Rhodium-catalysed Hydrogenation of Allene as Revealed by [¹⁴C]Propylene and [¹⁴C]Carbon Monoxide Tracer Studies

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The low-pressure hydrogenation of allene has been studied over alumina-supported rhodium catalysts. During a series of hydrogenation reactions the activity of the catalyst progressively decreases to a steady-state value and thereafter remains constant. The reaction proceeds in two distinct stages. During the first stage the selectivity for the formation of propylene is ca. 95%.

Hydrogenation of allene + [14 C]propylene mixtures shows that, in the first stage of the allene hydrogenation, the yield of propane from the hydrogenation of propylene is relatively small. Direct hydrogenation of adsorbed allene to propane is the major route to formation of the latter, the selectivity being a measure of the relative rates of hydrogenation of allene directly to propylene and propane.

Adsorption of [¹⁴C]propylene on freshly reduced catalysts occurs in two distinct stages: a non-linear primary region followed by a linear secondary region. No primary region is observed for propylene adsorption on steady-state catalysts or on freshly reduced catalysts in the presence of allene. However, [¹⁴C]propylene adsorption and hydrogenation occurs in the presence of allene on the secondary region with both freshly reduced and steady-state catalysts.

Adsorption of [¹⁴C]carbon monoxide shows that, whilst the decrease in activity of the catalyst to a steady-state constant value corresponds to the progressive build-up of a surface hydrocarbonaceous layer, the combined effects of allene and hydrogen on a carbon monoxideprecovered surface leads to an increase in the capacity of that surface for carbon monoxide adsorption. Treatment of the carbon-monoxide-precovered surface with hydrogen alone does not lead to such an increase. It is suggested that, under the influence of the allene hydrogenation reaction, the surface undergoes some reconstruction.

Evidence is presented to show the presence of separate surface sites for the hydrogenation of allene to propylene, the hydrogenation of allene to propane and for the hydrogenation of propylene to propane.

In a series of recent papers we have reported studies of the adsorption and hydrogenation of acetylene and ethylene over supported Group VIII metal catalysts.¹⁻⁴ It has been shown that the adsorption of C_2 hydrocarbons is characterised by a primary and a secondary region, the catalytically active species being located on the secondary region. Evidence has also been presented to show that the actual hydrogenation reaction occurs on a catalyst which is effectively covered by hydrocarbonaceous residues, these being the species responsible for the primary adsorption process.

Radiotracer studies of the effects of added ethylene on the hydrogenation of acetylene^{3, 4} have shown that the selectivity for the formation of ethylene from acetylene depends primarily upon the ability, or otherwise, of the metal catalyst to

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catalyse separate reaction pathways from adsorbed acetylene to ethylene and ethane, rather than upon the relative rates of hydrogenation of acetylene and ethylene in a sequential process. Thus, for example, over a silica-supported nickel catalyst⁴ the relative values of the rate constants in the reaction scheme



were evaluated to be $k_1 = 10$, $k_2 = 0.47$ and $k_3 = 1.83$ at 293 K.

Since these studies demonstrated the usefulness of using [¹⁴C]alkenes as a tracer for elucidating the mechanism of the selective hydrogenation of the diunsaturated hydrocarbon, and for determining the state of the 'metal' surface under hydrogenation conditions, it appeared desirable to extend the studies carried out with C₂ hydrocarbons to higher unsaturated hydrocarbons to examine the applicability of the model proposed for the hydrogenation of acetylene to other diunsaturated hydrocarbons. Allene was chosen for this study since it was found from previous studies⁵⁻¹⁰ that its hydrogenation behaviour closely resembles that of acetylene. The results of our studies using [¹⁴C]propylene as a tracer in the hydrogenation of allene over supported rhodium catalysts are reported below.

EXPERIMENTAL

CATALYSTS

The catalysts containing 5% w/w metal supported on γ -alumina (aluminium oxide C, supplied by Degussa Ltd) were prepared by impregnation of the support with an aqueous solution containing the required weight of metal as the chloride. After evaporation to dryness, the supported salt was heated in an air oven at 400 K for 24 h, ground to a fine powder and stored until required.

Before use, the supported salt was reduced *in situ* in a stream of hydrogen (flow rate $10 \text{ cm}^3 \text{ min}^{-1}$) at 493 K for 12 h. The catalyst was then allowed to stand for a further 6 h at 530 K in an atmosphere of purified hydrogen and finally evacuated at 530 K for 6 h, before being cooled under vacuum to ambient temperature.

