

PRIORITY COMMUNICATION

First Demonstration of *in Situ* Electrochemical Control of the Composition and Performance of an Alloy Catalyst during Reaction

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Interfacing a Pb^{2+} conducting solid electrolyte with a thin-film Pt catalyst permits *in situ* electrochemical control of surface composition and catalytic performance of the resulting bimetallic catalyst. Transport of Pb between the solid electrolyte and the Pt film provides a controlled, reversible, and reproducible way of altering the surface composition of the Pt/Pb-alloy surface. Large increases in acetylene partial hydrogenation selectivity may thus be achieved from 20% with pure Pt to 85% with a $\sim 26\%$ Pb-alloy surface. This is the first demonstration that the surface composition and catalytic performance of bimetallic-alloy catalysts can be electrochemically controlled under working conditions. © 2002 Elsevier Science (USA)

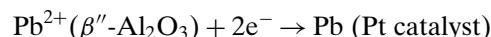
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INTRODUCTION

Electrochemical promotion (EP) may be used as a highly effective means of controlling the performance of working catalysts. Ions are pumped from a solid electrolyte to the surface of a porous, catalytically active metal film, which is in contact with the electrolyte. The resulting changes in catalyst surface properties can strongly and beneficially modify catalyst performance; comprehensive reviews of the phenomenology and underlying theory are available (1–3). In every case investigated thus far the promoter that is supplied to the metal surface corresponds to an adsorbed species derived from the electrochemically transported ion, for example, O_a in the case of O^{2-} -conducting solid electrolytes (1) and alkali surface compounds (4, 5) in the case of Na^+ - and K^+ -conducting electrolytes.

Here we report a significant extension of the technique. For the first time, EP was used to reversibly and reproducibly control the composition and, hence, the catalytic

performance of a *bimetallic surface alloy* tested for the partial hydrogenation of acetylene to ethylene. The solid electrolyte $\text{Pb } \beta''$ -alumina (a Pb^{2+} conductor) was synthesised and used to deliver/abstract metallic lead to/from the active surface of a platinum film while changes in catalytic performance were monitored. Thus, when a cathodic current flows between electrolyte and the Pt film the following reaction occurs:



Pb ions are discharged at the electrode/electrolyte boundary where they form Pb atoms which subsequently diffuse to the gas-exposed surface of the porous Pt film. As we shall see, XPS shows that this results in formation of a surface alloy. The implications of this advance in the EP technique are significant, given the importance of catalysis by alloys in both the academic (6) and industrial (7) arenas. We chose acetylene partial hydrogenation as the test reaction precisely because pure Pt exhibits very poor selectivity toward ethylene formation (8), probably the result of its overly strong interaction with adsorbed acetylene (9–12).

EXPERIMENTAL METHODS

Preparation of Pb- β'' -Alumina

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.* (13). 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 are described in detail elsewhere (4). In the current case, the estimated surface area of the Pt film was $\sim 100 \text{ cm}^2$. Inlet and exit gas analysis was carried out by online gas chromatography (SHIMADZU-14B; Haysep N column). The reactant gases consisted of pure hydrogen and pure acetylene (Distillers MG) diluted in ultrapure He

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(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 1.023×10^{-4} mol sec $^{-1}$ (150 cm 3 STP/m), with partial pressures $P(\text{C}_2\text{H}_2) = 6$ kPa and $P(\text{H}_2) = 60$ kPa. A $\text{C}_2\text{H}_2 : \text{H}_2 = 1 : 10$ ratio was used 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 counterelectrode by applying voltage bias to the latter. The 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 $4f_{7/2}$ emission at 84 eV; the Au reference spectra conveniently was obtained from the Au wire that formed the electrical connection to the working electrode.

RESULTS

X-ray Photoelectron Spectroscopy

First, the Pt film was supplied galvanostatically with a measured dose of Pb at 573 K until the XP spectrum indicated the presence of comparable amounts of Pt and Pb within the spectroscopic sampling depth (~ 5 nm). Then, this Pb was progressively electropumped away from the catalyst surface by applying a constant positive current ($+30 \mu\text{A}$), while repeatedly recording the Pb 4f emission. The resulting data are shown in the top panel of Fig. 1 from which it is clear that applied current did indeed induce a progressive decrease in the amount of Pb contained in the surface region of the catalyst. The measured change in catalyst potential over this interval was from ~ -500 to $+500$ mV. After 250 min, the current direction was reversed ($-30 \mu\text{A}$) to pass an equal amount of charge in the opposite direction; the corresponding XP spectra are shown in the bottom panel of Fig. 1. It can be seen that the system was well-behaved in that the initial condition was restored. The precise location of the Pb relative to the Pt surface (overlayer versus alloy) will be considered in the following. The Pt 4f spectra were also monitored, but were not especially informative. No binding energy shifts were observed as a function of composition, which in such systems is nevertheless compatible with alloy formation (14). The attenuation of the Pt signal at the highest Pb loading was $\sim 5\%$; the interpretation of this figure is model-dependent, as explained in the following.

