Radiochemical Studies of Chemisorption and Catalysis

VIII. The Behavior of ^{14}C-Ethylene and Tritium Adsorbed on Alumina-Supported Palladium, Rhodium, and Platinum Catalysts

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^{14}C-Ethylene and tritium tracer studies of the nature and reactivity of adsorbed species have been made using 5% alumina-supported palladium, rhodium, and platinum catalysts in a microcatalytic reactor between 20° and 200°C. The injection of ^{14}C-ethylene onto freshly reduced catalysts results in the formation of a strongly adsorbed species which is inactive in molecular exchange, hydrogenation, and displacement by acetylene. Using tritium, the relative abilities of the metals to promote ethylene self-hydrogenation have been determined to be Rh > Pt > Pd. The results show that the same catalyst surface exhibits different degrees of surface heterogeneity for different hydrocarbon molecules. The role of the catalyst support is also discussed, and evidence for the participation of the hydroxyl groups of the alumina in the reaction is described.

INTRODUCTION

In a previous paper (*1*) we showed that when hydrocarbons were injected on to a reduced alumina-supported palladium catalyst in a flow system, appreciable amounts of the hydrocarbon were retained by the catalyst. Furthermore, product analysis of the eluted hydrocarbon showed that, with alkenes and acetylene, appreciable quantities of the corresponding saturated hydrocarbon were produced.

This paper describes a further study of the adsorption of ethylene on alumina-supported palladium, platinum, and rhodium catalysts using carbon-14 and tritium as tracers in an attempt to understand further the nature and reactivity of adsorbed species at metal surfaces.

EXPERIMENTAL

Apparatus. The apparatus was the same as that described previously (*1*) except that a proportional counter was connected to the outlet from the gas chromatograph. The proportional counter was constructed to the design of Schmidt-Bleek and Rowland

(*2*) and was operated using a filling of helium and methane in the ratio of 10:1 at a flow rate of 60 ml min^{-1}. Under these conditions the plateau length was $\geqslant$ 200 V with a slope of less than 3% per 300 V.

Materials. The catalysts (Johnson, Matthey & Co. Ltd.) consisted of 5% w/w palladium, platinum, or rhodium supported on α-alumina. The total areas (BET) and the metal areas, as determined by CO adsorption, were as follows:

Catalyst:	Palladium	Rhodium	Platinum
BET area (m^{2}g^{-1})	111	141	147
Metal area (m^{2}g^{-1})	5.0	0.8	0.2

Each catalyst sample was activated, immediately before use, at 200°C for approximately 30 min in a stream of hydrogen (30 ml min^{-1}).

Helium, hydrogen, and ethylene were supplied and purified as described previously (*1*). Methane (Air Products Ltd. "CP grade"), which was blended with the helium eluant from the gas chromatograph

TABLE 1
Chemical and Radiochemical Analysis of Eluants from $^{14}C\text{-}C_2H_4$ Adsorption on Palladium Catalysts[a]

