^{14}C]-ethylene on a "clean" catalyst sample and the adsorption of a 1:1 mixture of [^{14}C]ethylene and nonradioactive carbon monoxide on the same catalyst sample following the cleaning procedure.

Effect of Hydrogen Upon Adsorbed Species on Rh/Silica and Rh/Alumina

The effect of hydrogen upon [^{14}C]-ethylene adsorbed upon a "clean" catalyst and upon a carbon monoxide prepoisoned

TABLE 4

C_2H_4 DISPLACEMENT OF ^{14}CO AND CO DISPLACEMENT OF $^{14}C_2H_4$ ON 5% Rh/SiO_2

Adsorbate	Counts min^{-1}	Displacing gas	Pressure Torr	Final counts min^{-1}	Removal percent
^{14}CO	11811	C_2H_4	40	11360	4
$^{14}C_2H_4$	10226	CO	2-3	9090	11
$^{14}C_2H_4$	5470	CO	10	4800	12

catalyst was investigated by admitting 30 Torr of hydrogen to the catalyst vessel at ambient temperature, and monitoring the change in surface count rate with time. Typical results for 5% Rh/silica and 5% Rh/alumina are shown in Figs. 8 and 9, respectively. Table 5 shows the results obtained for 5% Rh/silica catalyst. For both silica- and alumina-supported catalysts the admission of hydrogen resulted in an initial rapid decrease in surface count rate, followed by a slower decrease. In Fig. 8, the rapid fall in count rate when hydrogen was introduced corresponded approximately to the counts ascribed to the primary adsorption process. We therefore suspected that initially hydrogen was removing species primarily from the metal component of the catalyst. This view is substantiated by the observation (Fig. 8) that when a carbon monoxide prepoisoned catalyst was used, the initial fast decrease in surface counts was not observed on admission of hydrogen.

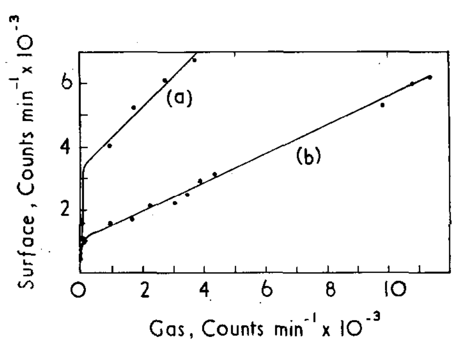

FIG. 7. (a) $^{14}C_2H_4$ adsorption on 5% Rh/SiO_2. (b) Adsorption of a 1:1 mixture of $^{14}C_2H_4$, CO on the same catalyst after cleaning procedure.

The percentage of adsorbed [^{14}C]ethylene, removed by hydrogen, decreased as the extent of secondary adsorption was increased. Thus in Table 5 the extent of adsorption increased in the order $2 < 3 < 1 < 4$, whereas the percentage removal was in the order $2 > 3 > 1 > 4$. The effect of partially precovering a 5% Rh/SiO_2 catalyst with [^{14}C]C_2H_4 to an extent well below the turning point was also investigated. For this catalyst, the final count after adsorption was 3612 counts min^{-1}

TABLE 5

$^{14}C_2H_4$ REMOVAL FROM 5% Rh/SiO_2 BY HYDROGEN, 30 TORR[a]

	Counts min^{-1}				
Expt	Turning point in $^{14}C_2H_4$ adsorption	Evacuation for 1 hr Before	Evacuation for 1 hr After	Fall in counts, by H_2 treatment	Percent removed
1	4500	16120	15635	9400	60
2	4500	5236	5011	3550	71
3	4500	11845	11681	7150	61
4	4500	21402	19657	11300	58

[a] Note: Same catalyst for each experiment: same secondary gradient: fall in counts measured by extrapolating final slow fall to zero time and subtracting this count from count after evacuation.

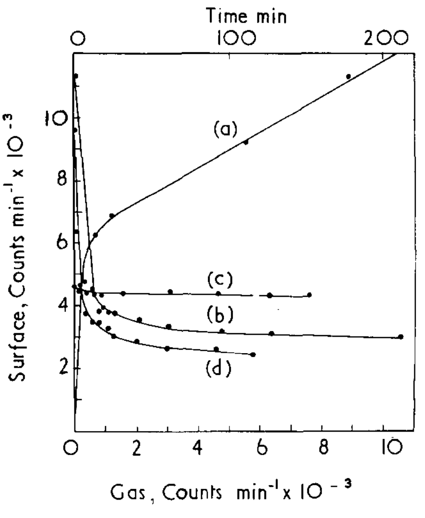

FIG. 8. Removal of adsorbed species by hydrogen from 5% Rh/SiO$_2$ catalyst. (a) $^{14}C_2H_4$ adsorption. (b) Removal by H_2. (c) Removal in case of CO-pretreatment. (d) Removal by C_2H_4/H_2 mixture. Time scale applies to (b), (c), and (d).

