JOURNAL OF CATALYSIS **179,** 231–240 (1998)
ARTICLE NO. CA982179

In Situ Electrochemical Promotion by Sodium of the Selective Hydrogenation of Acetylene over Platinum

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Received February 20, 1998; revised May 28, 1998; accepted June 1, 1998

The applicability of electrochemical promotion (EP) has been extended to an investigation of the Pt-catalysed hydrogenation of acetylene to ethylene and ethane, the first example of the use of EP in catalytic selective hydrogenation. The system exhibits strong promotion by spillover Na supplied from a β''-alumina solid electrolyte. In the hydrogen-rich regime, reversible, potential-dependent, increases in ethylene selectivity of an order of magnitude are achievable under the influence of $\sim$0.02 monolayer Na, while maintaining high acetylene conversion. Thus, EP by Na induces Pt, normally a poor selective hydrogenation catalyst, to behave like Pd. Butenes, butadiene, and benzene are observed as minor products whose formation is also promoted by Na. A simple reaction model based on the destabilising effect of charge transfer from Na to adsorbed ethylene accounts for the principal findings.

Key Words: **promotion; sodium; electrochemical; acetylene selective hydrogenation; platinum; β''-alumina; promoter phase.**

INTRODUCTION

Electrochemical promotion (EP), discovered and developed by Vayenas *et al.*, is a new way of controlling catalyst performance (1). The phenomenon occurs when catalytic reactions take place on a variety of metal films in contact with a solid electrolyte, where the latter acts as a source of electrochemically controlled promoter species that directly modify the behavior of the catalyst film (the working electrode). It has been shown (1) that the electrochemically induced changes in catalyst potential over a range of $\sim$1 V measured with respect to a reference electrode (ΔV_{WR}) are identical to the change in catalyst workfunction, leading to concomitant changes in adsorption enthalpies and reaction activation energies. This, in turn, can lead to major changes in catalytic activity and selectivity. The effects on activity and selectivity are generally reversible, and the phenomenon provides an effective and controllable method for the *in situ* tuning of working catalytic systems. Useful information about the reacting system can be obtained in either of two modes. Measurements of the steady-state reaction rate under potentiostatic conditions provide information about kinetics and mechanism. Transient (galvanostatic) measurements are used to estimate the metal surface area and to provide an approximate scale for Na coverage of the Pt surface (θ_{Na}). They can also yield information about the effective dipole moment of the promoting Na species in the presence of coadsorbed reactants.

The EP phenomenon has been reported for a number of catalytic reactions on Pt, Rh, Pd, Ag, Ni, and IrO_2 catalyst films with a variety of solid electrolytes including oxygen (2–4), sodium (1,5–7), fluorine (8), and hydrogen (9) ion conductors. These EP systems are characterised by a very large value of the ratio between the change in turnover rate and the rate of charge transport through the electrolyte (up to 10^5). In other words, they are strongly non-Faradaic: one is not dealing with conventional electrocatalysis. Reported gains in reaction rate with respect to the unpromoted (clean surface) rate lie in the range 2–100.

For the most part, the catalytic processes studied thus far consist of total oxidation reactions, with results also reported for selective oxidation (10) (of ethylene over Ag) and for the decomposition and dehydrogenation (11) of methanol (over Ag). However, interesting results have also been reported for CO and CO_2 hydrogenation (12) over Pd and Rh interfaced to yttria-stabilised zirconia (O^{2-} conductor), ethylene hydrogenation (9) over Ni interfaced to $CsHSO_4$ (H^+ conductor), and 1-butene isomerisation/hydrogenation (13) over Pd/C interfaced to Nafion (H^+ conductor). To diversify the catalytic chemistry that can be addressed by EP, we report here the first study of a selective hydrogenation process using an Na^+ conductor as the electrochemically active support: the catalytic conversion of acetylene to ethylene (and ethane) over Na-modified Pt using Na β''-alumina (a Na^+ conductor) as the active support. It is well known that Pd is an excellent selective hydrogenation catalyst for the efficient conversion of acetylene to ethylene. Indeed, Pd is extensively used industrially (14,15) for this very purpose—the catalytic removal of acetylene impurity from ethylene feedstreams. Pt, on the other hand, is much less selective as a hydrogenation catalyst, producing mainly ethane under most conditions (16). Previously,

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0021-9517/98 $25.00

in regard to the NO + CO (17) and NO + propene reactions (18), we showed that EP by Na could be used to induce Pt to behave like Rh. Here, we show that in regard to selective hydrogenation, EP by Na induces Pt to behave like Pd.

METHODS

The platinum catalyst (working electrode, W) consisted of a porous continuous thin film ($\sim$1 cm^2 geometric area) deposited by sputtering on one face of a 10×15-mm Na β''-Al_2O_3 wafer. Au reference (R) and counter (C) electrodes were deposited on the other face of the solid electrolyte wafer, also by sputtering. Electrical contact with the W, R, and C electrodes was by means of 0.5-mm-diameter Au wires, which also served to suspend the Pt/β''-Al_2O_3/Au sample in a quartz, atmospheric-pressure well-mixed reactor (50 cm^3). All three electrodes were exposed to the reactant gas mixture (17,18), and the system behaved as a single-pellet, continuous stirred tank reactor (CSTR) as described elsewhere (19).

It is useful to recall the mode of operation. Consider starting with the Pt catalyst film covered by some Na. Under potentiostatic conditions, imposition of a positive potential ($V_{WR} > 0$) between working electrode (i.e., the Pt catalyst film) and reference electrode results in current flow between the working electrode (catalyst) and Au counterelectrode corresponding to the following anodic reaction at the Pt working electrode:

$$\mathrm{Na(Pt)} \rightarrow \mathrm{Na^+}(\beta''\text{-}\mathrm{Al_2O_3}) + e^-.$$

This occurs until the amount of Na pumped away from the Pt causes the value of V_{WR} to reach the desired preset value, at which point the current vanishes. Application of $V_{WR} < 0$ causes the reverse, cathodic, reaction to occur: Na^+ ions from the solid electrolyte are reduced at the three-phase (gas/electrode/electrolyte) boundary and spill over onto the Pt film until the required preset value of V_{WR} is achieved.

Inlet and exit gas analysis was carried out by a combination of online gas chromatography (Shimadzu-14B, Porapak-N columns) and online mass spectrometry (VG Supavac). Acetylene, ethylene, and ethane were monitored by gas chromatography and butenes, butadiene, and benzene were monitored by mass spectrometry, having performed the necessary calibrations. Reactants were solvent-free acetylene (99.6%) (Linde Gases) and hydrogen (99.999%) (MG Distillers) diluted in ultrapure He (99.996%) (MG Distillers); these were fed to the reactor by mass flow controllers (Brooks 5850 TR). The total flow rate was kept constant at $\sim$30 cm^3 STP/min, with partial pressures P_{H_2} and $P_{C_2H_2}$ varying between 6 and 60 kPa, respectively.

An Amel Model 553 galvanostat–potentiostat was used to carry out measurements in both galvanostatic and potentiostatic modes. In the galvanostatic mode, constant current, I, was applied between the catalyst (W) and the counterelectrode (C) while monitoring the potential, V_{WR}, between the catalyst and the reference electrode (R) (17). As described below, the galvanostatic transient behaviour of V_{WR} in He was used to obtain an estimate of the Pt surface area (20). Additionally, galvanostatic transients in H_2, acetylene, and H_2 + acetylene yield information about the effective dipole moment of the promoting Na species in the presence of coadsorbed reactants; they also provide an approximate scale for Na coverage of the Pt surface (θ_{Na}).