Expt. No.	Injection No.	Substance injected	Temp. (°C)	Methane ml	Methane cpml × 10⁻⁵	Ethane ml	Ethane cpml × 10⁻⁵	Ethylene ml	Ethylene cpml × 10⁻⁵	% Hydrocarbon retained
*Molecular Exchange*
1	1	$^{14}C\text{-}C_2H_4$	200°	0.01	0.02	0.30	0.42	0.02	0.07	36
	2	C_2H_4		0.005	0.00	0.25	0.00	0.11	0.00	28
2	1	$^{14}C\text{-}C_2H_4$	100°	—	—	0.09	0.30	0.31	0.38	20
	2	$^{14}C\text{-}C_2H_4$		—	—	0.03	0.15	0.42	0.40	10
	3	C_2H_4		—	—	0.00	0.00	0.46	0.00	8
3	1	$^{14}C\text{-}C_2H_4$	20°	—	—	0.02	0.08	0.42	0.39	12
	2	$^{14}C\text{-}C_2H_4$		—	—	0.00	—	0.49	0.40	2
	3	C_2H_4		—	—	0.00	—	0.50	0.01	0
*Hydrogenation*
7	1	$^{14}C\text{-}C_2H_4$	200°	0.01	0.01	0.20	0.42	0.08	0.15	43
	2	$^{14}C\text{-}C_2H_4$		—	—	0.15	0.38	0.20	0.30	30
	3	H_2(2 ml)		0.01	0.01	0.00	—	—	—	—
8	1	$^{14}C\text{-}C_2H_4$	100°	0.01	0.01	0.06	0.21	0.36	0.36	16
	2	H_2(2 ml)		—	—	0.02	0.10	0.00	—	—
9	1	$^{14}C\text{-}C_2H_4$	20°	—	—	0.01	0.06	0.46	0.39	6
	2	H_2(2 ml)		—	—	0.03	0.10	—	—	—
*Acetylene Displacement*
4	1	$^{14}C\text{-}C_2H_4$	200°	0.01	0.01	0.30	0.45	0.01	0.24	35
	2	C_2H_2		—	—	0.04	0.00	0.01	0.00	91
5	1	$^{14}C\text{-}C_2H_4$	100°	—	—	0.10	0.20	0.30	0.47	20
	4	C_2H_2		—	—	—	—	0.02	0.00	96
6	1	$^{14}C\text{-}C_2H_4$	20°	—	—	—	—	0.42	0.36	16
	4	C_2H_2		—	—	—	—	0.02	0.01	90

[a] Injection size, 0.5 ml (NTP) except where stated. Specific activity of $^{14}C\text{-}C_2H_4$, 4.0×10^4 counts ml^{-1}.

to form the counter filling, had a purity of >99% and was used without further purification.

Tritium and ^{14}C-ethylene were obtained from the Radiochemical Centre, Amersham. These were diluted to the required specific activity with inactive hydrogen and ethylene, respectively.

Results

^{14}C-Ethylene adsorptions. Following the activation of the catalyst at 200°C, helium was flowed through the catalyst bed for 5 hr at 200°C. The catalyst was then cooled to the reaction temperature in a flow of helium. ^{14}C-Ethylene was injected onto the catalyst at 20°, 100°, and 200°C and this was followed by injections of either inactive ethylene, hydrogen, or acetylene to investigate the reactivity of the retained species in molecular exchange, hydrogenation, and displacement. The results for the chemical and radiochemical analysis of the reactor eluant following these injections are shown in Tables 1, 2, and 3 for palladium, rhodium, and platinum catalysts, respectively.

In these and the ensuing tables, the activities are expressed as counts per milliliter. These were obtained by dividing the total integrated counts from the flow counter by the volume of hydrocarbon as determined by the gas chromatograph.

From the results presented in Tables 1, 2, and 3, it can be seen that in some instances, the activities of the eluant hydrocarbons are different from that of the ethylene injected onto the catalyst. These discrepancies are particularly noticeable when the yields of eluted hydrocarbon are small, and probably arise due to errors in the estimation of the areas of very small peaks in the chromatograph.

Tritium exchange and adsorption. The reduction of catalysts by treatment in hydrogen at elevated temperature may leave residual hydrogen on the catalyst surface. It was therefore necessary to investigate the following questions: (i) How efficient was our helium treatment for the removal of surface hydrogen? (ii) Assuming that helium did not remove all the residual hydrogen, what is the reactivity of the hydrogen in the production of alkanes from injections of alkenes? Both of these questions were answered by using tritium as a tracer. Immediately following the catalyst activation, the residual surface hydrogen was exchanged, either by allowing the catalyst to stand under 10 ml of tritiated hydrogen for 1 hr (static exchange), or by injecting 2 ml of tritiated hydrogen into the helium stream and allowing it to pass through the catalyst bed (flow exchange). Using the latter technique the efficiency of the helium treatment for hydrogen removal was investigated by monitoring the reactor eluant with the proportional counter until the background level was achieved. The time required for this to be achieved and the total count recovered in the eluant are shown in Table 4.

From these results it can be seen that the catalysts retained considerable quantities of hydrogen. The reactivity of this hydrogen was examined by injecting 0.5-ml volumes of ethylene onto the catalyst and analyzing the eluant for radioactivity. The results are shown in Table 5.

