

## The Adsorption and Retention of Hydrocarbons by Alumina-Supported Palladium Catalysts

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The adsorption of  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_8$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_3\text{H}_6$ ,  $\text{C}_2\text{H}_2$ , and cyclo- $\text{C}_3\text{H}_6$  on alumina-supported palladium catalysts has been studied at 20°, 100°, and 200°C. Product analyses and percentages of hydrocarbon retained in an unreactive form by the catalyst are reported.

The percentage retention of the various hydrocarbons increases in the sequence: alkanes < cyclopropane < alkenes < acetylene. The results are discussed in terms of surface heterogeneity and the dissociative adsorption of hydrocarbons by carbon-hydrogen bond cleavage. Carbon-carbon bond rupture appears to be unimportant except at 200°C.

### INTRODUCTION

In metal-catalyzed reactions of hydrocarbons self-poisoning and the accumulation of surface residues are often assumed to occur (1). However few systematic studies of the formation of surface residues have been reported.

The existence of inactive species on a catalyst surface has been demonstrated by studies of the stoichiometry of reactions, e.g., self-hydrogenation of ethylene (2, 3), and by the use of radioactive tracers (4, 5). Infrared spectroscopic studies have shown that on hydrogen-free metal surfaces, hydrocarbons are dissociatively adsorbed, thereby forming hydrogen-deficient residues and possibly also surface polymers (6, 7, 8). Dissociative adsorption and the formation of surface residues has also been demonstrated by field-emission microscopy (9, 10).

Unfortunately comparisons between the various reports are difficult since different workers have used different catalyst preparations, experimental conditions, and procedures. The aim of the study presented in this report was to investigate the adsorption and retention of a whole range of hydrocarbons on a supported metal catalyst under a variety of conditions. Previous work (5) had shown that with alumina-supported

palladium catalysts a large percentage of initially adsorbed ethylene was retained on the catalyst surface in an inactive form. Consequently, alumina-supported palladium was chosen for the present study.

### EXPERIMENTAL

**Apparatus.** The apparatus, similar to that described by Kokes *et al.* (11), consisted of a microcatalytic reactor coupled to a Beckmann GC2A gas chromatograph. The reactor itself consisted of a pipette-shaped Pyrex glass vessel fitted at each end with a glass-metal seal. This was coupled to the gas chromatograph via  $\frac{1}{8}$ -inch diameter copper tubing and Crawford, Swagelock connectors. Where necessary (see Fig. 1) stainless steel switch valves were used, thus ensuring a grease-free system. The catalyst (0.5 g) was placed in the bulb portion of the reactor and was held in place by a plug of clean silica wool. The temperature of the catalyst was maintained by surrounding the reactor with an electric furnace, and was measured by a thermocouple positioned in a well in the side of the reactor vessel. Immediately above and below the catalyst were situated injection ports which were sealed by  $\frac{1}{4}$ -inch serum caps. These permitted hydrocarbon samples to be intro-

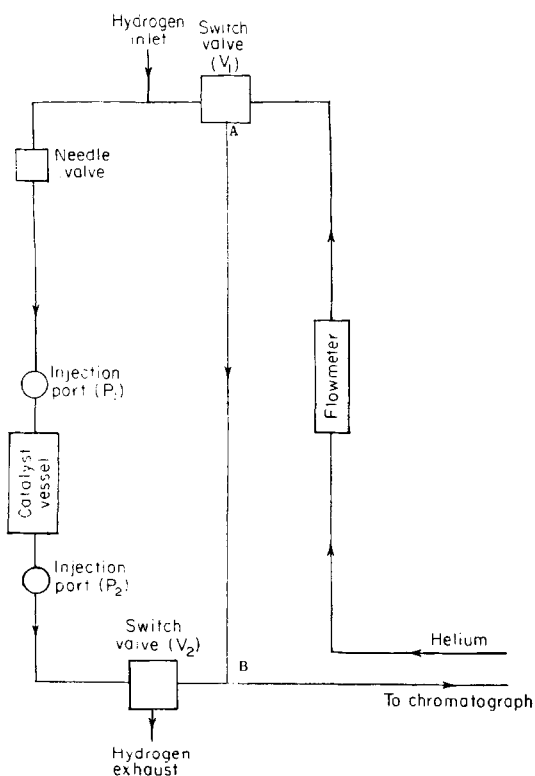


Fig. 1. Block schematic diagram of microcatalytic reactor.

duced into the carrier-gas stream and thence onto the catalyst, or directly onto the chromatographic column for calibration purposes. Injections were made using Hamilton Gas-Tight syringes fitted with Chaney adaptors. Using this system the desired volume of gas could be sampled with an accuracy of  $\pm 0.01\%$ .