In the potentiostatic mode, a constant potential, V_{WR}, was maintained between the catalyst and the reference electrode during reaction. Constant V_{WR} corresponds to fixed Na loading, so these measurements gave information about activity, selectivity, and kinetics under steady-state conditions for a given Na loading. Most experiments were carried out in the potentiostatic mode by following the effect of changes in the applied catalyst potential (V_{WR}) on reaction rates and selectivity. That is, one observes the response of the catalytic system to electrochemically induced changes in the Na coverage of the Pt surface under reaction conditions. Periodic reversal of the direction of Na^+ pumping (required to regenerate a clean Pt surface on the working electrode) was effective in eliminating possible difficulties due to Na depletion of the electrolyte. In this connection, note that an amount of sodium equivalent to a coverage of $\sim$1 monolayer on the Pt film corresponds to $\sim 10^{-4}$ of the Na content of the electrolyte wafer. At the start of each series of experiments, the Pt surface was electrochemically cleaned by pumping Na away from the Pt film with the catalyst potential held at +400 mV until the current in the WC circuit fell to zero.

Two methods were used to clean the Pt film: (i) heating in oxygen (673 K, 100 cm^3 STP/min) and (ii) electrochemical cleaning (catalyst potential held at +400 mV until the Na^+ current vanished). The oxidative procedure removed carbonaceous residues; the electrochemical treatment removed Na. Typically, some deposition of carbon or inert hydrocarbonaceous material on the catalyst surface on exposure to the reactant mixture was observed, the effect being dependent on temperature and gas composition. At any given temperature, the level of carbon deposition was essentially constant during the experimental run, and in hydrogen-rich environments the data indicate that the extent of deposition was very small.

To check overall reproducibility of behaviour, data were acquired with two different samples, A and B, whose active Pt surface areas were similar. All previous studies involving EP by Na β''-alumina used temperatures in excess of 414 K to ensure adequate conduction in the solid electrolyte. Sample A was therefore used for investigating performance at temperatures >433 K. Since it was found (i) that carbon deposition increased with increased temperature and

(ii) that the largest Na-induced changes in ethylene selectivity occurred when carbon deposition was minimised, sample B was used for a more detailed study of the low-temperature behaviour (433 and 373 K). It is interesting to note that Na β''-alumina performs well as an EP active support at these low temperatures. Therefore, the prospects for extending its application to other areas of catalysis are encouraging.

RESULTS

The main products under all conditions were ethylene and ethane: these were monitored by gas chromatography, as was the degree of acetylene conversion. Very small amounts of C_4 compounds (butene and butadiene) and even smaller amounts of C_6 compounds (benzene and cyclohexane) were detected mass spectrometrically for $T > 533$ K and $H_2 : C_2H_2 \leq 2$. The combined yield of these products was always $\leq$1% of the total conversion and they are therefore ignored in calculating the ethylene selectivity. However, their presence is certainly interesting from a mechanistic point of view, as discussed below.

Effect of Catalyst Potential (V_{WR}) on Steady-State Reaction Rates

It is useful to summarise the major features of the system.

Na pumping to the initially clean Pt surface always increases its selectivity toward ethylene formation. This selectivity enhancement is most pronounced at (i) high hydrogen partial pressures and (ii) lower temperatures.

The steady-state activity is highest at high hydrogen partial pressure.

Deposition of carbon (or hydrocarbonaceous) material, which is dependent on temperature and acetylene partial pressure, decreases activity and increases selectivity. It is negligible at temperatures <433 K.

The activity and selectivity results shown in Figs. 1 and 2 were obtained using sample B by (i) cleaning the Pt surface oxidatively to remove carbon (673 K, 100 cm^3 STP/min), (ii) imposing a catalyst potential (V_{WR}) of +400 mV to pump Na away from the Pt, and then (iii) monitoring performance as a function of V_{WR}, i.e., Na loading, under potentiostatic conditions. In both cases, the 433 K data were

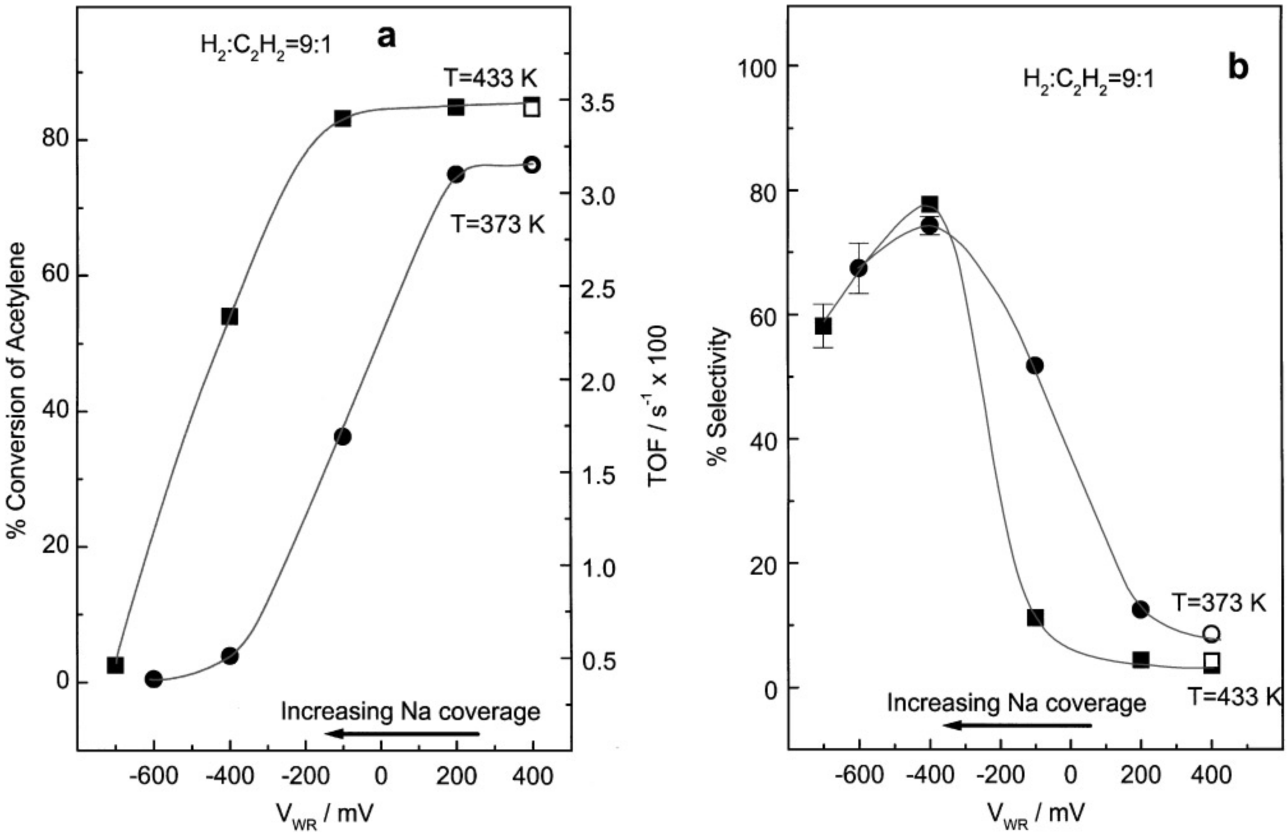

FIG. 1. Effect of catalyst potential, V_{WR}, on conversion of acetylene (a) and selectivity towards ethene formation (b) for sample B with $H_2 : C_2H_2 = 9 : 1$. Conditions: $P_{H_2} = 60$ kPa, $P_{C_2H_2} = 7$ kPa, $P_{He} = 34$ kPa, total flow rate $F_t = 30.3$ cm^3 STP/min. V_{WR} was initially set at +400 mV and was increased in steps until the maximum negative voltage was applied. V_{WR} was then returned to its original value of +400 mV and the open symbols correspond to measurements taken at this point.

