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Radiochemical Studies of Chemisorption and Catalysis

VII. Direct Observation of Ethylene-C^{14} Behavior on Nickel, Rhodium, Palladium, Iridium, and Platinum During Chemisorption and Hydrogenation

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Ethylene-C^{14} tracer studies have been made of the adsorption and hydrogenation of ethylene at 20°C using 5% alumina-supported nickel, rhodium, palladium, iridium, and platinum catalysts. The effects of an equimolar mixture of nonradioactive ethylene and hydrogen, nonradioactive ethylene, and hydrogen on preadsorbed ethylene-C^{14} have been observed using an end-window G-M counter placed within the catalyst vessel.

In all cases only part of the preadsorbed ethylene was removed from the surface and it was independent of the subsequent treatment. Average percentages of initial radioactivity retained in the surface were Pd, 63.5%; Ni, 24.0%; Rh, 22.5%; Ir, 16;% and Pt, 6.5%. Evacuation following ethylene-C^{14} adsorption gave similar retention values. With nickel catalysts, pretreatment with hydrogen at 20°C did not change the retention of radioactivity, and at surface saturation an equilibrium between gas-phase and adsorbed ethylene was observed.

Ethylene-C^{14} containing 8% acetylene-C^{14} behaved similarly to ethylene-C^{14} with respect to retention of radioactivity. However, acetylene-C^{14} could displace ethylene from the metal surfaces.

Attempts to elucidate the nature of the adsorbed species have been made, correlations being sought between retention, heat of adsorption, and the ability of the metals to break carbon–hydrogen bonds. A possible correlation between retention and selectivity for acetylene hydrogenation is also discussed.

INTRODUCTION

Since the work of Pease and Stewart (*1*) first gave support to Taylor's views on the nature of surfaces (*2*), there has been a continual accumulation of evidence which shows that surfaces are heterogeneous (*3*). This manifests itself, for example, in varying rates of adsorption on sites of different energies (*4*). There is also a considerable body of evidence for various modes of adsorption of a single species on a given adsorbent (*5*). It is unlikely that these adsorbed complexes are all reactive in catalytic processes: Indeed Selwood (*6*) has shown that 46% of the species arising from ethylene adsorption on silica-supported catalysts could not be removed by treatment with hydrogen.

Attempts have been made in this laboratory (*7*) to measure the fraction of the total adsorbed species which is reactive during catalysis. This has been extended in the present paper to a study of a series of transition metals supported on alumina. The procedure involved the direct monitoring of surfaces by means of a Geiger-Müller (G-M) tube, while the surface was gradually saturated with ethylene-C^{14}. The fate of the adsorbate was then observed after admission of a reaction mixture consisting of equimolar amounts of ethylene and hydrogen. The extent of molecular exchange between gas-phase and adsorbed ethylene was also studied.

APPARATUS AND MATERIALS

Hydrogen could be passed through the reaction vessel (Fig. 1) for *in situ* reduction

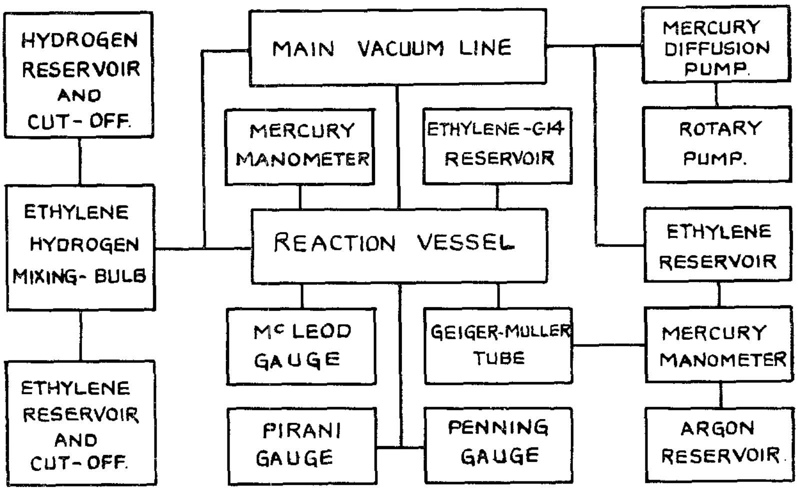


FIG. 1. Schematic diagram of apparatus for G-M observation of catalysts during adsorption, hydrogenation, etc.

of catalysts at 500°C. The vessel contained a G-M tube for monitoring the radioactivity on these catalysts after sorption of ethylene-C^{14}. Gas pressures were measured by a manometer, a McLeod gauge, or a Speedivac Pirani-Penning gauge, No. 2A, for 1 to 10^{-5} Torr.

