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# Supported Metal Catalysts: Preparation, Characterisation, and Function

## III. The Adsorption of Hydrocarbons on Platinum Catalysts

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Adsorption of ethene in the absence and presence of carbon monoxide has been investigated over Pt/alumina (I), Pt/silica (I), and Pt/molybdena (I) catalysts prepared by impregnation, and a Pt/molybdena (C) catalyst prepared by co-crystallization in the temperature range 188–296 K. Static $^{14}$C-ethene radiotracer adsorption measurements show that on each catalyst only a fraction of the adsorbed ethene is reversibly adsorbed at 293 K; this fraction increases in the order Pt/alumina < Pt/silica ≪ Pt/molybdena. Dynamic flow adsorption studies show that, on Pt/alumina and Pt/silica, retention of ethene is accompanied by self-hydrogenation to ethane. Retention, but no self-hydrogenation, is observed with both Pt/molybdena catalysts. Following reduction/activation and thermal treatment in helium at 573 K, the Pt/silica surface retains appreciable quantities of hydrogen, which reacts with adsorbed ethene producing ethane. Preadsorption of carbon monoxide totally blocks the surface of Pt/alumina, Pt/silica and Pt/molybdena (C) for ethene adsorption. However, preadsorption of ethene only partially poisons the surface of Pt/alumina and Pt/silica for carbon monoxide adsorption. With Pt/molybdena (C), preadsorption of ethene promotes a threefold increase in the capacity of the surface for carbon monoxide chemisorption. On Pt/molybdena (I) carbon monoxide and ethene are adsorbed noncompetitively at separate sites. With Pt/alumina and Pt/silica, coadsorption of ethene and carbon monoxide results in an enhancement in the amounts of ethane formed, relative to those formed when ethene alone is adsorbed. This is interpreted in terms of the chemisorption of carbon monoxide causing the release of hydrogen retained on the catalyst surface following the reduction/activation/thermal desorption procedure. This effect is more pronounced with Pt/silica than with Pt/alumina, the amounts of hydrogen released relative to the total Pt content of the catalyst ($Pt_{(total)}$ : H) being, respectively, 2.38 and 1.06. FTIR examination of ethene adsorbed on Pt/silica shows bands ascribable to surface alkyl ($-CH_3$ and $>CH_2$) species. Evidence for an interaction between the retained hydrocarbon and the –OH groups of the silica support has also been obtained. No hydrocarbon bands were obtained from species retained by the Pt/alumina catalyst during ethene adsorption. However, DRIFT spectra of ethene retained by the Pt/molybdena (I) catalyst suggest the formation of small amounts of aromatic residues.

## INTRODUCTION

In Parts I and II (*1, 2*) of this series details are given of the preparation, physical characterisation, and chemisorption of carbon monoxide on platinum/silica (I), platinum/alumina (I), platinum/molybdena (I), and platinum/molybdena (C) catalysts: (I) and (C) indicate catalysts prepared by impregnation and co-crystallization methods, respectively.

In previous studies using $^{14}$C-radiotracer techniques we have shown that, under static conditions, the chemisorption of alkenes

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and alkynes on a variety of supported metal catalysts (*3–8*) is characterised by a primary process, in which permanently retained hydrocarbonaceous ($C_xH_y$) species are chemisorbed on the metal surface, and a secondary process which is responsible for the adsorption of the catalytically active species. We have also shown that the extent and nature of the primary adsorbed hydrocarbonaceous species are a function of both the metal and the catalyst precursor state. As such the chemisorption of unsaturated hydrocarbons provides a method whereby the metal function of supported catalysts may be conveniently characterised. We have also found (*9–11*) that the chemisorption of alkenes and alkynes under pulsed-flow conditions leads to similar results regarding the nature and extent of the primary adsorption process to those obtained under static conditions. Against this background we now report results of a study of the chemisorption of ethene on the various platinum catalysts and an extension of our earlier methods to a study of the competitive chemisorption of ethene and carbon monoxide over the same catalysts.

## EXPERIMENTAL

### APPARATUS AND METHODS

Adsorption isotherms for $^{14}$C-ethene were determined at ambient temperature up to pressures of 1.33 kPa in a static system of similar design to that described elsewhere (*4, 5*). Infrared spectra were obtained using a Nicolet 5DXC Fourier Transform spectrometer, at 2 cm$^{-1}$ resolution, in either the transmission mode (Pt/silica and Pt/alumina) using the cell described in Part II (*2*), or the diffuse reflectance mode using a Barnes DRIFT cell equipped with an environmental chamber. Dynamic chemisorption measurements were made using a pulse-flow microreactor system, as described in Part II (*2*), using typical pulse sizes of 2 cm$^3$, 6.67 kPa.

## RESULTS

### *Ethene Adsorption Measurements*

*Platinum/alumina* (*I*). The isotherms for the adsorption of $^{14}$C-ethene at 295 ± 2 K on three different samples (A, B, and C) of Pt/alumina, which had been reduced in flowing hydrogen at a standard temperature of 573 K, are shown in Figs. 1a and 1b. On the freshly reduced catalysts the shapes of the isotherms are similar in each case, showing an initial rapid increase in surface count rate followed by a linear region, which persists up to a gas pressure of $\leq$0.53 kPa, followed by another steep increase in surface count rate as the gas pressure is further increased. With samples A and B, evacuation of the surface following adsorption resulted in a decrease in surface radioactivity to varying extents dependent on the time of evacuation. With Sample B, evacuation for a total of 70 min resulted in a 38% decrease in surface radioactivity. Subsequent treatment of the evacuated surface with 1.33 kPa $^{12}$C-ethene resulted in a further 27.5% decrease in the surface count rate.

With Sample C (Fig. 1b), the procedure was modified such that, when the adsorption isotherm had reached a point in the intermediate secondary region, the system was left to equilibrate for 95 min, during which time a further amount of radioactivity slowly accumulated on the surface. In contrast with the behaviour of samples A and B, subsequent evacuation of this equilibrated surface for 590 min resulted in only a 1% decrease in surface radioactivity.

