Hydrogenation of Propyne over Palladium Catalysts

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The hydrogenation of propyne on a range of supported palladium catalysts has been investigated. The catalysts all showed 100% selectivity to propene. A non-steady-state regime was observed when the catalysts were brought on line. During this period there was significant carbon laydown resulting in a surface Pd : C ratio of 1 : 3 with two of the catalysts tested. Once this level of laydown was reached, steady-state operation was achieved. In the steady state the amount of carbon laydown was reduced and activity was reproducible; the orders of reaction for propyne and dihydrogen were obtained. The order with respect to dihydrogen varied between 1.3 for the Pd/zirconia to 0.6 for the Pd/silica, while the order for propyne varied between 0.0 and 0.4. Analysis of the surface species by infrared spectroscopy revealed the presence of a horizontal and vertically bonded propyne, a di-sigma adsorbed propene and propylidyne. A mechanism for the reaction system has been postulated.

Since the early reports of Sabatier et al.,¹ a vast number of studies on the catalytic hydrogenation of unsaturated hydrocarbons have been reported (for a review, see ref. 2). Although a large part of this literature concerns the hydrogenation of alkynes most of it refers to the hydrogenation of ethyne. The literature on the hydrogenation of propyne by comparison is relatively sparse. This may have been due in part to the ability to make and detect ethyne by relatively straightforward techniques, whereas the pre-war production of propyne was considerably more difficult. An example of this can be found in the experimental section of the earliest study on the hydrogenation of propyne by Conn et al.,3 who measured the heat of hydrogenation over a 10% Pt/asbestos catalyst. However, even when propyne was more readily available there was only a limited number of reports. The first study which investigated the kinetics was by Bond and Sheridan⁴ who studied the reaction of propyne and hydrogen over pummice-supported nickel, platinum and palladium. For palladium, an activation energy of 16.5 kcal mol⁻¹ (69.1 kJ mol⁻¹) was determined and a first-order pressure dependence in hydrogen and zero-order in propyne was observed. A later study by Mann and Khulbe⁵ reported an activation energy of 10.5 kcal mol⁻¹ (44 kJ mol⁻¹) and pressure dependences of -0.52 ± 0.11 for propyne and 1.25 ± 0.05 for hydrogen. All of these past studies have been carried out using staticreactor systems monitoring pressure-fall against time. A more recent study by Jackson and Kelly⁶ examined the hydrogenation of propyne over a Pt/silica catalyst under a pulseflow regime over a range of temperatures (333-673 K) and gas ratios $(C_3H_4:H_2, 2.5:1-1:3)$. The orders of reaction with respect to propyne for propene formation were determined to be -0.02 at 333 K, -0.04 at 373 K and -0.13 at 423 K. The order of reaction with respect to hydrogen was determined to be 0.60 at 333 K.

There is considerable interest in the selective hydrogenation of alkynes to alkenes over palladium catalysts, especially ethyne to ethene. However, the selective hydrogenation of propyne is also an industrial process. Therefore, given the limited literature and the experimental methods used it seemed appropriate to undertake a study of propyne hydrogenation over a range of supported palladium catalysts. To that end we have examined the catalysts by infrared spectroscopy, by static reaction methods, and by pulse-flow reaction techniques.

Experimental

Pulse-flow Reaction

Apparatus

A pulse-flow microcatalytic reactor system was used throughout this study. The sample of catalyst was supported on a glass sinter in the centre of the reactor (8 mm id, down flow), which was placed inside a furnace. Catalyst temperatures were measured by means of a thermocouple placed in contact with the catalyst bed. Catalysts (typically 0.5 g) were reduced in a 2% H_2-N_2 flow (25 cm³ min⁻¹) while the temperature was raised from 293 to 473 K at 3 K min⁻¹, and held at 473 K for 0.5 h. The gas flow was then changed to helium. The catalysts were cooled from 473 to 273 K in flowing helium $(47.5 \text{ cm}^3 \text{ min}^{-1})$. Pulses of reactant gas $(3.347 \text{ cm}^3, 200 \text{ and})$ 400 Torr) were injected into the helium carrier-gas stream immediately above the catalyst. On elution from the catalyst bed the full pulse was analysed by on-line gas chromatography. The amount of gas adsorbed/reacted, from any pulse, was determined from the difference between calibration peak areas and the peak areas obtained following injections of pulses of comparable size onto the catalyst.

