

Electrochemical Promotion by Potassium of the Selective Hydrogenation of Acetylene on Platinum: Reaction Studies and XP Spectroscopy

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Received: February 11, 2002; In Final Form: March 20, 2002

In the partial hydrogenation of acetylene, potassium, pumped to a thin film Pt catalyst from the electro-active support K β'' -alumina, very strongly promotes ethylene formation. In the best case, K-promotion increases ethylene selectivity from <20% (for the un-promoted catalyst) to 90%. XPS and photoelectron microscopy show that under these conditions submonolayer amounts of K are uniformly distributed on the Pt surface and that alkali transport, like the catalytic behavior, is fully reversible as a function of catalyst potential. Auxiliary experiments strongly suggest that ethylene, or a surface species derived from it, is a key intermediate in the total hydrogenation of acetylene to ethane. Promotion of selective hydrogenation by potassium may be rationalized in terms of K-induced weakening and strengthening respectively of ethylene and hydrogen adsorption. Comparison with earlier results indicates that the associated electronic effects are relatively insensitive to the chemical identity of the alkali.

Introduction

The palladium-catalyzed removal of acetylene impurity from ethylene feed streams^{1–3} is technically important, although despite intensive technical development the reaction mechanism is still not well understood.⁴ In comparison to palladium, platinum is a very poor selective hydrogenation catalyst,⁵ producing mainly ethane under most conditions, probably because of its overly strong interaction with adsorbed acetylene.^{6–9} However, we may deliberately exploit this fact in order to shed light on the reaction mechanism by using promoted Pt catalysts to study the partial hydrogenation of acetylene. In the case of platinum catalysts, one would expect promoter effects to be relatively large and certainly much greater than in the case of Pd. Proceeding thus, we may hope to elucidate promoter action and, hence, reaction mechanism.

Recently, using the technique of electrochemical promotion (EP), we showed that when sodium was supplied to a thin Pt film catalyst from a solid electrolyte support the selectivity for partial hydrogenation of acetylene to ethylene was greatly enhanced.¹⁰ Here, we report on extension of this work in several important ways. First, we investigated the effects of potassium promotion in order to examine whether chemically specific effects are significant. Second, spectroscopic measurements were performed in order to establish that EP by K of a Pt film does indeed involve reversible supply of the potassium to the surface of the platinum catalyst; these data were previously unavailable. Finally, auxiliary experiments with ethylene were carried out to examine certain aspects of the reaction mechanism.

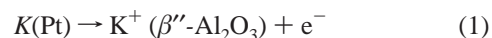
The EP technique, discovered and developed by Vayenas and his school,¹¹ entails electrochemical pumping of ions from a solid electrolyte to the surface of a porous, catalytically active metal film with which it is in contact. A recent concise review of the phenomenology, methodology, and underlying theory of electrochemical promotion by alkalis is available.¹² In the present case, the solid electrolyte was K- β'' alumina (a K⁺

conductor). Under forward bias (catalyst working electrode negative relative to counter electrode), K⁺ ions are transported to the catalyst electrode where they are discharged at the metal electrode/solid electrolyte/gas three phase boundary. The resulting species (K) are thought to spill over onto the surface of the metal catalyst, thus altering its reactive behavior. For example, EP by Na of the Pt-catalyzed NO+CO and NO+ propene reactions^{13,14} induces platinum to behave like rhodium. As we shall see, in the case of acetylene selective hydrogenation, EP by alkali causes platinum to behave like palladium.

Experimental Methods

The method of sample preparation and cleaning, the reactor geometry, analysis system, and electrochemical setup have already been described in detail.¹⁰ The overall methodology closely follows that established by Vayenas and co-workers.¹⁵ Briefly, the platinum catalyst (working electrode, W) consisted of a porous continuous thin film (~1 cm² geometric area) deposited by DC sputtering on one face of a 10 mm × 15 mm K- β'' -Al₂O₃ 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 sample in a quartz vessel (35 cm³), and the overall system behaved as a single pellet stirred tank reactor.¹⁶

The mode of operation is as follows. Imagine starting with the Pt catalyst film covered by some K. 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 counter electrode corresponding to the following anodic reaction at the Pt working electrode:



This occurs until the amount of K pumped away from the Pt causes the value of V_{WR} to reach the desired pre-set value, at

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which point the current vanishes. Application of $V_{\text{WR}} < 0$ causes the reverse, cathodic, reaction to occur: K^+ 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 pre-set value of V_{WR} is achieved.