With each of the samples, readsorption of $^{14}$C-ethene following evacuation and/or molecular exchange with $^{12}$C-ethene gave isotherms which showed more normal behaviour with only one primary and secondary region, as shown in Figs. 1a and 1b.

Results for total amounts of ethene adsorbed and the amounts of ethane produced during the pulsed-flow chemisorption of ethene at 294, 273, and 193 K are shown in Table 1. At 294 K, adsorption of the first pulse of ethene resulted in 63% (≡ 4.08 ×

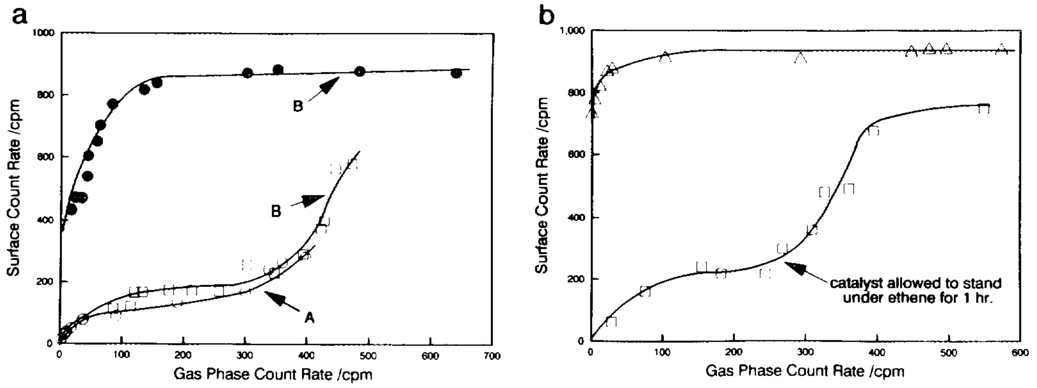

FIG. 1. (a) Adsorption of $^{14}$C-ethene on Pt/alumina (I) (0.3386 g; curva A) and (0.2765 g; curve B) at 293 K. Curve A: (○) first adsorption on freshly reduced catalyst. Curve B: (□) first adsorption on freshly reduced catalyst; (●) second adsorption following evacuation of first isotherm at 293 K; $^{14}$C-ethene specific activity = 0.258 mCi mmol$^{-1}$). (b) Adsorption of $^{14}$C-ethene on Pt/alumina (I) (0.2765 g) at 293 K. (□) first adsorption on freshly reduced catalyst; (△) second adsorption following evacuation of first isotherm at 293 K; $^{14}$C-ethene specific activity = 0.258 mCi mmol$^{-1}$).

$10^{18}$ molecules g$^{-1}$) hydrogenation to ethane, the remainder being retained by the catalyst; 26% (≡ 1.68 × $10^{18}$ molecules g$^{-1}$) of the second pulse was hydrogenated to ethane and a further 22.2% (≡ 1.44 × $10^{18}$ molecules g$^{-1}$) was retained. Further pulses of ethene produced no further hydrogenation, although some adsorption occurred until surface saturation was eventually achieved. When the catalyst had been left under flowing helium at 294 K for 60 min and then subjected to further pulses of ethene, 33.2% (≡ 2.15 × $10^{18}$ molecules g$^{-1}$) of the first pulse was hydrogenated and 30.9% (≡ 2.00 × $10^{18}$ molecules g$^{-1}$, corresponding to 26.8% of that initially retained) was retained. After the surface had been resaturated with ethene, the catalyst was heated

TABLE I

Adsorption of Ethene on Supported Platinum Catalysts

| Catalyst | Temperature (K) | Amount $C_2H_4$ adsorbed (molecules g-catalyst$^{-1}$) × $10^{18}$ | Amount $C_2H_6$ formed (molecules g-catalyst$^{-1}$) × $10^{18}$ | Thermal desorption (molecules g-catalyst$^{-1}$) × $10^{18}$ | | |
|---|---|---|---|---|---|---|
| | | | | $CH_4$ | $C_2H_6$ | $C_2H_4$ |
| Pt/Alumina (I) | 193 | 28.02 | 1.81 × $10^{18}$ | — | — | — |
| | 273 | 7.16 | 3.73 × $10^{18}$ | — | — | — |
| | 294 | 3.83 | 5.82 × $10^{18}$ | 1.05 | 0.41 | 0.00 |
| Pt/Silica (I) | 191 | 113.1[a] | 0 | — | — | — |
| | 273 | 0.40 | 0 | — | — | — |
| | 294 | 0.33 | 1.69 × $10^{18}$ | >0 | >0 | 0 |
| Pt/molybdena (I) | 188 | 15.00 | 0 | — | 1.44 | 10.50 |
| | 273 | 14.00 | 0 | — | 0.18 | 2.11 |
| | 294 | 3.87 | 0 | — | — | — |

[a] Amount retained determined from thermal desorption.

to 573 K in the helium flow. This resulted in the desorption of 1.05 × $10^{18}$ molecules $g^{-1}$ methane and 4.1 × $10^{17}$ molecules $g^{-1}$ ethane.

Adsorption of ethene on a freshly reduced catalyst at 273 K also resulted in the formation of ethane; from the first pulse 30% (≡ 1.70 × $10^{18}$ molecules $g^{-1}$) was hydrogenated and the remainder (5.51 × $10^{18}$ molecules $g^{-1}$) was retained, whilst 26% (≡ 1.48 × $10^{18}$ molecules $g^{-1}$) of the second pulse was hydrogenated and 20% (≡ 1.14 × $10^{18}$ molecules $g^{-1}$) was retained. No further hydrogenation was observed with subsequent pulses, although further adsorption occurred until effective saturation of the surface was achieved.