**Materials.** The catalysts consisted of 5% w/w palladium supported on  $\alpha$ -alumina. The total area of the catalyst was  $111 \text{ m}^2\text{g}^{-1}$  (BET), while the metal area, determined by CO adsorption, was  $5.0 \text{ m}^2\text{g}^{-1}$ . Catalyst samples were activated immediately before use at  $200^\circ\text{C}$  for approximately 30 min in a stream of hydrogen ( $30 \text{ ml min}^{-1}$ ).

Helium (Fisons Ltd.) of purity  $> 99.995\%$  was used as carrier gas and was further purified by passage through a  $5\text{\AA}$  molecular sieve maintained at liquid nitrogen temperature. Cylinder hydrogen (British Oxygen Co.) was first purified by passage through a Deoxo Hydrogen Purifier and thence through

a  $5\text{\AA}$  molecular sieve trap cooled in liquid nitrogen.

Methane (Air Products Ltd.), ethylene, acetylene, and cyclopropane (British Oxygen Co. Ltd.) were fractionally distilled, and ethane, propane, and propylene (Matheson Co., Inc.) were degassed before use. The impurity level of each hydrocarbon following the above treatment was  $< 0.5\%$  as determined by gas chromatography.

**Experimental procedure.** Figure 1 shows a block schematic diagram of the apparatus. The catalyst was reduced as described above. During this period helium was allowed to flow through the chromatographic column via the bypass AB. At the end of the reduction period the catalyst vessel was flushed with helium, at a flow rate of  $60 \text{ ml min}^{-1}$ , for a minimum of 30 min. Hydrocarbon samples were then introduced to the catalyst via injection port ( $P_1$ ) and the eluant products were separated on a 10 ft long silica gel column which was operated at either  $70^\circ$  or  $130^\circ\text{C}$ . Calibration samples were introduced at frequent intervals via injection port ( $P_2$ ). Quantitative estimation of the chromatographic analyses was obtained from the peak area as determined by an electronic integrator.

## RESULTS

The primary aim of the first series of experiments was to find the pattern of reactivity and retention for a range of hydrocarbons on the palladium-alumina catalyst. Equal volumes of  $0.5 \text{ ml}$  (NTP) of the various hydrocarbons were each injected on to a freshly reduced catalyst at  $20^\circ$ ,  $100^\circ$ , and  $200^\circ\text{C}$ . In each case the extent of the retention, by the catalyst, of the first injection of hydrocarbon, and the composition of the eluted hydrocarbon products was examined. From the results shown in Table 1 it can be seen that the percentages of the first hydrocarbon dose retained by the catalyst increase in the order:

alkanes  $<$  cyclopropane  $<$  alkenes  $\ll$  acetylene

The volume of gas used for the first injection was calculated to give a reasonable excess over that required for monolayer coverage. However, since the measurements

