Successful application of electrochemical promotion to the design of effective conventional catalyst formulations

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Abstract

Electrochemical promotion (EP), discovered and developed by Vayenas and co-workers provides a novel in situ reversible and highly controllable means of catalyst promotion. We found that Pt-group metal catalysts exhibit strong EP by sodium during reactions related to emission control catalysis, such as NO reduction by hydrocarbons. Close similarities are found between the performance of Pt-film catalyst promoted electrochemically with Pt highly dispersed on large surface area carriers (e.g. γ-Al$_2$O$_3$) promoted by conventional means (impregnation). These similarities include (i) the overall kinetic behaviour and (ii) the dependence of the activity and selectivity on Na loading. Using both methods of Na-promotion, the catalytic reduction of NO by propene over Pt exhibited rate enhancements as high as *two orders of magnitude* accompanied by very pronounced increases of the system selectivity towards N$_2$. The results serve to validate further the interpretation offered for the EP (or NEMCA) phenomenon. More importantly, they demonstrate that the insight obtained from EP studies can be used to design conventional type effective catalyst formulations that were previously untried, thus opening up new areas for investigation in the frontiers between catalysis and electrochemistry.   © 2000 Elsevier Science B.V. All rights reserved.

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Materials: C$_3$H$_6$; NO; Pt; Au; β''-Al$_2$O$_3$; γ-Al$_2$O$_3$; H$_2$PtCl$_6$; NaNO$_3$

1. Introduction

Heterogeneous catalysis has played and will continue to play a major role in pollution control. It provides best solution for reduction of NO$_x$ and oxidation of VOCs produced by mobile and stationary combustion processes [1,2]. Currently, 'three-way' catalytic converters (TWCs) are used for the simultaneous removal of all three main pollutants (NO$_x$, CO and hydrocarbons) from automotive emissions [2]. These use formulations based variously on Pt, Pd and Rh. Although TWCs are very effective in oxidising CO and hydrocarbons they are substantially less effective in reducing the NO$_x$ emissions. With regard to NO$_x$ reduction, note that Pt is relatively ineffective for the dissociative chemisorption of NO [3], whereas Pd exhibits strong structure sensitivity for this process, which is favoured by step sites [4]. On the other hand Rh is highly effective for NO dissociative chemisorption and is therefore the key component responsible for NO$_x$ reduction in TWCs.

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Considerable effort has recently been expended on enhancing the catalytic properties of Pt-group metals by additives (promoters) [5,6] in order to (i) reduce the noble metal loading required in TWC and (ii) to reduce or replace the usage of Rh because of its scarcity in comparison with Pt and Pd. It is therefore of interest to discover means of enhancing the catalytic performance of the other noble metals (Pt and Pd) in reactions for which Rh is the currently preferred catalyst [1,2].

Although, the performance of conventional heterogeneous metal catalyst is commonly enhanced by the addition of promoters, their exact role in industrial heterogeneous catalysis is well understood only for a limited number of systems [7]. This partly due to the difficulty of achieving in situ control of promoter concentration on the catalyst surface under reaction conditions. Electrochemical promotion (EP) [8] overcomes some limitations. It provides a novel in situ reversible and highly controllable means of catalyst promotion and allows for a systematic study of the role and mode of action of promoters in heterogeneous catalysis. In brief, solid electrolytes are used as reversible in situ promoter donors or poison acceptors to affect the catalytic activity and/ or selectivity of metals interfaced with them [8]. We have used EP to investigate the efficiency of Na as a promoter of Pt for reactions of environmental importance, such as CO oxidation [9] and NO reduction by CO [10] and by C_3H_6 [11]. It was shown that Na supplied electrochemically from a β''-Al_2O_3 solid electrolyte, a Na^+ ion conductor, strongly affects both catalytic activity and selectivity of all the above reactions [9–11].

Guided by these EP studies, we then investigated Na promotion of NO_x reduction by C_3H_6 over conventional catalysts, i.e. catalysts in which the active phase is highly dispersed on large surface area carriers. Thus we studied the $NO + C_3H_6$ reaction over catalysts in which the active phase (Pd) was dispersed on YSZ carrier, and this catalyst was dosed by impregnation with different sodium loadings [5]. Significant Na-induced increases in reaction rate by up to an order of magnitude, as well as remarkable improvement of N_2-selectivity were achieved [5].