At 193 K, ethene adsorption on a freshly reduced catalyst sample showed complex behaviour. After the adsorption of four pulses (≡ 2.27 × $10^{18}$ molecules $g^{-1}$) ethane began to desorb. After seven pulses had been passed over the catalyst elution of ethene, along with ethane, began, whilst by the ninth pulse only ethene was eluted from the reactor. The total amount of ethene passed over the catalyst was 6.77 × $10^{19}$ molecules $g^{-1}$; the respective amounts of ethane and ethene desorbed were 1.81 × $10^{18}$ and 3.79 × $10^{18}$ molecules $g^{-1}$, giving a total ethene retention of 28.0 × $10^{18}$ molecules $g^{-1}$ on the catalyst.

*Platinum/silica (I).* Figure 2 shows the $^{14}$C-ethene adsorption isotherms at 295 ± 2 K on a freshly reduced sample of catalyst. The isotherm shows a primary and a secondary region and evacuation of the precovered surface at 295 K removed up to 50% of the adsorbed species. A repeated adsorption–evacuation–adsorption cycle indicated that the amounts of ethene adsorbed in the secondary region were reproducible, the slight increase in surface count rate in the second isotherm being attributable to an increase in the extent of adsorption in the primary region. Molecular exchange with 0.67 kPa $^{12}$C-ethene following a $^{14}$C-ethene adsorption-evacuation cycle resulted in a decrease of 11% in the surface count rate.

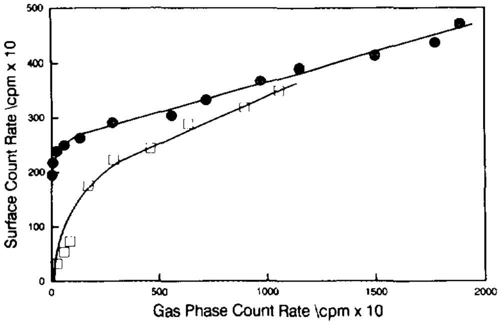

FIG. 2. Adsorption of $^{14}$C-ethene on Pt/Silica (I) (0.287 g) at 293 K: (□) first adsorption on freshly reduced catalyst; (●) second adsorption following evacuation of first isotherm at 293 K ($^{14}$C-ethene specific activity = 0.258 mCi $mmol^{-1}$).

Pulsed-flow adsorption of ethene on freshly reduced catalyst samples was examined at 294, 273 and 194 K. The results are summarised in Table 1. At 294 K, 25% (≡ 1.42 × $10^{18}$ molecules $g^{-1}$) of the first pulse was hydrogenated to ethane. However, only 5% of the ethene pulse (≡ 0.28 × $10^{18}$ molecules $g^{-1}$) was retained by the catalyst. In consequence, assuming that all of the hydrogen associated with the retained ethene is available for ethane formation, the catalyst must have provided *a minimum of* 4.54 × $10^{18}$ atoms H $g^{-1}$ to account for the ethane yield. No further hydrogenation occurred in subsequent pulses, although some further retention of ethene was observed. After the ethene-saturated surface had been left in the helium flow at 294 K for 60 min and then subjected to further pulses of ethene, 22% (≡ 1.25 × $10^{18}$ molecules $g^{-1}$) of the first pulse was hydrogenated to ethane, although *no further retention* of ethene could be detected. The ethene-saturated catalyst was heated to 573 K in flowing helium. This resulted in the desorption of both methane and ethane, although the amounts produced were too small for quantitative measurement.

At 273 K, ethene retention was observed, but no hydrogenation to ethane was detected, whilst at 194 K, ethene began to desorb from the catalyst after two pulses. As

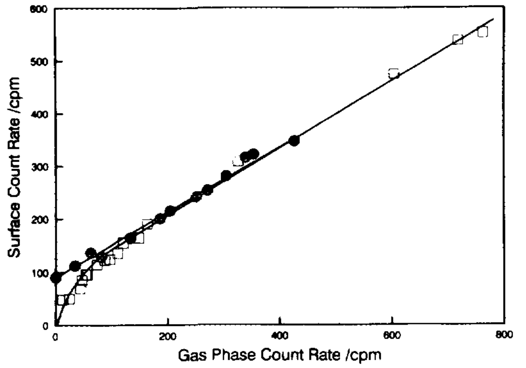

FIG. 3. Adsorption of $^{14}C$-ethene on Pt/molybdena (I) (0.8563 g) at 293 K. (☐) first adsorption on freshly reduced catalyst; (●) second adsorption following evacuation of first isotherm at 293 K ($^{14}C$-ethene specific activity = 0.258 mCi mmol$^{-1}$).

shown in Table 1, thermal desorption from the catalyst sample which had been saturated with ethene at 194 K showed that the amount of ethene retained at 194 K was $11.3 \times 10^{18}$ molecules g$^{-1}$.

*Platinum/molybdena (I).* Two $^{14}C$-ethene adsorption isotherms obtained at 293 K with freshly reduced samples of the platinum/molybdena catalyst are shown in Fig. 3. It can be seen that, whilst the shapes of the isotherms are not of the expected form, showing instead a gradual increase in surface count rate with increasing gas pressure, the behaviour is reproducible. Much of the ethene is only weakly adsorbed, the amounts removed by evacuation for 80 min being, respectively, 84 and 76% for the first and second isotherms. Equilibration of the $^{14}C$-ethene precovered surface with 1.07 kPa $^{12}C$-ethene over 40 min resulted in *no* molecular exchange between the surface and gas phase.

In the pulsed-flow adsorptions of ethene on freshly reduced catalyst samples at 294, 273, and 188 K, no production of ethane was observed. At 294 K the shape of the eluted peak was found to be broad and diffuse due to chromatographic effects of the catalyst bed, even after the surface had been saturated. The total amounts of ethene adsorbed at each temperature are given in Table 1. Thermal desorption of the adsorbed ethene, by heating from the adsorption temperature to 573 K in the helium flow, resulted in the production of both ethane and ethene. Following adsorption at 273 K, the respective amounts of ethane and ethene produced were $0.18 \times 10^{18}$ and $2.11 \times 10^{18}$ molecules g$^{-1}$, whilst after adsorption at 188 K the corresponding figures were $1.44 \times 10^{18}$ and $10.50 \times 10^{18}$ molecules g$^{-1}$. No quantitative thermal desorption data could be obtained following adsorption at 294 K.