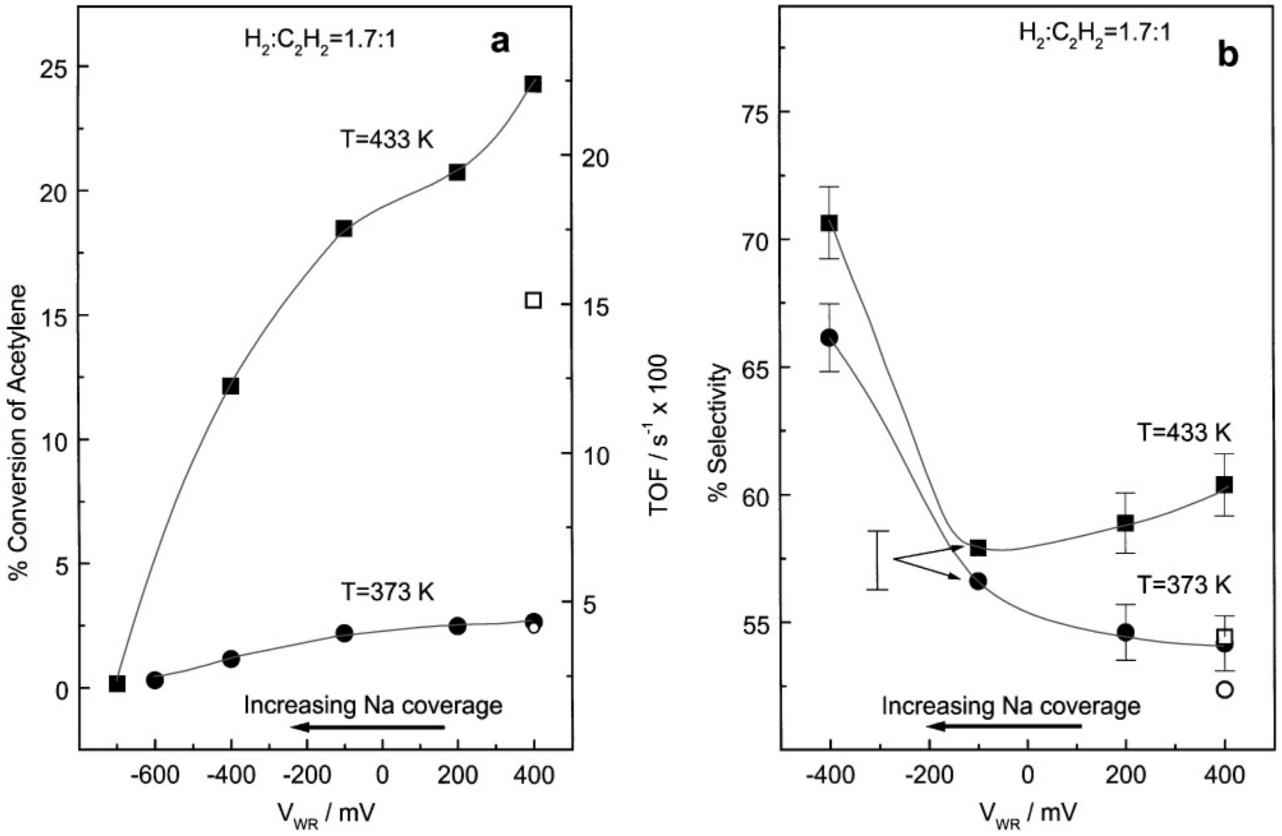

FIG. 2. Effect of catalyst potential, V_{WR}, on conversion of acetylene (a) and selectivity towards ethene formation (b) for sample B with $H_2:C_2H_2 = 1.7:1$. Conditions: $P_{H_2} = 40$ kPa, $P_{C_2H_2} = 24$ kPa, $P_{He} = 37$ kPa, total flow rate $F_t = 27.8$ cm^3 STP/min. V_{WR} was initially set at +400 mV and was increased in steps until the maximum negative voltage was applied. V_{WR} was then returned to its original value of +400 mV and the open symbols correspond to measurements taken at this point.

taken before the 373 K data, without an intervening oxygen treatment. Figure 1a shows the dependence of activity (measured as percentage acetylene converted) on catalyst potential (Na coverage) under standard conditions of total flow rate (see above) for two different temperatures, 373 K and 433 K, for $P_{H_2} : P_{C_2H_2} = 9:1$. Figure 1b shows the corresponding variations in selectivity towards ethylene production, defined as

$$S = \frac{P_{C_2H_4}}{P_{C_2H_4} + P_{C_2H_6}}. \qquad [1]$$

Starting with the electrochemically cleaned surface ($V_{WR} = +400$ mV), it is apparent that Na supply to the Pt surface leads to a very large increase in ethylene selectivity at both temperatures: at 433 K, the selectivity increases from ~4% on the Na-free surface to 78% at a catalyst potential of −400 mV, at which point the acetylene conversion is still in excess of 50%. A striking feature is the coincidence between the pronounced increase in ethylene selectivity and the drop in activity which occurred as the catalyst potential (V_{wr}) was decreased, i.e., as more Na is pumped to the Pt surface. It is important to note that the catalyst's performance was entirely reversible with V_{WR}: the original activity and selectivity were fully restored on returning V_{WR} to +400 mV, which corresponds to the Na-free surface (see the open symbol data points at the right-hand sides of Fig. 1; in Fig. 1b the reproducibility is sufficiently good that at 373 K the open circle at 400 mV coincides with the filled circle). This demonstrates that the very pronounced changes in catalyst performance can indeed be ascribed to the effects of electrochemically pumped Na, and that accumulation of surface carbon is negligible during the course of these experiments in a hydrogen-rich reactant at 373 and 433 K.

The observed good reversibility with V_{WR} has another implication. It is known that under H_2 atmospheres Na β''-alumina may undergo hydronium ion incorporation by exchange with the Na^+ ions located in the conducting planes of the electrolyte. The data illustrated in Fig. 1 were acquired during a period of 3 h exposure to a hydrogen-rich atmosphere, at the end of which returning V_{WR} to its original value led to exactly the same reaction rate and catalytic selectivity. This indicates that effects due to hydronium ion incorporation cannot have been large.

Figures 2a and 2b show the corresponding data obtained with a much richer acetylene gas feed ($P_{H_2} : P_{C_2H_2} = 1.7:1$).

