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# In Situ Control of the Composition and Performance of a Bimetallic Alloy Catalyst: The Selective Hydrogenation of Acetylene over Pt/Pb

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The application of a  $\text{Pb}^{2+}$  conducting solid electrolyte ( $\text{Pb-}\beta''$  alumina) to electrochemical control of catalyst performance is reported. XPS data show that pumping of Pb to/from a thin film platinum catalyst from/to the solid electrolyte provides a controlled, reversible, and reproducible way of altering the surface composition of the resulting Pt/Pb surface alloy under conditions of acetylene hydrogenation. With increasing Pb concentration a large increase in partial hydrogenation selectivity occurs from 20% (pure Pt surface) to 85% ( $\sim 26\%$  Pb surface alloy). The results demonstrate that the surface composition and catalytic performance of bimetallic alloy catalysts can be dramatically and reversibly altered under working conditions by electrochemical means.

## Introduction

The phenomenon of electrochemical promotion (EP) has been successfully applied to a variety of catalytic systems, including reactions taking place in solution. The technique 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. The resulting changes in electronic and other properties of the catalyst surface alter the adsorption enthalpies of adsorbed species and the activation energies of reactions involving these species: these effects can strongly and beneficially modify catalyst performance. It is generally found that electrochemically induced changes in catalyst activity and selectivity are reversible with catalyst potential ( $V_{\text{WR}}$ ) measured with respect to a reference electrode. Thus EP provides an effective and controllable method for the in situ tuning of working catalytic systems.

The EP effect has been observed with both anionic and cationic conductors, which variously transport oxygen,<sup>1</sup> alkali,<sup>2</sup> fluorine,<sup>3</sup> and hydrogen ions.<sup>4</sup> In the case of oxygen<sup>5–8</sup> and alkali<sup>9–11</sup> ion conductors XPS, UPS, and STM studies have played a crucial role in illuminating the underlying phenomena. Comprehensive recent reviews are available that address these two cases ( $\text{O}^{2-}$ ,<sup>12,13</sup> and alkali ion conductors<sup>13,14</sup>). In every case investigated thus far the electrochemically supplied promoter species is to be thought of as adsorbed at the surface of the particular metal catalyst under investigation. Under reaction conditions, the chemical state of the promoter is determined by its equilibration with the reactive gas atmosphere. Thus in the case of EP by Na or K of the Pt-catalyzed reduction of NO, post-reaction XPS<sup>15</sup> and XANES<sup>16</sup> studies show that, depending on the composition of the gas phase, the alkali is present as nitrate, nitrite, carbonate, or hydroxide.

Here we report a significant extension of the EP technique that offers the possibility of broadening its application to new areas of heterogeneous catalysis: in situ control of the composition of a surface alloy under reaction conditions. The importance of catalysis by alloys from both academic<sup>17</sup> and industrial<sup>18</sup>

perspectives is well established. The present advance is based on the use of a solid electrolyte that transports Pb to/from the catalytically active metal surface. XPS has been used to demonstrate the reversible accumulation/depletion of metallic lead in the surface region of a Pt film catalyst used for the selective hydrogenation of acetylene. This test reaction was chosen because pure Pt exhibits very poor selectivity toward ethylene formation,<sup>19</sup> probably the result of its overly strong interaction with adsorbed acetylene.<sup>20–23</sup> As we shall see, electro-pumped Pb greatly improves selectivity toward partial hydrogenation.

