

Electrochemical vs. Conventional Promotion: A New Tool to Design Effective, Highly Dispersed Conventional Catalysts

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Abstract. Pt-group metals exhibit strong Electrochemical Promotion (EP) by sodium during reactions related to emission control catalysis, such as NO reduction by hydrocarbons. Close similarities are found between electrochemically promoted catalysts and catalysts conventionally promoted and highly dispersed on large surface area supported materials. These similarities include (i) overall kinetic behaviour and (ii) the dependence of the activity and selectivity on Na loading. For example, using both methods of Na-promotion, the catalytic reduction of NO by propene exhibited rate enhancements by up to an order of magnitude accompanied by very pronounced increases of the system selectivity towards N₂. Among other things, our 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 successfully effective catalyst formulations that were previously untried, thus opening up new areas for investigation in the frontiers between catalysis and electrochemistry.

1. Introduction

Heterogeneous catalysis has and will continue to play a major role in pollution control of our atmosphere. Catalysis is the best solution for reduction of NO_x and oxidation of VOCs emissions produced by combustion processes [1].

Currently the "three-way" catalytic converters (TWCs) are used for the simultaneous removal of all three main pollutants (NO_x, CO and hydrocarbons) from automotive emissions. They use formulations based variously on Pt, Pd and Rh noble metals. Although, TWCs are very effective in oxidizing CO and HC, they are substantially less effective in reducing the NO_x emissions. Reactions involving the catalytic reduction of NO are today of major environmental importance with respect to the removal of toxic emissions from both stationary and mobile sources [1]. Because of its ability to chemisorb NO dissociatively, Rh is the key component in TWC converters for the reduction of NO_x.

Considerable effort has recently been expended on

enhancing the catalytic properties of Pt-group metals by additives (promoters) in order to (i) reduce the noble metals loading required in TWC and (ii) to reduce or replace the use of Rh because of its rarity in nature in comparison with Pt and Pd (~ 1:15) and its consequent significantly higher cost. It is therefore of interest to discover means of enhancing the catalytic performance of the other noble metals (Pt and Pd) for reactions at which Rh is the preferred catalyst in TWC because of its superior ability to dissociatively chemisorb NO, a process for which Pd and especially Pt is normally a relatively poor catalyst [1].

The performance of conventional heterogeneous metal catalyst is commonly enhanced by the addition of promoters that are used to modify the intrinsic metal surface chemistry. Their exact role in industrial heterogeneous catalysis is well understood only for a limited number of systems [2], while most fundamental studies have addressed their role in chemisorption only under ultra-high-vacuum conditions [2,3]. This is primarily due to

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the difficulty of achieving in-situ control of promoter concentration on the catalyst surface under reaction conditions.

Electrochemical Promotion (EP) [4] provides a novel in-situ reversible and highly controllable means of catalyst promotion. In brief, it uses solid electrolytes as reversible in situ promoter donors or poison acceptors to affect the catalytic activity and/or selectivity of metals interfaced with them. During the last ten years, EP has been studied for over fifty catalytic reactions on a variety of metal catalysts using a variety of solid electrolytes as *active supports* [5].

We have used electrochemical promotion (EP) to investigate the efficacy of Na as a promoter of Pt for reactions of environmental importance, such as CO oxidation [6] and NO reduction by CO [7] and by propene [8,9] or methane [10].

It was shown that Na supplied electrochemically from a $\beta''\text{-Al}_2\text{O}_3$ solid electrolyte, a Na^+ ion conductor, strongly affects both catalytic activity and selectivity of all the above reactions [7-10]. Based upon this promotion method we were led to a specific model for the mechanism of Na promotion which explains well all the experimental observations [7-10].

