

Radiochemical Studies of Chemisorption and Catalysis

IX. The Behavior of ^{14}C -Ethylene, ^{14}C -Propylene and Tritium Adsorbed on Alumina- and Silica-Supported Platinum Catalysts

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^{14}C -Ethylene, ^{14}C -propylene, and tritium tracer studies of the nature and reactivity of adsorbed species have been carried out between 20 and 350°C, using alumina- and silica-supported platinum catalysts, at metal concentrations between 5 and 0.1% (w/w). The results show that with both ethylene and propylene a large fraction of the initially adsorbed material is retained by the catalyst as an unreactive strongly adsorbed species. The extent of retention is greater with ethylene than with propylene. Using tritium, it has been found that the support as well as the metal participates in the reaction, the degree of participation being greater with alumina than with silica. Evidence is presented to show that hydrogen migration between the metal and the support is of importance.

INTRODUCTION

The existence of hydroxyl groups on the surface of alumina or silica has been demonstrated by several workers (1-5). Estimates of the concentration of these hydroxyl groups have been made by Hall and co-workers (1, 2), using a differential hydrogen analysis technique in which the exchange of the hydroxyl hydrogen atoms with deuterium is followed as the temperature is slowly and continuously increased. From these studies these workers concluded that the surface density of terminal hydroxyl groups was approximately the same for silica and alumina. However, the silica hydroxyl groups were less readily exchanged than the alumina hydroxyl groups. Hall and Lutinskii (2) also showed that the presence of approximately 0.7% platinum on the alumina did not materially change the concentration of surface hydroxyl groups on the alumina, nor did it appear to enhance the rate of exchange of the hydroxyl groups with deuterium.

Carter *et al.* (5) have reported the ki-

netics of the exchange of deuterium with the surface hydroxyl groups of alumina in alumina-supported platinum catalysts. These workers concluded that the presence of platinum increased the rate of exchange relative to that for pure alumina, although increasing the platinum concentration from 0.001 to 0.6% tended to decrease the exchange rate. It was also concluded that the method of preparation of the catalysts was important in that chloride ions, from the chloroplatinic acid used as the source of platinum, replaced some of the surface hydroxyl groups. Similar effects have been observed with fluoride ion (2).

In spite of these extensive studies with "hydrogen," comparatively little appears to be known about the reactivity of the hydroxyl hydrogen atoms in the reactions of hydrocarbons at the surfaces of supported metal catalysts. In a recent paper (6) we described some studies of the interaction of hydrocarbons and hydrogen with alumina-supported metal catalysts using a radioactive tracer technique. From these results it was concluded that the hydroxyl

groups could participate in the exchange of hydrocarbons.

The object of the present work was to study in more detail the role of the support, in the reactions of hydrocarbons over alumina- and silica-supported metal catalysts.

EXPERIMENTAL METHODS

Catalysts. The catalysts consisted of platinum supported on γ -alumina (Peter Spence Ltd) at concentrations of 5, 1, or 0.1% (w/w) platinum, and platinum on "Aerosil" silica (Degussa Ltd.) at platinum concentrations of 5 or 1% (w/w). The catalysts were prepared by adding an aqueous solution containing the required weight of chloroplatinic acid (H_2PtCl_6) to an aqueous suspension of the support-material. The excess water was evaporated off and the supported salt was finally dried in an air oven at 120°C for several hours. Immediately before use the supported salt was reduced to the metal at 350°C in a stream of hydrogen.

Apparatus and materials. The apparatus was as described previously (7). Briefly, it consisted of a microcatalytic reactor coupled to a Beckman GC2A gas chromatograph and a gas-flow proportional counter. A 4-ft long silica gel column was used at a temperature of 70 to 130°C with helium as carrier gas.

Helium, methane, and hydrogen were purified as described previously (6). Ethylene and propylene (Matheson Co. Inc.) contained no impurities detectable by gas chromatography and were merely degassed before use. Tritium and ^{14}C -ethylene were obtained from the Radiochemical Centre, Amersham, ^{14}C -propylene was obtained from New England Nuclear Corporation. The radioactive materials were diluted to the required specific activity with inactive material before use.