In the following we report on the promotional effects of Na for highly dispersed Pt on γ-Al_2O_3 catalysts. In this case the results are even more striking: activity enhancement *of two orders of magnitude* and large increases in N_2 selectivity from ~ 15% over the un-promoted Pt to values as high as 95% over optimally Na-promoted Pt. In effect Pt is induced to behave like Rh for the dissociation of NO. We have deliberately used conditions similar to those employed in the EP by sodium of Pt catalyst electrode in order to permit direct comparison between the two methods of promotion. Close similarities were found between electrochemically promoted Pt and conventionally promoted highly dispersed Pt.

2. Experimental methods

2.1. Electrochemical promotion (EP) experiments

In the case of electrochemical promotion (EP) experiments a galvanic cell of the type of Pt/β''-Al_2O_3 (Na^+ conductor)/Au, was constructed: a porous but continuous thin Pt film (as working electrode) deposited on a 20 mm diameter disc of β''-Al_2O_3 solid electrolyte. Au reference and counter electrodes were attached to the other face of the solid electrolyte wafer. The galvanic cell was then suspended in a quartz, atmospheric pressure, well-mixed reactor. The behaviour of such a 'single pellet', continuous flow stirred tank reactor (CSTR) with all three electrodes exposed to the reactant gas mixture, has been discussed in detail elsewhere [12]. The catalytically active surface area of the Pt catalyst electrode film was found 197 cm^2 or 5×10^{-7} mol of Pt. The procedure of electrodes deposition is described in detail elsewhere [11].

An AMEL 553 galvanostat–potentiostat is used in order to supply constant currents (galvanostatic operation) or potentials (potentiostatic operation) between the working and counter, or the working and reference electrodes, respectively. In this way controllable amounts of Na^+ ions, i.e. promoter species, are supplied to the catalyst film [9–11]. In the case of galvanostatic operation the sodium coverage can be directly calculated via Faraday's law. On the other hand, when the potentiostatic mode of operation is used, the galvanostatic transient behaviour of V_{WR} is necessary to calibrate the Na coverage scale [9–11]. The Pt electrode film was

also studied by XPS under bias conditions. The sample arrangement, instrumentation and construction details are given elsewhere [11].

2.2. Conventional promotion experiments

The basic catalyst used was Pt highly dispersed over a γ-Al_2O_3 carrier, subsequently dosed by several loadings of Na promoter using conventional impregnation methods. The BET surface area of the γ-Al_2O_3 support was 90 m^2 g^{-1}. Metal dispersion of catalysts was measured by H_2 chemisorption at 298 K. The hydrogen to metal ratio (H/M) was calculated by assuming 1:1 hydrogen to metal stoichiometry. Relevant data are summarised in Table 1. Seven samples (C1–C7 in Table 1) with different Na loadings were produced. Catalyst preparation and characterization details can be found elsewhere [14]. Catalyst testing was performed in a fixed bed, single pass, atmospheric pressure, plug flow reactor, consisting of a 0.4-cm I.D. quartz tube. Catalyst loadings were typically ~8 mg. The testing apparatus also consisted of a feed unit and an analysis unit utilizing variously a combination of on-line gas chromatography (Shimadzu-14B), with on-line CO_2–NDIR spectroscopy (Fisher-Rosemount, Binos 100 NDIR CO_2 analyser) or with on-line mass spectrometry (Balzers QMG 064) for the analysis of reactants and products. N_2, NO, N_2O, CO, CO_2 and C_3H_6 were measured via GC, using a molecular-sieve 5A column at 353 K (for the separation of N_2, NO, CO) and a porapak-N column at the same temperature (for the separation of CO_2, N_2O and C_3H_6). AMUs 17 (NH_3), 28 (N_2 + CO), 30 (NO), 32 (O_2), 41 (C_3H_6), 44 (CO_2 + N_2O) were also continuously monitored via mass spectrometry.

3. Results

The only detectable reaction products were N_2, N_2O, CO_2 and H_2O. Overall carbon and nitrogen mass balance closures within 5% were found by a combination of G.C. and mass spectroscopic analyses.