Guided by these EP studies, we investigated Na promotion of NOx reduction by propene over conventional dispersed catalysts. We have deliberately used conditions similar to those employed in the EP work in order to permit direct comparison between the two sets of results. Close similarities are found between electrochemically promoted catalysts and catalysts conventionally promoted and highly dispersed on large surface area supported materials such as $\gamma\text{-Al}_2\text{O}_3$. Among other things our results serve to validate further the interpretation offered for the EP (or NEMCA) phenomenon. The insight obtained from EP studies can be used to design successfully effective catalyst formulations that were previously untried.

2. Experimental

2.1. Electrochemical Promotion (EP) Experiments. In the case of electrochemical promotion (EP) experiments a continuous-flow, atmospheric pressure "single pellet" type, galvanic cell reactor [11] of volume 115 cm^3 was used. This galvanic cell consisted of a porous but continuous thin Pt film (as working electrode) deposited on a 20 mm diameter disc of $\beta''\text{-Al}_2\text{O}_3$ solid electrolyte. Au reference and counter electrodes were attached to the other

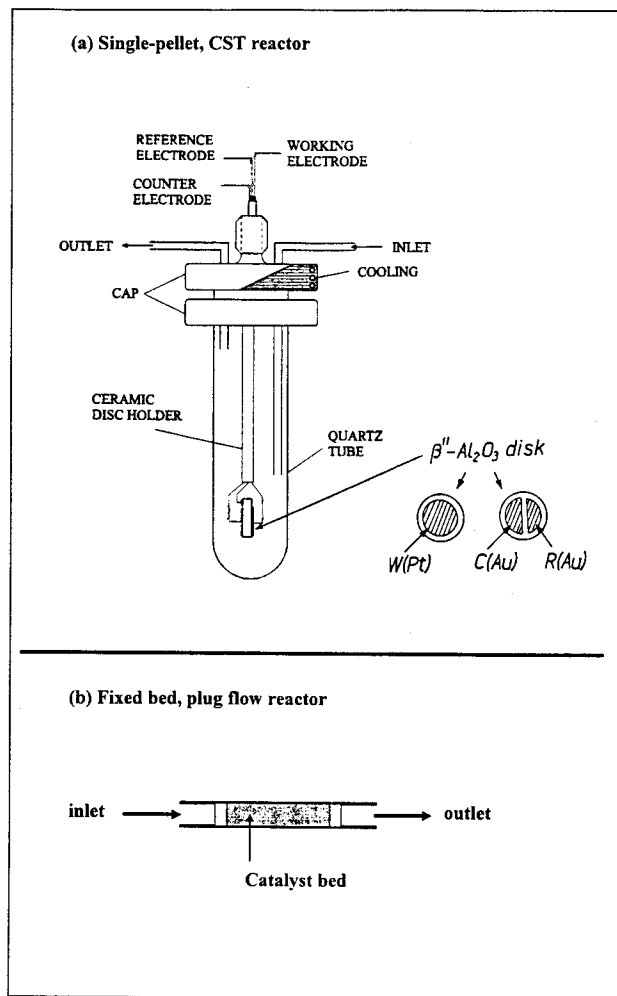


Fig. 1. (a): single pellet catalytic reactor-cell and electrode configuration used for EP experiments. (b): fixed bed plug flow reactor for conventional catalyst testing.

face of the solid electrolyte wafer (Fig. 1a). The catalytically active surface area of the Pt catalyst electrode film was measured by a titration technique [6] and found 197 cm^2 or 5×10^{-7} mols of Pt. The procedure of electrodes deposition is described in detail elsewhere [6,8].

This Pt/ $\beta''\text{-Al}_2\text{O}_3$ /Au galvanic cell was suspended in a quartz, atmospheric pressure, well-mixed reactor. The behaviour of such a single pellet, continuous stirred tank reactor (CSTR) with all three electrodes exposed to the reactant gas mixture, has been described and discussed in detail elsewhere [11].