Experimental procedure. Each catalyst sample (0.45 g) was activated in a stream of hydrogen (flow rate = 30 ml min⁻¹) at 350°C for 4 hr. In the tritium exchange experiments, the catalyst, after activation, was allowed to stand under 2 ml (NTP) of tritiated hydrogen at 350°C for 1 hr. At

the end of this period, the helium flow was directed over the catalyst. The temperature was maintained at 350°C until the count rate of the reactor eluant reached background level (approx 45 min), indicating that all the "desorbable" hydrogen had been removed from the catalyst. The catalyst was then cooled to the required temperature in the helium flow stream.

In the carbon-14 adsorption experiments following activation, helium stream flowed over the catalyst at 350°C for 1 hr, and the flow was continued until the required reaction temperature was attained. Samples of reactants were injected onto the catalyst using Hamilton Gas-Tight syringes.

RESULTS

^{14}C -Ethylene and ^{14}C -Propylene Adsorption and Exchange

The adsorption and exchange between adsorbed ^{14}C -olefin and inactive olefin in the gas phase was studied over 1% Pt/ Al_2O_3 and 1% Pt/ SiO_2 in the temperature range 20 to 350°C. The catalyst surface was first saturated with ^{14}C -labeled olefin by injecting successive 0.5-ml volumes (usually three) of the olefin onto the catalyst until no further adsorption was observed to occur. 0.5 ml of inactive olefin was then injected on to the catalyst and the reactor eluant was analyzed for radioactivity. The results for ethylene and propylene are shown in Tables 1 and 2, respectively. In these tables the product analyses refer to the first injection of ^{14}C -olefin on to the catalyst, while the adsorption values refer to the total amount of ^{14}C -olefin adsorbed on the catalyst at that particular temperature. In these and all subsequent tables the radioactive content of the eluant products is expressed as counts per milliliter (cpml).

Possible effects of differing strengths of adsorption of different olefins upon the exchangeability of the adsorbed species were investigated by studying the exchange between pre-adsorbed ^{14}C -propylene and inactive ethylene in the gas phase over 1% Pt/ Al_2O_3 between 20 and 350°C. The results are shown in Table 3.

TABLE 1
THE EXCHANGE BETWEEN ADSORBED $^{14}\text{C}_2\text{H}_4$ AND GAS-PHASE ETHYLENE
Injection size = 0.5 ml; sp act $^{14}\text{C}_2\text{H}_4$: 1.0×10^4 cpml (Pt/ Al_2O_3); 1.6×10^4 cpml (Pt/ SiO_2).

Catalyst	Temp (°C)	Injection	Adsorp- tion (ml)	Methane			Ethane		Ethylene		Exchange as % of adsorption
				(ml)	(ml) $\times 10^{-4}$	(cpml)	(ml) $\times 10^{-4}$	(cpml)	(ml) $\times 10^{-4}$	(cpml)	
1% Pt/ Al_2O_3	20	$^{14}\text{C}_2\text{H}_4$	0.10	—	—	0.01	1.00	0.39	1.0	—	
		C_2H_4	0.00	—	—	—	—	0.50	0.01	5.0	
	100	$^{14}\text{C}_2\text{H}_4$	0.08	—	—	0.04	0.80	0.38	1.1	—	
		C_2H_4	0.00	—	—	—	—	0.50	0.01	2.9	
	200	$^{14}\text{C}_2\text{H}_4$	0.10	—	—	0.12	0.80	0.27	1.0	—	
		C_2H_4	0.00	—	—	0.03	0.01	0.47	0.0	0.1	
	350	$^{14}\text{C}_2\text{H}_4$	0.10	0.18	1.0	0.12	1.00	0.10	1.0	—	
		C_2H_4	0.02	0.12	0.2	0.15	0.08	0.21	0.02	16.0	
1% Pt/ SiO_2	20	$^{14}\text{C}_2\text{H}_4$	0.04	—	—	0.03	1.60	0.43	1.70	—	
		C_2H_4	0.00	—	—	—	—	0.50	0.02	25.0	
	100	$^{14}\text{C}_2\text{H}_4$	0.04	—	—	0.01	1.50	0.45	1.70	—	
		C_2H_4	0.00	—	—	—	—	0.50	—	—	
	200	$^{14}\text{C}_2\text{H}_4$	0.14	—	—	0.03	1.60	0.33	1.60	—	
		C_2H_4	0.00	—	—	0.01	1.00	0.49	0.03	4.0	
	350	$^{14}\text{C}_2\text{H}_4$	0.05	0.02	1.0	0.07	1.60	0.45	1.40	—	
		C_2H_4	0.03	0.01	0.4	0.06	—	0.40	—	0.1	

TABLE 2
THE EXCHANGE OF PREADSORBED $^{14}\text{C}_3\text{H}_6$ WITH GAS-PHASE PROPYLENE
Injection size = 0.5 ml; sp act 6.0×10^4 cpml.