Inlet and exit gas analysis was carried out by a combination of on-line gas chromatography (Shimadzu-14B; Porapak-N columns) and on-line mass spectrometry. Reactants were solvent free acetylene (99.6%; Linde Gases) and hydrogen (99.999%; MG Distillers) diluted in ultrapure He (99.996%; MG Distillers) and fed to the reactor by mass flow controllers (Brooks 5850 TR). The total flowrate was kept constant at $\sim 70 \text{ cm}^3 \text{ STP/min}$, with the H_2 partial pressure fixed at 70 kPa, C_2H_2 partial pressure varying between 3.5 and 35 kPa, and made up with He to a total pressure of 1 atm in every case. An Amel model 553 galvanostat-potentiostat was used to carry out catalytic measurements under potentiostatic conditions. Measurements of V_{WR} transients in He were carried out under galvanostatic conditions so as to provide an estimate of the actual metal surface area, following the method previously described in detail,^{10,17} thus permitting calculation of turnover frequencies (TOFs). Initial cleaning of the sample was carried out by heating in oxygen (673 K, $100 \text{ cm}^3 \text{ STP/min}$, 4 h); before commencing each experiment, the surface was also electrochemically cleaned by pumping K away from the Pt film with the catalyst potential held at +400 mV until the current in the WC circuit fell to zero.

Photoemission experiments were performed at reaction temperature and under electrochemical control at the ESCA microscopy beamline, ELETTRA, Trieste. The methods used in this apparatus for sample mounting and manipulation have already been described.¹⁸ Photoelectrons were collected with a multichannel hemispherical analyzer mounted at 70° with respect to the sample normal and the incident photon beam (microspot of $0.15 \mu\text{m}$ diameter). All experiments were performed with the working electrode grounded and at a photon energy of 490 eV. The scanning photoelectron microscope operated in two modes: imaging and spectroscopic. Elemental mapping was performed by scanning the sample with respect to the focused beam with the analyzer tuned to the desired kinetic energy. A multichannel detector made it possible to acquire 16 images simultaneously, including background intensities. As a result, thermal drift did not affect background correction. In spectroscopic mode, core level spectra could be recorded from microspots on features selected from the elemental maps. Quoted binding energies are referred to the Au $4f_{7/2}$ emission at 83.8 eV originating from the Au wire that formed the electrical connection to the working electrode. Prior performing the synchrotron experiments all carbonaceous deposits have been removed from the sample by heating in oxygen ($5 \times 10^{-7} \text{ mbar}$, 630 K, 20 min).

Results and Discussion

XP Spectroscopy and Scanning Photoelectron Microscopy.

Figure 1a shows K 2p XP spectra obtained at 473 K as a function of catalyst potential V_{WR} under UHV conditions. All of the raw data could be fitted by use of two components, as shown, the origin of which is discussed below. Spectra were acquired in the time sequence 1–7. The initial spectrum (+400 mV) corresponds to the electrochemically cleaned sample. Progressively decreasing V_{WR} from +400 to -800 mV resulted in a systematic increase in the K 2p intensity, i.e., in the amount of potassium present on the catalyst surface (-800 mV was the lowest catalyst potential achievable under these conditions).