TABLE 1  
RETENTION DATA AND PRODUCT ANALYSIS OF FIRST INJECTION OF 0.5 ML OF HYDROCARBON

Hydrocarbon	Temp. (°C)	Eluant analysis (ml)							% Age retention
		CH <sub>4</sub>	C <sub>2</sub> H <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	C <sub>3</sub> H <sub>6</sub>	cyclo-C <sub>3</sub> H <sub>6</sub>	
Methane	200°	0.48	—	—	—	—	—	—	4
	100°	0.48	—	—	—	—	—	—	4
	25°	0.49	—	—	—	—	—	—	2
Ethane	200°	0.01	—	—	0.47	—	—	—	2
	100°	—	—	—	0.47	—	—	—	3
	20°	—	—	—	0.44	—	—	—	6
Ethylene	200°	0.01	—	0.00	0.30	—	—	—	39
	100°	—	—	0.00	0.33	—	—	—	34
	20°	—	—	0.05	0.32	—	—	—	26
Acetylene	200°	0.02	0.00	0.003	0.08	—	—	—	82
	100°	—	0.01	0.00	0.05	—	—	—	88
	20°	—	0.06	0.00	0.02	—	—	—	84
Propylene	200°	0.02	—	—	0.03	0.28	0.02	—	37
	100°	—	—	—	0.00	0.23	0.12	—	30
	20°	—	—	—	0.00	0.21	0.14	—	30
Propane	200°	0.01	—	—	0.04	0.40	—	—	14
	100°	—	—	—	—	0.50	—	—	0
	20°	—	—	—	—	0.50	—	—	0
Cyclo-propane	200°	0.01	—	—	0.03	0.26	0.00	0.03	39
	100°	—	—	—	—	0.36	—	0.02	24
	20°	—	—	—	—	0.14	—	0.29	15

TABLE 2  
TOTAL RETENTION OF HYDROCARBONS BY Pd/Al<sub>2</sub>O<sub>3</sub> CATALYST<sup>a</sup>

Hydrocarbon	Temp. (°C)	No. of injections	Total vol. adsorbed (ml)	% Recovery from—	
				1st injection	Last injection
Methane	200°	2	0.03	96	98
	100°	1	0.02	96	96
	25°	2	0.02	98	98
Ethane	200°	2	0.05	98	96
	100°	2	0.05	97	97
	20°	2	0.10	94	94
Propane	200°	4	0.12	86	95
Ethylene	200°	6	0.54	61	98
	100°	3	0.34	67	90
	20°	3	0.13	80	94
Propylene	200°	3	0.33	63	74
Acetylene	200°	3	1.22	18	22
	100°	3	0.67	12	72
Cyclo-propane	200°	2	0.29	61	80

<sup>a</sup> Injection size, 0.5 ml (NTP).

were made in a flow system it was necessary to establish whether the results obtained from the first injection represent a true saturation of the surface or whether further injections of hydrocarbon were necessary before equilibrium was achieved. Table 2 shows the results obtained from multiple injections of hydrocarbon.

From these results it can be seen that, with the exception of methane and ethane, where adsorption was complete after one injection, several injections were necessary before equilibrium was achieved. It is also of interest to examine the variation in the product distribution with injection number and Table 3 shows typical results obtained for ethylene at 100° and 200°C, propylene at 200°C, and propane at 200°C. From these results it can be seen that as the amount of hydrocarbon passed through the catalyst increases, so the amount retained on the catalyst surface and the amount of hydrogenated product in the eluant decrease.

## DISCUSSION

Several interesting points emerge from the results quoted above. Consideration of the percentage retentions of the various hydrocarbons shows that, at each temperature studied, the following sequence is observed:

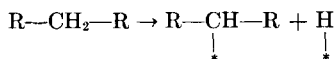
alkanes < cyclopropane < alkenes << acetylene.

This is not unexpected since it is the sequence of increasing strengths of adsorption of hydrocarbons (12).

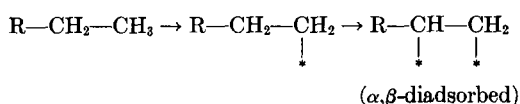
The effects of increasing temperature and increasing carbon chain length are less well defined. With methane and ethane there appears to be no effect of temperature upon the retention. However, with propane the retention of the first injection increases from 0% at 100°C and below to 14% at 200°C. Two factors may contribute to the retention of alkanes. First, since adsorption necessarily involves dissociation, i.e.,