Reactor Measurements

Starting with the pure Pt film, the effect of Pb concentration on catalyst performance at 433 K was investigated

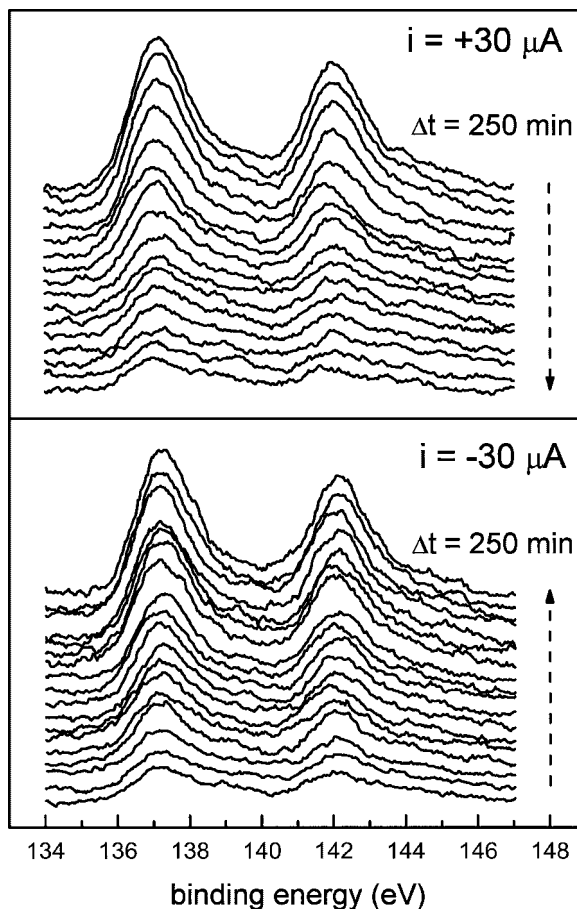


FIG. 1. Pb 4f XP spectra obtained at 573 K as a function of time. The top panel shows the effect of applying positive currents ($+30 \mu\text{A}$), whereas the bottom panel shows the effect of applying negative currents ($-30 \mu\text{A}$).

by measuring the reactor output under the conditions described in the Experimental Methods section. Controlled amounts of Pb were then electropumped to/from the catalyst under galvanostatic conditions in He at 573 K. The feed gas was switched to the acetylene/ H_2 /He mix and the catalyst performance was measured at 433 K; the process was repeated for different amounts of Pb supplied. As a strong check on the system's behaviour, the various data points in Fig. 2 were obtained by successively either supplying or removing Pb between one measurement and the next. The order in which these data were acquired is given in Fig. 2, which shows the dependence of ethylene selectivity and acetylene conversion on Pb loading; point 1 was acquired first; point 14 last. The only products ever observed were ethylene and ethane, with the mass balance always closing within 2%.

It is apparent that the Pb-free catalyst exhibited very low selectivity toward ethylene formation ($\sim 20\%$), as would be expected (8). However, the addition of only $\sim 5\%$ Pb (see the following text for quantification) produced a large