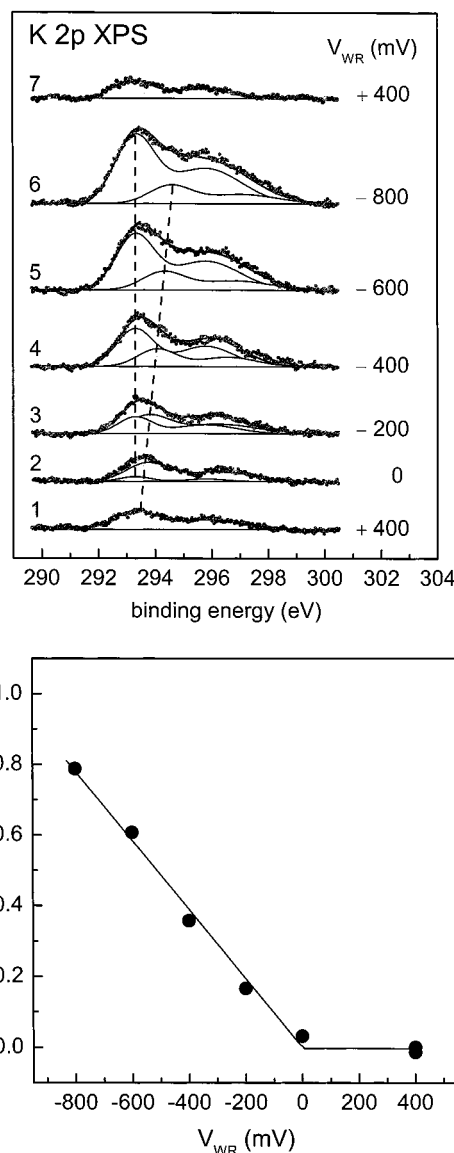


Figure 1. (a) Synchrotron core level spectroscopy: K 2p spectra as a function of V_{WR} . (b) Integrated K 2p intensity from potassium on platinum catalyst versus V_{WR} .

Finally, increasing V_{WR} from -800 to $+400 \text{ mV}$ restored the “clean surface” spectrum. Thus, electropumping of K is fully reversible with catalyst potential, in very good accord with the reversible and reproducible catalytic response observed under reaction conditions at atmospheric pressure, to be described below.

The two components of the K 2p emission behave as follows. One component exhibits invariant binding energy (BE) and its intensity increases with decreasing V_{WR} , i.e., as K is electro-pumped to the catalyst. This is ascribed to potassium at the surface of the (grounded) Pt catalyst film. The other component exhibits constant intensity and a systematic shift in apparent BE. This shift is numerically equal to the change in V_{WR} (i.e., the change in catalyst potential), strongly suggesting that this K 2p emission arises from the underlying solid electrolyte whose electrostatic potential differs from that of the Pt film by the change in V_{WR} . That the solid electrolyte is indeed visible to XPS through cracks and pores in the metal film is confirmed by the observation of Al 2s emission from the same source.

Figure 1b shows the integrated intensity of the K 2p emission of the component associated with potassium on the Pt surface

as a function of V_{WR} . Two points are apparent. First, there is a region ($\sim +500$ to ~ 0 mV) over which decreasing the catalyst potential does not pump XPS-detectable K on the Pt surface. Second, for $V_{WR} < \sim 0$ mV, decreasing the catalyst potential causes a linear increase in the K 2p intensity. The first observation implies that at ~ 0 mV the Pt surface has been fully depleted of K by electro-pumping, so that further increase in catalyst potential does not result in a corresponding decrease in the amount of K present on the Pt surface. The second observation shows that once detectable K is present on the Pt surface the K coverage changes linearly with V_{WR} .

In the case of EP of Rh films by Na, we have shown that in the regime where alkali coverage varies linearly with V_{WR} , there is also a linear correspondence between ΔV_{WR} and $\Delta\phi$, the change in catalyst work function.¹⁹ This shows that the alkali coverages lie in the low submonolayer range,²⁰ and a quantitative analysis of the $\Delta\phi$ and XPS data allowed us to estimate that the maximum alkali coverage attained in those experiments was ~ 0.02 monolayers. When the same analysis is carried out with the present data, the conclusion is that the maximum potassium coverage achieved in these experiments was on the order of ~ 0.05 monolayers.

Element mapping was performed by rastering the sample with respect to the focused photon beam with the analyzer tuned to either the Pt 4f_{7/2} or K 2p_{3/2} photoelectrons. In this way, intensity maps were obtained as a function of V_{WR} at spatial resolution $0.15\ \mu\text{m}$, with the sample held at 473 K.

Because we are not dealing with an optically flat surface, the raw photoelectron maps are a convolution of chemical information with topographical effects. The topographical effects, because of the intrinsic roughness of the sample surface, arise because the angle between the surface normal and the detector axis (which affects the intensity of the measured photoemission yield) changes from point to point. We therefore treated the data using the algorithm recommended by Kiskinova et al.,^{21,22} to remove intensity variations because of topographical features.