3.1. Electrochemically promoted Pt

Electrochemical promotion experiments are carried out in both galvanostatic or potentiostatic mode, by following the effect of a step change of the applied current on catalytic rate and potential or by following the effect of the applied constant catalyst potential V_{WR} on the reaction rate, respectively. Due to the high temperature (~1025 K) used during electrode deposition on β''-Al_2O_3 disc, small amounts of Na inevitably migrate to the Pt catalyst surface from the β''-Al_2O_3 structure. In order to clean the Pt surface from this thermally diffused sodium, a positive potential V_{WR} is applied between the catalyst and the reference electrode at relatively high temperatures ($\gtrsim 400$ K) until the current ($I > 0$) between the catalyst and the counter electrode vanished. This current corresponds to the reaction:

$$Na(Pt) \rightarrow Na^+ (\beta''\text{-}Al_2O_3) + e^- \qquad (1)$$
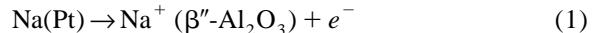
Of course, application of negative currents results in application of Na to the Pt catalyst electrode via the reverse reaction (1). Our earlier XPS studies [11] have demonstrated directly the reversible pumping of Na *to/from* β''-Al_2O_3 *from/to* the Pt catalyst film. In those studies we found that the amount of Na on Pt

Table 1
Properties of the 0.5 wt% Pt/γ-Al_2O_3 catalysts

	Catalyst code						
	C1	C2	C3	C4	C5	C6	C7
Na-loading (wt%)	0	0.52	1.57	2.60	4.18	5.22	10.4
H_2 uptake (cm^3 STP g^{-1})	0.085	0.250	0.160	0.100	0.082	0.081	0.071
Dispersion, (%)[a]	30	87	56	35	29	28	25

[a] Dispersion = surface metal atoms/total number of metal atoms in the catalyst = $2A_m \times V_M/22\,400 \times$ (wt% of metal). Where A_m = atomic weight of the metal, V_M = hydrogen uptake in cm^3 STP g^{-1}.
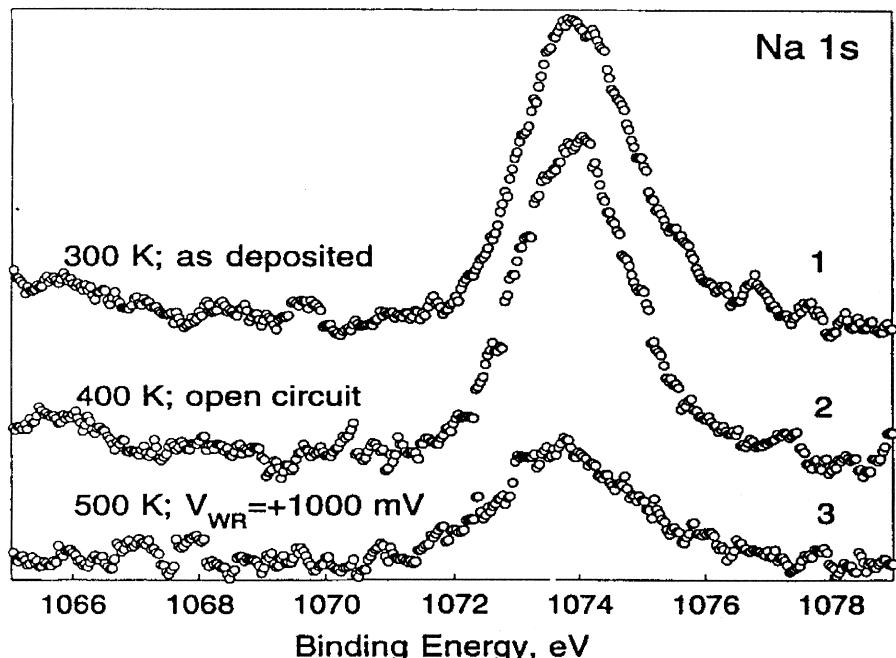
Fig. 1. Na1s XPS illustrating electrochemical pumping of vacuum-deposited Na away from the surface under UHV conditions at sufficiently high temperature and positive catalyst potential.

varies monotonically with catalyst V_{WR}, in a reproducible and reversible manner [11].