The same general trends in activity and selectivity with increasing Na coverage are apparent. Thus, a clear increase in selectivity at negative catalyst potentials is again apparent, though the effect is less pronounced, mainly because the initial selectivity is relatively high (~50%). Correspondingly, compared with the $P_{H_2} : P_{C_2H_2} = 9:1$ case, increased Na loading acts to decrease activity, although the activity is substantially lower under any given conditions of temperature or catalyst potential. Note that the 373 K data again show full recovery of the initial (low) activity on pumping Na away from the catalyst at the end of the measurements. However, the 433 K results show that some irreversible loss in both activity and selectivity occurred during the course of the measurements (see the open symbol data points in Fig. 2a). We ascribe this to deposition of carbon or hydrocarbonaceous material caused by the acetylene-rich reactant gas at this higher temperature; evidence in support of this inference is given below. Note that in Fig. 1b error bars are smaller than the plotting symbols, unless indicated otherwise.

For temperatures above ~433 K the effects of "carbon" deposition become significant, as illustrated by the results in Fig. 3, which show the temperature dependence of conversion and selectivity, respectively, for $P_{H_2} : P_{C_2H_2} = 9:1$, at constant flow rate and for a constant V_{WR} (+400 mV): that is, the data refer to the Na-free catalyst. These experiments were carried out with sample B; i.e., prior to these measurements the sample had not been exposed to high temperatures, thus minimising carbon deposition. It can be seen that in the absence of Na, as the temperature was increased from 433 K, the selectivity increased from 12 to 70% at 563 K, while the activity actually fell at the highest temperature. The results illustrated in Fig. 3 suggest that the observed behaviour is due to the effects of significant carbon deposition at higher temperatures. This is confirmed by the ○ data points in Fig. 3, which were taken after cooling the sample from 563 to 433 K: they correspond to lower activity and higher selectivity than the original 433 K data. Further confirmation is provided by the 433 K △ data points in Fig. 3, which were taken after subjecting the sample to oxidative cleaning (3 h, 100 cm^3 STP/min, 673 K). The △ data points actually correspond to somewhat higher activity and lower selectivity than the original 433 K data (indicating that some residual carbonaceous material must have been present on the Pt surface at the start of this series of experiments).

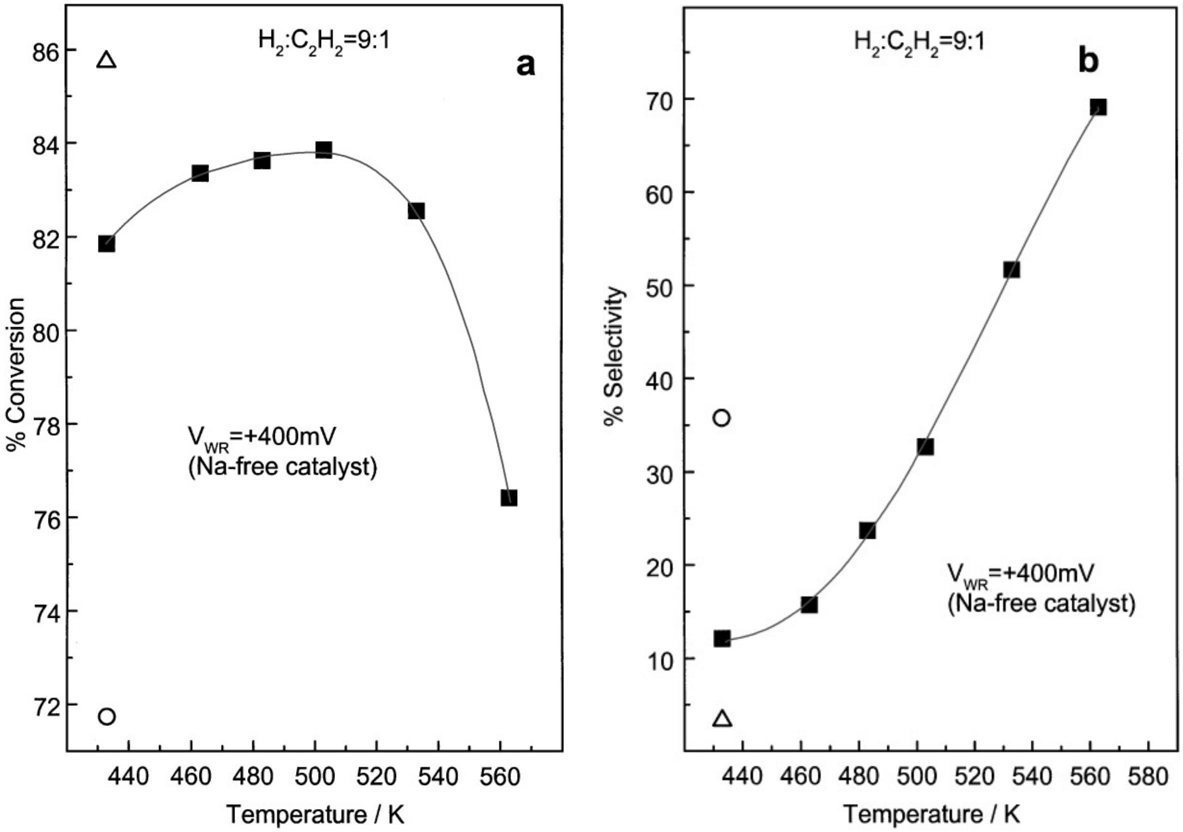

FIG. 3. Effect of temperature on acetylene conversion (a) and selectivity towards ethene (b) for Na-free catalyst, sample B, with $H_2 : C_2H_2 = 9:1$. Conditions: $P_{H_2} = 60$ kPa, $P_{C_2H_2} = 7$ kPa, $P_{He} = 34$ kPa, total flow rate $F_t = 30.3$ cm^3 STP/min with T increasing from 433 to 563 K. ○, on returning to the initial temperature: △, after subsequent cleaning in oxygen (673 K, 3 h, 100 cm^3 STP/min) followed by cooling to 433 K.