Reservoirs for hydrogen and ethylene, and a mixing bulb, were connected to the reaction vessel through mercury cutoff valves.

The G-M counter filling consisted of argon and ethylene.

Catalyst vessel and internal arrangement. The catalyst holder could be moved from the hot reduction region to the cold G-M counter region. The holder could be moved back and forth during the monitoring stages for determination of surface and gas-phase count rates. For these reasons the catalyst vessel was attached to the apparatus by a ball and socket joint, Fig. 2. This permitted rotation of the catalyst vessel, so that the catalyst holder could slide back and forth when required. The catalyst was

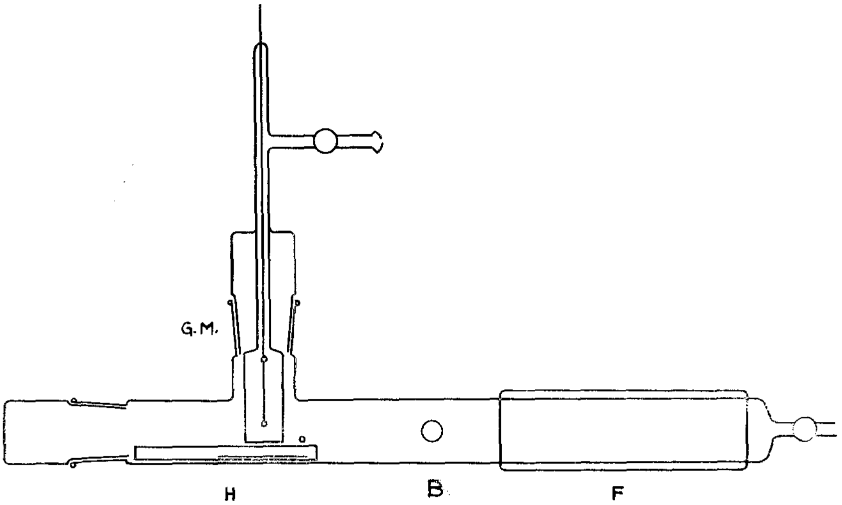


FIG. 2. Arrangement of G-M tube over catalyst in holder H. The reaction vessel could be rotated about the ball and socket joint B. F is the furnace region for catalyst reduction.

spread over half the length of the holder. Counts were taken of gas-phase plus surface activity, and then the gas-phase contribution was obtained by taking count rates over the empty portion of the holder. There the G-M tube was exposed to the same gas volume as before. The surface count rate was obtained by difference.

The geometry of the system was strictly reproducible for a given specimen of catalyst. Thus the holder was placed firmly against the end of the vessel before a gas-phase plus surface count was taken. Two dimples in the walls of the vessel prevented rotation of the holder.

For a given total amount of ethylene-C^{14} in the gas phase, or adsorbed on a catalyst it was shown by experiment that no measurable variations in count rate occurred with change in pressure.

Geiger-Müller counter. The end-window G-M tube (Fig. 3) had a cylindrical stainless steel cathode, 5 cm long and 2.4 cm in diameter. A recess in one end held a stainless steel ring with a crosspiece. A circular piece of mica was inserted and this was followed by a second ring exactly like the first. A large retaining ring, which fitted the recess in the cathode, was mounted as shown.

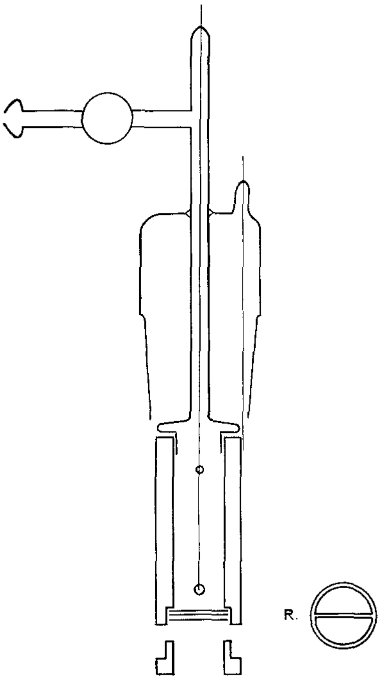


FIG. 3. G-M Counter for use within a reaction vessel, in vacuum or low pressure. R shows the mica supports.