Further XPS measurements show (Fig. 1) that under UHV, electro-pumped Na is identical in behaviour and in chemical state with Na supplied by vacuum deposition from a Na evaporation source. In Fig. 1, spectrum 1 depicts the XPS of the catalyst film when Na was vacuum-deposited. Heating to 400 K under open circuit conditions causes no change (spectrum 2). At 500 K (when the β''-Al_2O_3 becomes appreciable conducting) and with $V_{WR} = +1000$ mV, the deposited Na is strongly pumped away from the surface (spectrum 3). This result has prompted our attention to the design of conventional catalyst formulations in which the information acquired from EP studies were directly applied.

Fig. 2 shows the results of a typical EP experiment under galvanostatic transient conditions. It depicts the effects of applying a constant negative current (Na supply to the catalyst) on catalyst potential (V_{WR}) and on the amu 28 (N_2) (note that no CO was detected by GC analysis) and 44 ($CO_2 + N_2O$) MS signals. The experimental procedure was as follows:

first, the surface was electrochemically cleaned of Na by application of a positive potential (0.3 V) until the positive current (Na removal from the catalyst) has vanished. This current corresponds to the reaction (1). The potentiostat was then disconnected ($I = 0$ at $t = -1$ min) and V_{WR} relaxed to the value imposed by the composition of the gas phase. Then, at $t = 0$ the galvanostat was used to impose a constant current $I = -100$ μA; This pumps Na *to* the catalyst surface (the reverse of reaction (1)) at a rate $I/F = 1.04 \times 10^{-9}$ mol Na s^{-1}. The corresponding Na coverage, θ_{Na}, increases according to Faraday's law:

$$\theta_{Na} = -It/FN \tag{2}$$

where t is the time of current application, F is Faraday's constant and N is the number of available surface Pt sites (5×10^{-7} mol Pt). Under these conditions, i.e. Na pumping *to* the catalyst surface, a pronounced decrease in the catalyst potential V_{WR}, and consequently in the catalyst work function ($e\Delta V_{WR} = \Delta(e\Phi)$ [13]) and a very pronounced increase in the production rate of N_2 and CO_2 was
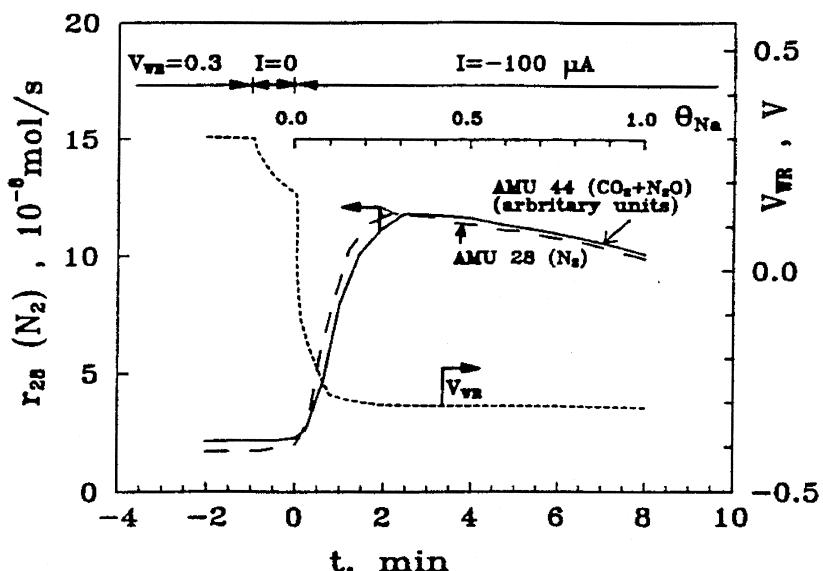
Fig. 2. Transient effect of applied constant negative current (Na supply to the catalyst) on the amu 28 (N_2) and 44 ($CO_2 + N_2O$) mass spectrometer signals and on the catalyst potential (V_{WR}); conditions: $p_{NO} = 1.3$ kPa, $p_{C_3H_6} = 0.6$ kPa, $T = 648$ K.

observed. The rates pass through a maximum when V_{WR} is about -0.3 V ($\theta_{Na} \sim 0.5$). The $CO_2 + N_2O$ signal (amu 44) is given in arbitrary units in Fig. 2 because the separate contributions of CO_2 and N_2O could not be measured under transient conditions. However, under steady-state conditions the separation of CO_2 and N_2O products was performed via GC analysis. Potentiostatic imposition of the initial V_{WR} restored all rates to their initial, unpromoted, values corresponding to clean Pt.