(expected turning point 5000). The rapid change in count rate when hydrogen was admitted amounted to a fall in surface coverage by ^{14}C-species of 81%.

Once again this substantiated the view that hydrogen removed species in the initial stage from the metal.

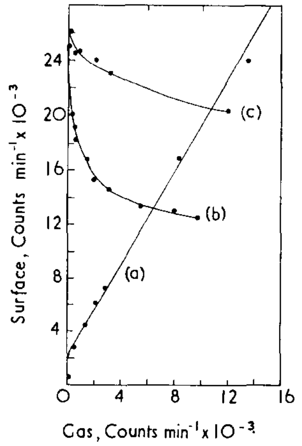

FIG. 9. Removal of adsorbed species by hydrogen from 5% Rh/Al$_2$O$_3$ catalyst. (a) $^{14}C_2H_4$ adsorption. (b) Removal by H_2. (c) Removal in case of CO-pretreatment.

[^{14}C]*Carbon Monoxide Adsorption on Ethylene Precovered Surfaces of 5% Rh/Silica*

In an attempt to establish the existence of bare metal sites following ethylene adsorption, [^{14}C]ethylene was adsorbed on the catalyst, followed by evacuation of the reaction vessel for 1 hr. [^{14}C]Carbon monoxide was then admitted to the catalyst in small aliquots and the change in surface count rate monitored. The results, in Fig. 10 and in Table 6, show the final [^{14}C] ethylene surface count rate following adsorption and after evacuation, the uptake of [^{14}C]carbon monoxide, obtained by extrapolating the plateau count rate to zero gas-phase count rate and subtracting the [^{14}C]ethylene count rate after evacuation, and the corresponding [^{14}C]carbon monoxide monolayer count rate on the "clean" catalyst. From these results, it can be seen that the [^{14}C]carbon monoxide uptake was approximately 25% of the monolayer value.

DISCUSSION

The adsorption of carbon monoxide on supported rhodium catalysts and on evaporated rhodium films has been studied by

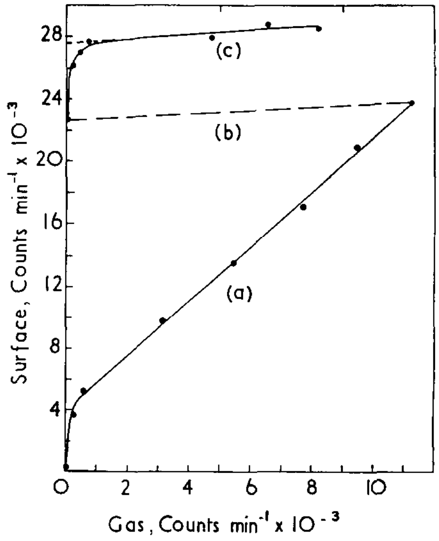

FIG. 10. ^{14}CO adsorption on 5% Rh/SiO$_2$ following adsorption of $^{14}C_2H_4$. (a) Initial $^{14}C_2H_4$ adsorption. (b) Effect of evacuation for 1 hr. (c) Subsequent ^{14}CO adsorption.

TABLE 6

^{14}CO ADSORPTION AFTER $^{14}C_2H_4$ ADSORPTION ON 5% Rh/SiO_2[a]

Counts min^{-1}			
After $^{14}C_2H_4$ adsorption	After evacuation	From ^{14}CO uptake	^{14}CO monolayer
20808	19094	2200	4700
13747	12777	2500	6000
23684	22670	5000	16000
13649	13746	2600	10300
9572	8910	4000	9500

[a] Note: ^{14}CO uptake measured by extrapolating plateau to zero gas-count rate. The count rate after evacuation ($^{14}C_2H_4$) was subtracted from count so obtained.