MATERIALS

Cylinder allene and cylinder propylene (Mathieson Inc.) were found to contain no impurities detectable by gas chromatography and were merely degassed before use. [¹⁴C]Propylene was prepared by the catalytic dehydration of [1,3-¹⁴C]propan-2-ol (0.25 mCi, specific activity = 9.1 mCi mmol⁻¹), supplied by the Radiochemical Centre, Amersham. The dehydration was performed by injecting 0.1 cm⁻³ quantities of the labelled propanol, diluted to the required specific activity with non-radioactive propan-2-ol (Hopkins and Williams Co), into a stream of dried nitrogen passing through a catalyst bed consisting of 7.2 g alumina-H (Spence) containing 10% w/w potassium chloride. The product water was removed from the reactor effluent by an ice-water trap and the [¹⁴C]propylene by a liquid-nitrogen trap. After degassing to remove the nitrogen carrier gas, the purity of the [¹⁴C]propylene was found by radiogas chromatography to be 99%: the overall yield of the product was ca. 70%. In experiments where a high specific activity of the [¹⁴C]propylene was required, a sample of [1-¹⁴C]propylene (New England Nuclear Co) with a specific activity of 5 mCi mmol⁻¹ was used. [¹⁴C]Carbon monoxide was prepared from [¹⁴C]carbon dioxide (Radiochemical Centre, Amersham) by reduction with metallic zinc as described earlier.¹

APPARATUS

The apparatus was similar to that described previously.¹ It consisted of a constant volume reactor (520 cm³) fitted with two intercalibrated Geiger-Muller counters to permit the direct observation of the adsorbed species during adsorption and subsequent processes. The reactor was connected to a mercury-free conventional high-vacuum system. Pressures in the reactor were measured using a calibrated pressure transducer (S.E. type SE/V/10D), the output from which was recorded continuously on a potentiometric recorder.

The reactor was also connected to a gas-sampling system (volume 5.2 cm³) which was coupled to a combined gas chromatograph-proportional counter. This permitted the sampling and analysis of the reaction products throughout the course of a reaction.

The analysis was performed using a 6 m column packed with a 30% w/w dispersion of dimethylsulpholane supported on Chromosorb P (30-60 mesh). The column was operated at ambient temperature using helium (Air Products Ltd) as carrier gas at a flow rate of $60 \text{ cm}^3 \text{ min}^{-1}$. On elution from the column, the eluant was mixed with the required amount of methane (Air Products Ltd) before it entered the gas proportional counter.

PROCEDURE

Adsorption of $[1^4C]$ propylene or $[1^4C]$ carbon monoxide was investigated by admitting small aliquots of the labelled adsorbate to the catalyst vessel and determining the surface and gas-phase count rates after each addition.

In the hydrogenation reactions a premixed sample of hydrogen and the hydrocarbon, usually in the ratio 3:1, was admitted to the reaction vessel to the required pressure. The reaction was followed by the pressure fall recorded by the pressure transducer, samples being extracted at any desired pressure fall for analysis. In the course of a typical reaction five or six samples were analysed at various times. All the adsorption and hydrogenation measurements were made at 293 K.

RESULTS

HYDROGENATION OF ALLENE AND CATALYST ACTIVITY

For the hydrogenation of allene at 12.0 Torr* with hydrogen at 36.0 Torr over 0.05 or 0.10 g catalyst, plots of pressure against time showed the reaction to occur in two distinct stages, the onset of the second stage being accompanied by an increase in rate at a pressure fall of 12.0 ± 0.5 Torr. Up to this acceleration point the reactions were accurately first order in total pressure.

In a series of similar hydrogenation reactions over the same sample of catalyst, it was observed that from reaction to reaction the activity progressively decreased until a 'steady-state' activity was eventually attained, as shown in fig. 1. This deactivation process did not have any effect upon the acceleration point in the reaction, although the selectivity for propylene formation, S, defined as

$$S = p(C_{3}H_{6}) / [p(C_{3}H_{6}) + p(C_{3}H_{8})]$$

increased slightly from 0.940 with a freshly reduced catalyst to 0.950 for a steady-state catalyst.

The deactivation process could only be effected by carrying out a series of allene hydrogenation reactions. Pretreatment of the catalyst at 293 K with allene at 200 Torr for 2 h, storage of the catalyst under the hydrogen-rich reaction products for up to 12 h, or storage under an atmosphere of hydrogen at 293 K had no effect either upon the rate of deactivation or upon the final steady-state activity of the catalyst. The original activity of the catalyst could, however, be reproducibly restored by treatment

* 1 Torr
$$\equiv 101325/760$$
 Pa.

of the catalyst in an atmosphere of hydrogen (760 Torr) at 623 K for 1 h. During this regeneration process the only hydrocarbon product detected in the gas phase over the catalyst was propane, although because of the small quantities involved quantitative determination of the actual amount formed was not possible.