TABLE 3  
COMPLETE ELUANT ANALYSIS FOR ETHYLENE, PROPYLENE, AND PROPANE ADSORPTIONS

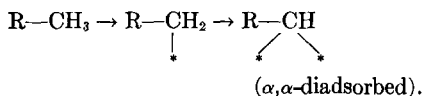
Injection No.	Eluant analysis (ml)					% Hydrocarbon retained	% Hydrogenation of recovered hydrocarbon
	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>3</sub> H <sub>8</sub>	C <sub>3</sub> H <sub>6</sub>		
<i>A. Ethylene injections (0.5 ml) at 200°C</i>							
1	0.01	0.30	0.00	—	—	39	100
2	0.00	0.29	0.02	—	—	38	93
3	0.00	0.18	0.22	—	—	20	45
4	0.00	0.09	0.38	—	—	6	19
5	0.00	0.06	0.43	—	—	2	12
6	0.00	0.05	0.44	—	—	2	10
<i>B. Ethylene injections (0.5 ml) at 100°C</i>							
1	0.00	0.33	0.00	—	—	34	100
2	0.00	0.23	0.15	—	—	25	61
3	0.00	0.04	0.41	—	—	10	9
<i>C. Propylene injections (0.5 ml) at 200°C</i>							
1	0.02	0.06	0.00	0.23	0.00	44	100
2	0.00	0.01	0.00	0.24	0.07	36	78
3	0.00	0.00	0.00	0.10	0.27	26	27
<i>D. Propane injections (0.5 ml) at 200°C</i>							
1	0.01	0.04	0.00	0.40	0.00	14	—
2	0.005	0.03	0.00	0.45	0.00	6	—
3	0.00	0.02	0.00	0.46	0.00	6	—
4	0.00	0.01	0.00	0.47	0.00	5	—



the ease of formation of the dissociatively adsorbed species will be reflected in the retention. Second, with  $\text{C}_2$  and higher alkanes we have the additional possibility of carbon-carbon bond cleavage. Kemball *et al.* (13, 14) have shown that in alkane-deuterium exchange over palladium films, above  $\sim 140^\circ\text{C}$  (i) the ease of exchange increases in the order methane < ethane < propane, and (ii) whereas methane exchanges by a stepwise process, ethane and propane readily undergo multiple exchange. These observations lead to the conclusion that while palladium will readily form an  $\alpha, \beta$ -diadsorbed species



it will not readily catalyze the formation of an  $\alpha, \alpha$ -diadsorbed complex



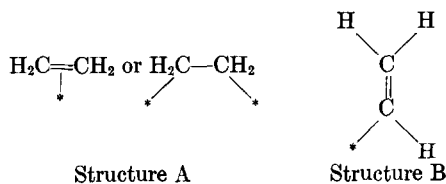
Thus we might expect our sequence of retention to be propane  $\geq$  ethane  $>$  methane, assuming only carbon-hydrogen bond fission.

Table 1 shows that at  $200^\circ\text{C}$  small amounts of methane were obtained from ethane, and methane and ethane were obtained from propane. Thus at  $200^\circ\text{C}$  some carbon-carbon bond fission must also occur and the results suggest that this is more important with propane. Our observed sequence for the retention of alkanes at  $200^\circ\text{C}$  can thus be explained in terms of carbon-hydrogen and carbon-carbon bond fission. However, the foregoing discussion does not explain the observation that at temperatures  $\leq 100^\circ\text{C}$  the retention of propane was 0% although both ethane and methane were adsorbed by the catalyst. Consideration of the adsorbed states of the alkanes shows that on adsorption the magnitude of the decrease in entropy increases in the order methane < ethane < propane, and consequently on these grounds one might expect the effect of temperature on adsorption to be more marked with propane than with ethane. Alternatively, the

low retention of propane at low temperatures may be due to less extensive dissociative adsorption at these temperatures and the consequential increase in the probability that a monoadsorbed propyl radical will react with adsorbed hydrogen and return to the gas phase.

The retentions of ethylene and propylene, though very similar to each other when considered along with those for the alkanes and acetylene, showed some characteristic differences. At each temperature more ethylene than propylene was retained by the catalyst; the effect of carbon chain length is the reverse of that observed for alkanes.

With alkenes, unlike alkanes, there is the possibility of adsorption either as an associatively bonded species (structure A) or as a dissociatively bonded species (structure B).