The reactivity of the retained hydrogen was further investigated by tritiating the catalyst surface by the static exchange method and subsequently injecting 0.5-ml volumes of ethylene and acetylene onto the

TABLE 2

CHEMICAL AND RADIOCHEMICAL ANALYSES OF ELUANTS FROM
^{14}C-C$_2$H$_4$ ADSORPTION ON RHODIUM CATALYSTS[a]

Expt. No.	Injection No.	Substance injected	Temp. (°C)	Eluant analysis								% Hydrocarbon retained
				Methane		Ethane		Ethylene		Acetylene		
				ml	cpml×10⁻⁵	ml	cpml×10⁻⁵	ml	cpml×10⁻⁵	ml	cpml×10⁻⁵	
Molecular Exchange												
1	1	^{14}C-C$_2$H$_4$	200°	0.02	0.02	0.22	1.00	—	—	—	—	54
	2	C$_2$H$_4$		—	—	0.27	0.00	—	—	—	—	46
	3	C$_2$H$_4$		—	—	0.18	0.00	0.18	0.00	—	—	28
2	1[b]	^{14}C-C$_2$H$_4$	20°	—	—	—	—	0.49	0.41	—	—	2
	2	C$_2$H$_4$		—	—	—	—	0.48	0.00	—	—	4
Hydrogenation												
3	1	^{14}C-C$_2$H$_4$	100°	—	—	0.11	1.00	0.25	1.00	0.25	0.80	28
	2	H$_2$(2 ml)		0.02	1.10	—	—	—	—	—	—	—
Acetylene Displacement												
4	1	^{14}C-C$_2$H$_4$	200°	0.005	0.20	0.27	0.87	—	—	—	—	46
	2	C$_2$H$_2$		—	—	0.01	0.00	—	—	—	—	98
5	1[b]	^{14}C-C$_2$H$_4$	100°	0.01	—	0.07	0.38	0.23	0.41	—	—	39
	2	C$_2$H$_2$		—	—	—	—	0.015	0.0	0.13	0.0	71

[a] Injection size, 0.5 ml (NTP) except where stated. Specific activity ^{14}C-C$_2$H$_4$, 1.0×10^5 counts ml⁻¹
[b] Activity ^{14}C-C$_2$H$_4$ = 4.0×10^4 counts ml⁻¹.

TABLE 3
CHEMICAL AND RADIOCHEMICAL ANALYSIS OF ELUANT FROM
^{14}C-C$_2$H$_4$ ADSORPTIONS ON PLATINUM CATALYSTS[a]

| | | | | Eluant analysis | | | | | | | | | % Hydro-carbon retained |
| | | | | Methane | | Ethane | | Ethylene | | Acetylene | | | |
Expt. No.	Injection No.	Substance injected	Temp. (°C)	ml	cpml×10⁻⁵	ml	cpml×10⁻⁵	ml	cpml×10⁻⁵	ml	cpml×10⁻⁵	
				Molecular Exchange								
1	1	^{14}C-C$_2$H$_4$	200°	—	—	0.22	0.42	0.04	0.10	—	—	48
	3	^{14}C-C$_2$H$_4$		—	—	0.04	0.17	0.42	0.32	—	—	8
	4	C$_2$H$_4$		—	—	0.03	0.00	0.44	0.00	—	—	6
2	1	^{14}C-C$_2$H$_4$	100°	—	—	0.005	0.08	0.46	0.35	—	—	4
	2	^{14}C-C$_2$H$_4$		—	—	—	—	0.48	0.32	—	—	2
	3	C$_2$H$_4$		—	—	—	—	0.49	0.00	—	—	2
3	1	^{14}C-C$_2$H$_4$	25°	—	—	—	—	0.48	0.41	—	—	4
	2	^{14}C-C$_2$H$_4$		—	—	—	—	0.49	0.40	—	—	2
	3	C$_2$H$_4$		—	—	—	—	0.50	0.00	—	—	0
				Hydrogen Treatment								
9	1	^{14}C-C$_2$H$_4$	100°	—	—	0.01	0.01	0.47	0.44	—	—	4
	2	^{14}C-C$_2$H$_4$		—	—	—	—	0.50	0.38	—	—	0
	3	H$_2$(2 ml)		0.01	0.01	—	—	—	—	—	—	—
				Acetylene Displacement								
10	1	^{14}C-C$_2$H$_4$	200°	—	—	0.13	0.17	0.10	0.51	—	—	54
	2	^{14}C-C$_2$H$_4$		—	—	0.04	0.10	0.31	0.45	—	—	30
	3	^{14}C-C$_2$H$_4$		—	—	0.03	0.03	0.39	0.41	—	—	16
	4	C$_2$H$_2$		—	—	0.00	—	0.04	0.00	0.23	0.0	46
11	1	^{14}C-C$_2$H$_4$	20°	—	—	—	—	0.46	0.24	—	—	8
	2	^{14}C-C$_2$H$_4$		—	—	—	—	0.47	0.26	—	—	6
	3	C$_2$H$_2$		—	—	—	—	0.005	0.00	0.41	0.0	14