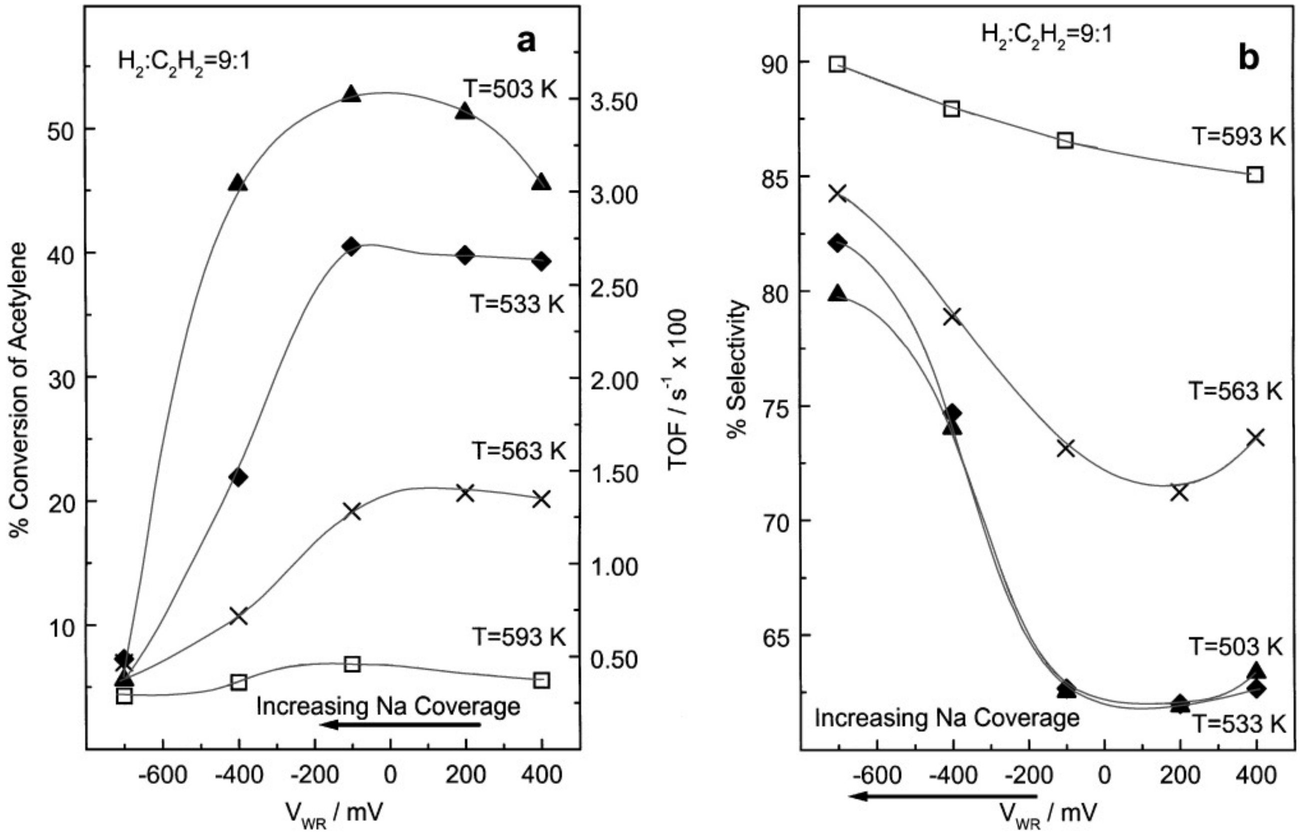

FIG. 4. Effect of catalyst potential, V_{WR}, on conversion of acetylene (a) and selectivity towards ethene formation (b) for sample A with $H_2:C_2H_2 = 9:1$. Conditions: $P_{H2} = 60$ kPa, $P_{C2H2} = 7$ kPa, $P_{He} = 34$ kPa, total flow rate $F_t = 30.3$ cm^3 STP/min.

In view of the effects of significant carbon deposition at temperatures in excess of 533 K, exacerbated by operating in an acetylene-rich environment, further measurements were restricted to temperatures of 503 to 533 K with $P_{H2}:P_{C2H2} = 9:1$, using sample A. The resulting data are shown in Fig. 4. Once again, the pronounced decrease in activity coincides with the marked increase in selectivity, the onset of the effect occurring at approximately −100 mV at both temperatures.

Figure 5 illustrates the dependence of butenes + butadiene ($m/z = 39$) production rates on catalyst potential. The production rate for butenes alone ($m/z = 41$) mirrors the $m/z = 39$ results. It can be seen that Na promotion increases selectivity towards formation of these minor products. Data were also obtained for the benzene formation. However, as noted above, this product was formed in even smaller amounts and the scatter in the data does not permit any conclusion to be drawn about the V_{WR} dependence of the benzene rate.

Galvanostatic Behaviour

Figure 6 shows galvanostatic transients obtained in pure He and in four different gas environments at 433 K and 1 atm pressure, after cleaning the sample in oxygen (oxygen flow rate of 100 cm^3 STP/min, $T = 673$ K for 3 h). In the case of pure He, the experimental procedure was as follows: first ($t \leq 0$), the surface was electrochemically cleaned of Na by application of a positive potential (V_{WR}) of +400 mV until the current between the catalyst and counterelectrode vanished. This current corresponds to the reaction

$$\mathrm{Na(Pt)} \rightarrow \mathrm{Na}^+(\beta''\text{-}\mathrm{Al_2O_3}) + e^-. \qquad [2]$$

The potentiostat was then disconnected and the galvanostat used to impose a constant cathodic current $I = -10\ \mu$A at $t = 0$, thus pumping Na to the catalyst surface at a rate $I/F = 1.04 \times 10^{-9}$ mol Na/s. The initial change in V_{WR} is given by (1)

$$\frac{d(e\Phi)}{dt} = \frac{ed(V_{WR})}{dt} = \frac{e\mu_0}{\varepsilon_0}\frac{dC_{Na}}{dt} = \frac{e\mu_0 I}{\varepsilon_0 eA} = \frac{\mu_0 I}{\varepsilon_0 A}, \qquad [3]$$

where I = current, C_{Na} = atoms of sodium per square meter, μ_0 = initial dipole moment of sodium on platinum, and A = surface area of the catalyst in square meters. It has been shown that this method gives reasonable agreement with more conventional surface area measurements (1). Thus the value of A may be computed from the initial slope of the

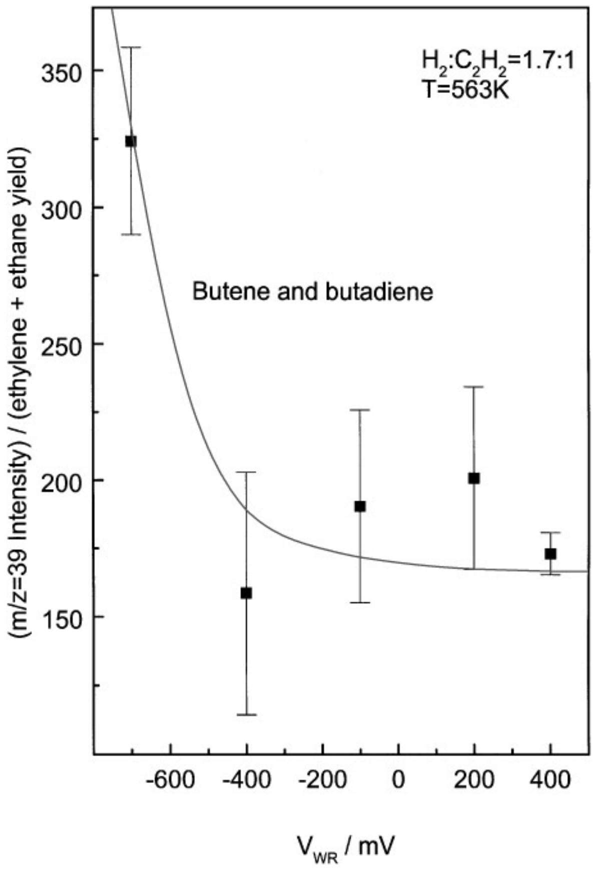

FIG. 5. Effect of V_{WR} on selectivity towards butene and butadiene where selectivity is defined as ($m/z = 39$ intensity)/(ethylene + ethane yield). Conditions: $P_{\mathrm{H_2}} = 40$ kPa, $P_{\mathrm{C_2H_2}} = 24$ kPa, $P_{\mathrm{He}} = 37$ kPa, total flow rate $F_t = 27.8$ cm^3 STP/min, $T = 563$ K, sample A.