Figure 2 shows $6.4\ \mu\text{m} \times 6.4\ \mu\text{m}$ Pt 4f_{7/2} (raw data), K 2p_{3/2} (raw data), and topography corrected K 2p_{3/2} intensity maps taken as a function of V_{WR} . These maps correspond to the spectra shown in Figure 1a in that the former were taken from a microspot located at the center of each image. The Pt 4f_{7/2} maps show a bright feature that probably corresponds to a Pt crystallite, whereas the dark features are likely due to cracks or pores in the Pt surface or shadowing of Pt particles. These images show that (i) the Pt signal does not attenuate as K is electrochemically supplied to the platinum surface and (ii) there is a very small thermal drift over the time scale of the experiment. The K 2p_{3/2} maps show a mark increased in intensity as V_{WR} is decreased. Although the raw data suggest that potassium is not uniformly distributed on the Pt surface, these images contain intensity modulations because of topography. After correction, the images indicate that the alkali is relatively uniformly distributed on the Pt surface, with its concentration increasing with decreasing catalyst potential.

Our spectroscopic data show that Pt 4f intensity did not change as K was supplied to the surface (data not shown). Under our conditions ($h\nu = 490$ eV, Pt 4f emission kinetic energy = 420 eV) the sampling depth was ~ 1 nm, so that the absence of Pt 4f attenuation is consistent with low submonolayer coverage by K. These results demonstrate very clearly that changes in V_{WR} cause reversible changes in the average K concentration at the platinum surface. Accordingly, the V_{WR} -reversible changes in catalyst behavior to be described below may confidently be

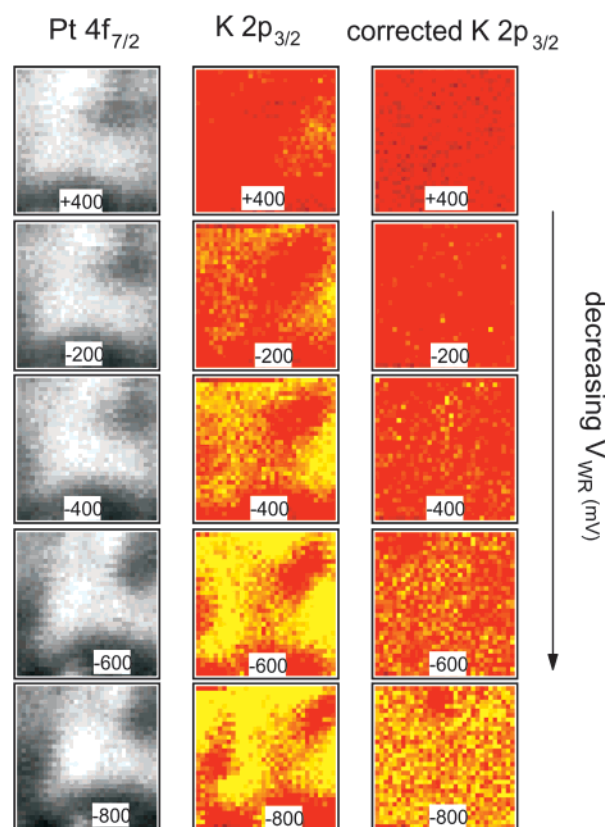


Figure 2. Pt 4f_{7/2} and K 2p_{3/2} photoelectron intensity maps as a function of V_{WR} at 473 K. Image size $6.4 \times 6.4\ \mu\text{m}^2$.

ascribed to the effect of potassium on the adsorbed species. Moreover, we see that the potassium is uniformly dispersed over the Pt surface with no particular tendency to accumulate at grain boundaries. Therefore, our interpretation of the catalytic data should take account of this feature also.

Reactor Studies. Before carrying out each experiment, the sample was cleaned in flowing oxygen (100 scc/m) at 620 K for 4 h followed by cooling to the temperature required for the performance of the experiment. Catalytic testing was carried out in the temperature range of 350–650 K, and the C₂H₂:H₂ partial pressure ratio was varied (at a constant total flow rate of 70 scc/m) from 1:2 to 1:20. Over this wide range of conditions, the system's behavior was qualitatively the same, and the only products observed were ethylene and ethane. Therefore, we show data only for the case of C₂H₂:H₂ = 1:20, though related results obtained under other conditions are also described.