Catalyst	Temp (°C)	Injection	Adsorp- tion (ml)	Ethane			Propane		Propylene		Exchange as % of adsorption
				(ml)	(ml) $\times 10^{-4}$	(cpml)	(ml) $\times 10^{-4}$	(cpml)	(ml) $\times 10^{-4}$	(cpml)	
1% Pt/ Al_2O_3	20	$^{14}\text{C}_3\text{H}_6$	0.12	—	—	0.05	6.20	0.37	6.00	—	
		C_3H_6	—	—	—	—	—	0.50	0.50	34.7	
	100	$^{14}\text{C}_3\text{H}_6$	0.06	—	—	0.05	6.00	0.40	6.00	—	
		C_3H_6	—	—	—	—	—	0.50	0.20	12.1	
	200	$^{14}\text{C}_3\text{H}_6$	0.08	0.01	6.0	0.15	6.00	0.26	6.20	—	
		C_3H_6	—	—	—	0.08	0.40	0.42	0.20	9.6	
350	$^{14}\text{C}_3\text{H}_6$	0.08	0.06	0.0	0.25	5.95	0.10	6.20	—		
	C_3H_6	—	0.03	1.2	0.15	0.20	0.25	0.20	7.4		
1% Pt/ SiO_2	20	$^{14}\text{C}_3\text{H}_6$	0.07	—	—	0.02	6.10	0.41	6.00	—	
		C_3H_6	—	—	—	—	—	0.50	0.22	24.0	
	100	$^{14}\text{C}_3\text{H}_6$	0.06	—	—	0.03	6.00	0.41	6.00	—	
		C_3H_6	—	—	—	—	—	0.50	0.40	26.4	
	200	$^{14}\text{C}_3\text{H}_6$	0.08	—	—	0.04	5.30	0.37	6.00	—	
		C_3H_6	—	—	—	0.02	0.80	0.48	0.20	10.7	

TABLE 3
THE EXCHANGE BETWEEN PREADSORBED $^{14}\text{C}_3\text{H}_6$ AND GAS-PHASE ETHYLENE

Catalyst: 1% Pt/Al₂O₃; injection size = 0.5 ml; sp act $^{14}\text{C}_3\text{H}_6$, 3.6×10^4 cpml.

Temp (°C)	Injection	Adsorp- tion (ml)	Methane		Ethane		Ethylene		Propane		Propylene	
			(ml)	(cpm/ $\times 10^{-4}$)	(ml)	(cpm/ $\times 10^{-4}$)	(ml)	(cpm/ $\times 10^{-4}$)	(ml)	(cpm/ $\times 10^{-4}$)	(ml)	(cpm/ $\times 10^{-4}$)
20	$^{14}\text{C}_3\text{H}_6$	0.08	—	—	—	—	—	—	0.01	3.70	0.41	3.60
	C ₂ H ₄	0.05	—	—	—	—	0.45	—	—	—	—	—
100	$^{14}\text{C}_3\text{H}_6$	0.10	—	—	—	—	—	—	0.02	3.70	0.38	3.50
	C ₂ H ₄	0.04	—	—	0.01	0.0	0.45	—	—	—	—	—
200	$^{14}\text{C}_3\text{H}_6$	0.02	—	—	—	—	—	—	0.07	3.50	0.40	3.50
	C ₂ H ₄	0.02	0.01	0.0	0.07	—	0.40	—	—	—	—	—
350	$^{14}\text{C}_3\text{H}_6$	0.06	—	—	0.02	0.01	0.01	0.0	0.21	3.60	0.16	3.60
	C ₂ H ₄	0.00	0.03	0.0	0.27	0.04	0.20	0.06	—	—	—	—

Interaction of Hydrocarbons with Tritium-Exchanged Catalysts

The results presented above show that when an olefin is injected on to a freshly reduced catalyst, the products contain appreciable amounts of the corresponding alkane. In a previous paper (6) we reported similar results for a 5% Pt/Al₂O₃ catalyst and we presented evidence to suggest that the alkane may arise by reaction between the olefin and hydrogen retained by the catalyst following the activation procedure. Furthermore it was suggested that this hydrogen may be associated with the support rather than the metal.