The catalysts could be brought to the 'allene steady-state' activity by carrying out a series of 9 or 10 acetylene hydrogenations on a freshly reduced catalyst sample at 293 K using a 3:1 hydrogen: acetylene reaction mixture. After this pretreatment the



Fig. 1. Deactivation process for the first (●) and the second (○) stage of the reaction of allene at 12.0 Torr with hydrogen at 36.0 Torr over 0.10 g rhodium-alumina.



Fig. 2. Adsorption isotherm for [14C]propylene on freshly reduced 0.30 g rhodium-alumina. (The figure shows two adsorptions on same catalyst.)

first-order rate constant for the subsequent allene hydrogenation was 3.5×10^{-3} min⁻¹, compared with a value of 4.1×10^{-3} min⁻¹ when a series of allene hydrogenations had been used to 'run-in' the catalyst.

ADSORPTION OF [14C] PROPYLENE ON FRESHLY REDUCED AND STEADY-STATE CATALYSTS

Since it did not prove possible to obtain or synthesise ¹⁴C-labelled allene, the adsorption of [¹⁴C]propylene was used as a probe to investigate the catalyst surface under allene hydrogenation conditions. On a freshly reduced sample of rhodium-alumina catalyst (0.30 g) the adsorption isotherm, shown in fig. 2, was of a similar

form to that observed previously for the adsorption of [14C]ethylene and [14C]acetylene, ¹⁻³ showing a non-linear primary region and a linear secondary region. The extent of adsorption in the linear secondary region continued to increase with increasing pressure; no plateau was reached even though gas pressures > 4 Torr were used. Similar [14C]propylene adsorption isotherms were observed with 5% rhodium-silica catalysts.¹¹



Fig. 3. Effect of various treatments on [14C]propylene adsorbed on 0.30 g rhodium-alumina.
(a) Build-up of isotherm; (b) evacuation; (c) admission of [12C]propylene at 12.5 Torr; (d) admission of H₂ at 36.0 Torr for 1 h; (e) catalyst regeneration in H₂ 760 Torr at 623 K for 1 h; (f) admission of H₂ at 36.0 Torr for 24 h.

Table 1. Effect of various treatments on preadsorbed [14C]propylene on rhodium-alumina catalysts

treatment	surface count rate/counts min ⁻¹
catalyst A (freshly reduced; 0.30 g)	
(a) build-up of adsorption isotherm	2033
(b) admission of 24 Torr propylene + hydrogen at 24 Torr to (a) for 1 h	1415
(c) evacuation of (b) for 1 h	1509
(d) admission of hydrogen at 36.0 Torr to (c)	583
(e) turning point in isotherm	1400
catalyst B (freshly reduced; 0.30 g)	
(a) build-up of adsorption isotherm	2515
(b) evacuation of (a) for $1 h$	2318
(c) admission of allene + hydrogen (1:2) at 36.0 Torr to (b) for 2 h	1412
(d) count rate of (c) after 24 h	1320
(e) evacuation of (d) for 1 h	1350
(f) admission of hydrogen at 36.0 Torr to (e) fo	r6h 953
(g) turning point in isotherm	1405

The effects of various treatments on the preadsorbed [14C]propylene were investigated to examine the reactivity of the adsorbed species under similar conditions to those pertaining in allene hydrogenation. The results are summarised in fig. 3 and table 1.

The gas-phase hydrocarbon in contact with the surface during the build-up of the adsorption isotherm was analysed after the addition of each aliquot of [14C]propylene

by radio-gas chromatography. This showed that during the build-up of the primary region (up to the turning point in the adsorption isotherm) the only hydrocarbon in contact with the surface was *propane*. The formation of propane ceased at the onset of the secondary region, when the gas phase consisted of the propane formed in the initial primary adsorption and unadsorbed propylene.



Fig. 4. Adsorption isotherm for [¹⁴C]propylene on freshly reduced rhodium-alumina (0.30 g) in the absence (○, ×) and presence (●) of allene at 12.0 Torr.



Fig. 5. Adsorption isotherms for [¹⁴C]propylene on rhodium-alumina (0.10 g) at various stages of catalyst deactivation to steady state. (The figures in parenthesis refer to number of allene hydrogenations performed on catalyst before isotherm determination.)

The adsorption of [¹⁴C]propylene in the presence of allene was investigated as follows: a freshly reduced catalyst was exposed to 12 Torr allene for 1 h. Without removing the allene from the reaction vessel, aliquots of [¹⁴C]propylene were admitted to the catalyst and the adsorption isotherm determined. This is shown in fig. 4, from which it can be seen that on the allene-precovered surface no primary adsorption of propylene occurred, although secondary adsorption occurred, but to a lesser extent than with a 'clean' catalyst surface. Subsequent evacuation of the catalyst did not remove any of the adsorbed propylene.