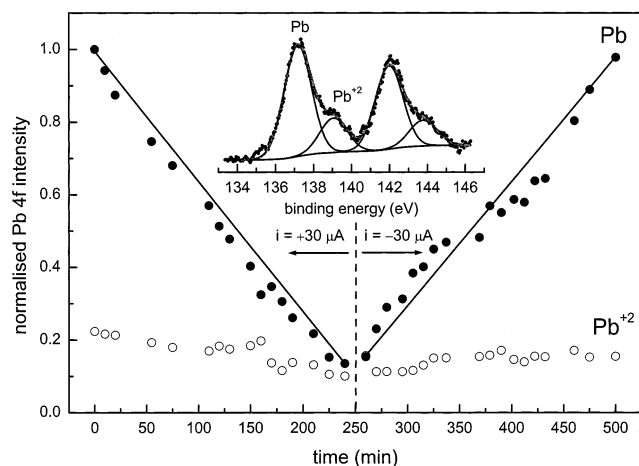
## Experimental Methods

The  $\text{Pb-}\beta''$  alumina was prepared by repeated molten salt ion exchange of a wafer of  $\text{Na-}\beta''$  alumina following the procedure described by Petric et al.<sup>24</sup> Gravimetric and EDX measurements indicated that the degree of Pb for Na exchange was  $>99.7\%$ . The methods used for (i) depositing the electrodes on the solid electrolyte wafer, (ii) sample mounting, (iii) metal surface area measurement, and (iv) catalytic testing have been described in detail elsewhere.<sup>15</sup> In the present case, the estimated surface area of the Pt film was  $\sim 100 \text{ cm}^2$ .

Inlet and exit gas analysis was carried out by on-line gas chromatography (SHIMADZU-14B; Haysep N column). The reactant gases consisted of pure hydrogen and pure acetylene (Distillers MG) diluted in ultrapure He (99.996%) and were fed to the well-mixed reactor by mass-flow controllers (Brooks 5850 TR). The total flow rate was kept constant in all experiments at  $1.023 \times 10^{-4} \text{ mol s}^{-1}$  ( $150 \text{ cm}^3 \text{ STP/min}$ ), with partial pressures  $P(\text{C}_2\text{H}_2) = 6 \text{ kPa}$  and  $P(\text{H}_2) = 60 \text{ kPa}$ . A  $\text{C}_2\text{H}_2/\text{H}_2 = 1:10$  ratio was used in order to minimize carbon deposition.

XPS measurements were carried out in a VG ADES 400 UHV spectrometer system. The EP sample was mounted on a machined ceramic block resistively heated by embedded, electrically insulated tungsten filaments. XP spectra were acquired with  $\text{MgK}_\alpha$  radiation with the Pt catalyst electrode always at ground potential; appropriate electrochemical potentials were imposed between the Pt working electrode and the Au counter electrode by applying voltage bias to the latter. The

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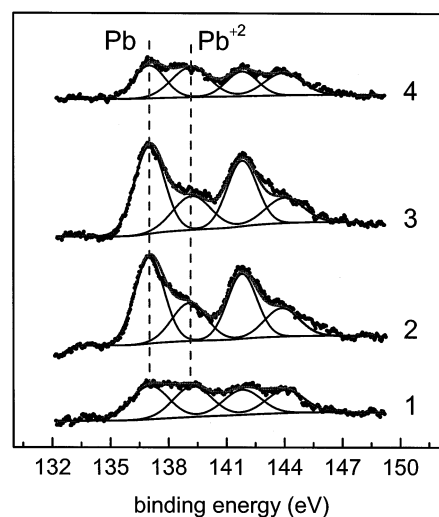
**Figure 1.** Integrated intensities of the Pb and Pb<sup>2+</sup> components corresponding to the data presented in Figure 1 as a function of time. The inset shows that the Pb 4f XP spectra are composed of two doublets with the following Pb 4f<sub>7/2</sub> binding energies (BE) values: 137.1 and ~139 eV

potential ( $V_{WR}$ ) of the Pt working electrode with respect to the Au reference electrode was also monitored. Quoted binding energies are referred to the Au 4f<sub>7/2</sub> emission at 84 eV, the Au reference spectra being conveniently obtained from the Au wire that formed the electrical connection to the working electrode.