The mica window, of sufficient transparency to pass β radiation from carbon-14, 2.57 mg cm^{-2}, did not have the strength to withstand large pressure differences, unless it was supported by crosspieces. The electrical leads were of 1-mm tungsten wire, and the anode of 0.2-mm wire. The components were assembled with Araldite.

The argon–ethylene filling for the tube, pressure 12 cm, had a partial pressure of the quenching gas, ethylene, of 4 cm. The counter had a plateau of slope 4% per 100 V, an externally set dead time of 500 μsec, and a quenching pulse of 240 V.

Catalysts. The nickel, rhodium, palladium, iridium, and platinum catalysts were of 5% metal supported on alumina. With the exception of nickel, these were supplied by Johnson Matthey and Co., Ltd. They were mixed as an aqueous slurry with montmorillonite, and spread evenly over the holder. When dried at 100°C they adhered firmly to it (*8*).

The sodium-calcium Wyoming-Bentonite montmorillonite, from Fullers' Earth Union, Ltd., was freed from these elements by ion exchange with 0.1 *M* hydrochloric acid. Back-titration gave an exchange capacity of 80 meq/100 g, in good agreement with the makers specification of 80 to 90 meq/100 g.

Gases. Hydrogen, from British Oxygen Company, Ltd., was passed through activated charcoal in traps immersed in liquid nitrogen.

Ethylene, from the same supplier, was condensed on a liquid-nitrogen-cooled finger. Residual gas was pumped away. The liquid nitrogen was removed and ethylene distilled into its reservoir. The mercury cutoff valve was closed before the cold finger reached room temperature.

Ethylene-C^{14}, code no CFA141, from the Radiochemical Centre, Amersham, was of activity 1–5 mCi/mM. It was claimed to be free from acetylene: The limit of detection was 2%.

EXPERIMENTAL PROCEDURE AND RESULTS

The catalysts were reduced in the reaction vessel by passing hydrogen over them at 500°C for 6 hr. The reaction vessel was then evacuated for 6 hr, with the catalyst at 500°; pumping was continued overnight at 20°.

Gases were admitted to the reaction vessel through a trap at −70°C; this prevented mercury vapor from entering the vessel.

A small amount of ethylene-C^{14} was admitted to the catalyst at 20°C and the adsorption observed by means of the G-M counter. The catalyst was moved under the counter and the total count rate obtained. The holder was then moved so that the counter monitored only the gas-phase contribution. The difference gave the surface radioactivity of the catalyst. Ethylene-C^{14} admission and counting continued until no further increase in surface activity was observed. The pressure of the ambient gas was measured on the McLeod gauge.

Typical adsorptions are shown in Fig. 4.

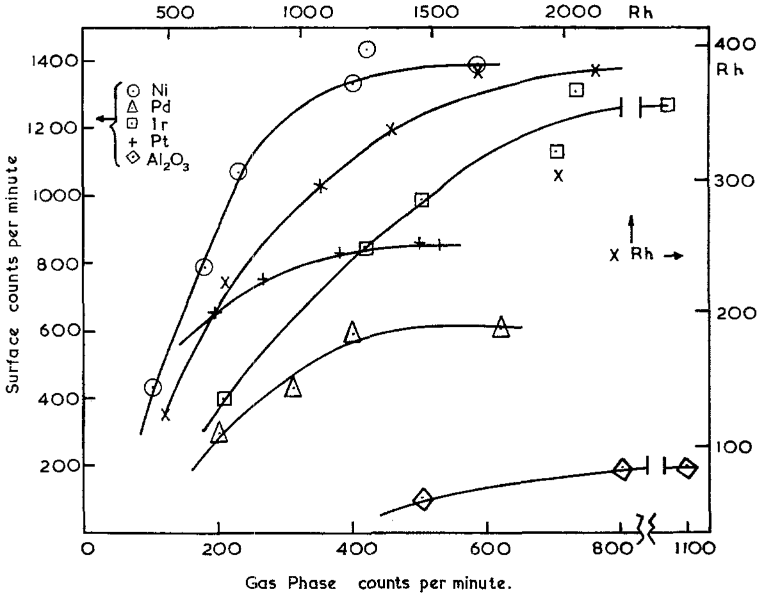


FIG. 4. Graphs showing surface radioactivity and gas-phase radioactivity for the adsorption of ethylene-C^{14} at 20°C on 5% metal on alumina catalysts: ⊙, Ni; △, Pd; ⊡, Ir; +, Pt; ◇, Al_2O_3; ×, Rh.