In an attempt to investigate the behaviour of adsorbed propylene and the surface during the deactivation of the catalyst to a steady state by allene hydrogenation, the adsorption of $[1^{4}C]$ propylene was investigated at various stages on the catalyst

N. C. KUHNEN, S. J. THOMSON AND G. WEBB

deactivation curve. The results are shown in fig. 5. Since in determining the isotherms the surface count rates were corrected for background activity, any permanently retained surface propylene residues from one adsorption are not included in the subsequent isotherm. The results in fig. 5 thus show that, as the catalyst approaches its steady state, the extent of coverage of the primary region with permanently retained surface residues progressively increases to the point where the primary region is totally covered. Thus in the steady state only secondary adsorption of propylene is observed.

	treatment	surface count rate/counts min ⁻¹
(a)	surface counts after build-up of isotherm	576
Ìb)	evacuation of (a) for 1 h	398
(c)	admission of propylene at 12.0 Torr to (b)	384
(d)	evacuation of (c) for 1 h	372
(e)	admission of allene at 12.0 Torr to (d)	372
Ì)	admission of hydrogen at 36.0 Torr to (e) for 2 h	271





Fig. 6. Adsorption isotherms of [¹⁴C]propylene on a steady-state rhodium-alumina catalyst (0.20 g) in the absence (○) and presence (●) of allene at 12.0 Torr.

The reactivity of the propylene adsorbed on the secondary region of a steady-state catalyst was also investigated using a 0.20 g sample of catalyst, which had been 'runin' to the steady state by carrying out a series of 10 allene hydrogenations. The results are summarised in table 2.

Comparison of the amounts of $[{}^{14}C]$ propylene adsorbed on a steady-state catalyst in the absence and presence of 12.0 Torr allene showed that the presence of the latter reduced the adsorptive capacity of the surface by *ca*. 40% (fig. 6).

HYDROGENATION OF ALLENE + $[^{14}C]$ propylene mixtures

The addition of $[1^4C]$ propylene to the allene + hydrogen reaction mixture was used to gain further insight into the mechanism of the selective hydrogenation on a

steady-state rhodium-alumina catalyst. The amounts of radioactivity in the individual reaction products was determined using radio-gas chromatography.

Table 3 shows the results obtained for the hydrogenation of allene at 12.0 Torr pressure with hydrogen at 36.0 Torr pressure when $[^{14}C]$ propylene at 1.26, 2.01 and 5.10 Torr pressure was added to the reaction mixture before admission to the reaction vessel.

Two interesting features emerge from these results. First, the yield of $[1^4C]$ propane only constitutes a small proportion of the total propane yield, relative to the amount expected from the amounts of $[1^4C]$ propylene and $[1^2C]$ propylene present in the reaction vessel, and secondly, the yield of $[1^4C]$ propane increased linearly as the

Table	3.	Product	distributions	from	the	hydrogenation	of	allene	in	the	presence	of
variou	S j	pressures	of [14C]prop	ylene	(weig	t of catalyst	= 0	0.10 g;	[<i>p</i> (]	H_2	= 36.0 To	orr;
				[<i>p</i> (C	$_{3}H_{4})]_{0}$	= 12.0 Torr						

conversion (%)	$p({}^{12}C_{3}H_{6})$	$[p(C_3H_8)]_{total}$	$p({}^{14}C_{3}H_{8})$	$[p(C_3H_8)]_{direct}$	S'
	(A) [¹⁴ C]propylene	at 5.10 Torr a	dded	
26.7	2.89	0.16	0.015	0.15	0.950
43.9	4.78	0.24	0.028	0.22	0.956
64.8	7.07	0.35	0.040	0.29	0.960
71.3	7.74	0.41	0.044	0.34	0.958
87.8	10.42	0.56	0.052	0.46	0.958
	(B)) [¹⁴ C]propylene a	at 2.01 Torr a	dded	
10.3	1.11	0.07	0.002	0.06	0.950
23.8	2.59	0.13	0.006	0.12	0.956
38.9	4.17	0.23	0.008	0.21	0.953
57.5	6.26	0.32	0.012	0.28	0.957
96.2	10.30	0.61	0.020	0.50	0.954
	(C)) [¹⁴ C]propylene a	at 1.26 Torr a	dded	
18.1	1.98	0.10	0.003	0.10	0.952
40.7	4.58	0.24	0.006	0.22	0.954
64.8	7.01	0.39	0.009	0.34	0.954
93.3	9.35	0.54	0.015	0.43	0.955

reaction proceeded (fig. 7) and was directly proportional to the amount of $[^{14}C]$ propylene present in the original reaction mixture. Assuming that the $[^{12}C]$ propylene formed by the hydrogenation of the allene behaves in the same manner as the added $[^{14}C]$ propylene, it is possible to calculate, from the extent of hydrogenation and the yield of $[^{14}C]$ propane, the amounts of $[^{12}C]$ propane formed by the subsequent hydrogenation of propylene, itself formed by allene hydrogenation, and hence to calculate the 'inherent selectivity', defined as

$$S' = p(C_3H_6) / [p(C_3H_6) + p({}^{12}C_3H_8)].$$

These results are shown in table 3.