galvanostatic transient from a knowledge of the zero-coverage dipole (μ_0) moment of Na on clean Pt. Using $\mu_0 = 5.3$ D (21) leads to a value of ~65 cm^2 for the Pt metal area. (Quoted TOFs are based on this value for the metal surface area.) In the case of the other gases the procedure was the same, with the relevant gas (or gas mixture) substituted for He. In every case, as with pure He, reversing the direction of current flow (i.e., pumping Na away from the Pt surface) restored V_{WR} to its initial value. Table 1 summarises the corresponding values for the apparent zero-coverage dipole moment of Na in the presence of the various coadsorbates ($\mu_0^\dagger$), deduced from the $d(V_{\mathrm{WR}})/dt$ at $t = 0$. These results indicate that the adsorbate layer formed by coadsorbed acetylene does not strongly perturb the dipole moment of adsorbed Na, whereas, for example, adsorbed hydrogen does strongly affect this quantity: $\mu_0(\mathrm{He}) = 1.75$ C m × 10^{29}; $\mu_0^\dagger(\mathrm{H}) = 1.1$ C m × 10^{29}. The implication is that H is a strongly electropositive adsorbate whose presence significantly reduces the degree of charge transfer from Na to Pt. This is consistent with the known behaviour of hydrogen on the three principal crystal planes of Pt (22–24) where substantial decreases in work function are found at saturation coverage. A 1.7 : 1 H_2 : C_2H_2 mixture yields a value of $\mu_0^\dagger$ that is intermediate between the pure H_2 and pure acetylene cases. Interestingly, the 9 : 1 H_2 : C_2H_2 mixture yields the lowest value of $\mu_0^\dagger$ (0.7 C m × 10^{29}) suggesting the presence of a strong electron donor which strongly reduces charge transfer from Na to Pt.

TABLE 1

Apparent Zero-Coverage Dipole Moment of Na on Pt in the Presence of Coadsorbates

Gas composition	μ_0 (C m × 10^{29})
He	1.75[a]
H_2	1.1
C_2H_2	1.7
H_2 : C_2H_2 = 1.7 : 1	1.5
H_2 : C_2H_2 = 9 : 1	0.7

[a] Reference (21).

The galvanostatic results also provide a useful indication of the approximate Na coverages present during the steady-state potentiostatic experiments. Figure 6 shows that in the presence of He, the decrease in V_{WR} ($= \Delta\phi$) is ~1100 mV

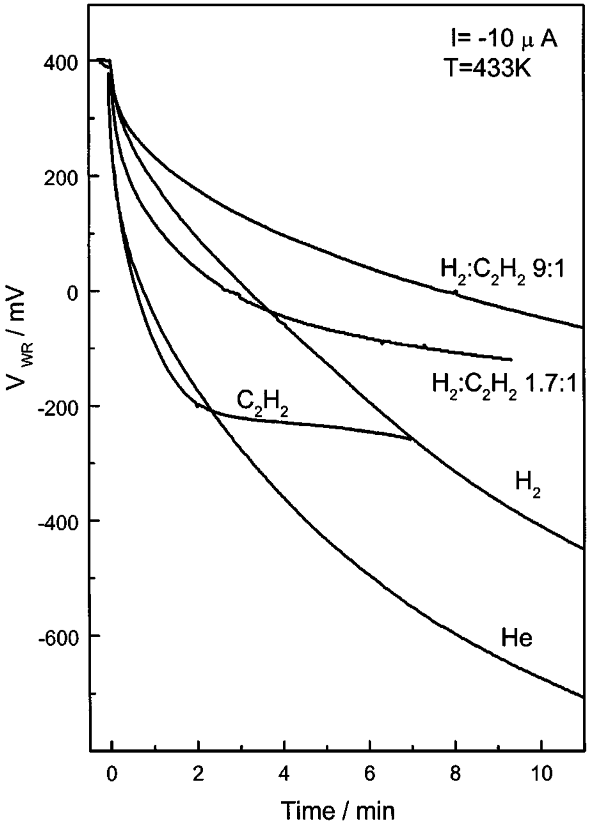

FIG. 6. Galvanostatic transients measured in various gas atmospheres. Conditions: $P_{\mathrm{total}} = 101$ kPa, total flow rate $F_t = 30.3$ cm^3 STP/min, $T = 433$ K, $I = -10$ μA, sample B.

after 10 min at $-10\ \mu$A. For Na on a clean transition metal surface, this corresponds to a sodium coverage on the order of 0.1 monolayer (25). Using this figure as a calibration value, and by extrapolating the galvanostatic transients obtained in reaction gas to any given value of V_{WR}, one obtains an approximate value for the corresponding Na coverage. Thus in the case of the data shown in Fig. 1, the selectivity starts to rise at approximately +200 mV, which corresponds to a sodium coverage of about 0.02 monolayer, peaking at approximately −400 mV (∼0.3 monolayer Na). Correspondingly, acetylene conversion is essentially unaffected at about +200 mV ($\theta_{Na} \sim 0.02$) but is substantially reduced at −400 mV. At this latter potential, the long extrapolation of the galvanostatic transient that is required to estimate the Na coverage (nominally ∼0.3 monolayer) may be associated with a large uncertainty in the derived Na coverage. However, the key point is that selectivity promotion commences at very low Na loadings ($\theta_{Na} \sim 0.02$, accurate), maximising when the Na loading is about one order of magnitude greater.

DISCUSSION

As noted in the Introduction, the selective hydrogenation of acetylene to ethylene with minimal production of ethane is of industrial importance. Palladium is the preferred catalyst for this process, and, partly as a consequence, there have been numerous academic studies of acetylene selective hydrogenation over Pd (26). Corresponding studies on Pt are much rarer, probably because Pt is not normally regarded as an efficient selective hydrogenation catalyst (16). Our results demonstrate that electropumping of Na to the surface of a Pt catalyst can lead to large, reversible changes in activity and selectivity towards the partial hydrogenation of acetylene under conditions where carbon deposition is negligible (Figs. 1,2). A striking result is that in hydrogen-rich atmospheres, Na pumping results in ethylene selectivity of ∼80%, approaching that achievable with palladium catalysts (Fig. 1b).

A detailed interpretation of the data in terms of a plausible reaction mechanism requires some knowledge of the surface species and elementary steps that actually are of importance under reaction conditions. There have been numerous studies of ethylene chemisorption on well-characterised platinum single-crystal surfaces [see, for example, Ref. (27) and references therein]; even so, no scheme of reactions has been found that satisfactorily explains all features of the observed hydrogenation behaviour under conditions of catalytic turnover. In the case of acetylene chemisorption, corresponding fundamental information is much scarcer and our knowledge of the relevant surface species is correspondingly more scant. Therefore, for purposes of discussion, it is convenient to describe the system in terms of the following very simple scheme of four surface reactions. (Neglect of the "direct" process $C_2H_2 + 4H \rightarrow C_2H_6$ does not alter the conclusions.)

$$C_2H_2 + 2H \rightarrow C_2H_4 \qquad [4]$$

$$C_2H_4 \rightarrow C_2H_4(g) \qquad [5]$$

$$C_2H_4 + 2H \rightarrow C_2H_6 \qquad [6]$$

$$C_2H_6 \rightarrow C_2H_6(g) \qquad [7]$$

Selectivity toward ethylene formation depends on the relative rates of [5] and [6]. Specifically, increasing the rate of [5] relative to [6] will increase ethylene selectivity. As noted above, both Na and H are electropositive adsorbates. Therefore, if Na promotion weakens the chemisorption bond of ethylene, favouring [5] relative to [6], increasing ethylene selectivity should result, as observed. We shall return to this point after considering what surface species are likely to be present under reaction conditions.