Galvanostatic transient provides an easy and quick way for scanning promoter dosing to a wide range and thus searching the resulting effects on catalyst performance at a given set of gaseous feed composition and temperature conditions. It offers a very quick and easy way to find at any set of conditions what is the optimal promoter loading. This is potentially important from a technological point of view, since such information could be used to design conventional catalysts for practical applications.

3.2. Conventionally promoted Pt

Fig. 3a depicts the effect of sodium content on the CO_2, N_2, and N_2O turnover frequencies (TOF: molecules of product per surface Pt atom per sec-

ond), respectively, for the seven catalysts listed in Table 1, promoted by different amounts of sodium. The results clearly shows a dramatic enhancement of reaction rates induced by Na. Rate enhancement ratios (defined as: $\rho = r$ (rate of promoted catalyst)/r_o (rate of unpromoted catalyst)) as high as ~ 300, 150 and 10 for N_2, CO_2 and N_2O, respectively, are achieved in the case of the optimally promoted catalyst C5 (4.18 wt% Na).

3.3. Comparison of the two methods of promotion

Reconstructing the EP data of Fig. 2, we can produce Fig. 3b which offers a more spectacular comparison between the data taken out by the two ways of Pt-promotion for the $NO + C_3H_6$ reaction. In Fig. 3b, sodium coverage was calculated by the use of Faraday's law as described earlier. The similarity of EP results (Fig. 3b) to those obtained by conventional promotion (Fig. 3a) upon varying sodium loading is remarkable.

For purposes of convenient comparison with EP data, a nominal percentage surface coverage by Na could be calculated for each of the catalysts C1–C7, based on the assumption that all the promoter is present at the surface and distributed uniformly over
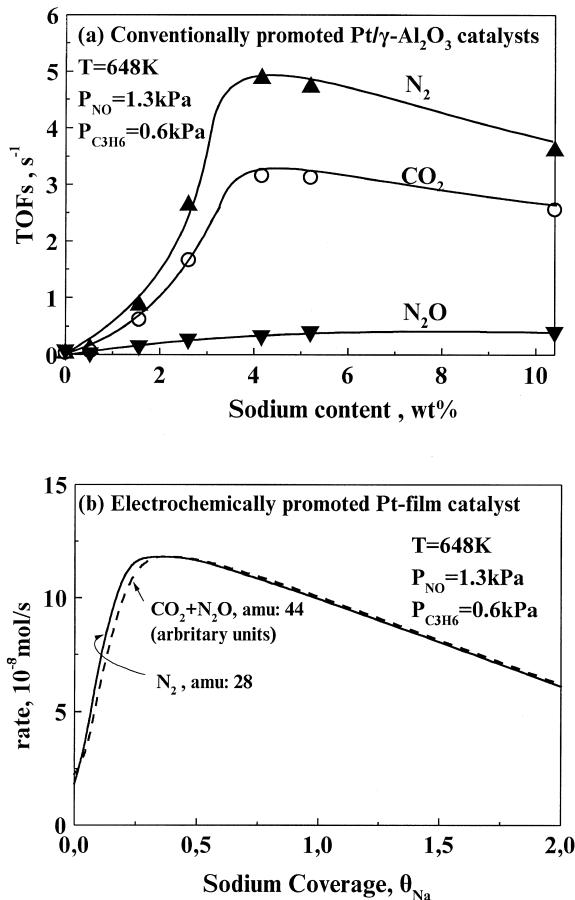
Fig. 3. Comparison of EP and conventional promotion data at $T = 648$ K taken under similar reactor inlet conditions: $p_{NO} = 1.3$ kPa, $p_{C_3H_6} = 0.6$ kPa. (a) Conventionally promoted Pt/γ-Al$_2$O$_3$ catalysts, (b) electrochemically promoted Pt-film catalyst using the transient galvanostatic mode of operation.

Fig. 4. Comparison of electrochemically promoted and conventionally promoted Pt at $T = 648$ K with respect to N$_2$-selectivity. Reactor inlet conditions: $p_{NO} = 1.3$ kPa, $p_{C_3H_6} = 0.6$ kPa.

well-correlated effects were observed for the variation of N$_2$ selectivity of the system, defined as:

$$S_{N_2} = r_{N_2} / (r_{N_2} + r_{N_2O}) \qquad (3)$$

where r_{N_2} and r_{N_2O} are the production rates of N$_2$ and N$_2$O, respectively, upon varying sodium coverage (Fig. 4).