[a] Injection size, 0.5 ml (NTP) except where stated. Specific activity ^{14}C-C$_2$H$_4$, 4.0 × 10^4 counts ml⁻¹.

catalyst. The results from static exchange experiments are shown in Table 6.

DISCUSSION

^{14}C-Ethylene Adsorption

The injection of inactive ethylene onto palladium, rhodium, and platinum catalysts, after they had been exposed to ^{14}C-ethylene resulted in the recovery of ethylene at all temperatures used, and ethane with palladium and rhodium at 200°C. In all cases both the recovered ethane and ethylene were inactive showing that (i) molecular exchange between surface and gas-phase ethylene did not occur, and (ii) ethane production did not involve the wholesale participation of previously adsorbed ethylene or residues. These observations suggest that on our catalysts the retained species is a strongly bonded dissociatively adsorbed species, rather than an associatively bonded species such as that generally assumed to be the reactive form of ethylene in catalytic hydrogenation (3). Furthermore, the inactivity of the ethane suggests that separate

TABLE 4
DESORPTION OF "HYDROGEN" BY HELIUM
TREATMENT AT 200°C[a]

Catalyst	Total HT count in eluant (×10⁻⁸)	Time to reach background	Atoms of H retained (×10⁻²⁰)
Rh-A	70.5	4 min	1.063
Rh-B	62.0	6 min	1.065
Pd-A	235.0	>11 hr	1.034
Pd-B	252.0	5½ hr	1.031
Pt-A	47.0	10 min	1.067

[a] Wt. of catalyst, 0.5 g; Total HT injected, 2 ml = 6.0 × 10^6 counts.

TABLE 5

ETHYLENE ADSORPTION ON TRITIATED CATALYSTS (FLOW EXCHANGE)[a]

Catalyst	Injection No.	Methane		Ethane		Ethylene	
		ml	cpml $\times$ 10^{-5}	ml	cpml $\times$ 10^{-5}	ml	cpml $\times$ 10^{-5}
Pd/Al$_2$O$_3$	1	0.01	18	0.30	12.5	—	—
	2	—	—	0.28	9.6	0.04	23
Pd/Al$_2$O$_3$	1	0.01	10	0.27	12.9	—	—
	2	—	—	0.25	10.3	0.07	18.6
Rh/Al$_2$O$_3$	1	0.02	0.8	0.23	6.5	0.01	2
	2	—	—	0.18	5.7	0.01	2
Rh/Al$_2$O$_4$	1	0.01	0.3	0.27	4.8	—	—
	2	—	—	0.16	3.1	0.10	1.6
Pt/Al$_2$O$_4$	1	—	—	0.08	6.1	0.38	2.2
	2	—	—	0.03	2.8	0.48	1.4
Pt/Al$_2$O$_3$	1	—	—	0.07	7.1	0.30	2.3
	2	—	—	0.03	3.4	0.42	1.3

[a] Volume of ethylene, 0.5 ml per injection.

types of surface site are involved in residue formation and hydrogenation.