An AMEL 553 galvanostat-potentiostat was used in order to supply constant currents (galvanostatic operation) or potentials (potentiostatic operation) between the working and counter, or the working and reference elec-

trodes, respectively. In this way controllable amounts of Na^+ ions, i.e., promoter species, were supplied to the catalyst [6,12]. As will be shown in the result section, 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 [6-9, 12].

2.2. Conventional Promotion Experiments. Conventionally supported and promoted catalysts were tested in an atmospheric pressure fixed bed, single pass, plug flow reactor (Fig. 1b), consisting of a 0.4-cm ID quartz tube. Catalyst loadings were typically about 7-8 mg, the sample being diluted further by admixture with about 100 mg, 100-325 mesh $\alpha\text{-Al}_2\text{O}_3$.

These dispersed supported Pt catalysts were prepared by impregnation of the supporting material, $\gamma\text{-Al}_2\text{O}_3$ (Akzo Chemicals) using a solution of H_2PtCl_6 (Alfa Products). The solution was of appropriate strength so as to yield 0.5 wt% metal loading. Sodium promoter was added to the catalyst by subsequent impregnation with NaNO_3 solution of suitable concentrations. The resulting suspension was dried in a rotating flask by evaporation at 353 K and then overnight at 383 K. The catalyst precursors were heated in flowing He ($1\text{h}/673\text{ K}/100\text{ cm}^3\text{min}^{-1}$), followed by H_2 reduction for 1h at the same temperature and H_2 flux. Seven samples with different Na loadings were produced (coded as C1-C7 in Table 1).

For purposes of convenient comparison with EP data, a nominal percentage surface coverage by Na has been calculated for each of the catalyst C1-C7, based on the assumption that all the promoter is present at the surface and distributed uniformly over the entire available area ($\text{Pt} + \gamma\text{-Al}_2\text{O}_3$), without any incorporation into the bulk. In fact, an extended XPS and Auger study of similar supported catalysts (Pd/YSZ dosed by Na) [13], showed that coverage of catalyst by Na increases monotonically with promoter loading and that there is no tendency towards promoter agglomeration at higher loadings. However, a very small but constant tendency to accumulate subsurface or dissolved Na with increasing promoter loading was observed.

The catalyst testing apparatus consisted of a feed unit, the reactor and the analysis unit utilizing variously a combination of on-line gas chromatography (Shimadzu 14B), with on-line IR spectroscopy (Fisher-Rosemount, Binos 100 NDIR CO_2 Analyser) or with on-line mass

Table 1. Properties of the 0.5 wt % Pt/ $\gamma\text{-Al}_2\text{O}_3$ catalysts

a/a	Na-loading wt%	Nominal Na coverage %	H_2 uptake $\text{cm}^3\text{STP/g}$	Dispersion %
C1	0	0	0.085	30
C2	0.52	10	0.250	87
C3	1.57	30	0.160	56
C4	2.60	50	0.101	35
C5	4.18	80	0.082	29
C6	5.22	100	0.081	28
C7	10.4	200	0.071	25

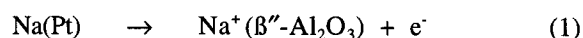
spectrometry (Balzers QMG 064) for the analysis of reactants and products.

XPS measurements were carried out in a VG ADES 400 UHV spectrometer. The sample arrangement and other instrumentation and construction details are given elsewhere [8].

3. Results

3.1. Electrochemical Promotion Data. Electrochemical promotion experiments can be 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. For the latter case the relationship between V_{WR} and Na coverage, θ_{Na} , established via the galvanostatic transient behaviour can be used in order to estimate the level of sodium coverage.