EFFECTS OF CARBON MONOXIDE ON THE ADSORPTION OF PROPYLENE AND THE HYDROGENATION OF ALLENE

Previous studies of the hydrogenation of acetylene over supported Group VIII metals^{3, 4} had shown that the presence of carbon monoxide tended to poison selectively

the sites responsible for the production of ethane from acetylene and therefore to increase the selectivity. The effects of carbon monoxide on allene hydrogenation were therefore investigated to see if similar effects were apparent in this system.

The adsorption of $[1^{4}C]$ carbon monoxide on freshly reduced and steady-state catalysts in the absence and presence of allene was investigated. The adsorption isotherms are shown in fig. 8. Note that, in contrast to the propylene adsorption isotherms, the carbon monoxide isotherms showed only a primary region and are of a shape expected for Langmuir-type behaviour. The effects of various treatments on the adsorbed carbon monoxide were also investigated, and the results are summarised in table 4.



Fig. 7. Variation of the yield of [¹⁴C]propane with conversion for the hydrogenation of allene at 12.0 Torr with hydrogen at 36.0 Torr in the presence of [¹⁴C]propylene at ○, 1.26; ①, 2.01 and □, 5.10 Torr over 0.10 g rhodium-alumina.

The effects of the presence of adsorbed carbon monoxide on the catalytic activity of the freshly reduced and steady-state catalysts for allene hydrogenation were also investigated. Table 5 summarises the effect on the first-order rate constant of various treatments of the catalyst with carbon monoxide before the hydrogenation of a 3:1 hydrogen+allene mixture. The presence of preadsorbed carbon monoxide resulted in a slight increase in the selectivity of the catalyst from 0.950 to 0.982.

It was noticed during the experiments in which a carbon monoxide-pretreated catalyst was treated with an allene + hydrogen mixture that, following reaction and subsequent evacuation of the catalyst, the amount of carbon monoxide which could be adsorbed on the catalyst was in excess of that required to complete the monolayer on the original catalyst. Thus the amount of carbon monoxide which could be adsorbed after the hydrogenation reaction was greater than the amount displaced by the allene + hydrogen mixture. This implies that the actual hydrogenation reaction



Fig. 8. Adsorption isotherms for [¹⁴C]carbon monoxide on freshly reduced rhodium-alumina (0.20 g) in the absence (\times) and presence (\bigcirc) of allene at 12.0 Torr and on a steady-state rhodium-alumina catalyst (0.20 g) in the absence (\bigcirc) and presence (\square) of allene at 12.0 Torr.

Table 4. Effect of evacuation, allene, allene hydrogenation and hydrogen on the amounts of
adsorbed [14C]carbon monoxide (weight of cagalyst = 0.20 g)

	(A)	(B)	(C)	(D)
(1) saturation surface count rate/counts min	-1 9366	1246	2500	1165
 (2) CO removed by evacuation for 1 h/counts min⁻¹ 	251	34	313	14
(3) CO removed by adding allene at 12.0 Torr to (1)/counts min ⁻¹	1265		0	
 (4) CO removed by adding hydrogen at 36.0 Torr to (1)/counts min⁻¹ 	18			-
 (5) CO removed by adding allene + hydrogen (1:3) at 48.0 Torr to (1)/counts min⁻¹ 	25	0	46	18

(A) Freshly reduced catalyst; (B) freshly reduced catalyst pretreated with allene at 12.0 Torr; (C) steady-state catalyst; (D) steady-state catalyst pretreated with allene at 12.0 Torr.

catalyst conditions	k/\min^{-1}
(1) freshly reduced	4.29×10^{-1}
2) freshly reduced, treated with CO and then evacuated	8.9×10^{-4}
3) freshly reduced in the presence of CO at 1.0 Torr	0
4) freshly reduced, treated with CO in the presence of allene at 12.0 Torr	$4.6 imes 10^{-2}$
5) steady state	$6.0 imes 10^{-2}$
6) steady state treated with CO then evacuated	3.1×10^{-3}
7) steady state in the presence of CO at 1.0 Torr	0
 steady state, treated with CO in presence of allene at 12.0 Torr and then evacuated 	1.2×10^{-2}

Table 5.	5. Variation of first-order rate constant with pretreat	ment of	`catalyst	with	carbon
	monoxide (weight of catalyst = 0.20 g, T =	= 293 ±	1 K)		