Figure 3 shows the effect of catalyst potential, V_{WR} , on the conversion of acetylene to ethylene and ethane for C₂H₂:H₂ ratio of 1:20 at 430 K and atmospheric pressure. The total flow rate was 70 scc/m, and the gas composition was 3.5 kPa of C₂H₂, 70 kPa of H₂, with He as a makeup gas so as to achieve a constant total pressure of 1 atm. Conversion is defined as

$$\frac{\text{mol of C}_2 \text{ products formed}}{\text{mol of reactant consumed}} = \frac{P_{\text{C}_2\text{H}_4} + P_{\text{C}_2\text{H}_6}}{P_{\text{C}_2\text{H}_2} + P_{\text{C}_2\text{H}_4} + P_{\text{C}_2\text{H}_6}} \quad (2)$$

where the partial pressures refer to values at the reactor exit.

It is apparent that under these conditions the acetylene conversion fell from $\sim 60\%$ to $\sim 10\%$ as V_{WR} varied between +400 (alkali-free surface) and -400 mV (maximum achievable potassium coverage). Most importantly, this behavior was fully and repeatedly reversible with V_{WR} . This, in the light of the

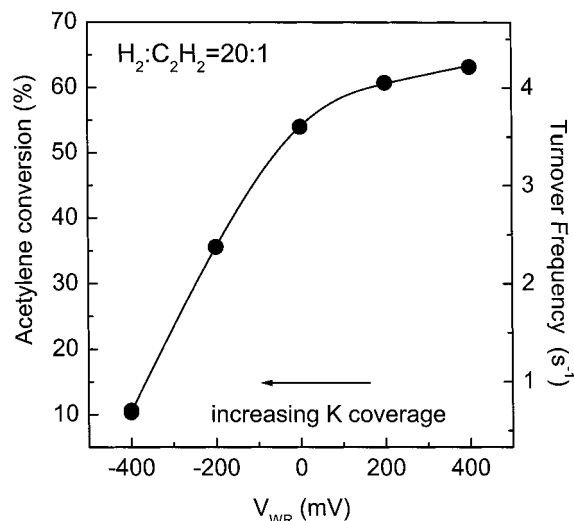


Figure 3. Acetylene conversion as a function of catalyst potential V_{WR} . Conditions: $T = 430$ K, $H_2:C_2H_2 = 20:1$, total flow rate = 70 scc/m.

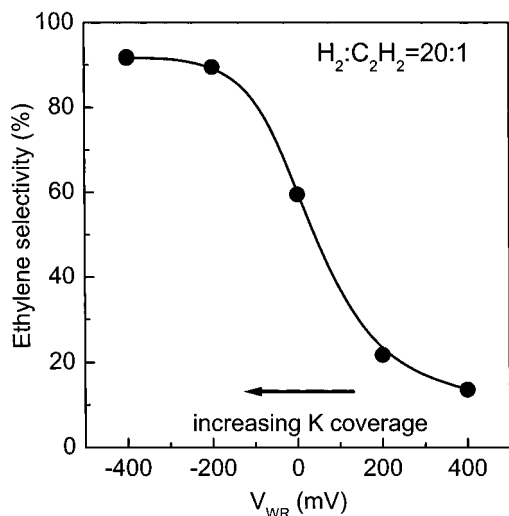


Figure 4. Selectivity toward ethylene formation as a function of catalyst potential V_{WR} . Conditions: $T = 430$ K, $H_2:C_2H_2 = 20:1$, total flow rate = 70 scc/m.

above XPS results, confirms that the observed modification of catalytic behavior may be confidently ascribed to the electrochemically controlled variation of a uniformly distributed potassium promoter phase. As already mentioned, our spectroscopic measurements show that the highest alkali coverage achieved is on the order of ~ 0.05 monolayers.¹⁹ Under more acetylene-rich conditions, C_2H_2 conversion decreased, as would be expected, but the qualitative behavior of the conversion/ V_{WR} curves was essentially the same, as was their reversibility.