An equimolar mixture of hydrogen and ethylene was then admitted to the catalyst vessel which had a volume of about 900 cc. Total count rates were taken of radioactivity on the catalyst and in the gas phase until constant count rates were observed. During this time the course of the ethylene hydrogenation at 20°C was followed manometrically. The results for platinum and nickel are shown in Fig. 5.

Curves showing variation of total activity with time either showed an increase or decrease. Once constancy of count rates had been obtained, it was invariably found that the surface radioactivity had decreased, and that the gas-phase radioactivity had increased.

When change in the total observed count rate ceased, the catalyst holder was moved and the gas-phase activity determined. If no change with time was found for the gas-phase activity, the count rates were subtracted from the total activity to give the surface activity. From these results we obtained the percentage of the initially adsorbed radioactivity from ethylene-C^{14} which remained on the surface during catalytic hydrogenations. All results are summarized in Table 1.

After the hydrogenation of ethylene, the gases in equilibrium with the surface were pumped away; the pressure at this stage was 10^{-4} Torr. More ethylene-C^{14} was then admitted. The molecular exchange between adsorbed and gas-phase ethylene was studied by admitting nonradioactive ethylene to the reaction vessel to pressures between 2 and 5 cm. Total and gas-phase counts were taken; the results are shown in Table 1.

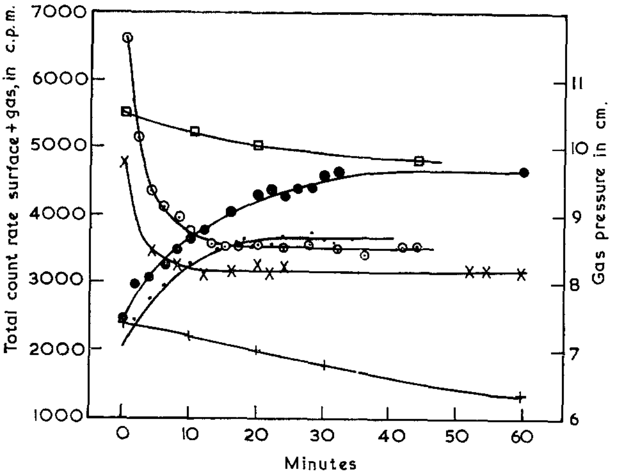


FIG. 5. The graphs show total count rates, surface plus gas phase, during hydrogenation of ethylene over nickel, ●, and Pt, ⊙, previously exposed to ethylene-C^{14}. Curves are also drawn for total activity against time for ethylene molecular exchange over Ni, •, and Pt, ×. Pressure–time graphs are shown for hydrogenation of ethylene over Ni, +, and Pt, ⊡. All experiments at 20°C.

TABLE 1

COUNT RATES FROM ADSORBED SPECIES

	Counts per minute from surface[a]						
		After					
Catalyst	Initially	Ethylene hydrogenation	Ethylene exchange	Admission of hydrogen	Evacuation	Pressure fall in cm during hydrogenation	Pressure at saturation in Torr
Pd/Al_2O_3	5303	3758(70%)	3966(72%)	3464(63%)	3478(63%)	9.6 to 6.1 in 110 min	
	603	358(60%)	367(61%)	370(61%)	349(58%)	7.3 to 6.2 in 30 min	8.4×10^{-2}
Rh/Al_2O_3	2102	167(23%)	176(24%)	130(18%)	156(20%)	8.3 to 4.8 in 162 min	
	381	72(21%)	97(27%)	89(24%)	85(24%)	9.5 to 6.8 in 40 min	7.8×10^{-2}
Pt/Al_2O_3	7005	406(6%)	779(11%)	584(8%)	217(3%)	10.4 to 9.8 in 44 min	
	849	68(8%)	45(5%)	44(5%)	39(5%)	8.6 to 8.0 in 30 min	3.5×10^{-2}
Ir/Al_2O_3	1260	227(18%)	213(18%)	168(14%)	172(14%)	10.8 to 10.2 in 30 min	2.7×10^{-2}
Ni/Al_2O_3	1898	499(26%)	509(26%)	493(24%)	510(25%)	7.4 to 6.8 in 30 min	
	1383	334(24%)	285(20%)	343(24%)	331(23%)	5.5 to 4.9 in 30 min	4.6×10^{-2}
Al_2O_3	203	—	~8(7%)	—	—	0	4.7×10^{-2}