Table 6. Accumulative adsorption of [14C]carbon monoxide on a freshly reduced catalyst

catalyst treatment	surface count rate/counts min ⁻¹	additional counts/counts min ⁻¹
(1) freshly reduced	5 973	
(2) evacuated, allene hydrogenation, evacuated	6 516	543
(3) evacuated, allene hydrogenation, evacuated	7 039	523
(4) evacuated, allene hydrogenation, evacuated	7 200	161
 (5) evacuated, allene hydrogenation, allowed to stand under reaction products for 12 h, evacuated 	8 567	1367
(6) evacuated, allene hydrogenation, evacuated, H_2 (36.0 Torr) for 12 h, evacuated	10 090	1523

frees some sites for further adsorption of carbon monoxide, and the phenomenon was investigated further. After determination of the carbon monoxide adsorption isotherm on a freshly reduced (0.10 g) sample of catalyst, the catalyst was evacuated until there was no change in the surface count rate. A premixed sample of 12.0 Torr allene and 36.0 Torr hydrogen was then admitted to the reaction vessel and the reaction allowed to go to completion. The reaction vessel was again evacuated and the amount of carbon monoxide taken up by the catalyst determined. This procedure was repeated a further two times, the extent of carbon monoxide adsorption increasing each time. The whole procedure was repeated twice further, but on these occasions the catalyst was left under the reaction products for 12 h before evacuation and readsorption of carbon monoxide. The results are summarised in table 6.

Note that adsorption of carbon monoxide, followed by evacuation and readsorption of carbon monoxide, did not produce any significant increase in the surface count rate, whilst treatment of the carbon monoxide precovered surface with hydrogen at 36.0 Torr for 12 h, followed by evacuation and readsorption of carbon monoxide, resulted in an increase of only 8% in the monolayer capacity of the catalyst surface. A similar enhancement of the adsorption of carbon monoxide following allene hydrogenation was observed with a steady-state catalyst. The results for this catalyst are shown in table 7.

catalyst treatment	surface count rate/counts min ⁻¹
(a) saturation surface count rate	2243
(b) evacuation of (a) for 1 h	2000
 (c) saturation surface count rate of (b) following allene hydrogenation, evacuation and readmission of [¹⁴C]CO 	2832
(d) evacuation of (c) for 1 h	2710

Table 7. Accumulative adsorption of $[{}^{14}C]$ carbon monoxide on a steady-state catalyst

DISCUSSION

The results presented in fig. 1 show that, as was observed previously in the hydrogenation of acetylene over a range of Group VIII metal catalysts,¹⁻⁴ the rhodium-alumina catalyst, when used for a series of allene hydrogenations, tended to deactivate to a steady-state activity. Both the first and second stages of the allene hydrogenation were deactivated by similar amounts. Treatment of the catalyst with allene alone for extended periods, before carrying out the hydrogenation reactions, did not have any significant effect on the deactivation process. This suggests that the deactivation does not simply arise from a build-up of carbidic or other hydrogen-deficient carbonaceous residues on the surface, resulting from the dissociative adsorption of the allene, but rather from a process involving the interaction of allene with hydrogen on the catalyst surface.

Comparison of the amounts of [¹⁴C]propylene adsorbed on freshly reduced and steady-state catalysts (fig. 5) shows that the deactivation process results in a loss of the hydrocarbon primary region, in the sense that this region becomes completely filled with permanently retained hydrocarbonaceous species. The similarity in the amounts of [¹⁴C]carbon monoxide adsorbed on freshly reduced and steady-state catalysts in the presence of allene (see fig. 8) leads to the surprising conclusion that the concentration of sites responsible for this adsorption is the same in the two cases. If we assume that the carbon monoxide adsorption can also occur on these sites, it follows that the deactivation process cannot be ascribed to the blocking of the hydrogen adsorption sites, thereby reducing the concentration of adsorbed hydrogen for the hydrogenation reaction.

It is clear that, as in acetylene hydrogenation, the presence of hydrogen is essential for the 'running-in' of the catalyst to its steady-state activity. It is also significant that the same steady-state activity is attained when the catalyst is run-in either with acetylene + hydrogen or allene + hydrogen reaction mixtures, suggesting that the species responsible for this process are similar from the two hydrocarbon sources.

Comparison of the amounts of [¹⁴C]propylene adsorbed on the primary region of a freshly reduced catalyst with the saturation value for the adsorption of [¹⁴C]carbon monoxide on the same catalyst shows that the ratio of propylene to carbon monoxide molecules on the surface is 1:3.89. This ratio should be compared with a ratio of 1:2.64 for ethylene to carbon monoxide molecules adsorbed on the same catalyst.¹² Assuming, as suggested from infrared spectroscopic studies, an average bond order of 1.3 for the adsorption of carbon monoxide in rhodium,¹³ the average bond order