Figure 4 shows the corresponding dependence on V_{WR} of the selectivity toward ethylene production for acetylene: $H_2 = 1:20$ at 430 K. The unpromoted catalyst exhibited very low selectivity ($\sim 10\%$). By intermediate catalyst potential ($V_{WR} \sim 0$ mV = intermediate K coverage), the selectivity had increased rather sharply to $\sim 60\%$. Finally, by $V_{WR} = -400$ mV, the ethylene selectivity reached $\sim 90\%$. Notice that, although K strongly enhances ethylene selectivity at the cost of overall conversion, at $\sim 80\%$ selectivity we still achieve $\sim 45\%$ acetylene conversion. Again, for more acetylene-rich compositions, the qualitative behavior was similar, although, as would be expected, the lower the H_2 partial pressure, the higher the initial "clean surface" selectivity. Thus, for $C_2H_2:H_2 = 1:10$ and $1:5$ the initial unpromoted selectivities were $\sim 25\%$ and $\sim 70\%$, respectively.

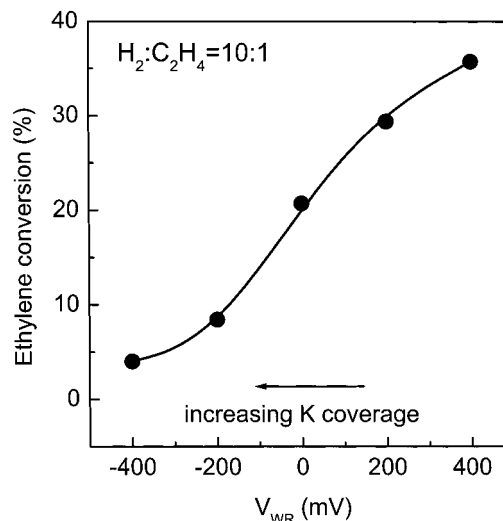


Figure 5. Ethylene hydrogenation to ethane as a function of catalyst potential V_{WR} . Conditions: $T = 430$ K, $H_2:C_2H_4 = 10:1$, total flow rate = 70 scc/m.

However, in every case, the maximum limiting selectivity achieved at -400 mV was 90%.

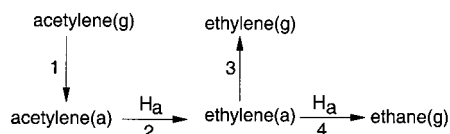
Note that although the ΔV_{WR} range was the same in the spectroscopic and reactor measurements, the measured V_{WR} values differ in the two cases. This offset is due to the effect of the gas atmosphere on the electrodes. It arises because (i) the Au reference electrode is really a pseudo-reference-electrode in that it is exposed to a different gas environment in the two cases and (ii) the absolute work function of the alkali-free Pt working electrode is different in the presence and absence of the reaction gas.

To further understand the reaction mechanism, a limited study of the effects of potassium on ethylene hydrogenation was carried out using the same temperature and flow rates as those employed for the acetylene experiments. Moreover, the regime of ethylene partial pressures explored encompassed those that occurred in the acetylene hydrogenation studies. Representative results (ethylene: $H_2 = 1:10$) are shown in Figure 5 ($P_{H_2} = 70$ kPa, $P_{C_2H_4} = 7$ kPa). For this partial pressure ratio, the ethylene conversion changed from $\sim 35\%$ to $\sim 5\%$ as potassium was pumped toward the Pt film. It is immediately clear that K strongly quenches the hydrogenation of ethylene to ethane, and as with acetylene hydrogenation, the V_{WR} dependence was reversible.

There is an extensive literature dealing with the spectroscopy of possible hydrocarbon species produced by ethylene and acetylene adsorption on platinum group metal surfaces and the possible interconversions between these species.²³⁻²⁶ Even in the case of unmodified Pt surfaces, significant unresolved disagreements persist.^{23,26} Nevertheless, we may propose a simple mechanism that may be used to rationalize our results and which takes account of relevant single-crystal data. For present purposes, the key issues concern the effects of alkali on the adsorption of reactants and reactant intermediates.