[a] Percentages of retained radioactivity are shown in parentheses. These have been corrected for dead-time losses.

The ethylene over the catalyst was then pumped away and hydrogen admitted. The effect this had on the radioactivity retained on the surface was observed. Finally the effect of evacuation was investigated. The results for these experiments are in Table 1.

Count rates. No count rate has been used in computing percentage retentions without being determined from at least 5000 counts. Since the count rates used in finding retentions are obtained by differences, they are effectively corrected for background activities. All count rates reported are uncorrected observed rates with the exception of the "saturation activity" values, which have been corrected for dead-time losses. Dead-time losses have also been taken into account in computing percentage retentions.

Count rates may not be compared between experiments on different catalysts because of the impossibility of spreading catalysts in exactly the same way to give reproducible geometry. Also ethylene-C^{14} of differing specific activities has been used.

Count rates can be compared within a given experiment on a catalyst: Here the counting geometry was reproducible.

Adsorption on alumina. It was necessary to know if alumina, which was the catalyst support, adsorbed ethylene to a significant extent. Alumina, 145 mg, was mixed with one-third of its weight of montmorillonite and subjected to the reduction treatment normally given to the metal catalysts.

Ethylene-C^{14} adsorption on the alumina was measured and this was followed by an exchange experiment. The results are shown in Table 1. It is not possible to give an absolute comparison between the amounts of ethylene-C^{14} adsorbed on alumina and on the catalysts. This is because it is impossible to reproduce the counting geometry from one series of experiments to another.

Nonetheless an approximate answer can be given, as is shown in Table 2. Not only is the total surface activity less for alumina than for any other surface, but the ratio of gas phase to surface activity is very much greater. We conclude that the amount adsorbed on alumina is low compared with that adsorbed on the catalysts.

TABLE 2
GAS/SURFACE COUNT RATES FOR VARIOUS ADSORBENTS

Adsorbent	Observed activities: Gas	Observed activities: Surface	Ratio gas/surface
Al_2O_3	3541	203	17
Pd/Al_2O_3	2069	5303	0.4
Rh/Al_2O_3	1751	719	2.4
Pt/Al_2O_3	1137	7005	0.2
Ir/Al_2O_3	3888	5203	0.8
Ni/Al_2O_3	3018	1898	1.6

Adsorption on oriented platinum metal. Platinum metal, which had been prepared with the 111 face exposed, was reduced in hydrogen at 500°C as before. The uptake of ethylene-C^{14} at 20°C was studied.

Adsorption was insignificant in that the ratio of gas-phase to surface counts was 18, as compared with 0.2 for the supported metal catalyst.

Poisoned catalysts. Palladium catalysts sometimes fail in the hydrogenation of ethylene. It was suspected that air was the contaminant in these cases and so a reduced palladium catalyst was exposed to air for 15 min at 3.1 mm. The results for ethylene-C^{14} adsorption, hydrogenation, exchange, and evacuation are shown in Table 3, A and B.

Effect of hydrogen pretreatment. In the previous experiments ethylene had been admitted first to the catalyst. The effect of preadmission of hydrogen was examined by preparing a catalyst in the usual way and then admitting hydrogen to a pressure of 4.5 cm for 15 min. The hydrogen was removed by evacuation, and ethylene-C^{14} adsorbed; the usual experiments were then performed (Table 3, C).

Study of equilibrium between gas-phase and adsorbed species. Ethylene-C^{14} was adsorbed on a nickel catalyst until increase in the pressure of the gas phase gave no increase in surface counts, viz. 1386 counts/min. Evacuation for 30 min reduced the surface count rate to 504 cpm; 10 min further evacuation left this unchanged. These figures corresponded to 32% retention, well above the 25% previously found for nickel after hydrogenation.