infrared spectroscopy (*26*, *27*). The results of these studies suggest that, on rhodium, carbon monoxide is probably adsorbed predominantly in the linear mode, with a small contribution from other species (*26*, *28*, *29*). However, since extinction coefficients for the adsorbed species are not known, it is difficult to assign quantitatively relative surface coverages to the various modes of adsorption on spectroscopic evidence alone. A more reliable value for the ratio of the number of carbon monoxide molecules adsorbed to the number of metal sites available can be obtained by the volumetric method used by Sinfelt and Yates (*30*, *31*). By assuming that monolayer coverage for carbon monoxide was obtained at a gas pressure of 100 Torr, and comparing the amounts of hydrogen adsorbed by the same catalyst samples, over a range of metal concentrations, a [CO(ads.)/metal site] ratio of approximately unity was derived (*31*). These workers also showed (*30*) that for a 5% rhodium/silica catalyst good agreement between crystallite size determined by hydrogen chemisorption and by X-ray line broadening was obtained. Thus, it may be concluded that with silica-supported rhodium catalysts both hydrogen and carbon monoxide adsorption provides good methods for the determination of the area of the metal component.

In the present work the turning point in the carbon monoxide adsorption isotherm was taken as the limit of monolayer coverage. This turning point is demonstrated more clearly in the radiochemical measurements than in the volumetric measurements of Sinfelt and Yates (*31*). Thus, it may be assumed that in the present work a [CO(ads.)/metal site] ratio of unity or slightly less is applicable.

A striking feature of the results presented above is the observation that the turning point in the ethylene adsorption isotherms consistently corresponded to a surface count rate equal to half the surface count rate at the turning point in the carbon monoxide adsorption isotherms for the same catalyst sample. Since the specific activity of [^{14}C]ethylene and [^{14}C]-carbon monoxide was the same, namely 0.1 mCi/m*M*, this observation indicates that each ethylene molecule occupies twice as many sites as each carbon monoxide molecule. Comparison of the areas of the two molecules, calculated from the van der Waals radii, suggest that this could be the case. It is also likely that the primary adsorption of ethylene occurred exclusively on the metal and that the turning point in the ethylene adsorption corresponds to the completion of a monolayer on the metal. This conclusion is supported by the observation (*25*) that, for a number of catalysts, ethylene monolayer formation was complete at pressures below 0.1 Torr: that is, within the pressure range found for primary adsorption in the present studies.

Further evidence for the above conclusion comes from the observation that the extent of primary adsorption increased threefold when the metal loading was increased from 5% to 15% w/w for Rh/silica although, significantly the gradient of the secondary adsorption was independent of the metal loading. Electron microscopy showed similar particle size distributions for the two catalysts. These observations, together with the observation that carbon monoxide poisoning of the metal resulted in the disappearance of the primary adsorption without materially affecting the secondary adsorption, lead to the conclusion that primary adsorption may be identified with the metal component, secondary adsorption with sites located on the surface of the support.

The greater extent of secondary adsorption compared with primary adsorption suggests that the former occurs on a catalyst component of substantially greater area than that of the metal, namely the silica or alumina support. However, comparisons of the gradients observed for secondary adsorption and the gradients obtained for adsorption of ethylene onto silica or alumina in the absence of metal, clearly indicate that the presence of metal facilitates the secondary adsorption process. Furthermore, although a large fraction of the adsorbate is removed by evacuation in the case of alumina and silica, evacuation has little effect upon the material involved in secondary adsorption when rhodium metal is present on the support. It is apparent, therefore, that the metal component plays an active part in secondary adsorption, although the adsorbed material does not remain on the metal. It is suggested that migration occurs from the metal to the support. This postulate raises the question as to the nature of the metal sites responsible for the migration and the mechanism whereby migration occurs. It seems likely that the metal sites responsible for migration are located at the edges and corners of the metal islands and that they are quite dissimilar from metal sites nearer to the center of the islands. It may further be envisaged that each of these edge and corner sites renders a certain area of the support available for hydrocarbon retention. As the number of these sites is increased, for example, by increasing the metal concentration per unit area of support, overlap of the "catchment" areas on the support must occur. It is possible, therefore, to envisage that there is a critical concentration of sites above which increase in metal concentration does not alter the amount of hydrocarbon retained by the support at a particular hydrocarbon pressure. This concentration will depend upon the areas of the support involved in the catchment process. Sancier (*20*) has deduced that atomic hydrogen is capable of migrating a distance of 0.5 nm across the support. Even if hydrocarbon migration is far more restricted than this, the areas involved may be large and thus the critical concentration of metal sites quite small.