N. C. KUHNEN, S. J. THOMSON AND G. WEBB

of the propylene adsorbed on the primary region is 3, whilst that for ethylene is 2. This result, together with the observation that only propane was present in the gas phase during the build-up of the primary region, is strong evidence to suggest that, in the primary adsorption process, the hydrocarbon molecule undergoes carbonhydrogen bond fission and that all the carbon atoms in the molecule are attached to the surface. The average composition of the propylene species adsorbed in the primary region, calculated from the amounts of propane formed during this stage of the adsorption, is C₃H_{5.4}. On this basis we may deduce that the primary region corresponds to monolayer coverage of the metal by the hydrocarbon, the small amounts of carbon monoxide (ca. 13% of that required for monolayer coverage of a freshly reduced catalyst) which is adsorbed on either freshly reduced catalysts in the presence of allene, or on steady-state catalysts, corresponding to single metal sites, which are expected to exist on the hydrocarbon-covered metal surface.14 The observation that, on carbon monoxide-precovered surfaces, adsorption of propylene occurs in the secondary region to approximately the same extent as on freshly reduced catalysts, but shows no primary adsorption region when carbon monoxide is preadsorbed, also supports the conclusion that the primary region corresponds to direct adsorption on the metal.

From the results presented in tables 1 and 2, it is clear that the catalytically active adsorbed propylene species is located in the secondary region, although the primary adsorbed propylene species will react with hydrogen, and at a much slower rate than the rate of hydrogenation. The question arises as to the location of the secondary adsorbed species; in particular, whether or not these species are adsorbed on the metal. The results obtained for the adsorption of carbon monoxide on both freshly reduced and steady-state catalysts are of particular interest in this context.

From the amounts of carbon monoxide adsorbed at saturation on the freshly reduced catalyst, a value of 0.45 can be calculated for the number of adsorbed carbon monoxide molecules per rhodium atom in the catalyst. This value is in close agreement with that quoted by Yates *et al.*¹³ for rhodium–alumina catalysts and with the value quoted by these workers for the hydrogen:rhodium ratio. The results presented in tables 5 and 6 show the surprising feature that, when carbon monoxide-precovered rhodium–alumina catalysts had been used for allene hydrogenation, the adsorptive capacity of the surface for carbon monoxide increased. The extent of this increase was substantially greater than the amount of carbon monoxide which could be removed from the precovered surface, either by evacuation or by admission of allene to the surface.

From our observations it is apparent that the increase in the carbon monoxide uptake cannot be accounted for by loss of carbon monoxide from the surface during the allene hydrogenation, either by direct displacement or by incorporation of carbon monoxide in the reaction products, since the surface count rate was observed to remain constant during the hydrogenation reaction. Furthermore, the surface saturation count rate was increased following exposure to the reaction mixture.

Hydrogen treatment of the carbon monoxide-precovered surface did not give rise to any marked enhancement in the carbon monoxide adsorptive capacity of the catalyst. A small rise of 8%, compared with a freshly reduced and evacuated catalyst, was observed after the first treatment of the precovered catalyst with hydrogen. However, no further rise in the [14C]carbon monoxide surface count rate was observed following further hydrogen treatment of the precovered surface. Thus hydrogenation of the adsorbed carbon monoxide to produce an absorbed formyl or similar species, which has been reported to occur on polycrystalline rhodium,¹⁵ but according to Solymosi¹⁶ does not occur with rhodium–alumina catalysts, can be ruled

out as being responsible for the enhancement of uptake. A further reduction of the catalyst by hydrogen treatment can also be ruled out, since different reduction procedures for producing freshly reduced catalysts had no effect on the initial carbon monoxide saturation count rate.

Note that it appears to be the treatment of the catalyst with the allene + hydrogen reaction mixture which leads to the enhancement of the carbon monoxide uptake by the surface. As shown in table 6, for freshly reduced catalysts the enhancement is greatest when the allene hydrogenation (12 h under reaction products) evacuation cycle is carried out. The enhancement cannot be simply due to the removal of hydrocarbonaceous species by the prolonged treatment in hydrogen, or the removal of adsorbed carbon monoxide from the surface, since the surface count rate remains constant. We conclude that the enhancement indicates that, during allene hydrogenation, a rearrangment of the surface occurs resulting in the freeing of metal sites on the surface. The precise origins of this rearrangement cannot be established from the present studies. It could arise due to the incorporation of adsorbed carbon monoxide into the permanently retained surface hydrocarbonaceous residues, located on the hydrocarbon primary region, or it could be due to the movement of metal atoms through the hydrocarbonaceous primary layer, under the influence of the hydrogenation reaction. Such a phenomenon has been observed in the nickel-catalysed steamreforming reactions of hydrocarbons,¹⁷ although much higher temperatures were involved than those used in the present study. Burwell et al.¹⁸ have also claimed that the hydrogenation of di-t-butylacetylene on supported platinum catalysts involves the movement of surface metal atoms in a process which they termed 'corrosive chemisorption'.