*Platinum/molybdena (C).* Attempts to study ethene adsorption in the pulsed-flow system were unsuccessful in that, whilst adsorption did occur, it was extremely weak and this resulted in ethene continually bleeding from the system. This rendered impossible attempts to measure, in the dynamic mode, total amounts adsorbed. However, when examined in the static system at 295 K, $^{14}C$-ethene adsorption isotherms were obtained as shown in Fig. 4. Unlike the behaviour with the Pt/molybdena (I) catalyst, these isotherms were of the expected form with distinct primary and secondary regions. Evacuation, for 77 min at 295 K, following the adsorption of $^{14}C$-ethene on to a freshly reduced surface resulted in the removal of 81% of the adsorbed species.

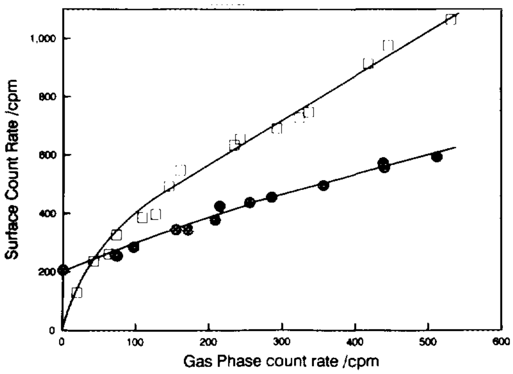

FIG. 4. Adsorption of $^{14}C$-ethene on Pt/molybdena (C) (0.8563 g) at 293 K: (☐) first adsorption on freshly reduced catalyst; (●) second adsorption following evacuation of first isotherm at 293 K ($^{14}C$-ethene specific activity = 0.258 mCi mmol$^{-1}$).

Readsorption of $^{14}$C-ethene on this evacuated surface to a residual gas pressure of 0.53 kPa, followed by evacuation for 78 min at 295 K, resulted in a 62% decrease in surface radioactivity, and subsequent equilibration with 1.20 kPa $^{12}$C-ethene for 40 min showed a further 21% of the surface radioactivity could be exchanged.

### *Coadsorption of Ethene and Carbon Monoxide*

The effects of preadsorbing carbon monoxide on the adsorption of ethene and vice versa, and the coadsorption of carbon monoxide and ethene together, were examined in the dynamic mode over each catalyst.

*Platinum/alumina (1).* No ethene adsorption was detected at 273 K on a carbon monoxide precovered surface. The amounts of carbon monoxide adsorbed and the subsequent thermal desorption results were identical to those reported in Part II (*2*). However, when, on a freshly reduced catalyst sample, ethene was preadsorbed to saturation at 273 K, subsequent admission of a pulse of carbon monoxide resulted in the desorption of 28% (≡ 1.97 × 10$^{18}$ molecules g$^{-1}$) of the adsorbed ethene. The ratio $CO_{(ads.)} : C_2H_{4(des.)}$ was 4.3 : 1. A second pulse of carbon monoxide also displaced some ethene such that the ratio $\Sigma CO_{(ads.)} : \Sigma C_2H_{4(des.)}$ was 4.2 : 1. Further pulses of carbon monoxide, whilst undergoing adsorption, did not displace any further amounts of ethene. No ethane was detected as a desorption product. The total amount of ethene displaced by the carbon monoxide was 3.35 × 10$^{18}$ molecules g$^{-1}$. Subsequent heating in the helium flow to 573 K resulted in the desorption of carbon dioxide (4.71 × 10$^{18}$ molecules g$^{-1}$), such that $CO_{(ads.)} : CO_{2(des.)} = 3.0 : 1$, ethene (0.22 × 10$^{18}$ molecules g$^{-1}$) and ethane (0.11 × 10$^{18}$ molecules g$^{-1}$).

When carbon monoxide and ethene ($CO : C_2H_4 = 1 : 1$) were co-pulsed over a freshly reduced catalyst at 273 K, carbon monoxide adsorption, ethene hydrogenation and ethene retention were all observed; 92% of the carbon monoxide in each of the first three pulses was adsorbed, whilst further smaller amounts of carbon monoxide were adsorbed from the fourth and fifth pulses, after which no further adsorption was observed. The total amount of carbon monoxide adsorbed was 15.5 × 10$^{18}$ molecules g$^{-1}$. Ethane formation and ethene retention were observed with each of the first four pulses. The respective amounts of ethane formed and ethene retained were as follows:

| Pulse number | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| Ethane formed (%) | 84 | 77 | 69 | 65 |
| Ethene retained (%) | 16 | 23 | 28 | 0. |

No adsorption or hydrogenation was observed after four pulses. The respective total amounts of carbon monoxide and ethene adsorbed were 15.5 × 10$^{18}$ and 2.76 × 10$^{18}$ molecules g$^{-1}$. These values compare with 19.79 × 10$^{18}$ and 7.16 × 10$^{18}$ molecules g$^{-1}$ for the respective separate adsorptions on freshly reduced catalysts. Thermal desorption by heating in the helium flow to 573 K resulted in the production of carbon dioxide (4.15 × 10$^{18}$ molecules g$^{-1}$), ethane (1.56 × 10$^{18}$ molecules g$^{-1}$) and ethene (1.39 × 10$^{18}$ molecules g$^{-1}$). The ratio $CO_{(ads.)} : CO_{2(des.)}$ was 3.74 : 1, compared with a value of 4.3 : 1 when carbon monoxide alone was adsorbed on a freshly reduced catalyst.