Two test procedures were used with this system, one to determine the order of reaction with respect to the reactants, the other to determine the effect of temperature. Therefore aliquots of C_3H_4 - H_2 mixtures in the following ratios, 2:1, 1.5:1, 1:1, 0.7:1, 0.5:1, 0.4:1 and 0.3:1, were pulsed repeatedly over the catalyst and the results analysed. Hence a variation in gas ratios of approximately one order of magnitude was used to specify the reaction orders. In a similar manner with a fresh catalyst, and using a fixed ratio of 1:1 ($C_3H_4:H_2$), the catalyst was tested at the following temperatures 273, 278, 283, 288 and 298 K.

Static Reaction

In the static-reactor system the catalysts were maintained in an evacuated glass reactor $(157.6 \text{ cm}^3, 2.5 \text{ cm} \text{ diameter})$ at room temperature. The sample of catalyst was supported on a glass sinter halfway down the reactor; in this way gas added to the evacuated reactor was pulled through the catalyst bed. The catalysts (typically 1.5 g) were reduced by admitting hydrogen into the reactor, leaving for 0.3 h, then evacuating the reactor. This procedure was repeated six times for each catalyst. A 1 : 3 propyne-hydrogen mixture (typically 56 Torr) was added to the reactor and the rate of reaction was monitored by following the pressure fall of the system with time.

Infrared Spectroscopy

All spectra were taken, in transmission mode, using a Nicolet 5DXC FT-IR Spectrometer with a resolution of 4 cm^{-1} equipped with an environmental cell.⁷

The catalysts were reduced, in situ at 293 K, by admitting dihydrogen to the cell, leaving for 0.3 h, then evacuating the cell. This was repeated six times. Spectra were taken of the catalyst in the evacuated cell before and after reduction. A spectrum was recorded immediately after 20 cm³ of reactant gas mixture (C_3H_4 : $H_2 = 1$: 3), at atmospheric pressure, was injected into the cell. A second spectrum was recorded 0.25 h later. The cell was then evacuated and another spectrum taken. Into the evacuated cell 20 cm³ of [²H]dihydrogen at atmospheric pressure was injected and a spectrum recorded. The cell was evacuated and a final spectrum of the catalyst taken. Support materials were similarly examined.

X-Ray Photoelectron Spectroscopy

XPS analyses were performed using an SSI M-probe spectrometer with Al-K α X-rays for photoionisation and 2 eV electrons for charge correction. Each sample was contained in a 5 mm diameter aluminium pan and was supported directly on a sample stub. The stub itself was covered with a fine stainless-steel mesh to assist in the neutralisation of charge build-up.

Catalyst Preparation

Four catalysts were prepared by impregnation. For three of the catalysts, palladium chloride (PGP Industries Ireland) was dissolved in sufficient dilute hydrochloric acid to fully wet the supports, zirconia (Degussa, S. A. 50 m² g⁻¹), silica (3M Cab-o-sil, S. A. 203 m² g⁻¹), and alumina (Degussa Aluminium Oxid C, S. A. 102 m² g⁻¹). The resulting mixtures were evaporated to dryness at 353 K. The weight loadings obtained were 0.83% m/m Pd/silica, 0.81% m/m Pd/alumina and 0.99% m/m Pd/zirconia.

The fourth catalyst was prepared by dissolving palladium nitrate (Johnson-Matthey) in sufficient deionised water to wet fully the alumina support (Harshaw, S. A. 180 m² g⁻¹). The resulting mixture was evaporated to dryness at 353 K. After it had been dried, the sample was heated in air to 823 K at 1.5 K min⁻¹ and held at this temperature for 3 h. The weight loading obtained was 0.64% m/m Pd/alumina.