Using this model, it can be seen that an increase in metal concentration from 5 to 15% need not necessarily alter the secondary gradient if the critical site concentration lies below that obtained with the 5% catalyst.

Pre-exposure of the catalyst to nonradioactive carbon monoxide did not alter the secondary gradient and thus, according to the above model, carbon monoxide did not change the number of metal sites involved in the migration. While, at first sight, this appears to be rather surprising, it should be noted that pre-exposure to carbon monoxide was followed by evacuation for 1 hr, resulting in the removal of approximately 10% of the adsorbed carbon monoxide. Similar observations have been made using Pt/silica catalysts by Cormack and Moss (*32*), and these workers ascribe the carbon monoxide removed by evacuation to that adsorbed at edge and corner sites. Thus, while pre-exposure to carbon monoxide poisoned all the metal sites, the subsequent evacuation made available the metal sites for migration, although the large majority of metal sites (those responsible for primary adsorption) are unaffected by evacuation and remain poisoned.

This explanation of our results is further substantiated by the results observed in experiments where nonradioactive carbon monoxide was present in the gas-phase during [^{14}C]ethylene adsorption. Under these conditions, it might be expected that the metal sites responsible for both primary and secondary ethylene adsorption would be affected by carbon monoxide, in agreement with the experimental observations.

Attempts to use carbon monoxide to detect metal sites, which remain unoccupied following ethylene adsorption, proved unsuccessful since although a considerable uptake of ^{14}CO was observed (see Table 6), this uptake can be accounted for by the displacement of ethylene from the surface by carbon monoxide. The results show that carbon monoxide displaces 10–12% of the adsorbed ethylene. Thus, assuming that two carbon monoxide molecules can occupy the sites occupied by one ethylene molecule, uptakes of ^{14}CO of 20–25% of the [^{14}C]ethylene count rate following evacuation, in agreement with the experimental observations, can be explained in terms of displacement. The results presented in Table 6 are therefore inconclusive in establishing the existence of bare sites on ethylene-covered surfaces.

The admission of hydrogen to ethylene-precovered surfaces resulted in the removal of a fraction of the ethylene involved in both primary and secondary adsorption. However, when the 5% Rh–silica catalyst was exposed to carbon monoxide and then evacuated before ethylene adsorption, i.e., when only secondary adsorbed ethylene was present, the subsequent admission of hydrogen removed little of the adsorbed ethylene. Thus, direct hydrogenation of the ethylene adsorbed on the support does not take place. Either slow migration of adsorbed hydrocarbon back to the metal is necessary for hydrogenation, or activation of the hydrogen by the metal, prevented by the presence of adsorbed carbon monoxide, is a necessary prerequisite to the hydrogenation of the secondary species. With 5% Rh–alumina catalysts, similar measurements suggest that direct hydrogenation can occur to a limited extent. This is consistent with a slight hydrogenation activity observed with alumina (*33*, *34*).

From the foregoing discussion it can be concluded that the results reported in this study are consistent with a model in which the primary adsorption is located on the metal component, and the secondary adsorption is located on the support component. An alternative explanation of the secondary adsorption may be sought in terms of polymerization of ethylene on the surface. Such a polymerization would have the effect of increasing the [^{14}C]-ethylene adsorption beyond that expected for monolayer coverage, as measured from [^{14}C]carbon monoxide adsorption. However, this explanation can be rejected for the following reasons. First, it is unlikely that the poisoning of the metal surface would leave the degree of polymerization, and hence the secondary adsorption gradient, unaffected. The sites most likely to be affected by the carbon monoxide, those in the metal crystal planes (*32*), are also those likely to be involved in polymerization (*37*). Second, since electron microscopic studies of our catalyst show that the particle size is not materially affected by increasing the metal concentration, it might be expected that the effect of increasing metal concentration would be to increase proportionately the number of polymerization sites, thereby increasing the secondary adsorption gradient. The experimental results show that the secondary gradients for 5% Rh–silica and 15% Rh–silica are virtually identical. Finally, as we shall show in a later paper in this series (*38*), thermal desorption studies of ethylene adsorbed on supported rhodium catalysts indicate that the degree of polymerization of ethylene is relatively small.

We conclude, therefore, that ethylene is adsorbed on both the metal and the support and that the ability of adsorbed ethylene to migrate from the metal to the support has been demonstrated for supported rhodium catalysts.

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