A fundamental contribution to the subject was made by Cremer *et al.* (28), who used sum frequency generation spectroscopy to investigate the surface species resulting from acetylene chemisorption on Pt(111) as a function of temperature. They observed initial formation of η^2-μ_3-vinylidene (Pt=C=CH$_2$), with ethylidene (M=CH−CH$_3$), di-σ-ethylene, μ-vinylidene, and ethylidyne (M≡C−CH$_3$) appearing as the temperature was raised above 125 K. For present purposes, the key finding is the eventual appearance of di-σ-ethylene, which, in the absence of gaseous hydrogen, undergoes decomposition to μ-vinylidene, ethylidene, and eventually ethylidyne. (The presence of ethylidyne implies considerable disproportionation of acetylene, and of course these results were obtained by adsorbing gaseous acetylene in the absence of gaseous hydrogen.)

We now attempt to answer in more detail the question Why does Na drastically improve the performance of clean Pt as a selective hydrogenation catalyst? A simple explanation involving the effects of adsorbate–metal charge transfer may be offered as follows: this is consistent with (i) the reactor data, (ii) the galvanostatic transients, and (iii) the compelling observations of Cremer *et al.* regarding the evolution of hydrocarbon species on Pt following acetylene chemisorption. First, recall that according to Ref. (1), $\Delta V_{WR} = \Delta\phi$(catalyst), and that single-crystal/UHV studies show that on Pt(111) both acetylene and ethylene are strongly electropositive adsorbates. That is, chemisorption involves substantial charge transfer to the metal (29), leading to workfunction decreases of the order of 1000 mV at saturation coverage. In line with these UHV results, recent $\Delta\phi$ measurements obtained by the Kelvin probe technique (30) show that saturation ethylene adsorption at 10^{-3} mbar on polycrystalline Pt at 473 K reduces the metal workfunction by 1400 mV. Thus, both sets of data are in line with our galvanostatic measurements.

The zero-coverage Na dipole moments extracted from the galvanostatic data suggest that there is rather little electronic interaction between Na and acetylene and a strong interaction between Na and hydrogen. Since all three adsorbates are electropositive, one expects mutual lowering of chemisorption bond strengths (31), the effect being most pronounced for Na/hydrogen. Furthermore, these data show that at high hydrogen partial pressures (i.e., $H_2:C_2H_2=9:1$, for which the optimum catalytic performance is achieved) the active surface includes a species that interacts very strongly with Na (see Table 1). Keeping in mind the results (28) of Cremer *et al.*, we propose that this species is the precursor to ethylene desorption, possibly di-σ adsorbed ethylene. We further propose that, in the presence of hydrogen, reaction [4] corresponds to the hydrogenation of vinylidene to form this di-σ adsorbed ethylene. Note that our identification of the strongly electropositive species formed under hydrogen-rich conditions with ethylene is in good accord with the findings of Hlavathy and Tetenyi (30), who observed $\Delta\phi=-1500$ mV for ethylene on Pt at 523 K and 10^{-3} mbar. That is, at temperatures relevant to the present work, ethylene does indeed yield a very strongly electropositive species on polycrystalline Pt.

We therefore propose that Na interacts especially strongly with the partly hydrogenated product, i.e., di-σ C_2H_4 or its precursor, weakening its chemisorption bond and increasing its desorption rate, thus increasing selectivity for ethylene formation. Addition of Na always leads to an increase in selectivity at the cost of some activity loss and, under certain conditions ($\theta_{Na}\sim 0.02$), can induce high selectivity while maintaining high activity, relative to clean unpromoted Pt (Fig. 1). The activity decline is associated with the blocking of adsorption sites by Na ($\theta_{Na}>0.3$) and by its destabilising influence on both reactants at neighbouring sites, especially hydrogen. The net effect is a decrease in reactant coverage and a lower reaction rate. Why does the activity pass through a maximum at high Na loadings (Fig. 1b)? It is not possible to offer a simple persuasive explanation on the basis of the available evidence. The spatial distribution of the Na promoter species as a function of promoter loading may be important. Thus if there is any tendency for the Na promoter to agglomerate at the highest loadings, a falloff in selectivity could result. Further experiments are planned to address this point (scanning photoelectron microscopy).

The control data presented in Figs. 2a and 4 suggest that higher temperatures and acetylene-rich environments favour carbon deposition, as might be expected. This interpretation is supported by the results illustrated in Fig. 3 which show that at the end of a series of variable-temperature experiments, oxidative treatment returns activity and selectivity towards the initial values. Deposition of hydrocarbonaceous species increases selectivity and can drastically reduce activity, thereby minimising the beneficial influence of Na (Figs. 2,3). Maetz and Touroude (32, 33) have actually demonstrated directly the importance of such effects due to hydrocarbon deposits in controlling the selective hydrogenation of but-1-yne over Pd and Pt catalysts. In our case, at sufficiently high temperatures (>503 K), increased hydrocarbonaceous deposits actually cause the activity to fall with temperature (Fig. 4). Thus at 593 K, in the absence of Na, one has a selective but very inactive catalyst which shows a modest response to Na promotion, ultimately yielding a very selective but very inactive catalyst. Given that ethylidyne is readily formed on Pt by adsorption of both ethylene and acetylene, it seems possible in the present case that ethylidyne is present as the precursor to deposition of hydrocarbonaceous residues which act to inhibit hydrogenation, especially total hydrogenation, thus raising selectivity.

A large body of data obtained using single-crystal samples indicates (34) that acetylene trimerisation to benzene on Pd(111) surfaces occurs according to the sequence

$$2C_2H_2 \rightarrow C_4H_4\ (+C_2H_2) \rightarrow C_6H_6,$$

where the C_4H_4 intermediate is a tilted metallocycle (35) capable of reacting with a variety of adducts, including acetylene itself. In the presence of adsorbed hydrogen, it reacts to form butadiene, butenes, and butane (36).

Unlike Pd(111), clean Pt(111) is ineffective for the trimerisation of acetylene, because on clean Pt(111) acetylene forms (“vertical”) vinylidene (28), the precursor to ethylene, rather than weakly adsorbed “flat-lying” acetylene (37), which is the precursor to C_4H_4 formation [this same work (36) showed that on Pd(111) “flat-lying” acetylene converts to vinylidene with increasing temperature]. Addition of Sn atoms to the Pt(111) surface leads to benzene formation (38), presumably via the C_4H_4 intermediate, by weakening the acetylene–surface bonding. Our results (Fig. 6) indicate that Na acts in a similar fashion to Sn, promoting acetylene coupling and hence the formation of butenes and butadiene. Under UHV-TPR conditions (38), in the absence of a supply of hydrogen, acetylene coupling to benzene is the predominant process. Under our conditions, in the presence of excess gaseous hydrogen, most of the acetylene undergoes hydrogenation to C_2 products (via vinylidene) but a small fraction of “flat-lying” adsorbed acetylene molecules survive to couple, resulting in C_4 products and benzene. The implication is that Na may tend to stabilise “flat-lying” acetylene against conversion to vinylidene.