To distinguish between the two alumina-supported catalysts the sample prepared using Harshaw alumina will be designated Pd/alumina(H), while the other sample, prepared using Degussa alumina, will be designated Pd/alumina(D).

The dispersion of the catalysts was determined, after a standard reduction, by carbon monoxide chemisorption. The catalysts were reduced in a 2% H₂-N₂ flow (25 cm³ min⁻¹) while the temperature was raised from 293 to 473 K at 3 K min⁻¹, and held at 473 K for 0.5 h. The gas flow was then changed to helium. The catalysts were cooled from 473 to 273 K in flowing helium (47.5 cm³ min⁻¹) and then pulses of carbon monoxide were passed over the samples. The dispersions, assuming a ratio of 1 : 2 for CO : Pd, were calculated to be 33% for Pd/silica, 29% for Pd/alumina(D), 96% for Pd/ zirconia and 19% for Pd/alumina(H).

Results

Pulse Reaction

Non-steady State

The four catalysts were tested, at 273 K and a C_3H_4 : H_2 ratio of 1:1, using the pulse-flow apparatus; three went through an initial non-steady-state period before activity

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Table 1 Non-steady-state hydrogenation of propyne over Pd/silica⁴

pulse	number of mole	cules ($\times 10^{19}$) of	carbon deposit ^b	
	propene	propyne	(×10 ¹⁹)	cumulative
ref.		1.18		
1	0.20	0.73	0.75	0.75
2	0.21	0.87	0.30	1.05
3	0.21	0.90	0.21	1.26
4	0.21	0.87	0.30	1.56
5	0.22	0.87	0.27	1.83
6	0.23	0.87	0.24	2.07
7	0.24	0.90	0.12	2.19
8	0.24	0.90	0.12	2.31°

^a Temperature 273 K, propyne : dihydrogen 1 : 1, carrier flow rate 47.5 cm³ min⁻¹, weight of catalyst 0.5 g. ^b Carbon deposit expressed as a number of carbon atoms. ^c Total amount of carbon deposited 2.31 \times 10¹⁹, number of surface Pd atoms 7.7 \times 10¹⁸.

Table 2 Non-steady-state hydrogenation of propyne over $Pd/alumina^{a}$

	number of mo	lecules ($\times 10^{19}$)	carbon deposit ^b	
pulse	propene	propyne	(×10 ¹⁹)	cumulative
ref.		1.18		
1	0.00	0.43	2.25	2.25
2	0.00	0.48	2.10	4.35
3	0.00	0.60	1.74	6.09
4	0.00	0.61	1.71	7.8
5	0.03	0.64	1.53	9.33
6	0.08	0.57	1.59	10.92
7	0.08	0.58	1.56	12.48
8	0.11	0.58	1.47	13.95
9	0.12	0.58	1.41	15.36
10	0.15	0.61	1.26	16.62
11	0.43	0.63	0.36	16.98 ^c

a Temperature 273 K, propyne : dihydrogen 1 : 1 carrier flow rate 47.5 cm³ min⁻¹, weight of catalyst 0.5 g. ^b Carbon deposit expressed as a number of carbon atoms as distinct from propyne molecules. ^c Total amount of carbon deposited 16.98×10^{19} , number of surface Pd atoms 3.4×10^{18} .