To investigate this problem further the interaction of ethylene and propylene with tritium exchanged alumina- and silica-supported platinum catalysts has been studied between 20 and 300°C at platinum concentrations of 5, 1, and 0.1% (w/w). Similar experiments were also carried out with pure alumina and silica as catalysts.

The catalysts were exchanged in tritium at 350°C and the extent of tritium retention following the helium treatment was calculated. Table 4 shows the amount of tritium retained per gram of catalyst, together with the ratio of tritium to the total number of metal atoms per gram of catalyst.

In one series of experiments the reactivity of the retained hydrogen towards ethyl-

ene was investigated by injecting successive 0.5-ml volumes of ethylene onto the catalyst at constant temperature. Figure 1 shows some typical results for the yield of ethane (ml) and the tritium content of the ethylene (cpml) as a function of the volume of ethylene injected on to the catalyst.

From these results two important factors emerge. First, the "hydrogenation activity" decreases more rapidly than the "exchange activity"; second, ethylene exchange occurs in the absence of hydrogenation.

In another series of experiments the effect of temperature upon the reactivity of the retained hydrogen towards ethylene was studied as a function of the platinum content of the catalysts. After helium pretreat-

TABLE 4
EXTENT OF TRITIUM RETENTION BY CATALYSTS

Two ml of HT injected on to catalyst = ca. 4×10^6 counts.

Catalyst	H atoms re- tained/g of catalyst ($\times 10^{-20}$)	H-atoms Pt-atoms
Pt/Al ₂ O ₃ , 5%	1.69	1.02
1%	1.73	6.50
0.1%	1.86	64.0
Al ₂ O ₃	1.88	—
Pt/SiO ₂ , 5%	1.98	1.39
1%	1.98	6.80
SiO ₂	1.97	—

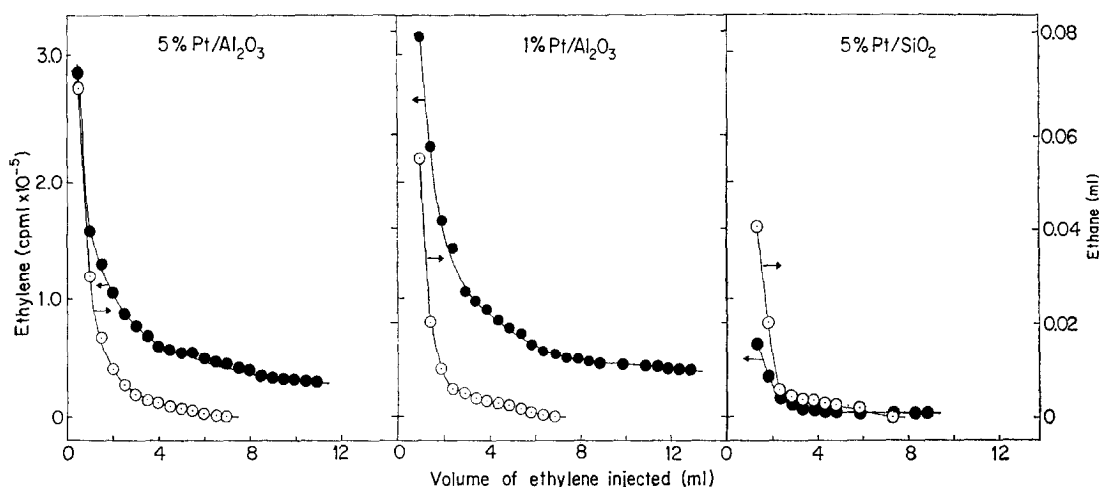


FIG. 1. Variation of ethane yield (ml) (○); and yields of exchanged ethylene (cpml) (●) with the total volume of ethylene injected on to various platinum catalysts at 100°C.

TABLE 5
THE REACTION OF ETHYLENE WITH TRITIATED CATALYSTS

Injection size = 0.5 ml.