Due to the high temperature ($\sim 1025\text{K}$) used during electrode deposition on $\beta''\text{-Al}_2\text{O}_3$ disc, small amounts of Na inevitably migrate to the Pt catalyst surface from the $\beta''\text{-Al}_2\text{O}_3$ structure. In order to clean the Pt surface from this thermally diffused sodium, a positive potential V_{WR} was applied between the catalyst and the reference electrode at relatively high temperatures ($> \sim 400\text{ K}$) until the current ($I > 0$) between the catalyst and the counter electrode vanished. This current corresponds to the reaction:



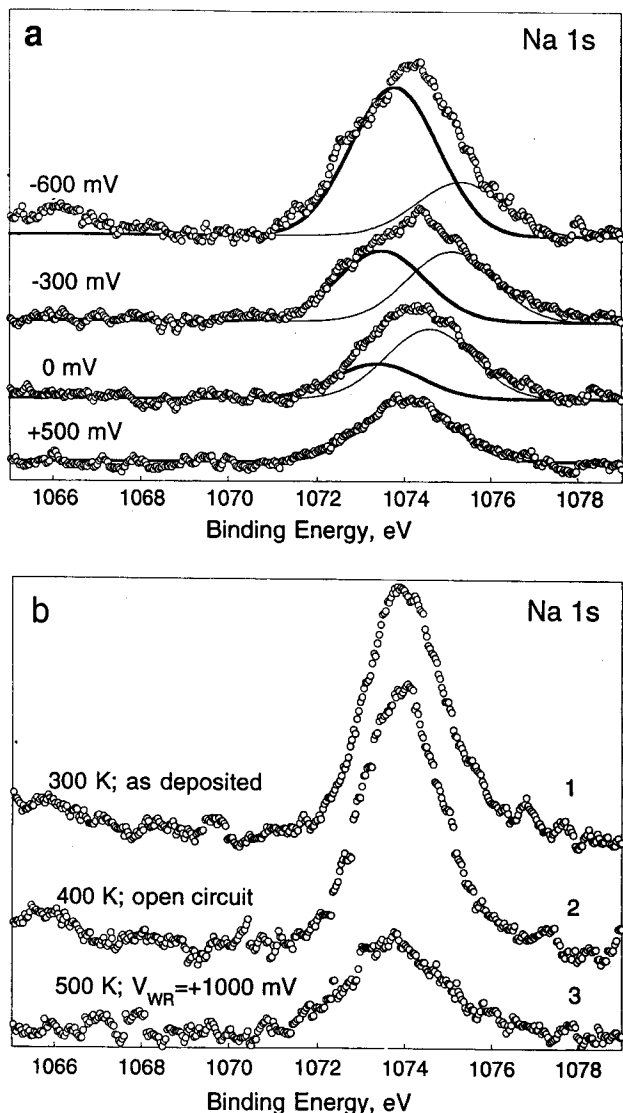


Fig. 2. Na 1s XPS. (a): Showing effect of catalyst potential in pumping sodium *to/from* the Pt film under UHV conditions at 600 K. (b): Illustrating electrochemical pumping of vacuum-deposited Na away from the surface under UHV conditions at sufficiently high temperature and positive catalyst potential.

Of course, application of negative currents result in application of Na to the catalyst via the reversible reaction (1). Our XPS studies, discussed below, have demonstrated directly the reversible pumping of Na *to/from* β'' - Al_2O_3 *from/to* the Pt catalyst.

3.1.1. XPS Studies of Electrochemically Promoted Catalysts. Fig. 2 shows Na 1s spectra acquired at 600K in ultra high vacuum under electrochemical bias conditions that replicate those in the reactor. The electrochemically cleaned surface ($V_{WR} = +500$ mV) exhibits a feature at 1074 eV BE which is due to Na in the β'' - Al_2O_3 visible

through cracks in the porous Pt film. At $V_{WR} = -600$ mV, two features are now present, that at 1073.5 eV being due to Na pumped to the Pt surface. Note that the β'' - Al_2O_3 derived peak has shifted to ~ 1075.5 eV, i.e., by an amount about equal to the change in V_{WR} (1.1 eV), as expected [8]. The Pt film is at ground potential and Na 1s photoemission from the Pt should of course appear at fixed kinetic energy, independent of V_{WR} . Thus our XP spectra clearly reveal the relationship between the two types of Na sampled by photoemission.