4. Discussion

The present results show that the catalytic properties of Pt can be markedly affected by sodium promotion. This is manifested by both methods of promotion, electrochemical and conventional promotion, with notable similarities between the results of the two methods.

A detailed analysis of the electrochemical promotion data [11] in connection with our earlier works on EP of the CO + NO reaction [10] led as to infer that the promotional effect is due to enhanced NO chemisorption and dissociation on the Pt surface induced by Na addition. Na-induced NO dissociation produces adsorbed atomic oxygen, which is responsible for initiating the ensuing oxidation reactions of adsorbed propene. The mechanisms of the reaction and the way of action of Na promoter have been

the entire available area (Pt + γ-Al$_2$O$_3$), without any incorporation into the bulk. In a resent extended XPS and Auger study of similar supported catalysts (Na dosed Pd/YSZ) [5], we showed that coverage of catalyst by Na increases monotonically with promoter loading and that there is no tendency towards promoter agglomeration at higher loadings. On the basis of this assumption we could calculate a nominal sodium coverage of a value of ~40% for the catalyst C5 (4.18 wt% Na) which exhibits the maximum rate enhancement. This value is in good agreement with the optimal Na coverage indicated by electrochemical promotion data (Fig. 3b). Similar

described in recent communications [6,11]. Here we are going to analyse the similarities and the differences between electrochemical and conventional promotion for a reaction/promoter system for which the mechanism of the promoter action is well understood [6,11]. Thus, a study of Figs. 3 and 4, shows the following similarities between the two kinds of promotion: (i) Both promotion methods very strongly enhance the rates of N_2 and CO_2 production, while the effect on the N_2O production rate is much less pronounced. (ii) A rapid exponential increase in reaction rates with sodium coverage is followed in both cases by a less pronounced inhibition. (iii) The optimal promoter loading was found to be in both cases about $\theta_{Na} = 40$–50%, while (vi) the selectivity towards N_2 follows the same behaviour passing through a maximum, which corresponds to the optimally promoted catalyst.

One may also notice the following differences: (a) In the case of conventional promotion the enhancement ratio ρ (r/r_o) values are much more pronounced than with EP. This may be connected with the very different Pt particle sizes in the two cases. (b) The Na-free EP catalyst exhibited an unpromoted rate significantly higher than that of Na-free conventional Pt/γ-Al_2O_3 dispersed catalyst: the latter is practically ineffective for the $NO + C_3H_6$ reaction. This may be explained as follows. Previously, we used XP spectroscopy to investigate the location and the chemical state of electrochemically supplied Na modifier on Pt-film catalysts [11]. Our XPS data showed that there is always a residual amount of Na on the catalyst surface due to thermal diffusion from the β″-Al_2O_3 substrate. That is, the electrochemically cleaned Pt is not entirely Na-free so that its catalytic properties are already affected to some extent by residual Na adatoms. This explains why the so called 'Na-free' EP catalyst appears to have a relatively good activity for the reaction of NO + propene, whereas the true Na-free (unpromoted) Pt/γ-Al_2O_3 is almost ineffective, in good agreement with literature [15]. This happens presumably because surface sites are blocked by propene derived carbonaceous species, which are strongly adsorbed on catalyst surface [11]. Here we propose that Na can eliminate this problem by enhancing the strength of the NO adsorption bond, thus enhancing the NO population on the catalyst surface, as well as enhanc-

ing the NO dissociation, which is proposed as the critical reaction-initiating step.

5. Conclusions

The catalytic reduction of NO by propene over Pt exhibits strong electrochemical promotion by Na. Promotion is due to the sodium-induced increase in strength of NO chemisorption relative to propene. This is accompanied by weakening of the N–O bond, thus facilitating NO dissociation, which is proposed to be the critical reaction-initiating step. XPS data confirm that electropumped Na is indistinguishable from Na put down by vacuum deposition.

Close similarities exist between the performance of Pt-film catalyst promoted electrochemically with highly dispersed, on high surface area supporting materials (e.g. γ-Al_2O_3), Pt promoted by conventional means. These findings serve to validate further the interpretation offered for the EP phenomenon, and the use of this phenomenon as a *tool* for exploring the effects of a range of promoters before applying them to the design of efficient catalyst formulations.

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