Table 3 Non-steady-state hydrogenation of propyne over Pd/zirconia^a

pulse	number of mole	carbon deposit ^b		
	propene	propyne	(1019)	cumulative
ref.		1.18		
1	0.58	0.00	1.57	1.57
2	0.54	0.00	1.68	3.25
3	0.53	0.14	1.32	4.57
4	0.48	0.32	0.98	5.55
5	0.45	0.44	0.73	6.28
6	0.42	0.46	0.74	7.02
7	0.40	0.51	0.69	7.71
8	0.39	0.59	0.50	8.21
9	0.36	0.57	0.62	8.83
10	0.34	0.60	0.59	9.42°

a Temperature 273 K, propyne : dihydrogen 1 : 1, carrier flow rate 47.5 cm³ min⁻¹, weight of catalyst 0.5 g. ^b Carbon deposit expressed as a number of carbon atoms as distinct from propyne molecules. ^c Total amount of carbon deposited 9.42×10^{19} , number of surface Pd atoms 2.7×10^{19} .

became constant. Tables 1–3 show a pulse-by-pulse analysis of the three catalysts approaching steady state. The $Pd/Al_2O_3(D)$ catalyst did not show any activity in the pulseflow experiments even when the temperature was increased. The end of the non-steady state was characterised by a dramatic reduction in the extent of carbon deposition and a reproducibility in the extent of hydrogenation (Table 4). At the end of the non-steady state the C : Pd_s ratio was 3 : 1 for

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Table 4 Steady-state reaction and orders of reaction for propyne and dihydrogen

Pd/alumina (H)			Pd/silica			Pd/zirconia		
rate/ μ mol g ⁻¹ s ⁻¹	C ₃ H ₄ : H ₂	deposition (%)	rate/ μ mol g ⁻¹ s ⁻¹	C ₃ H ₄ : H ₂	deposition (%)	rate/ μ mol g ⁻¹ s ⁻¹	C ₃ H ₄ : H ₂ (%)	deposition
9.77	2.01	< 0.2	6.27	1.98	0.9	16.95	2	2.3
9.3	1.48	< 0.2	6.25	1.5	< 0.2	16	1.49	4.6
9.03	1	< 0.2	5.42	0.99	2	16.12	1	5.1
9.78	0.67	2.3	7.25	0.67	0.2	29.37	0.67	3.2
11.47	0.5	1	8	0.5	0.4	38.86	0.5	3.6
14.44	0.35	< 0.2	9.73	0.33	< 0.2			
catalyst			propyne order		dihydrogen order			
Pd/zirconia				0.0 ± 0.1		1.3 ± 0.3		
Pd/silica			0.2 ± 0.0		0.6 ± 0.1			
Pd/alumina (H)			0.1 ± 0.0		0.7 ± 0.1			

Pd/zirconia, 3:1 for Pd/silica and 50:1 for Pd/alumina(H). The C: Pd_s ratio was obtained by summing the amount of carbon deposition over the non-steady state and ratioing against the number of surface Pd atoms as determined from the carbon monoxide chemisorption.

Steady State

Once in the steady state, the variation of reaction rate over the range 273–298 K was determined, using a $1:1 C_3 H_4: H_2$ ratio (Fig. 1). As the conversion rapidly increased with temperature, determination of the orders of reaction was performed at 273 K to minimise any effects of mass transfer. Reaction at 273 K over the Pd/zirconia catalyst (the most active) was repeated at a different flow rate and the absence of diffusion control was confirmed. The ratio of propyne to hydrogen was varied and the orders of reaction in hydrogen and propyne determined (Table 4). The orders were calculated using a series of simultaneous equations based on the assumption that the rate equation was of the form, r = $k[C_3H_4]^{x}[H_2]^{y}$. At each gas ratio at least three pulses of the reaction mix was passed over the catalyst; the results in Table 4 were used with the other data to determine the reaction orders.

A pulse-flow experiment was undertaken to investigate the hydrogenation of propene over the Pd/ZrO_2 catalyst. When a 1:2 propene: hydrogen mixture was pulsed over the catalyst at 273, 298 and 323 K, no hydrogenation reaction was observed.

The behaviour of the Pd/Al_2O_3 (D) catalyst was noticeably different from the other samples tested. When a 1:3 propyne: hydrogen mixture was pulsed over this catalyst at temperatures ranging from 298 to 473 K, no propene or propane was detected from any of the pulses.