Molecular exchange on this surface was

TABLE 3

COUNT RATES FROM ADSORBED SPECIES

Experiment No.	Catalyst	Counts per minute from surface[a]					Pressure fall (cm) during 30-min hydrogenation	"Saturation" pressure of ethylene (Torr)
			After					
		Initially	Ethylene hydrogenation	Ethylene exchange	Admission of hydrogen	Evacuation		
A	Pd/Al_2O_3[b]	233	106(45%)	—	106(45%)	101(43%)	Nil	1.8×10^{-2}
B	Pd/Al_2O_3[b]	673	647(99%)	677(103%)	679(103%)	658(100%)	Nil	6.6×10^{-2}
C	Ni/Al_2O_3[c]	2927	707(23%)	761(25%)	762(25%)	741(24%)	9.9 to 9.3	3.9×10^{-2}
D	Ni/Al_2O_3[d]	2107	442(21%)	458(21%)	445(21%)	447(21%)	7.2 to 6.6	
E	Ni/Al_2O_3[e]	1386	—	347(25%)	—	504(32%)	—	2.9×10^{-2}
F	Pt/Al_2O_3[f]	1027	67(7%)	94(9%)	63(6%)	59(6%)	10.6 to 10.0	4.0×10^{-2}
G	Ir/Al_2O_3[f]	3581	486(13%)	434(12%)	310(8%)	278(7%)	8.5 to 7.9	3.4×10^{-2}
H	Ir/Al_2O_3[f]	10782	2438(22%)	1919(17%)	903(8%)	1962(17%)	10.7 to 10.1	1.1×10^{-2}
I	Pd/Al_2O_3[f]	265	170(65%)	191(73%)	158(60%)	145(55%)	9.1 to 8.1	5.9×10^{-2}
J	Ni/Al_2O_3[f]	2637	568(22%)	599(22%)	487(18%)	468(17%)	10.6 to 10.0	1.1×10^{-1}

[a] Percentage retained radioactivity shown in parentheses, corrected for dead time losses.

[b] Exposed to air at 3.1 mm for 15 min at 20°C.

[c] Ni pretreated with H_2.

[d] Ni covered with C_2H_4 then exposed to C^{14}-labeled C_2H_2 and C_2H_4.

[e] Catalyst exposed to C^{14}-labeled C_2H_4 followed by evacuation, then exchange with ordinary ethylene.

[f] Preadsorption of C^{14}-labeled C_2H_2 and C_2H_4.

studied by introducing ordinary ethylene to a pressure of 4.4 cm. The surface count rate fell to 347 cpm, corresponding to 25% retention, as before. Evacuation then left the retention unchanged at 25%. The results are in Table 3, E.

Effect of introducing ethylene-C^{14} and acetylene-C^{14} to a surface previously exposed to inactive ethylene. Ethylene was admitted to a nickel catalyst to a pressure of 2.9×10^{-1} mm and left for 20 min. The vessel was evacuated and ethylene-C^{14} containing 8% acetylene-C^{14} was admitted. The surface count rate rose from zero to 2107 cpm. Hydrogenation of ethylene reduced the surface count rate to 442 cpm. This corresponds to a 21% retention of radioactivity; this and further experiments on this surface are recorded in Table 3, D.

Pretreatment of surfaces with a mixture of ethylene-C^{14} and acetylene-C^{14}. A mixture of ethylene-C^{14} and acetylene-C^{14} was admitted to surfaces of nickel, platinum, iridium, and palladium. The uptake of labeled species was observed, and the usual observations made on the surface after hydrogenation of ethylene, ethylene exchange, hydrogen treatment, and evacuation. The results are shown in Table 3: F, G, H, I, and J.

SUMMARY OF EXPERIMENTAL RESULTS

These experiments have shown that changes in the amounts of initially adsorbed material can be followed during the hydrogenation of ethylene.

The retention figures for hydrogenation are closely paralleled in the case of molecular exchange between the adsorbed species and the gas phase. It has also been shown that the retained material is not affected by the action of pure hydrogen, nor can it be removed by evacuation.