## Results and Discussion

**X-ray Photoelectron Spectroscopy.** At 573 K, the Pt film was supplied galvanostatically with a measured dose of Pb such that the XP spectrum indicated comparable amounts of Pt and Pb within the sampling depth (~5 nm). The fact that this state could be attained shows that the Pb formed at the electrode/electrolyte boundary ( $\text{Pb}^{2+} + 2e^- \rightarrow \text{Pb}$ ) does indeed spill over onto the gas-exposed surface of the Pt film. Then, the Pb was galvanostatically electro-pumped away from the Pt by applying a constant positive current (+30  $\mu\text{A}$ ), while repeatedly recording the Pb 4f emission. The raw data (not shown) clearly demonstrate that applied positive current leads to a progressive decrease in the amount of Pb at the Pt surface. After an elapsed time of 250 min, the direction of the current was reversed (−30  $\mu\text{A}$ ) so as to pass an equal amount of charge in the opposite direction. If the system were well-behaved, this procedure should correspond to pumping Pb toward the catalyst surface, so as to restore the initial condition. Again, the raw spectral data (not shown) bear out this expectation, demonstrating that electro-pumping provides a reversible, reproducible, and controllable means of altering the Pt/Pb composition at the surface of the catalyst. As we shall see, this reversibility and reproducibility are in good accord with the reversible and reproducible catalytic response observed under reaction conditions at atmospheric pressure. Under open circuit conditions the amount of Pb at the surface remains constant, so in this sense the promotion is permanent, as indeed it also is when alkalis are supplied electrochemically to such metal film catalysts.<sup>13</sup> The precise location of the Pb relative to the Pt surface (overlayer versus alloy) will be considered below.

We now give a quantitative analysis of the Pb 4f XP spectra which leads to significant conclusions. The observed 4f doublet is composed of two components corresponding to 4f<sub>7/2</sub> binding energies (BEs) of 137.1 and ~139 eV (Figure 1, inset). The lower BE component is due to metallic Pb present at the Pt surface, whereas the higher BE component is due to Pb<sup>2+</sup> present in the solid electrolyte, visible through cracks and pores in the



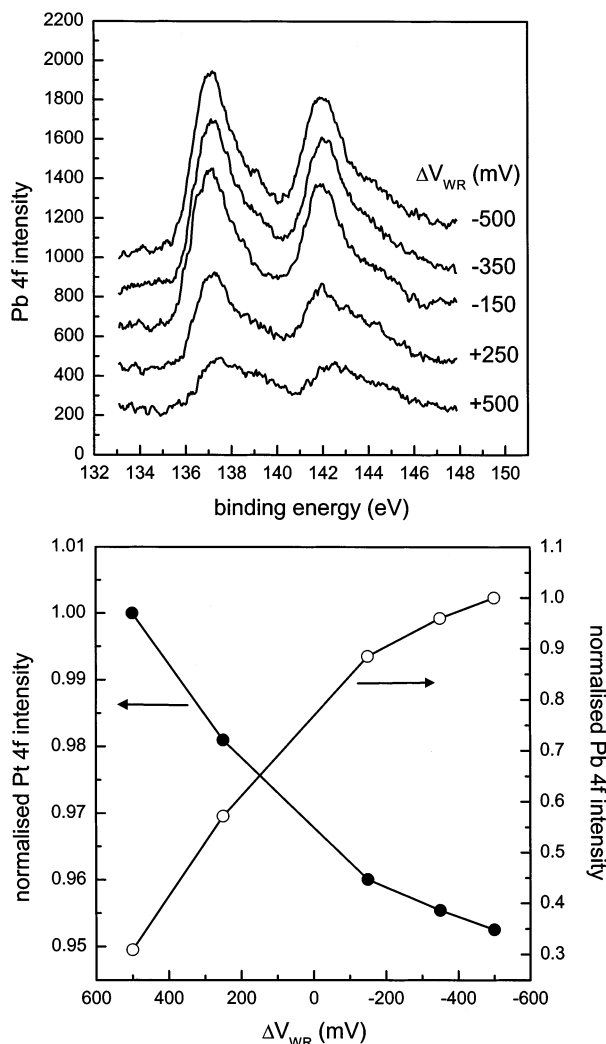
**Figure 2.** Pb 4f XPS spectra obtained under different conditions: (1) after electrochemically pumping Pb away from the Pt film; (2) after vacuum deposition of Pb from a Pb evaporation source at room temperature; (3) after heating the sample at 433 K; and (4) after electrochemically pumping Pb away from the Pt film.