Catalyst	Temp (°C)	Adsorption (ml)	Ethane		Ethylene		Methane	
			(ml)	(cpml × 10 ⁻⁵)	(ml)	(cpml × 10 ⁻⁵)	(ml)	(cpml × 10 ⁻⁵)
Pt/Al ₂ O ₃ , 5%	20	0.36	0.12	0.10	0.02	0.04	—	—
	100	0.22	0.07	5.40	0.23	2.80	—	—
	200	0.20	0.12	5.20	0.18	4.90	—	—
	300	0.16	0.10	5.00	0.00	—	0.24	0.0
1%	20	0.15	0.08	—	0.27	0.01	—	—
	50	0.01	0.00	—	0.49	0.03	—	—
	100	0.03	0.02	1.70	0.45	0.55	—	—
	200	0.04	0.08	3.00	0.38	2.10	—	—
	300	0.01	0.25	4.20	0.21	3.30	0.02	?
0.1%	20	0.04	—	—	0.46	2.00	—	—
	50	0.02	—	—	0.48	2.60	—	—
	100	0.05	—	—	0.45	6.00	—	—
	200	0.06	0.01	5.00	0.42	1.50	—	—
	300	0.04	0.10	7.30	0.32	4.40	0.02	20.0
Al ₂ O ₃	20	—	—	—	0.50	—	—	—
	50	—	—	—	0.50	—	—	—
	100	—	—	—	0.50	—	—	—
	200	—	—	—	0.50	0.03	—	—
Pt/SiO ₂ , 5%	100	0.25	0.04	0.76	0.35	0.60	—	—
	200	0.10	0.12	1.30	0.28	1.00	—	—
	300	0.08	0.20	1.20	0.02	1.00	0.20	1.90
1%	20	0.05	0.01	0.04	0.44	0.01	—	—
	100	0.10	0.02	0.25	0.38	0.10	—	—
	200	0.00	0.04	0.17	0.46	0.07	—	—
	300	0.03	0.25	1.20	0.19	1.00	0.05	1.60

TABLE 6
THE REACTION OF PROPYLENE WITH TRITIATED CATALYSTS

Injection size = 0.5 ml.

Catalyst	Temp (°C)	Adsorption (ml)	Ethane		Propane		Propylene	
			(ml)	(cpml × 10 ⁻⁵)	(ml)	(cpml × 10 ⁻⁵)	(ml)	(cpml × 10 ⁻⁵)
Pt/Al ₂ O ₃ , 1%	20	0.10	—	—	0.02	0.07	0.38	0.02
	100	0.07	—	—	0.03	7.50	0.40	4.00
	200	0.10	—	—	0.18	5.60	0.22	4.40
	300	0.02	0.28	24.0	0.18	3.00	0.02	1.60
0.1%	20	0.05	—	—	0.00	—	0.45	0.00
	100	0.05	—	—	0.01	0.1	0.44	0.05
	200	0.05	—	—	0.02	0.1	0.43	1.20
	300	0.07	0.02	17.0	0.07	5.0	0.34	2.40
Pt/SiO ₂ , 1%	20	0.12	—	—	0.03	2.8	0.35	0.50
	100	0.05	—	—	0.04	3.8	0.41	1.71
	200	0.10	—	—	0.04	4.7	0.36	3.30
	300	0.05	0.05	0.0	0.10	6.5	0.30	3.30

ment, the exchanged catalysts were cooled in helium to 20°C and the activity was investigated at temperatures from 20 to 300°C by injecting 0.5-ml volumes of ethylene onto the catalyst at each temperature. The results for the first injection of ethylene at each temperature are shown in Table 5.

Similar studies were made with propylene over 1 and 0.1% Pt/Al₂O₃ and 1% Pt/SiO₂; the results are shown in Table 6.

With both ethylene and propylene the amount of olefin exchange and the alkane yield increased with increasing temperature and decreased with decreasing platinum content. The extent of tritium exchange in the hydrocarbons was greater over the alumina than over the silica-supported catalysts at each temperature. Neither alumina nor silica was found to be active for ethylene adsorption or exchange below 300°C, although at this temperature the alumina showed appreciable exchange activity.

From these results it would appear that the presence of the metal activates the hydrogen associated with the support. It was therefore decided to investigate the interaction of hydrogen with the tritiated catalysts in an attempt to establish the mechanism whereby the exchange reaction occurs.

Table 7 shows the results obtained for the exchange of hydrogen with Pt/Al₂O₃, Pt/SiO₂, Al₂O₃, and SiO₂ catalysts in the temperature range 20 to 350°C.

DISCUSSION

The results presented above show that there are some significant differences between alumina- and silica-supported platinum catalysts with regard to the reactivity of adsorbed species.