Static Reaction

The pressure-time curves obtained during the reaction between propyne and hydrogen over freshly reduced catalysts consisted, generally, of an initial period where the pressure dropped sharply, followed by a constant-pressure regime (Fig. 2). After the initial fall in pressure no further decrease was observed even after 1 h. The extent of the pressure fall was consistent with the selective hydrogenation of propyne to propene, i.e. given a starting pressure of 56 Torr and a 1:3 propyne : dihydrogen ratio, a pressure of 42 Torr would represent total hydrogenation of propyne to propene. However the Pd/Al₂O₃(D) sample exhibited a pressure-time curve which was significantly different (Fig. 3). Initially the pressure fall was slow but after ca. 0.25 h the rate of pressure fall increased; however, after 0.3 h there was no further decrease in pressure. Again the pressure fall was consistent with the hydrogenation of propyne to propene.

Infrared Spectroscopy

Fig. 4(a) shows a typical spectrum obtained when a zeroreaction-time spectrum is subtracted from a 15 min reactiontime spectrum. Fig. 4 also shows propyne, propene and propane reference spectra labelled (b), (c) and (d), respectively. The positive peaks in spectrum (a) closely resemble the spectrum of propene, while the negative peaks are all indicative of propyne, showing the loss of propyne and the formation of propene. No bands indicative of propane were observed. This behaviour was observed for all the catalysts tested except the Pd/Al₂O₃(D) sample. Owing to the low activity of the Pd/Al₂O₃(D) catalyst, the reaction was left for 50 min before the spectrum was recorded. The behaviour observed after 50



Fig. 2 Pressure-fall against time curves for Pd/Al_2O_3 (H), Pd/SiO_2 and Pd/ZrO_2 . The starting pressures have been normalised to 100 units.



min was similar to that described for the other catalysts after 0.25 h, *i.e.* only propene was detected.

The residual species left on the surface of the Pd/zirconia catalyst after propyne hydrogenation were also investigated by infrared spectroscopy. Fig. 5(a) shows the spectrum obtained after the gas phase had been evacuated. The negative bands at ca. 3400 and 1600 cm^{-1} are indicative of water being lost from the system. The six bands at 2965, 2927, 2875, 1447, 1430 and 1381 cm⁻¹, indicate the presence of retained hydrocarbon species. Spectrum (b) of Fig. 5 shows the catalyst after [2H]dihydrogen had been added to the cell. This spectrum exhibits negative bands due to [1H]water and positive bands due to [²H]water. The bands at 2965 and 2875 ¹ increased in size by ca. 10%, whereas the band at 2927 cm⁻ cm^{-1} decreased in size by ca. 40%. Three new small bands were detected between 2160 and 2030 cm^{-1} and can be assigned to the deutero derivatives of the protium bands at 2965, 2927 and 2875 cm⁻¹. Bands at 1447 and 1380 cm⁻¹ remained unchanged, but the bands at 1430 and 1413 $\rm cm^{-1}$ increased in intensity. A new band, which was not visible in the absence of [²H]dihydrogen appeared at 2212 cm⁻¹. On evacuation, the bands 2965, 2927, 2875 cm^{-1} and their deuteriated derivatives were reduced by 15% as was the band at 2212 cm^{-1}

XPS Analysis of Catalysts

1.0

0.5

-0.0

-0.5

-1.0

(d)

(c)

(b)

(a)

absorbance (arb. units)

The four catalysts, which had been used in the static reactions, were examined by XPS to determine the oxidation state of the palladium and to confirm or otherwise the absence of chlorine. The Pd $3d_{5/2}$ peak was detected at 334.5

4000 3000 2000 1000 wavenumber / cm⁻¹ Fig. 4 Infrared spectra showing (a) the change between initial reaction and 15 min reaction, (b) the spectrum of propyne, (c) the spectrum of propene and (d) the spectrum of propane



Fig. 5 Infrared spectra showing (a) the surface species after the gas phase had been evacuated and (b) the surface species after the system had been subjected to a pressure of $[^{2}H]$ dihydrogen

eV in the Pd/zirconia sample and at 335.0 eV in the Pd/ alumina(H) catalyst. No residual chlorine was detected on either of these samples. The Pd/silica catalyst was analysed and again no chlorine could be detected. However, when the used Pd/alumina(D) sample was analysed it was found to contain significant quantities of residual chlorine (ratio atomic% Al : Cl 18 : 1). The Degussa support itself contained no detectable chlorine.