Pt metal film.<sup>9,10</sup> The main body of Figure 1 shows the time-dependence of the integrated intensities of these two components, extracted from the raw data mentioned above. It is clear that the amount of Pb within the XPS sampling depth decreases/increases linearly with time under galvanostatic pumping, depending on the direction of the current. This establishes that Pb transport from/to the catalysts surface is indeed proportional to the amount of charge passed. In complete contrast, the intensity due to the Pb<sup>2+</sup> component arising from the solid electrolyte remains essentially constant with time, thus confirming our spectral assignments.

Figure 2 depicts the results obtained in control experiments designed to confirm that the system does in fact function as we propose. Spectrum 1 shows the initial condition in which a relatively small amount of Pb was present on the catalyst. Spectrum 2 was obtained after vacuum deposition of Pb from a collimated evaporation source onto the Pt film at room temperature. It is apparent that the amounts of electrochemically supplied and vacuum-deposited Pb were comparable. Spectrum 3 was obtained after heating the sample to 433 K (reaction temperature, see below); this resulted in no significant change. Finally, spectrum 4 was obtained after electrochemically pumping Pb<sup>2+</sup> away from the Pt film. Overall, the results shown in Figure 2 demonstrate that (i) electro-pumped Pb is identical in behavior and in its chemical state with Pb supplied by vacuum deposition, and (ii) vacuum-deposited Pb is pumped away in exactly the same way as electrochemically supplied Pb.

The XPS data also enable us to address issues of relevance to the interpretation of the catalytic data presented below, namely (i) whether we are dealing with a Pb overlayer or a Pb/Pt surface alloy, and (ii) the surface composition.

That Pb<sup>2+</sup> is the only mobile ionic species present in the solid electrolyte is corroborated by the complete absence of Na 1s emission in the all XPS data. (Recall that the degree of Pb for Na exchange resulting from the preparation procedure was >99.7%). This implies that a dose of −30  $\mu\text{A}$  for 250 min (Figure 1) corresponds to a surface coverage of 9.3 ML, where for convenience 1 ML is defined as one Pb atom per surface Pt atom. Such a multilayer Pb film would result in 82% attenuation of the Pt 4f XP intensity (inelastic mean free path ~2 nm for 1181 eV photoelectrons). However, the observed attenuation

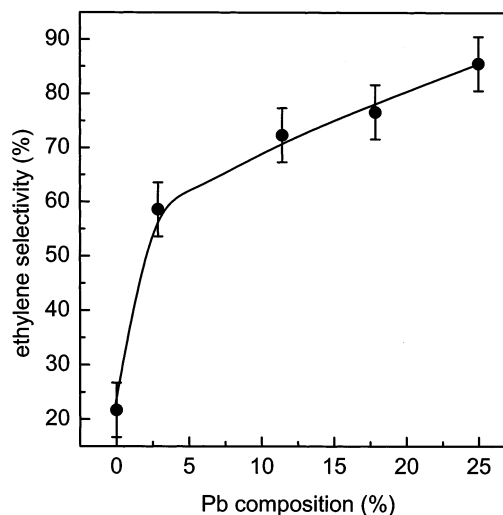


**Figure 3.** (a) Pb 4f XPS spectra as a function of decreasing the catalyst potential at  $T = 433$  K. (b) Integrated intensities of the Pb 4f and Pt 4f signals as a function of changes in catalyst potential at  $T = 433$  K.

was only  $\sim 5\%$ . The implication is that during electro-pumping the Pb is incorporated as a surface alloy whose thickness increases with Pb dosage.

This conclusion depends on there being no significant desorption of Pb from the sample during electro-pumping at 573 K. That this is indeed the case is suggested by temperature-programmed desorption data for Pb on polycrystalline Pt which show that Pb multilayer desorption is negligible below  $\sim 600$  K with Pb monolayer desorption occurring at  $\sim 1100$  K.<sup>25</sup> Nevertheless, to check on the possibility of Pb desorption at 573 K, experiments were carried out at 433 K at which temperature Pb desorption is certainly negligible (see Figure 2). Figure 3a shows the effect on the Pb 4f XP spectrum of potentiostatically supplying Pb at 433 K, and Figure 3b shows the integrated intensities of the Pb 4f and Pt 4f signals derived from the same experiment. It is evident that the Pb intensity increased by 70% while the Pt intensity was attenuated by  $\sim 5\%$ , comparable to the behavior found at 573 K (Figure 1). In passing, we note that there were no detectable shifts in the Pt BE. The total charge passed during these measurements corresponds to the supply of  $\sim 8.7$  ML Pb which is comparable to the amount of Pb supplied at 573 K (Figure 1), further confirming that evaporation of Pb was negligible at 573 K.