¹⁴C-Olefin Adsorption and Retention

The results presented in Table 1 show that the extent of adsorption of ethylene

TABLE 7
EXCHANGE OF HYDROGEN WITH
TRITIATED CATALYSTS

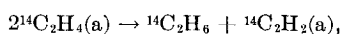
Injection size = 0.5 ml.

Temp (°C):	20	50	100	200	300
Catalyst (cpml × 10 ⁻⁵)					
Pt/Al ₂ O ₃ , 1%	1.0	1.1	1.4	1.4	1.9
0.1%	1.4	1.7	2.4	2.9	3.4
Pt/SiO ₂ , 1%	0.10	0.15	0.12	0.62	0.95
Al ₂ O ₃	0.34	0.60	0.85	1.10	1.70
SiO ₂	0.15	0.18	0.14	0.62	0.90

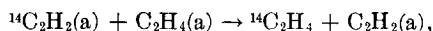
is greater on alumina-supported platinum than on silica-supported platinum. However, the injection of inactive ethylene on to ^{14}C -ethylene precovered surfaces shows that the amount of adsorbed ethylene which will undergo exchange is greater with the silica-supported catalyst. Both catalysts show similar behavior in that the amount of exchangeable ethylene decreases with increasing temperature. Similar results were obtained with propylene (see Table 2), although the total extent of adsorption was less than with ethylene, whereas the fraction of the adsorbed propylene which would undergo "molecular" exchange was greater than the corresponding value for ethylene.

It is of interest to note that with both ethylene and propylene below 200°C "molecular" exchange occurred by the direct replacement of adsorbed ^{14}C -olefin with inactive ethylene, whereas at 200°C and above, the exchanged fraction comprised both the olefin and the corresponding alkane. Only at 350°C does carbon-carbon bond fission appear to have been of importance.

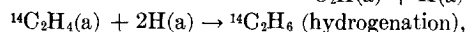
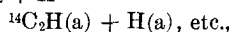
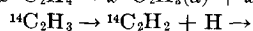
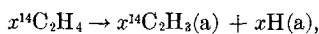
These results suggest that the species retained by the catalyst is a dissociatively adsorbed species and that exchange occurs by a self-hydrogenation process which may be represented as either (a);



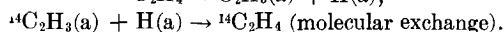
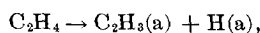
and



or, as seems more likely from the tritium tracer results discussed below, (b);

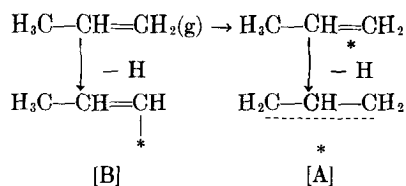


and



The greater ease of exchange of propylene relative to ethylene may be explained by considering that a fraction of the retained propylene exists on the surface as a

π -allyl complex [A] rather than as a less reactive σ -bonded dissociatively adsorbed species, e.g., adsorbed propenyl [B]:



Further evidence that a different type of adsorbed species may be in part responsible for the retention of propylene rather than ethylene comes from the results presented in Table 3. These show the effects of injecting inactive ethylene onto the surface of a 1% Pt/Al₂O₃ catalyst which was precovered with ^{14}C -propylene. The following interesting points emerge:

1. Ethylene adsorption can still occur on surfaces which have been effectively saturated with propylene, although the extent of adsorption is less than on a "clean" surface; (ii) at 200°C and below no radioactivity is displaced from the surface; and (iii) at 350°C the injection of inactive ethylene onto the catalyst results in the formation of radioactive ethane and ethylene, although no C₃-hydrocarbons are displaced.

From these observations we conclude that different types of site, and consequently different types of adsorbed species, are involved in the retention of ethylene and propylene, i.e., the catalyst surface shows differing degrees of heterogeneity depending upon the adsorbate hydrocarbon.