Discussion

In this study of propyne hydrogenation over palladium catalysts we have tried, by using a range of techniques and reactor configurations, to develop further our understanding of the kinetics and mechanism of the reaction, while keeping a link with previous studies. Let us first consider the pulseflow results.

Over a freshly reduced catalyst a non-steady-state regime was observed (Tables 1–3) when the catalysts were operated in a pulse-flow mode. The yield of propene varied considerably during this period and there was also significant carbon laydown (typically 10–40%). Such an approach to steady state is not unusual in the hydrogenation of unsaturated hydrocarbons. It is now well documented that the nonsteady-state behaviour relates to the growth of a hydrocarbonaceous overlayer on the surface of the catalyst, which is not removed in the course of the hydrogenation reaction.^{8–10} Indeed various authors have concluded that such an overlayer is essential for the effective operation of the catalysts.^{11–13}

For the Pd/silica and Pd/zirconia catalysts, the nonsteady-state regime ends when the amount of retained material saturates the palladium surface and gives a ca. 1:1 ratio of surface Pd to C₃ molecule. A similar ratio (3:1, C: Pd_s) was obtained when the Pd/zirconia catalyst was subjected to pulses having a different ratio $(1:3 C_3H_4:H_2)$ and at a different temperature.¹⁴ The species that make up this carbonaceous layer are those that were detected in the infrared spectroscopy study. Indeed the ratio obtained is in keeping with the mode of bonding of the adsorbed propyne in the presence of hydrogen. The specific nature of these species will be discussed below. This link between nonsteady-state behaviour and surface coverage has been observed previously. In ethene hydrogenation over osmium cluster catalysts¹⁰ the optimum rate was achieved when the amount of retained C2 units equalled the adsorption site density. In that study the authors concluded that the retained species transferred hydrogen to the adsorbed ethene. The mechanistic implications with respect to propyne hydrogenation are discussed below. With the Pd/alumina(H)sample the ratio was found to be vastly in excess of 1:1. In this case it appears that the support has also been involved in a carbon deposition process.

Once in the steady state the catalysts behaved reproducibly. The orders of reaction with respect to dihydrogen and propyne were calculated (Table 4). Mann and Khulbe⁵ obtained an order of -0.52 in propyne, while Bond and Sheridan⁴ obtained an order of zero for propyne. Our values are in good agreement with those of Bond and Sheridan. For dihydrogen, Mann and Khulbe obtained an order of 1.25, while Bond and Sheridan calculated an order in dihydrogen of 1. The value we obtained with the Pd/zirconia catalyst is in excellent agreement with that of Mann and Khulbe, however, the values of 0.7 for the Pd/alumina(H) catalyst and 0.6 for the Pd/silica catalyst are significantly lower than both previous studies and would indicate a stronger adsorption of hydrogen. This lack of agreement in the reaction order for hydrogen for propyne hydrogenation between static and pulse reactors is in keeping with studies on similar systems. Varying values for the reaction order in hydrogen have been obtained in ethyne hydrogenation,^{15,16} where it has also been found that orders determined by the initial rate method do not agree with those determined by a change in rate with respect to time.^{16,17} The reason for these differences is not clear, although it has been suggested that it may be due to reversible poisoning effects.² Some support for this view has been obtained in a recent study of propyne hydrogenation over a platinum catalyst,⁶ where it was found that the $H_2: C_3H_4$ ratio affected the extent to which the carbonaceous residue acted as a promoter or a poison.