An estimate of the composition of the Pb/Pt alloy film may be obtained from the ratio of the integrated Pt and Pb XP



**Figure 4.** Ethylene selectivity as a function of the Pb/Pt alloy composition. Conditions:  $T = 433$  K;  $H_2/C_2H_2 = 10:1$ .

intensities, allowance being made for photo-ionization cross sections.<sup>26</sup> Within the approximation that the surface alloy composition is constant within the sampling depth, the maximum Pb concentration shown in Figure 1 corresponds to  $\sim 26\%$  Pb.

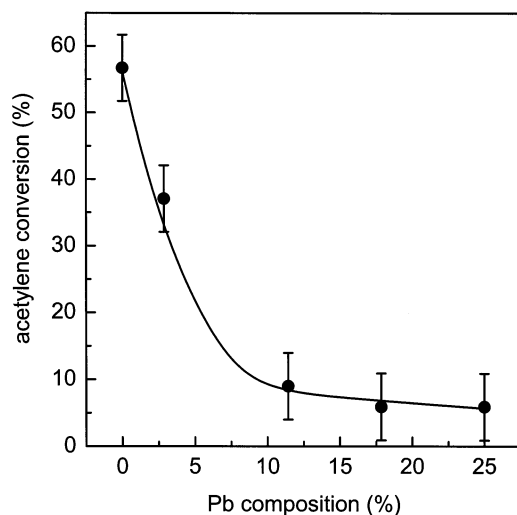
Our conclusion that Pt/Pb surface alloys are formed under our conditions is strongly corroborated by surface science studies of the adsorption of lead on polycrystalline platinum<sup>25</sup> and on Pt(111).<sup>27</sup> These show that intermixing of Pb and Pt occurs even at low temperatures. For example, Mazina-Ngokoudi and Argile<sup>27</sup> found that on Pt(111) intermixing with Pb occurred at temperatures as low as 180 K. The observed absence of detectable Pt 4f BE shifts is consistent with alloy formation. Thus in the closely related Pt(111)/Sn system where alloy formation was unequivocally established by STM and LEISS, there were again no detectable Pt BE shifts.<sup>28</sup>

In summary, Pb may be electrochemically delivered to or removed from the surface of a Pt thin film catalyst where it forms surface alloys in a reversible and reproducible manner. The alloy composition may be readily controlled in the range 0 to  $\sim 26\%$  Pb and the electro-pumped Pb is identical in both behavior and chemical state with Pb supplied by vacuum deposition.

**Reactor Measurements.** Catalytic testing was carried out using the conditions detailed in the Experimental Methods section. The only products ever observed were ethylene and ethane, the mass balance always closing within 2%. The effect of electro-pumped Pb on the activity and selectivity of the platinum catalyst was investigated as follows. After characterizing the catalytic performance of the pure Pt film at 433 K, the temperature was increased to 573 K in a helium atmosphere and a controlled amount of Pb was delivered to the catalyst under galvanostatic conditions. Then, after cooling in He to 433 K, the feed gas was switched to the acetylene/ $H_2$ /He mix and the catalyst performance was measured again. This procedure was adopted because although Pb pumping was possible at 433 K (reaction temperature), it was much quicker at 573 K.