*Platinum/silica (1).* When carbon monoxide was preadsorbed to saturation at 273 K on a freshly reduced catalyst sample, no subsequent adsorption of ethene occurred. However, when an ethene precovered surface was subjected to pulses of carbon monoxide, 1.6 × 10$^{18}$ molecules g$^{-1}$ of the latter were adsorbed, although *no* hydrocarbon was displaced either as ethene or ethane. Co-pulsing of a carbon monoxide–ethene mixture ($CO : C_2H_4 = 1.1 : 1$) resulted in the adsorption of *both* carbon monoxide and ethene *and* the production of ethane, but only from the first pulse. No retention or hydrogenation of ethene was observed in subsequent pulses. The respective amounts of ethane produced, ethene retained and carbon monoxide adsorbed were $0.36 \times 10^{18}$, $0.21 \times 10^{18}$, and $1.73 \times 10^{18}$ molecules $g^{-1}$. It is noteworthy that the formation of ethane in these coadsorption experiments contrasts sharply with the behaviour of ethene when pulsed alone over a freshly reduced catalyst, when no hydrogenation was observed.

*Platinum/molybdena (I).* In contrast with the behaviour of the Pt/alumina (I) and Pt/silica (I) catalysts, the amounts of carbon monoxide and ethene adsorbed by the Pt/molybdena (I) catalyst were almost independent of which adsorbate was admitted first, or whether the adsorbates were admitted together. Thus, on a carbon monoxide presaturated surface, on which $4.45 \times 10^{18}$ molecules CO $g^{-1}$ were adsorbed, pulsing of ethene to surface saturation resulted in the retention of $5.4 \times 10^{18}$ molecules $g^{-1}$, whilst presaturation of the surface with ethene, followed by carbon monoxide resulted in the adsorption of $5.64 \times 10^{18}$ molecules $C_2H_4$ $g^{-1}$ and $5.18 \times 10^{18}$ molecules CO $g^{-1}$. Co-pulsing of a $1.1:1 = CO:C_2H_4$ mixture over a freshly reduced catalyst resulted in the adsorption of $3.18 \times 10^{18}$ molecules CO $g^{-1}$ and $5.53 \times 10^{18}$ molecules $C_2H_4$ $g^{-1}$. *No* ethane was produced from any of the pulses.

*Platinum/molybdena (C).* Preadsorption of carbon monoxide at 293 K prevented the subsequent adsorption of ethene, although when ethene was preadsorbed on a freshly reduced catalyst subsequent pulsing of carbon monoxide resulted in the adsorption of $3.97 \times 10^{18}$ molecules $g^{-1}$. This latter figure should be compared with a carbon monoxide adsorption of only $1.40 \times 10^{18}$ molecules $g^{-1}$ on the freshly reduced catalyst in the absence of ethene.

Co-pulsing of a carbon monoxide-ethene mixture ($CO:C_2H_4 = 1.1:1$) over the freshly reduced catalyst at 293 K resulted in the adsorption of $3.88 \times 10^{18}$ molecules CO $g^{-1}$ and some ethene adsorption. However, because of the heavy tailing of the peaks, no accurate figure for the amount of the latter could be established. Carbon monoxide, carbon dioxide, and ethene were all detected as products during thermal desorption at 573 K, although the amounts were too small to enable quantitative values to be obtained.

### *FTIR Spectra of Adsorbed Ethene*

*Platinum/alumina (I).* Transmission spectra of a freshly reduced catalyst sample, which had been subjected to a pulse ($49.3 \times 10^{18}$ molecules) of ethene in a helium stream (flow rate 25 ml $min^{-1}$) at 298 K showed no bands ascribable to surface bound hydrocarbon species. Similarly, the transmission spectra obtained in a static mode when a catalyst sample, which had been reduced in deuterium, was left in contact with 5.87 kPa ethene at 298 K for up to 56 min failed to reveal any bands due to adsorbed hydrocarbon species.

*Platinum/silica (I).* No bands due to adsorbed hydrocarbon were observed when a freshly reduced catalyst sample was treated with a pulse ($4.93 \times 10^{18}$ molecules) of ethene in a helium stream (flow rate 28 ml $min.^{-1}$) at 298 K, although there was a slight loss in the intensity of the hydroxyl band (3840 $cm^{-1}$) and a slight increase in the intensity of bands due to chemisorbed water (ca. 3000 and 1460 $cm^{-1}$). However, when a static adsorption was carried out at 298 K by allowing 5.33 kPa ethene to equilibrate, for up to 53 min, with the catalyst sample, which had been reduced in deuterium, bands at 2990, 2948, and 2871 $cm^{-1}$, ascribable to the presence of surface $-CH_3$ and $>CH_2$, rather than $-CD_3$ or $>CD_2$, species were detected. The spectra are shown in Fig. 5.

These spectra also show that the bands persisted even after the catalyst had been evacuated for 10 min at 298 K and when the catalyst had been heated *in vacuo*, first to 385 K and then to 485 K. Associated with the appearance of the hydrocarbon bands were changes in the features of the bands due to Si–OH and Si–OD groups at, respectively, 3600 and 2600 $cm^{-1}$, indicating some interaction between the adsorbed hydrocarbon moiety and these groups.

It was found that evacuation and heating of the ethene precovered surface resulted in a gradual disappearance of the bands due to both isolated and "hydrogen"-bonded –OD groups and a corresponding increase in intensity of both types of –OH group. In a further experiment, the spectra obtained when a deuterium-reduced catalyst was exposed to 6.53 kPa ethene for 40 min at 298 K failed to reveal any bands ascribable to surface alkyl groups, although similar effects on the deuteroxyl and hydroxyl bands were observed. Subsequent exposure of this second sample to $C^{18}O$ led to the appearance of a band due to linearly bound $C^{18}O$ (Fig. 6), whose position was slightly shifted from 2038 to 2019 $cm^{-1}$ and whose intensity was substantially reduced compared with that obtained following adsorption of $C^{18}O$ on a freshly reduced catalyst.