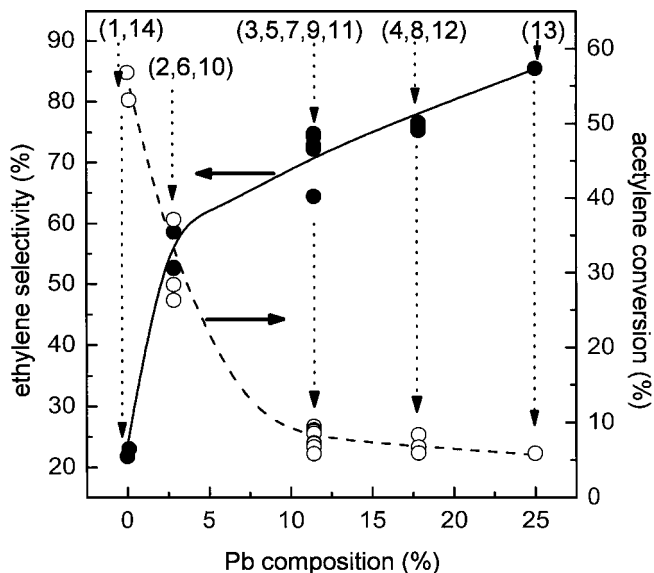


FIG. 2. Ethylene selectivity and acetylene conversion as a function of the Pb/Pt-alloy composition. Conditions: 433 K, $H_2 : C_2H_2 = 10 : 1$. Numbers refer to the order in which the data were taken (see text).

selectivity enhancement to $\sim 60\%$. This was followed by a slower rise in partial hydrogenation selectivity to a maximum value of $\sim 85\%$. Selectivity enhancement was accompanied by a decrease in reactant conversion, a common observation; even so, $\sim 60\%$ ethylene selectivity was achieved at 35% acetylene conversion. It is of course of interest to compare these conversion/selectivity data with those obtained from the pure-Pt film; these measurements are in progress.

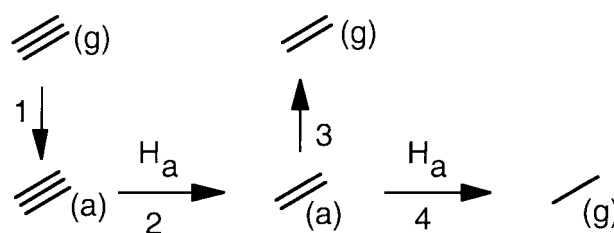
DISCUSSION

The XPS results show that electropumping provides a reversible, reproducible, and controllable means of altering the Pt/Pb composition at the surface of the catalyst (Fig. 1). Furthermore, this reversibility and reproducibility are in good accord with the reversible and reproducible catalytic response observed under reaction conditions at atmospheric pressure (Fig. 2). It is evident that the amount of Pb within the XPS sampling depth decreases/increases progressively with time under galvanostatic pumping, demonstrating that Pb transport from/to the catalysts' surface is indeed proportional to the amount of charge passed. However, questions remain in regard to whether we are dealing with (i) a Pb overlayer or a Pb/Pt surface alloy and (ii) the actual surface composition in any given case. We may address these issues as follows. A Pb dose of $-30 \mu A$ for 250 min (Fig. 1) is equivalent to a coverage of ~ 9.3 Pb monolayers (ML) where 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 was only $\sim 5\%$. The implication is that during electropumping the Pb is incorporated as a surface alloy whose thickness increases with Pb dosage. This conclusion depends on the condition of no significant desorption of Pb from the sample during electropumping and subsequent reaction measurements. 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 ~ 600 K with Pb monolayer desorption occurring at ~ 1100 K (15). The inference 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 (15) and on Pt(111) (16). These studies showed that surface intermixing of Pb and Pt occurs at temperatures as low as 180 K (16). An estimate of the composition of the Pb/Pt-alloy film in any given case may be obtained from the ratio of the integrated Pt and Pb XP intensities, with allowance made for photoionisation cross sections (17). If we assume that the surface alloy composition is constant within the XPS sampling depth, the maximum Pb concentration shown in Fig. 1 corresponds to a surface alloy consisting of $\sim 26\%$ Pb.

A simple and plausible reaction scheme that describes the reactor data is shown (Scheme 1). Pb-induced selectivity enhancement is probably due to a combination of electronic and ensemble effects that act to weaken the bonding of ethylene, thus favouring its desorption (Scheme 1, reaction 3) over further hydrogenation to ethane (Scheme 1, reaction 4). That is, 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 (Scheme 1, reaction 2), the decrease in acetylene conversion that accompanies the increase in ethylene selectivity is also understandable.

In conclusion, the surface composition of Pt/Pb surface alloy thin-film catalysts interfaced with Pb- β'' -alumina can be electrochemically controlled *in situ*, reversibly and reproducibly. Changes in surface composition of the bimetallic catalyst correlate with marked changes in performance. Surface enrichment with Pb strongly enhances selectivity toward selective hydrogenation of acetylene, a result which may be understood in terms of a simple reaction scheme. A



SCHEME 1

significant extension of the EP method was achieved. Further work is in progress to examine this interesting system in more detail.

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