It is interesting to consider the possible effects of such a surface rearrangement in terms of our observations. According to such a model, the deactivation of the catalyst to a steady-state activity could be interpreted as the establishing of a steady-state concentration of active metal sites by migration of individual metal atoms into the hydrocarbonaceous layer adsorbed on the primary region, these metal atoms being responsible for the secondary adsorption. Such a movement of metal atoms would also, of necessity, result in the occlusion of carbon atoms in the surface layers of the metal which would, in consequence, be relatively unreactive and which would tend, on hydrogen treatment at elevated temperature, to produce methane, in agreement with our observations.

The reaction of allene with hydrogen in the presence of [¹⁴C]propylene was studied in an attempt to investigate the relative importance of the two routes:

allene $\xrightarrow{k_1}$ propylene $\xrightarrow{k_2}$ propane allene $\xrightarrow{k_1}$ propylene $\xrightarrow{k_3}$ propane

in determining the selectivity in the reaction. The results reported in table 3 show that the amount of [¹⁴C]propane formed during these reactions was a small, but constant, fraction of the total propane yield. Furthermore, the yields of [¹²C]propane, formed by the further hydrogenation of propylene, calculated from the [¹⁴C]propane yields, are small compared with the total [¹²C]propane yield. Thus we conclude that the major route to the production of propane is directly from the hydrogenation of allene (adsorbed), rather than by the hydrogenation of propylene, formed by the first stage in the hydrogenation of allene. Using the model described earlier for the hydrogenation

and

of acetylene over nickel-silica catalysts,⁴ from the yields of [¹⁴C]propane values of $k_1 = 0.108$, $k_2 = 0.0007$ and $k_3 = 0.0054$ can be evaluated.

It was observed that the yield of [¹⁴C]propane in the reactions where [¹⁴C]propylene was added, was directly proportional to the initial pressure of [¹⁴C]propylene present in the reaction mixture. This fact, together with the above observations regarding the amounts of [¹⁴C]propane produced, suggests that the hydrogenation of [¹⁴C]propylene occurs independently of the hydrogenation of allene, and therefore that separate sites are involved in the two processes.

The latter conclusion is supported by the $[{}^{14}C]$ propylene adsorption measurements, which showed that in the presence of allene the adsorption of [14C]propylene could still occur, although the actual amounts were reduced by ca. 40% compared with those adsorbed in the absence of allene, implying that some of the allene and propylene compete for the same surface sites. Our observations are consistent with a model in which, on steady-state rhodium catalysts, three types of surface-hydrocarbon adsorption-hydrogenation sites may be recognised. Type I sites are responsible for the adsorption of allene and its hydrogenation directly to propane, Type II sites are those on which allene can adsorb and hydrogenate to propylene and Type III sites are those on which propylene is adsorbed and hydrogenated to propane, but on which allene adsorption and hydrogenation does not occur. Some propylene adsorption and hydrogenation may also occur in the absence of allene on either the Type I or II sites, thus accounting for the reduction in adsorption of propylene in the presence of allene. Further evidence for the separate identity of sites responsible for the hydrogenation of allene and propylene comes from the results for the hydrogenation of allene on carbon monoxide-poisoned catalysts. These show that the second stage of the reaction (the hydrogenation of propylene to propane) is less affected than the hydrogenation of allene to propylene, implying that, under the conditions used where the easily removed adsorbed carbon monoxide has been evacuated from the surface before the hydrogenation reaction was carried out, the Type III sites are not covered to any appreciable extent by carbon monoxide. The results of these studies also provide further evidence for the existence of Type I and II sites, since the presence of adsorbed carbon monoxide tended to increase the selectivity. Since the Type III sites are unaffected, this increase in selectivity must be due to a preferential poisoning of the Type I sites by the carbon monoxide.

Our conclusions regarding the mechanism of formation of propane directly from adsorbed allene are in agreement with the conclusions of Oliver and Wells,¹⁹ who from allene deuteration studies suggested that the formation of a 2,2-diadsorbed propylene intermediate was of importance in the production of propane from allene, and with the infrared spectrosopic studies of Khulbe and Mann,⁹ who also obtained evidence for the direct hydrogenation of allene to propane.

Comparison of the results presented in this paper with those obtained earlier for the hydrogenation of acetylene on supported Group VIII metals¹⁻⁴ leads to the general conclusion that in the hydrogenation of diunsaturated hydrocarbons the main factor which controls the selectivity is the ability or otherwise of the metal to promote a direct route to the formation of the alkane. As such, the origins of the selectivity may be seen as the result of two separate reaction pathways for the hydrogenation of adsorbed allene, rather than as a consequence of the competitive adsorption of the mono- and di-unsaturated hydrocarbon for the same sites on the catalyst surface.

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(PAPER 3/070)