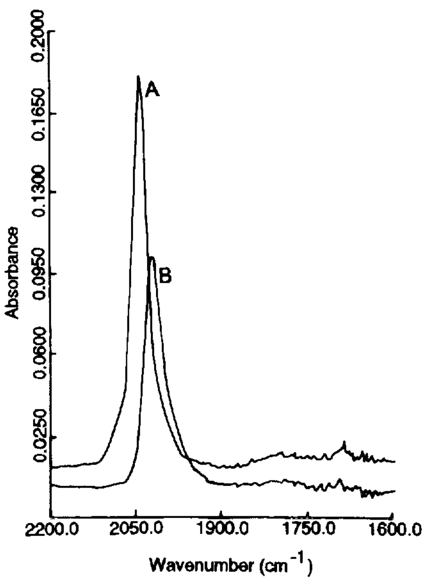

FIG. 6. Transmission FTIR spectrum of $C^{18}O$ adsorbed on (i) a freshly reduced Pt/silica (I) catalyst sample (spectrum A) and (ii) a Pt/silica catalyst which had been precovered with ethene and then evacuated before admission of $C^{18}O$ (spectrum B).

*Platinum/molybdena (I).* The DRIFT spectra obtained following the exposure of a freshly reduced catalyst sample, which had been diluted with 5 parts of diamond powder, to 30.67 kPa ethene at 298 K only showed bands ascribable to gas phase ethene. No bands due to surface adsorbed hydrocarbon species were observed.

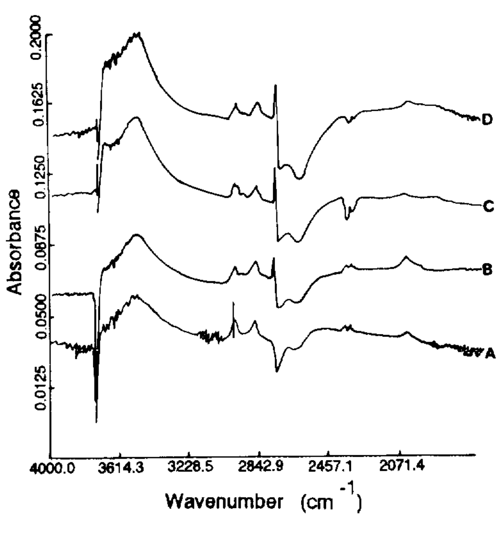

FIG. 5. Transmission FTIR difference spectra observed following exposure of a deuterium-reduced Pt/silica (I) catalyst sample to ethene for 53 min (spectrum A) and after a 10-min evacuation at 298 K (spectrum B), then 385 K (spectrum C), and finally at 485 K (spectrum D).

## DISCUSSION

The results presented above show that the various supported platinum catalysts exhibited marked differences in behaviour towards the adsorption and retention of ethene.

### *Platinum/Alumina (I)*

The pulsed-flow chemisorption results indicate that some dissociative adsorption of ethene occurred resulting in the formation of ethane and, during high-temperature thermal desorption, methane. Assuming that all of the hydrogen associated with the retained ethene is available for the formation of ethane and methane, an assumption which may not be correct in view of the carbon monoxide–ethene coadsorption results discussed below, the *average composition* of the surface adsorbed species can be calculated from the yields of hydrogenated products. These are, for ethene adsorbed at 294 K, $C_2H_{0.50}$ (after 1st pulse), $C_2H_{0.95}$ (after 2nd pulse) and, following adsorption and thermal desorption at 573 K, $C_2H_{0.76}$. For ethene adsorption at 273 K, the values are $C_2H_{2.30}$ (for 1st pulse), and $C_2H_{2.49}$ (after 2nd pulse). No values could be determined for adsorption at 194 K due to the complex behaviour observed. The total amounts of ethene strongly adsorbed on the surface decreased with increasing temperature; values for the $C_2 : Pt_{(total)}$ ratio were 1.01 : 1 (194 K), 0.33 : 1 (273 K), and 0.27 : 1 (294 K).

The dynamic chemisorption studies also showed that preadsorption of carbon monoxide to saturation at 273 K totally poisoned the catalyst surface for ethene adsorption. However, admission of carbon monoxide to an ethene-precovered surface resulted in the displacement of 47% of the adsorbed hydrocarbon as *ethene* and a total carbon monoxide adsorption on the ethene precovered surfaces corresponding to 62.6% of that adsorbed on a freshly reduced catalyst. These values suggest that the ethene molecules are bonded to two surface platinum atoms, assuming that, as discussed in Part II (*2*), the carbon monoxide is present predominantly as a linearly adsorbed species. In contrast with the displacement results, when an equimolar carbon monoxide–ethene mixture was co-pulsed over the catalyst, the predominant hydrocarbon species eluted from the reactor was *ethane*, rather than ethene. Indeed, *ethane* was produced even under conditions where *no ethene retention* was observed. The total amount of carbon monoxide adsorbed in the co-pulsing experiments corresponded to 78.4% of that adsorbed on a freshly reduced catalyst. In the coadsorption experiments, calculation of the hydrogen atom balance between the amounts injected and the amounts eluted from the reactor show that, even if all the hydrogen associated with the retained hydrocarbon species is available for ethane production, which cannot be the case in view of the carbon monoxide displacement results, where ethene was desorbed, the *catalyst itself* must provide at least a total of $1.15 \times 10^{19}$ atoms H $g^{-1}$, of which $4.37 \times 10^{18}$ atoms H $g^{-1}$ are provided in the first pulse. The total hydrogen provided by the catalyst, calculated on the above assumptions, corresponds to a $Pt_{(total)} : H$ ratio of 2.38 : 1. These coadsorption results are consistent with the results presented in Part II (*2*), which showed that, with a freshly reduced catalyst following the reduction/evacuation procedure, adsorption of the *second* and subsequent pulses of carbon monoxide resulted in the desorption of hydrogen, suggesting that the adsorption of carbon monoxide causes a decrease in the catalyst–hydrogen binding energy and a resultant release of surface retained hydrogen. In the present case it can be concluded that these catalyst hydrogen atoms, once released, will react with the ethene, rather than recombine and desorb as molecular hydrogen.