The ethylene selectivity results are illustrated in Figure 4 where the error bars are obtained from repeat experiments involving successively either supplying or removing Pb between one measurement and the next: this also provides a strong check on the system's reversibility. The maximum lead concentration corresponded to  $\sim 25\%$  Pb. The Pb/Pt alloy composition was estimated by using the relationship between the known amount of Pb supplied electrochemically (from the total charge passed





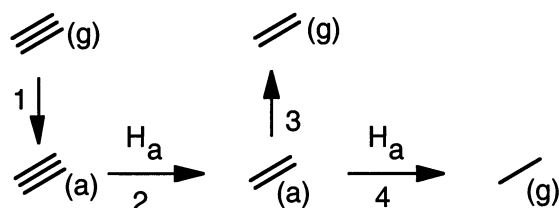
**Figure 5.** Acetylene conversion as a function of the Pb/Pt alloy composition. Conditions:  $T = 433\text{ K}$ ;  $\text{H}_2/\text{C}_2\text{H}_2 = 10:1$ .

through the cell) and the composition of the alloy film as determined by XPS and discussed above. It can be seen that the Pb-free catalyst exhibited very low selectivity toward ethylene formation ( $\sim 20\%$ ), as would be expected.<sup>19</sup> However the addition of only  $\sim 5\%$  Pb resulted in a large selectivity enhancement to  $\sim 60\%$ . This was followed by a slower rise in partial hydrogenation selectivity to a maximum value of  $\sim 85\%$ . Given the mode of data acquisition, Figure 4 also shows that the system does indeed behave reversibly under steady-state reaction conditions, in accord with the XPS data obtained under vacuum conditions.

Figure 5 shows the corresponding results for acetylene conversion. Interestingly, the pronounced drop in conversion occurs over the same range of composition as does the sharp rise in selectivity. Although selectivity enhancement is achieved at the expense of conversion, a common observation, note that  $\sim 60\%$  ethylene selectivity is achieved at 35% acetylene conversion, despite the very small active metal area compared to conventional dispersed catalysts.

Whether the actual composition of the bimetallic catalyst is closely approximated by the estimated surface composition depends on the validity of the assumption of constant alloy composition as a function of depth. Given the lower surface free energy of Pb compared to that of Pt,<sup>29</sup> it is possible that the actual surface composition is more Pb-rich than the estimates provided here. Further investigation is required in order to clarify this point. Whatever the case, the important point is that EP can be used for in situ control of the surface composition of a bimetallic alloy catalyst under reaction conditions, resulting in very large changes in catalyst performance.

A simple and plausible reaction scheme within which the present results may be understood is



The pronounced Pb-induced selectivity enhancement probably reflects a combination of electronic and ensemble effects that act to weaken the bonding of ethylene, thus favoring its

desorption (reaction 3) over further hydrogenation to ethane (reaction 4). This hypothesis receives support from UHV studies carried out on the analogous Pt(111)/Sn system<sup>25</sup> for which it was found that Sn acts to switch on acetylene trimerisation, a reaction that proceeds efficiently on pure Pd<sup>31</sup> but not at all on pure Pt. A similar effect is found here: under hydrogenation conditions, alloying with Pb causes Pt to behave like Pd due to weakened metal–hydrocarbon interaction. Since the presence of Pb also weakens the adsorption of acetylene, thus reducing its surface lifetime and reaction probability (reaction 2), the decrease in acetylene conversion that accompanies the increase in ethylene selectivity is understandable. It should, however, be noted that since consecutive reactions are involved here, a more rigorous test of these mechanistic proposals would call for measurements to be made at constant conversion for a series of different Pt/Pb surface compositions. Alternatively and more elegantly, one could investigate systems in which selectivity is determined by the competition between concurrent reactions. Such measurements are in progress.

## Conclusions

The surface composition of Pt thin film catalysts interfaced with Pb- $\beta''$  alumina can be electrochemically controlled, reversibly and reproducibly. This electro-pumped Pb is identical in its properties with Pb deposited by vacuum evaporation. Under our conditions the Pb spilt over at the electrode/solid electrolyte interface forms bimetallic Pt/Pb surface alloys whose composition may be varied at will. Application of EP by means of a Pb solid electrolyte permits in situ control of the performance of Pt/Pb bimetallic catalysts. Changes in surface composition of the bimetallic catalyst correlate with marked changes in performance: enrichment with Pb strongly enhances selectivity toward selective hydrogenation of acetylene.

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