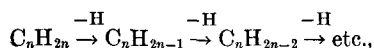
Tritium Adsorption and Retention

The results presented in Table 4 show that after all the desorbable "hydrogen" had been removed from the catalyst during the helium treatment, considerable quantities of hydrogen still remained on the catalyst. With the alumina-supported platinum catalysts the extent of retention increased with decreasing platinum concentration to a maximum value for alumina itself. However with the silica-supported catalysts, the retention values are independent of the platinum concentration. Consideration of the values for the total number of

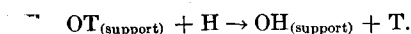
hydrogen atoms retained per platinum atom shows that the ratio is always in excess of unity. This fact together with the observation that the retention values for the different catalysts are independent of the platinum concentration over a fifty-fold increase leads to the conclusion that the retained hydrogen is associated with the support rather than the metal. From the BET surface areas for the alumina ($180 \pm 5 \text{ m}^2 \text{ g}^{-1}$) and the silica ($175 \pm 5 \text{ m}^2 \text{ g}^{-1}$), respective values of 1.05×10^{14} and 1.13×10^{14} H atoms retained cm^{-2} are obtained. These values are in good agreement with those quoted by Hall *et al.* (1) for the concentration of terminal hydroxyl groups on alumina and silica. They also agree with previously quoted values for 5% dispersions of rhodium, palladium, and platinum on alumina (6).

The injection of ethylene or propylene onto tritium exchanged catalysts (see Tables 5 and 6) results in the formation of tritiated alkanes and olefins. The question therefore arises as to the mechanism whereby the tritium associated with the support reacts with adsorbed olefin. The results in Tables 5 and 6 show that (i) decreasing the platinum concentration decreases the extent of retention, hydrogenation, and olefin exchange; and (ii) the extent of retention, hydrogenation, and olefin exchange are greater for alumina-supported platinum than for silica-supported platinum. Furthermore, below 300°C , neither alumina nor silica will itself catalyze the olefin exchange or hydrogenation reactions.

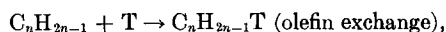
These observations are consistent with a mechanism in which the olefin undergoes dissociation on the metal;



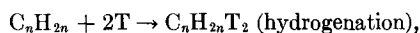
the extent of dissociation depending upon the experimental conditions. The hydrogen atoms, thus liberated, can freely migrate between the metal and the support, thereby equilibrating with the "retained" tritium;



The tritium can then react with adsorbed olefin to yield tritiated alkane and olefin;



and



both of these reactions occurring on the metal.

According to this mechanism the extent of tritium incorporation in the hydrocarbon will depend upon the ability of the adsorbed hydrogen to migrate from the metal to the support and *vice versa*. Studies of the exchange reaction between gas-phase hydrogen and the tritiated catalysts (see Table 7) show that the rate of exchange is greater than the rate of formation of tritiated products from ethylene or propylene. Thus hydrogen migration must be fast relative to the rate of reaction of adsorbed hydrocarbon species with hydrogen. The rate of hydrogen exchange is greater with alumina-supported platinum than with silica-supported platinum. This sequence of reactivity, which is the same as that observed by Hall *et al.* (1) for alumina and silica, is the same as that observed with ethylene and propylene. This again suggests that the incorporation of tritium in the hydrocarbon is dependent upon the ability of the hydrogen atoms to exchange with the support "hydroxyl" groups.

The results for reaction of hydrogen with tritiated catalysts (Table 7) differ from those obtained for the reaction of tritiated catalysts with olefins in two important respects. First, while for olefin exchange and hydrogenation the presence of metal was essential, both silica and alumina were themselves active for hydrogen exchange at 20°C and above. Second, whereas the amounts of olefin exchange and hydrogenation increased with increasing metal concentration, the rate of hydrogen exchange decreased as the platinum concentration was increased from 0.1 to 1%, although the presence of the metal increased the rate of exchange over that for pure alumina.

The enhancement of the rate of exchange by the presence of platinum is in agreement with the observations of Carter *et al.* (5); the decrease in rate with increasing platinum concentration probably reflects a de-

crease in the hydroxyl concentration due to their replacement by chloride ions from the chloroplatinic acid used in the preparation. In this context it is interesting to note that the total number of hydrogen atoms retained by the platinum-alumina catalysts (Table 4) decreased as the platinum concentration was increased from 0.1 to 5%.

In conclusion, the present results show that for alumina- and silica-supported platinum catalysts, the reactivity of adsorbed species is dependent upon the nature of the support. The results also show that on these catalysts hydrogen migration between metal and support readily occurs. This observation together with the observation that alumina, and to a lesser extent silica, itself is active in hydrogen exchange suggests that in reactions involving hydrogen and hydrocarbons, the support may play a significant role in determining the catalytic activity. A similar conclusion has been reached by Wells and Wilson (8) and by Sinfelt and Lucchesi (9).

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