The average amounts of initial surface radioactivity which are not removed at 20°C by ethylene hydrogenation, molecular exchange with ethylene, treatment with hydrogen, and evacuation, are expressed in percentages, as follows:

$$\begin{array}{ccccc} Pd & > Ni \approx & Rh & > Ir > & Pt \\ 63.5 & 24 & 22.5 & 16 & 6.5 \end{array}$$

Poisoning of the palladium catalyst by air has been demonstrated. Nevertheless adsorption of ethylene took place under these circumstances.

It was also shown that acetylene could cause desorption of even the portion of the adsorbed ethylene layer which was retained throughout the other experiments. Further-more the acetylene, once adsorbed, behaved, at least in the presence of hydrogen, in the same manner as ethylene with regard to extent of retention.

The over-all averages, for the percentage of initial surface radioactivity taken up from the acetylene-ethylene mixture, retained during hydrogenation, exchange, treatment with hydrogen, and evacuation were

$$\begin{array}{ccccccc} \mathrm{Pd} & > & \mathrm{Ni} & > & \mathrm{Ir} & > & \mathrm{Pt} \\ 63 & & 20 & & 13 & & 7 \end{array}$$

An experiment was also carried out to observe the effect of pretreatment of a surface with hydrogen before sorption of ethylene-C^{14}. No differences in retentions of radioactivity were found. Nickel was chosen for this experiment and it gave 24% retention; this is to be compared with 24% for the normal procedure.

With nickel initially adsorbed ethylene was shown to be partly in equilibrium with the gas phase, and was, as such removable by evacuation; 68% of the surface radioactivity could be removed by evacuation. A further 7% could be removed by exchange with ethylene.

Discussion

The retentions of C^{14} which we have observed are in agreement with the observations that ethylene adsorption on evaporated nickel, palladium, and tungsten is accompanied by the production of ethane by self-hydrogenation. Beeck (*9*) has suggested that acetylenic complexes resulting from the dissociative adsorption of ethylene poison the surface for ethylene hydrogenation. We have observed that not all the acetylene admitted to a nickel surface is retained as a poison; some is removed by hydrogenation.

Studies of ethylene decomposition as a function of temperature and pressure have been reported (*10–12*). The adsorbed residues have the form $(CH_n)_x$, where n is approximately 1 at 20°C (*10*), although with rhodium C–H bonds appear to be absent from the adsorbed residues (*13*).

Infrared studies of olefin adsorption indicate the presence of both olefinic and paraffinic C–H bonds (*5, 14*). With nickel-silica catalysts, magnetic susceptibility measurements (*6*) favor associative adsorption of ethylene at 0°C, the dissociatively adsorbed species becoming more important at 28°C.

In general, fragmentation appears to become increasingly important as the temperature is increased and occurs more readily with metal films than with supported metal catalysts (*15–18*). Heats of adsorption on evaporated films are higher than on supported metals (*19*) or bulk metal (*20*).

Our results indicate at least two modes for ethylene adsorption: one is involved in hydrogenation and molecular exchange; the other is an inert form which is retained on the surface. Similar studies using evaporated nickel films (*21*) showed that adsorption was irreversible on these catalysts. We may suppose that of the two types of bonding one is associative, the other dissociative. We now consider which mode of ethylene adsorption is active in hydrogenation and molecular exchange.

We consider first that the associatively bonded complex is reactive and the dissociative complex is unreactive and therefore responsible for the observed C^{14} retentions. This proposition is in agreement with Beeck (*9*) and Jenkins and Rideal (*22*) and should lead to correlations between our retention values and the relative abilities of the metals to rupture C–H bonds. The general pattern for heats of adsorption (*23*) gives Ni > Rh > Pt > Pd; a sequence in agreement with our results, except for Pd.

Hydrocarbon cracking (*24*) at 450–500°C gives the sequence Rh > W > Ni > Pt, and exchange reactions (*25, 26*) give the order of bond rupture activity as Ni > Rh > Pt > Pd. Deuterium exchange studies (*28*) also show that rhodium was poisoned by residues at 0°C, whereas Pd was not so poisoned below 100°C. Rh is more efficient also in C–C bond breaking than is Pd (*27*).

We conclude that the attempted correlation with the present results is satisfactory except for Pd.