The selectivity of the catalysts was, without exception, 100%, i.e. only the alkene was formed. Although high selectivity is a feature of palladium catalysts,^{2,4} total selectivity to the alkene is unusual. The reaction system can be described in terms of a standard $A \rightarrow B \rightarrow C$ model and to achieve high selectivity the rate of $B \rightarrow C \ll A \rightarrow B$. However this ignores the possibility of an $A \rightarrow C$ reaction, and indeed it has been shown that this route may be more important in terms of controlling selectivity than $B \rightarrow C$.⁹ In this reaction system, however, it is clear that the only reaction that takes place is $A \rightarrow B$. One of the reasons cited for high selectivity is the inability of the system to hydrogenate the alkene in the presence of the alkyne.⁵ Indeed in a static reactor the onset of the acceleration point is normally described as the point at which the alkyne has been consumed and hydrogenation of the alkene begins. Prior to the acceleration point the system is selective to the alkene because of the presence of alkyne blocking the surface to alkene adsorption.^{2,5} However, in the hydrogenation of ethyne, it was shown by use of isotopic tracers that such an argument was fallacious, as ethene was adsorbed even when the alkyne was present in excess.¹⁸ In this study we have also shown that, both in a static reactor and in the pulse-flow mode, the current catalysts do not hydrogenate propene even in the absence of propyne. This then leads to a second reason for the achievement of such selectivity. Selective poisoning of a catalyst can remove the ability to hydrogenate alkenes while allowing the hydrogenation of alkynes. However XPS analysis of the Pd/silica, Pd/zirconia and Pd/alumina(H) catalysts indicated that no poisons, such as sulfur or chlorine, could be detected on the catalyst surface. Therefore, the selectivity observed is not due to a selective poisoning process. At present we are unable to state with any confidence why these catalysts should be so highly selective. However, from propene exchange/ hydrogenation studies, it has been suggested² that propene may desorb more easily from a palladium catalyst than any 3273

other Group VIII metal, and clearly if the rate of desorption becomes too fast then no hydrogenation will take place. The XPS analysis of the Pd/alumina(D) catalyst, however, revealed that there was a significant quantity of residual chlorine remaining on the surface of this catalyst after reduction and hydrogenation reactions. This residual chlorine will be situated primarily on the alumina support but is the most likely cause of the low activity observed with this catalyst, probably due to back-migration. Clearly, the selectivity of this catalyst may not be due to the same causes as the other catalysts tested. The extent of carbon monoxide chemisorption may also be affected giving a low value for dispersion.

The final pressure obtained in the pressure fall against time experiments was indicative of selective hydrogenation to propene and this was supported by the difference spectra of the gas phase obtained from the infrared spectroscopy study. Repeat experiments on the used catalysts, with no intermediate reduction, gave the same result with no obvious loss in activity, showing that the catalyst had not been poisoned. The pressure fall against time curves obtained in the static reactor were similar to those obtained by Bond and Sheridan,⁴ who, within the limits of their analytical system, achieved a high selectivity to propene (>97%). However, our results do not agree with those presented by Mann and Khulbe.⁵ At hydrogen : propyne ratios greater than 1:1 the results of Mann and Khulbe⁵ do not show any evidence of high selectivity to propene; indeed, palladium gave very poor selectivity compared to other Group VIII metals tested. Examination of their results suggests that palladium only gave high selectivity at very low conversions and low hydrogen : propyne ratios. Given that palladium is the metal of choice for selective hydrogenation of both ethyne and propyne in the chemical industry, and that high selectivities are obtained at high conversions,^{19,20} we believe that the results obtained by Mann and Khulbe for palladium are not representative.