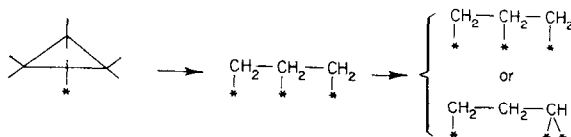
Structure A is generally assumed to be the reactive form of adsorbed olefins in catalytic hydrogenation (15). The possibility that the retention was due to an associatively bonded species was investigated by saturating the catalyst surface with ethylene and subsequently injecting several 0.5 ml volumes of hydrogen. At  $20^\circ$  and  $100^\circ\text{C}$  this procedure led to the removal of only trace amounts ( $\sim 0.02$  ml) of ethane, while at  $200^\circ\text{C}$  trace amounts ( $\sim 0.005$  ml) of methane only were observed. Thus we can assume that associatively adsorbed species are unimportant in retention.

Two interesting points emerge from the eluant analyses. First, at each temperature used the major product from the first injection of olefin is the corresponding alkane and this yield decreases with further injections. Second, at  $200^\circ\text{C}$  lower alkanes are formed, showing that some carbon-carbon bond cleavage occurs; this is slightly greater with propylene than with ethylene.

The formation of alkane may arise either by (a) self-hydrogenation, or (b) by reaction of associatively adsorbed olefin with hydrogen retained on the catalyst surface following

activation. By using tritium for catalyst activation we have shown (16) that both of these reactions occur on our catalysts although in the context of retention only the self-hydrogenation, which accounts for approximately 20% of the ethane field (16b), is of importance since this leads to the formation of hydrogen-deficient surface resi-

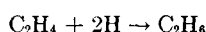
the origin of the hydrogen atoms being either (i) from dissociative adsorption or (ii) residual hydrogen from the reduction activation. Furthermore the processes leading to retention of cyclopropane are highly activated, i.e., rupture of the carbon-carbon bond to yield an  $\alpha,\gamma$ -diadsorbed species which may possibly undergo further dissociation



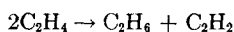
dues, e.g.,



and



or

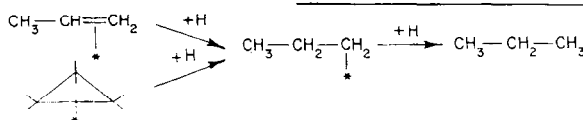


It has been reported (17) that on palladium films propylene undergoes more extensive self-hydrogenation than ethylene, although the volumes of gas required for monolayer coverage do not appear to have been taken into account. By considering the geometry of the adsorption of ethylene and propylene it can be seen that fewer molecules of propylene than of ethylene can be adsorbed per unit area of metal surface, due to the steric effects of the methyl group. Since our retention figures are based on the injection of equal volumes of ethylene and propylene, the slightly lower retention of propylene is readily explained by the above effects.

The adsorption of cyclopropane is of interest in that (i) the distribution of products from the first injection at 200°C is virtually identical with that observed from the first injection of propylene at 200°C (see Table 1) and (ii) the retention shows a more marked dependence upon temperature than does the retention of propylene. These results suggest that in the formation of products the same intermediates are involved in both cyclopropane and propylene reactions, i.e.,

The retention value of acetylene is very much higher than that observed with the alkenes. Furthermore, although the total volume of alkene adsorbed corresponds to approximately monolayer coverage, based upon the area determined assuming single-site adsorption of carbon monoxide, the total volume of acetylene is in excess of monolayer coverage of the metal. These observations are consistent with (i) the higher heat of adsorption of acetylene than of ethylene (18) and (ii) the greater ability of acetylene to polymerize to higher hydrocarbons (19). The latter may explain the excess adsorption over that required for monolayer coverage by considering that the polymer once formed can migrate on to the support. However further studies are required before it is possible to define precisely the nature of the retained acetylene.

In conclusion, it can be stated that the present study has demonstrated that (i) the palladium-alumina catalyst exhibits different degrees of heterogeneity depending upon the adsorbate hydrocarbon, i.e., for a given type of hydrocarbon the fraction of the catalyst surface active for retention relative to the total surface available for adsorption of that reactant depends upon the reactant itself. Thus, for example, the retentions for propylene and for ethylene are dissimilar (ii). Before it is possible to interpret accurately kinetic data it is necessary to characterize the catalyst by considering the adsorption of the



hydrocarbon molecule in terms of that fraction of the surface which is *active for catalysis*. This may be different from the metal area as determined by chemisorption of, for example, carbon monoxide or hydrogen.

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