We shall now consider the possibility that the reactive material is olefinic, the retained material associatively bonded. This is not in conflict with the IR studies for supported catalysts (*5, 14*). It is in agreement with the suggestion of an olefinic dissociatively adsorbed species as reactive intermediate

(*29*) and with recent ideas on the role of π-bonded olefinic species in catalysis (*30*).

The ability of a surface to form and retain an associative complex can be correlated with olefin exchange and isomerization:

$$\text{olefin (g)} \rightleftharpoons \underset{[\text{I}]}{\text{olefin (a)}} \underset{-\text{H}}{\overset{+\text{H}}{\rightleftharpoons}} \underset{[\text{II}]}{\text{alkyl (a)}} \xrightarrow{+\text{H}} C_2H_6\ \text{(g)}$$

The noble metals exhibit the following sequence for ethylene exchange relative to hydrogenation (*31*):

$$\text{Rh} > \text{Pd} > \text{Ru} > \text{Ir} \sim \text{Pt} \qquad (1)$$

For low-temperature butene isomerization (*32*) this becomes

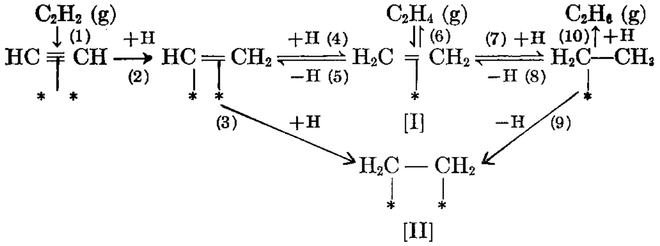
$$\text{Pd} > \text{Ru} > \text{Rh} > \text{Ir} \sim \text{Pt} \qquad (2)$$

This sequence indicates the tendency of the metals to favor state [I] over state [II] (*33*). These sequences, particularly for Pd, are in better agreement with our observations.

Further information regarding adsorbed states comes from selectivity studies which lead to the sequence (*34*), which we also observe:

$$\text{Pd} > \text{Rh} > \text{Pt} > \text{Ru} > \text{Os} > \text{Ir}$$

Since acetylene has been observed to behave like ethylene we have examined another possible scheme. The following scheme is proposed for acetylene hydrogenation:



In this model acetylene, adsorbed as a π complex, is hydrogenated to produce adsorbed ethylene. Some of this [I] may desorb (step 6) or undergo further hydrogenation to ethane (steps 7 and 10); some [II] may be retained on the surface. This is in accord with the identical behavior of ethylene and acetylene; it is possible that [I] is the species which can undergo molecular exchange, leaving species [II] retained on the surface to be "seen" by the G-M counter.

Those metals which show a strong tendency towards alkyl reversal, as judged by their ability to promote ethylene exchange, will favor the formation of [II]; the metals are:

$$\text{Rh} > \text{Pd} > \text{Ni} > \text{Ru} > \text{Os} > \text{Ir} \sim \text{Pt}$$

This sequence agrees with our observations except that the positions of Pd and Rh are reversed. Here we must take into account another aspect of the behavior of palladium. Rooney, Gault, and Kemball (*30*) have shown that in the exchange of several polymethylcyclopentanes, palladium alone readily promotes the interconversion between a π-olefinic and a π-allylic species at ambient temperature, i.e., palladium readily abstracts a hydrogen atom from the π-olefinic species. A similar situation is believed to occur in the isomerization of the *n*-butenes at ambient temperature (*35*). If this factor is considered, palladium can promote another route towards the adsorbed species [II]. This is shown in the above model by reactions (5) and (3) in which adsorbed ethylene [I] may revert to adsorbed alkenyl which on adding a hydrogen atom may yield either [I] or [II], depending upon whether the carbon–metal σ bond or the carbon–carbon π bond is broken.

In conclusion we may say that the surfaces studied are heterogeneous in that at least two types of bonding, leading to removable and retained species, are observed. The probability mirrors an underlying heterogeneity in the surfaces themselves.

The attempt to fit these catalysts into a general scheme involving supported metals and evaporated films has been reasonably successful. In this scheme a gradual variation in surface energy is envisaged, graduated from supported metals to non-sintered evaporated films.

Attempts to decide on the nature of these adsorbed complexes have proved moderately successful. However, it may be suggested that better correlations are obtained when the retained species are considered to be associatively bonded to these supported metal surfaces.

Acknowledgments

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