CONCLUSIONS

1. In hydrogen-rich atmospheres and at temperatures below 500 K, electrochemical promotion by ~0.02 monolayer Na converts Pt from a poor catalyst for the selective hydrogenation of acetylene to an active, selective catalyst, e.g., at 433 K, 78% selectivity at 54% acetylene conversion.

2. At higher temperatures, and especially in an acetylene-rich environment, deposition of carbon or carbonaceous species becomes significant. These reduce activity, increase selectivity, and diminish the promoting effect of Na.

3. Galvanostatic measurements indicate that adsorbed Na interacts strongly with H_a, relatively weakly with the species formed by acetylene adsorption, and very strongly with the adsorbed species formed by acetylene adsorption in the presence of hydrogen.

4. The results may be understood in terms of a mechanism whose most important feature is substantial weakening by Na of the chemisorption bond of the half-hydrogenated species, taken to be a form of adsorbed ethylene, possibly di-σ ethylene.

5. Butenes, butadiene, and benzene are formed as minor products, the selectivity towards C_4 species increasing with Na promotion. Thus Na also promotes acetylene coupling on Pt, in this respect resembling the effect of Sn on Pt(111) under UHV conditions.

ACKNOWLEDGMENTS

S.T. acknowledges the award of an EPSRC studentship and additional support from BP Chemicals. J.P.H.V. acknowledges the award of a European Community Research Fellowship. Financial support from the U.K. Engineering and Physical Sciences Research Council under Grant GR/K45562 is gratefully acknowledged. We thank Mintcho Tikhov for preparing the Au and Pt electrodes and Johnson Matthey plc for a loan of precious metals.

REFERENCES

1. Vayenas, C. G., Bebelis, S., Yentekakis, I. V., and Lintz, H.-G., *Catal. Today* **11**, 303 (1992).
2. Pliangos, C., Yentekakis, I. V., Verykios, X., and Vayenas, C. G., *J. Catal.* **154**, 124 (1995).
3. Bebelis, S., and Vayenas, C. G., *J. Catal.* **118**, 125 (1989).
4. Yentekakis, I. V., and Bebelis, S., *J. Catal.* **137**, 278 (1992).
5. Yentekakis, I. V., Moggridge, G. D., Vayenas, C. G., and Lambert, R. M., *J. Catal.* **146**, 292 (1994).
6. Marina, O. A., Yentekakis, I. V., Vayenas, C. G., Palermo, A., and Lambert, R. M., *J. Catal.* **166**, 218 (1997).
7. Lambert, R. M., Tikhov, M., Palermo, A., Yentekakis, I. V., and Vayenas, C. G., *Ionics* **5**, 366 (1995).
8. Yentekakis, I. V., and Vayenas, C. G., *J. Catal.* **149**, 238 (1994).
9. Politova, T. I., Sobyanin, V. A., and Belyaev, V. D., *React. Kinet. Catal. Lett.* **41**, 321 (1990).
10. Karavasilis, Ch., Bebelis, S., and Vayenas, C. G., *J. Catal.* **160**, 205 (1996).
11. Neophytides, S., and Vayenas, C. G., *J. Catal.* **118**, 147 (1989).
12. Vayenas, C. G., Jaksic, M. M., Bebelis, S. I., and Neophpytides, S. G., *in* "Modern Aspects of Electrochemistry" (J. O'M. Bockris, B. E. Conway, and R. E. White, Eds.), Vol. 29, pp. 57–202. Plenum, New York, 1996.
13. Ploense, L., Salazar, M., Gurau, B., and Smotkin, E. S., *J. Am. Chem. Soc.* **119**, 11550 (1997).
14. Godinez, C., Cabanes, A., and Villora, G., *Chem. Eng. Process.* **34**, 459 (1995).
15. Duca, D., Frusteri, F., Parmaliana, A., and Deganello, G., *Appl. Catal. A* **146**, 269 (1996).
16. Pradier, C. M., Mazina, M., Berthier, Y., and Oudar J., *J. Mol. Catal.* **89**, 211 (1994).
17. Palermo, A., Lambert, R. M., Harkness, I. R., Yentekakis, I. V., Marina, O., and Vayenas, C. G., *J. Catal.* **161**, 471 (1996).
18. Yentekakis, I. V., Palermo, A., Filkin, N. C., Tikhov, M. S., and Lambert, R. M., *J. Phys. Chem.* **101**, 3759 (1997).
19. Harkness, I. R., Hardacre, C., Lambert, R. M., Yentekakis, I. V., and Vayenas, C. G., *J. Catal.* **160**, 19 (1996).
20. Vayenas, C. G., Bebelis, S., and Despotopoulou, M., *J. Catal.* **128**, 415 (1991).
21. Schröder, W., and Hölzl, J., *Solid State Commun.* **24**, 777 (1977).
22. Atli, A., Abon, M., Bertolini, J. C., Boudeville, Y., Fallavier, M., Benmansour, M., and Thomas, J. P., *J. Phys. Chem.* **98**, 4895 (1994).
23. Shern, C. S., *Surf. Sci.* **264**, 171 (1992).
24. Pennemann, B., Oster, K., and Wandelt, K., *Surf. Sci.* **249**, 35 (1991).
25. Fischer, N., Sclupper, S., Fauster, T., and Steinmann, W., *Surf. Sci.* **314**, 89 (1994).
26. Winterbottom, J. M., *in* "Catalysis and Chemical Processes" (R. Pearce and W. R. Patterson, Eds.), Chap. 12. Blackie, London, 1981.
27. Zaera, F., *Langmuir* **88**, 1 (1996).
28. Cremer, P. S., Su, X., Shen, Y. R., and Somorjai, G. A., *J. Phys. Chem. B* **101**, 6474 (1997).
29. Abon, M., Billy, J., and Bertolini, J. C., *Surf. Sci.* **171**, L387 (1986).
30. Hlavathy, Z., and Tetenyi, P., *Surf. Sci.*, in press.
31. Garfunkel, E. L., Farias, M. H., and Somorjai, G. A., *J. Am. Chem. Soc.* **107**, 349 (1985).
32. Maetz, P., and Touroude, R., *J. Mol. Catal.* **91**, 259 (1994).
33. Maetz, P., and Touroude, R., *Appl. Catal. A* **149**, 189 (1997).
34. Lambert, R. M., and Ormerod, R. M., *in* "Surface Reactions" (R. J. Madix, Ed.), Chap. 4. Springer-Verlag, Berlin, 1994.
35. Ormerod, R. M., Hoffmann, H., Zaera, F., Yao, J. M., Saldin, D. K., Wang, L. P., Bennett, D. W., Tysoe, W. T., and Lambert, R. M., *Surf. Sci.* **295**, 277 (1993).
36. Lambert, R. M., and Ormerod, R. M., *J. Chem. Soc. Chem. Commun.* **20**, 1421 (1990).
37. Hoffmann, H., Zaera, F., Ormerod, R. M., Yao, J. M., Saldin, D. K., Wang, L. P., Bennett, D. W., Tysoe, W. T., and Lambert, R. M., *Surf. Sci.* **268**, 1 (1992).
38. Xu, C., Peck, J. W., and Koel, B. E., *J. Am. Chem. Soc.* **115**, 751 (1993).