Our starting point is the observation that, under the conditions used for acetylene hydrogenation, K strongly suppresses ethylene hydrogenation. This suggests that ethylene, or some surface species derived from it, is the reaction intermediate in acetylene total hydrogenation to ethane. (A conceivable alternative mechanism could be a direct reaction, not involving further reaction of the half-hydrogenated species.) It is known that on Pt{111} alkalis significantly enhance the adsorption strength of hydrogen, possibly by formation of a surface alkali

hydride.^{27–29} It is also known from HREELS, UPS, and XPS that on Pt{111} alkalis convert strongly adsorbed di- σ -bonded ethylene to more weakly adsorbed π -bonded ethylene.^{30,31} Furthermore, most recently, we have shown that on Pt{111} K acts to reduce the chemisorption strength of ethylene.²⁹ The following simple scheme is consistent with this information and with our present findings.



There are two important K-induced effects. In regard to ethane production, they work in the same direction, so formation of this product is drastically quenched. In the case of ethylene formation, they work in opposite directions, thus enhancing selectivity toward ethylene formation, but at the expense of acetylene conversion. Specifically, because of weakened Pt–C₂H₄ bonding, K should favor ethylene desorption (3) at the expense of further hydrogenation to ethane (4). This should enhance selectivity toward partial hydrogenation. Moreover, as noted above, K also acts to enhance the adsorption strength of hydrogen. This effect should tend to reduce the rate of reaction 4, either by increasing the associated activation energy, decreasing the concentration of “free” H_a, or both. Both effects of K operate in the same direction, so ethylene hydrogenation is very strongly suppressed and partial hydrogenation selectivity strongly promoted. Of course, the effect of K on H_a should also result in inhibition of reaction 2, in accord with the observed decrease in conversion. Thus, we may understand why potassium decreases overall acetylene conversion while at the same time strongly promoting ethylene selectivity.

Given our earlier results,¹⁰ it is of interest to enquire whether K and Na differ significantly in their effectiveness as selective hydrogenation promoters. A comparison of the present results with those obtained under the same conditions, but involving EP by Na, enables us to make a qualitative evaluation. This shows that over similar ranges of catalyst potential the two alkalis cause comparable changes in conversion and selectivity, although the maximum selectivity achieved with Na was 80% rather than 90%. Although it is reasonable to suppose that the V_{WR} /coverage relationship is similar for Na and K¹⁹ on Pt, it is unlikely that identical changes in catalyst potential result in identical changes in alkali coverage. Therefore, our conclusion is that there is no very great difference between these two alkalis in regard to promoter efficiency.

A final point concerns the chemical state of the K promoter under reaction conditions. Clearly, it cannot be present as metallic potassium. One would expect it to be present as an alkali compound or compounds whose identities are determined by the temperature and composition of the gas phase, just as with any conventional catalyst. Indeed, postreaction XPS and XANES analysis of Pt catalysts undergoing EP by Na for (i) the NO + propene reaction¹⁴ and (ii) the O₂ + propene reaction³² demonstrated unambiguously the presence of alkali nitrate and carbonate, respectively, at the Pt surface. In the present case, possible alkali promoter phases include surface hydrides or acetylides of potassium.

Conclusions

1. Potassium, pumped from the electro-active support K β'' -alumina, spills over to the surface of an overlying platinum film

where it strongly promotes selectivity toward the partial hydrogenation of acetylene.

2. These submonolayer amounts of K are uniformly distributed on the Pt surface, and the alkali transport and catalytic phenomena are fully reversible as a function of catalyst potential.

3. Ethylene, or a surface species derived from it, is a key intermediate in the total hydrogenation of acetylene to ethane.

4. Promotion of selective hydrogenation by potassium may be rationalized in terms of K-induced weakening and strengthening respectively of ethylene and hydrogen adsorption. Comparison with earlier results indicates that the associated electronic effects are relatively insensitive to the chemical identity of the alkali.

Acknowledgment. Financial support from the U.K. Engineering and Physical Sciences Research Council under Grant GR/M76706 is gratefully acknowledged. We thank Johnson Matthey plc for a loan of precious metals. F.J.W. acknowledges the award of a Cambridge University Oppenheimer Fellowship.

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