Hydrogen treatment of catalysts previously exposed to ^{14}C-ethylene resulted in the formation of small amounts of radioactive methane at 100°C with rhodium and platinum, and at 200°C with palladium. With palladium at 100° and 200°C, small amounts of radioactive ethane were produced. These results are of interest for two reasons. First, the yields of methane are consistent with the known abilities of rhodium and platinum films to catalyze carbon–carbon bond fission more effectively than can palladium (4). Secondly, while it has generally been found that, in kinetic studies, reactivation of catalysts can be satisfactorily achieved by treatment in hydrogen at 200°C for short periods (5), the above results show that this treatment does not remove strongly adsorbed residues. This again clearly indicates that catalyst

TABLE 6

ETHYLENE AND ACETYLENE ADSORPTION ON TRITIATED CATALYSTS (STATIC EXCHANGE)[a]

Catalyst	Injection No.	Temp. (°C)	Eluant analysis						% Retention
			Ethane		Ethylene		Acetylene		
			ml	cpml $\times$ 10^{-5}	ml	cpml $\times$ 10^{-5}	ml	cpml $\times$ 10^{-}	
					Acetylene				
Pd/Al$_2$O$_3$	1	200°	0.07	1.7	0.0	—	0.0	—	86
	3	200°	0.06	1.0	0.04	1.0	0.01	0.3	78
	3	100°	0.01	0.7	0.35	0.0	0.0	—	28
Rh/Al$_2$O$_3$	1	200°	0.0	—	0.1	0.4	0.07	0.0	84
	1	100°	0.0	—	0.0	—	0.43	0.0	16
Pt/Al$_2$O$_3$	1	200°	0.01	0.7	0.03	0.2	0.12	0.0	68
Al$_2$O$_3$	1 (5 ml)	200°	0.0	—	0.0	—	4.9	0.0	2
					Ethylene				
Pd/Al$_2$O$_3$	1	200°	0.26	1.7	0.0	—	—	—	47
	3	200°	0.18	1.4	0.16	0.8	—	—	32
Rh/Al$_2$O$_3$	1	200°	0.18	0.4	0.0	—	—	—	63
	2	200°	0.16	0.5	0.17	0.3	—	—	34
Pt/Al$_2$O$_3$	1	200°	0.01	0.7	0.03	0.2	—	—	38
Al$_2$O$_3$	1 (5 ml)	200°	0.0	—	4.75	0.0	—	—	5

[a] Volume of hydrocarbon, 0.5 ml per injection.

surfaces are heterogeneous and that sites which are involved in residue formation are not involved in hydrogenation. Although the temperature at which appreciable removal of residues was not established in the present studies, it is worth noting that with alumina-supported ruthenium catalysts, temperatures of around 450°C are required (6).

Although the injection of nonradioactive acetylene onto catalyst surfaces preexposed to ^{14}C-ethylene did not result in the displacement of radioactivity from the surface, the results are nevertheless of interest in that (i) even after the surface had been effectively saturated with ^{14}C-ethylene, acetylene adsorption still occurred, and (ii) nonradioactive ethane and/or ethylene resulted from the acetylene injections.

The extent of acetylene adsorption on ethylene-covered surfaces was almost as great as that on catalysts which had not previously been exposed to ethylene (see Table 7). This observation, together with the complete lack of reactivity of ethylene residues with acetylene indicates that the retained ethylene species is (i) not present as a reactive form of chemisorbed acetylene, which is considered to be associatively bonded (7), and (ii) not present in the same surface sites as the adsorbed acetylene. Thus the same catalyst surface must exhibit different types of heterogeneity for different

TABLE 7

PERCENTAGE OF THE INITIAL ACETYLENE DOSE RETAINED BY THE CATALYSTS

Temperature (°C):	20°	100°	200°
On catalysts unexposed to ethylene			
Palladium	84	84	84
Rhodium	8	18	84
Platinum	—	—	68
On catalysts covered to various degrees with ethylene[a]			
Palladium	90 (6)	96 (6)	91 (32)
Rhodium	—	71 (39)	98 (46)
Platinum	—	14 (6)	46 (16)

[a] Figures in parentheses are percentages of ethylene injection immediately before acetylene, which were retained by catalyst.

hydrocarbons. Further evidence for this latter postulate comes from the observation that the ethane and ethylene formed from the acetylene injections were nonradioactive.