The pressure fall against time curve for the Pd/alumina(D) sample appeared at first to be different from the others in that it seemed to have an acceleration point. However, closer examination of the Pd/silica profile confirmed that it also had evidence of an acceleration point. Indeed, the only difference between these two catalysts and the others may be the rate of reaction, with any acceleration point being hidden in the rapid pressure fall observed with the Pd/zirconia and the Pd/ alumina(H). Even so, the presence of an acceleration point is interesting as it is usually associated with the removal of all the alkyne and the initiation of the hydrogenation of the alkene. Clearly in this case that cannot be the explanation. In these tests, however, there was a bed of catalyst and heat transfer from the bed may not have been particularly efficient; therefore, it is possible that as the reaction proceeded the bed was self heating and that once a sufficient portion of the bed had increased in temperature an increased rate was observed.

The IR spectroscopic analysis of the reaction gave information on the nature of the surface species present during the hydrogenation of propyne. Table 5 summarises the main hydrocarbon bands. The spectra obtained give bands which are similar to those found by Shahid and Sheppard²¹ and Avery²² for propene adsorption. The spectrum recorded immediately after evacuation of the reaction mixture is similar to that assigned to a di-sigma adsorbed propene species [I, CH₃-CHM-CH₂M]. However, there are indications both from the intensities and the band positions that propylidyne [II, CH₃-CH₂-CM₃] was also present. The addition of the [²H]hydrogen to the system resulted in the appearance of isotopically exchanged C—H bands but at a very low level (<5% of the intensity of the main protium

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 Table 5
 Observed C—H absorption in IR spectra

Α	В	С	D	Е
2965 (s)	2965 (s)	2965 (s)	2965 (m&w)	2965 (s)
2927 (ms)	2927 (ms)	2927 (ms)	2920 (ms)	
2875 (m)	2875 (m)	2875 (m)	2880 (m)	2870 (w)
1447 (m)	1447 (m)	1447 (m)	1450 (m&w)	1450 (ms)
1430 (w)	1430 (m)	1430 (mw)	1425 (mw)	1435 (w)
1413 (w)	1413 (m)	1413 (mw)		
1381 (m)	1381 (m)	1381 (m)	1355 (ms)	1375 (w)

A, spectra taken after evacuation of the C_3H_4/H_2 mixture; B, $[^2H]H_2$ added to the cell; C, after evacuation of the $[^2H]H_2$ from the cell; D, the bands associated with a di-sigma species [I] (from ref. 20); E, the bands associated with propylidyne [II] (from ref. 20).

bands), indicating that very little exchange had taken place. This absence of exchange would be expected if the principal hydrogen-containing species was a methyl group which was not directly bonded to the catalyst surface. The appearance of the band at 2212 cm⁻¹ was unexpected as it can be assigned to a carbon-carbon triple bond stretch.²³ As it is highly unlikely that an adsorbed alkene species will have dehydrogenated we may assume that the alkyne species was present on the surface but not IR active. This condition may be achieved if the vibrational dipole of the bond is parallel to the metal surface, whereas when dihydrogen is adsorbed the propyne is bonded through the non-methyl-containing carbon atom in a vertical orientation (CH_3 -CC-M). Therefore, three distinct species can be identified from the IR spectra, (i) a di-sigmabonded propene, (ii) propylidyne and (iii) a sigma/pi-bonded propyne. These assignments and the interconversions are supported by the work of Koestner et al.,²⁴ who in an LEED study of propyne and propene on Pt(111) proposed parallelbonded propyne, di-sigma-bonded propene and propylidyne.

From the above results we can now propose a mechanistic scheme (Scheme 1) which accounts for the observed products and is in keeping with the infrared analysis of the surface species. The scheme is similar to that proposed by Webb² for ethyne hydrogenation, which was developed from isotope tracer studies. The numbered species indicate those that have been observed in the IR spectra, while the top line represents the formation of gas-phase propene. The first line down gives the mechanism of propylidyne formation, while the second line down gives the formation of the di-sigma-adsorbed propene; further hydrogenation of this species would result in the formation of propane. As this scheme is appropriate for both ethyne and propyne hydrogenation over Group 8-10metals, we believe that it has general applicability to the hydrogenation of terminal alkynes.

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