The static $^{14}C$-ethene adsorption isotherms, obtained for the first adsorption of ethene on a *freshly reduced* catalyst, show very unusual behaviour in that an intermediate plateau region is observed before further adsorption occurs when either substantially high ethene pressures ($\geq 0.53$ kPa) of the adsorbate are admitted or the catalyst is left in contact with a small pressure of ethene for a prolonged period. Subsequent isotherms on the same catalyst sample, which has been subjected to an adsorption–evacuation cycle, show the more usual behaviour with a well-defined primary and secondary region (*3*), the plateau of which corresponds with the *second* plateau of the first isotherm. Possible reasons for such behaviour are: (*i*) initial contact of the freshly reduced catalyst with ethene conditions it for further ethene adsorption by, for example, the lay-down of surface hydrocarbonaceous residues, and (*ii*) the surface of the freshly reduced catalyst is partially poisoned by some species which is slowly removed by interaction with adsorbed ethene.

The results obtained in both the dynamic and static chemisorption clearly show that surface hydrocarbonaceous residues are indeed formed on the surface. Similar observations have been made for ethene adsorption on other alumina-supported Group VIII metals (*5*) and on single crystal platinum surfaces (*12*). Furthermore, previous studies have shown that (i) the total amounts of hydrocarbon adsorbed in the pulsed-flow experiments may be equated with the amounts of hydrocarbon *retained* on the surface after adsorption and evacuation in static adsorption experiments and (ii) the composition of the retained $C_xH_y$ species is the same in both the pulsed-flow and static adsorption studies (*10*). However, in these earlier studies, no evidence has been obtained for such laydown giving rise to an enhancement in the amounts of ethene adsorbed. This, together with the observations made in the present study using silica-supported platinum which, from comparison of Figs. 1 and 2, shows an approximately eight times greater total ethene adsorptive capacity than the platinum/alumina (I) catalyst and which, as discussed below, shows the formation of a carbonaceous overlayer but a normal adsorption isotherm, leads to the conclusion that the enhancement of ethene chemisorption by carbon lay-down is unlikely to account for the observed behaviour with the platinum/alumina (I) catalyst.

Considering the alternative postulate that the behaviour is due to poisoning, the results presented in Part II (*2*), and results for the coadsorption of carbon monoxide and ethene presented above, show that the interaction of carbon monoxide with the freshly reduced catalyst results in the release of catalyst hydrogen. The possibility exists, therefore, that this hydrogen may effectively act as a partial poison for the initial adsorption of ethene and that the small initial ethene adsorption causes an effect similar to, but much slower than, that induced by carbon monoxide, with a *slow* release of the catalyst hydrogen and the creation of fresh sites for ethene adsorption. It is interesting to note that *no* evidence was obtained for the "two-stage" adsorption of ethene in the pulsed-flow chemisorption, suggesting that the effect is primarily associated with the nonretained, reversibly adsorbed ethene species, which is observed under static, but not under dynamic conditions.

In view of the strong evidence from the chemisorption measurements, particularly from the carbon monoxide displacement results, that ethene is retained as such on the catalyst surface, the absence in the FTIR spectra of any bands ascribable to hydrocarbon species is surprising. Clearly, the mode of adsorption of the retained species, even as $C_2H_4$, is such as to be infrared inactive. Similar observations have been reported previously by Sheppard (*13*) and by Avery (*14*) for the adsorption of various hydrocarbons on a variety of supported metal catalysts. The FTIR results also show that the permanently retained ethene species are not present on the surface as aliphatic polymer.

### *Platinum/Silica (I)*

In contrast to the complex behaviour observed in the case of Pt/alumina (I), the results obtained with Pt/silica (I) are relatively straightforward. From the pulsed-flow chemisorption results at 294 K, the amount of ethane produced was far in excess of that expected. Even if it is assumed that all the hydrogen associated with the retained hydrocarbon is available for ethane production, which cannot be the case in view of the FTIR results discussed below, the ethane yields show that the *catalyst itself* must provide *a minimum* of $2.12 \times 10^{18}$ atoms H $g^{-1}$, which is equivalent to a $Pt_{(total)}$ : H ratio of 1.06 : 1. The presence of catalyst hydrogen is also consistent with the conclusion reached from the carbon monoxide adsorption measurenents on the same catalyst (*2*), which showed that hydrogen remained on the surface of the freshly reduced catalyst even after high-temperature desorption in helium following reduction. The observation that, after the ethene-saturated surface was left in a helium flow at 294 K for an extended period, further amounts of ethane were formed when ethene was again pulsed over the catalyst, although no further ethene was retained, indicates that either there is a slow dissociation of the initially retained ethene, or retained hydrogen is released from the catalyst due to a slow surface restructuring under the influence of retained ethene, similar to that proposed for platinum/alumina (I). The values for the $Pt_{(total)}:H$ ratios clearly suggest that the freshly reduced platinum/silica (I) catalyst also contains hydrogen after reduction/activation. The amounts of ethane produced after the ethene adsorption–helium desorption–ethene adsorption cycle show that the catalyst, which is already bereft of hydrogen, must supply a further $2.96 \times 10^{18}$ atoms H $g^{-1}$. In contrast to the behaviour at 294 K, no hydrogenation was observed during ethene adsorption at either 273 or 194 K, although ethane was produced when carbon monoxide and ethene were coadsorbed on the catalyst at 273 K, suggesting that the presence of carbon monoxide liberates some hydrogen form the catalyst at this temperature. In comparison with platinum/alumina (I), the total amounts of ethene retained at each of the temperatures studied were very small; values for the $C_2:Pt_{(total)}$ ratio were 0.017 : 1 (294 K), 0.20 : 1 (273 K), and 0.75 : 1 (194 K), although these low values are not unexpected in view of the relatively small amounts of carbon monoxide adsorbed by the platinum/silica (I) catalyst, as shown in Part II (*2*), and the relatively large fraction of reversibly adsorbed ethene as determined in the $^{14}C$-ethene static chemisorption.