Tritium Exchange and Adsorption

The results presented in Table 4 show that after all the desorbable "hydrogen" had been removed by helium treatment considerable amounts of "hydrogen" remained on the catalyst. From the carbon monoxide surface area determinations the numbers of surface atoms can be calculated (8): For the rhodium, palladium, and platinum catalysts, respectively, the values are 4.5×10^{18}, 2.81×10^{19}, and 1.1×10^{18} atoms per 0.5 g of catalyst. Comparison of these values with the numbers of hydrogen atoms retained by the catalysts shows that the latter are in considerable excess of that required for monolayer coverage; the ratio of hydrogen atoms retained to number of surface metal atoms being for Rh, 23.6; Pd, 5.7; Pt, 97.1. The question thus arises as to the location of the hydrogen. Comparison of the total hydrogen retention with the total metal atoms present leads to hydrogen:metal ratios of 0.72 for Rh; 0.73 for Pd, and 1.38 for Pt. From the magnitude of these ratios it is clear that some of the retained exchangeable hydrogen must be associated with the alumina support.

From the total BET surface areas the amounts of hydrogen retained by the catalyst (metal + support) are calculated to be Rh, 1.51×10^{14}; Pd, 1.86×10^{14}; and Pt, 1.45×10^{14} atoms/cm². These figures agree well with those quoted by Hall and Lutinski (9) for the hydroxyl hydrogen content of platinum on alumina, and platinum on fluorinated alumina catalyst; values of between 1.4 and 2.8×10^{14} OH⁻/cm² being observed depending upon catalyst pretreatment. Our figures also agree with those of Wells and Wilson (10) who found that with cobalt-alumina catalysts 10^{21} H atoms/g of catalyst were exchangeable at 130°C. It would appear therefore that most if not all of the retained hydrogen is associated with the alumina support and that hydrogen

adsorbed on the metal is effectively removed by the helium pretreatment.

The relatively long times required for the removal of all the "desorbable" hydrogen from the palladium catalyst, when compared with the times for the rhodium and platinum catalysts, indicates that some hydrogen absorption occurs with palladium. This is not unexpected in view of the known ability of this metal for hydride formation. However, we believe that this absorbed hydrogen is removed by the helium pretreatment, the long times being a consequence of the slow diffusion of the absorbed hydrogen to the surface of the metal (11).

The results obtained from the injection of ethylene or acetylene on to tritiated catalysts (Tables 5 and 6) show that the retained "hydrogen" was active both in hydrogenation and olefin or acetylene exchange. The formation of ethane by the injection of ethylene onto the catalyst may be due to either (a) self-hydrogenation of ethylene or (b) reaction of adsorbed ethylene with the retained "hydrogen" following activation and tritium exchange. From the yields of ethane and the specific activities it is possible to calculate the dependence of ethane production upon ethylene self-hydrogenation. At 200°C the percentage of ethane formed by self-hydrogenation is Pd, 20%; Rh, 80%; and Pt 70%. This sequence reflects the relative abilities of the metal to form residual species by C–H bond fission, and correlates well with the percentage retentions of ethylene at 200°C (see Tables 1, 2, and 3) which tend to decrease in the order Rh > Pt > Pd.

The formation of tritiated products from the injection of unsaturated hydrocarbons is interesting in the light of the above discussion regarding the location of the retained "hydrogen." If, as appears likely, the hydrogen is associated with the hydroxyl groups of the alumina support, then it is necessary to consider the site of the interaction of adsorbed olefin with the hydrogen. Sinfelt et al. (12) have suggested that in ethylene hydrogenation over alumina-supported platinum catalysts, the ethylene is adsorbed on the alumina and that hydrogen migrates from the platinum to the alumina before reaction occurs. In view of the lack of reactivity of the alumina itself in the absence of metal (see Tables 5 and 6), a more likely explanation would appear to be that the hydrocarbon is adsorbed on the metal and that the tritium migrates from the alumina support to the metal before reaction takes place.

In conclusion, we can say that the tritium exchange results show that the support plays an important role in catalysis by alumina-supported metals; further work with silica and alumina-supported metals is at present being carried out in an attempt to establish more precisely the function of the support.

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