Whilst preadsorption of carbon monoxide caused complete blocking of the surface for ethene adsorption, carbon monoxide adsorption on either an ethene-precovered surface or in the presence of ethene under coadsorption conditions, could occur to the extent of ca. 80% of that observed for a freshly reduced catalyst. The presence of carbon monoxide in the adsorption mixture also effectively blocked the surface for ethene adsorption, which only occurred to an extent of 2.9% of that on the freshly reduced catalyst. Together these results indicate that the same surface sites are involved in the adsorption of carbon monoxide and ethene, the former being more strongly adsorbed under competitive conditions. However, the observation that *no* adsorbed hydrocarbon was displaced by carbon monoxide indicates that, once on the surface, the hydrocarbon species are strongly adsorbed. This latter conclusion is consistent with the FTIR results, which show that the surface alkyl species, once formed, are stable to desorption at 485 K.

The presence of strongly bound surface alkyl species is consistent with the adsorption of ethene as an ethylidyne species ($CH_3\text{–}C{\equiv}Pt$), as previously observed on single crystal platinum surfaces (*15*) and platinum/silica (I) catalysts (*16*). The FTIR spectra also showed that there was an interaction between the adsorbed hydrocarbon species and the hydroxyl groups associated with the support. Whilst the nature of this interaction is unclear, the observation that heating the ethene precovered surface resulted in a hydrogen exchange between the adsorbed hydrocarbonaceous species and the support hydroxyl groups indicates that either the hydrocarbon must be bonded, at least in part, to the support, or hydrogen released by further dissociation of the adsorbed hydrocarbon undergoes spillover on the silica-supported catalysts (*17*). The observation that the presence of preadsorbed ethene caused a lowering of the frequency of the linearly bound carbon monoxide, implying a greater degree of back donation to the $\pi^*$-orbitals of the carbon monoxide, strongly suggests that, in the adsorbed state, at least some of the hydrocarbon species donate electrons to the surface metal atoms. The decrease in intensity of the carbon monoxide band is consistent with a lower coverage, as indicated by the chemisorption results, although the decrease in $\theta_{CO}$ is not thought to cause the shift in the carbon monoxide stretching frequency to a lower wavenumber.

### *Platinum/Molybdena*

The $^{14}$C-ethene adsorption isotherms obtained with the catalyst prepared by impregnation showed little or no primary region and this, together with the observation that a major (80%) fraction of the adsorbed ethene is relatively easily removed by evacuation at the adsorption temperature, suggests that the ethene is only very weakly bound to the surface. However, this conclusion is not wholly supported by the pulsed-flow chemisorption data, which shows that significant amounts of ethene were retained at 294, 273, and 188 K, although no ethane formation accompanied the adsorption at any of the temperatures investigated. This suggests that ethene is associatively adsorbed and that *no* catalyst hydrogen is available for ethene hydrogenation, although there was clear evidence for the formation of a molybdenum bronze during the initial reduction of the catalyst (see Part I). The DRIFT spectra also indicate that a small fraction of the ethene is relatively strongly adsorbed on the catalyst surface, the bands at 1537 and 950 cm$^{-1}$, suggesting the presence of small amounts of surface aromatic species. The carbon monoxide–ethene coadsorption results are in marked contrast to the behaviour observed with the Pt/alumina, Pt/silica and the Pt/molybdena (C) catalysts in that the two adsorbates appear to be adsorbed noncompetitively at separate surface sites. However, it is not clear as to the origins of this difference in behaviour.

The results obtained for $^{14}$C-ethene chemisorption on the Pt/molybdena (C) catalyst, whilst differing in detail from those obtained with the Pt/molybdena (I) catalyst, also show that, when molybdena is used as the support, most (ca. 80%) of the ethene is relatively weakly adsorbed. The results obtained for the competitive adsorption of carbon monoxide and ethene at 293 K on the Pt/molybdena (C) catalyst are of particular interest in that, whilst preadsorption of carbon monoxide completely blocked the surface for ethene adsorption, the presence of ethene resulted in an almost three-fold *enhancement* in the amount of carbon monoxide adsorbed, this enhancement being the same when the ethene was either preadsorbed or was admitted together with the carbon monoxide. Clearly, the presence of ethene causes either some surface restructuring or reacts with some species on the surface which is capable of acting as a poison for the chemisorption of carbon monoxide.

## CONCLUSIONS

The results presented above show that there are significant differences in both the nature and the behaviour of the various supported platinum catalysts. In particular, striking differences between Pt/alumina (I) and Pt/silica (I) catalysts have been established both in terms of the nature of the adsorbed hydrocarbon species present on the surface following ethene chemisorption, and in the ability of the catalyst to retain hydrogen following reduction/activation, and subsequent thermal desorption, of the supported salt. In this context the ability of Pt/alumina (I) to retain significant amounts of hydrogen is of particular importance to the understanding of the nature of the active sites on this catalyst for hydrogenation reactions. The Pt/alumina (I) and Pt/silica (I) catalysts show similar particle size distributions, as measured by TEM, and the XPS spectra indicated that there was significant metal support interaction in the case of the Pt/alumina (*1*). This is supported by the differences observed in this adsorption study, which cannot be attributed simply to the differences in the platinum crystallites themselves, but must be due, at least in part, to an influence of the nature of the support on the metal.

The method of preparation of the Pt/molybdena catalysts has also been found to have a profound effect on their ability to adsorb carbon monoxide (*2*). Evidence has also been obtained for different types of adsorption site on the catalysts prepared by impregnation and co-crystallization. Significantly, although both catalysts formed a bronze during the reduction/activation, no evidence was obtained that the hydrogen stored in the catalyst as the bronze could act as a hydrogen source for the hydrogenation of ethene.

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