For intermediate values of V_{WR} the amount of Na on Pt varies monotonically with catalyst potential and the (constant intensity) Na 1s emission from the β'' - Al_2O_3 shifts with V_{WR} . This spectral behaviour was reproducible and reversible as a function of V_{WR} .

Fig. 2b demonstrates that under UHV conditions, electro-pumped Na is identical in behaviour and in chemical state with Na supplied by vacuum deposition from a Na evaporation source. Spectrum (1) shows the XPS of the catalyst film when Na was vacuum-deposited. Heating to 400 K under open circuit conditions caused 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 was strongly pumped away from the surface-spectrum (3).

3.1.2. EP under Transient Conditions. Figure 3 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

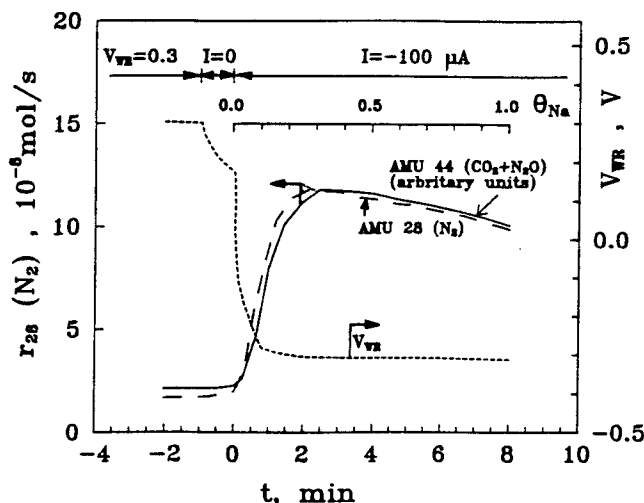


Fig. 3. Transient effect of applied constant negative current (Na supply to the catalyst) on the amu 28 (N_2) and 44 ($\text{CO}_2 + \text{N}_2\text{O}$) mass spectrometer signals and on the catalyst potential (V_{WR}); Conditions: $P_{\text{NO}} = 1.3$ kPa, $P_{\text{C}_3\text{H}_6} = 0.6$ kPa, $T = 648$ K.

catalyst potential (V_{WR}) and on the AMU 28 (N_2) and 44 (CO_2+N_2O) m.s. signals. The only detectable reaction products were CO_2 , N_2 , N_2O and H_2O .

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) vanished [6-8,12]. 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 gaseous composition. Then, at $t = 0$ the galvanostat was used to impose a constant current $I = -100 \mu A$; This pumped Na to the catalyst surface (the reverse of the reaction (1)) at a rate $I/F = 1.04 \times 10^{-9}$ mol Na/s. The corresponding Na coverage, θ_{Na} , starts increases according to Faraday's law:

$$\theta_{Na} = -It/FN \quad (2)$$

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 ($e\Delta V_{WR} = \Delta(e\Phi)$) [4] and a very pronounced increase (by a factor of ~ 10) in the production rate of N_2 was observed. The rates pass through a maximum when V_{WR} is about $-0.3V$ ($\theta_{Na} \sim 0.5$) (Fig. 3). The CO_2+N_2O signal (AMU 44) is given in arbitrary units in Fig. 3 because the separate contributions of CO_2 and N_2O could not be measured under transient conditions. Potentiostatic imposition of the initial V_{WR} restored all rates to their initial, unpromoted, values corresponding to clean Pt, thus demonstrating that the system is perfectly reversible.

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 provides a very quick and easy way to find under reaction 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.

Galvanostatic transients are also required for establishing the relationship, $\theta_{Na}(V_{WR})$, between V_{WR} and Na coverage θ_{Na} under reaction conditions, simply by following the time dependence of V_{WR} and using Eq.(2) (Fig. 3). In general, this relationship depends also on gaseous

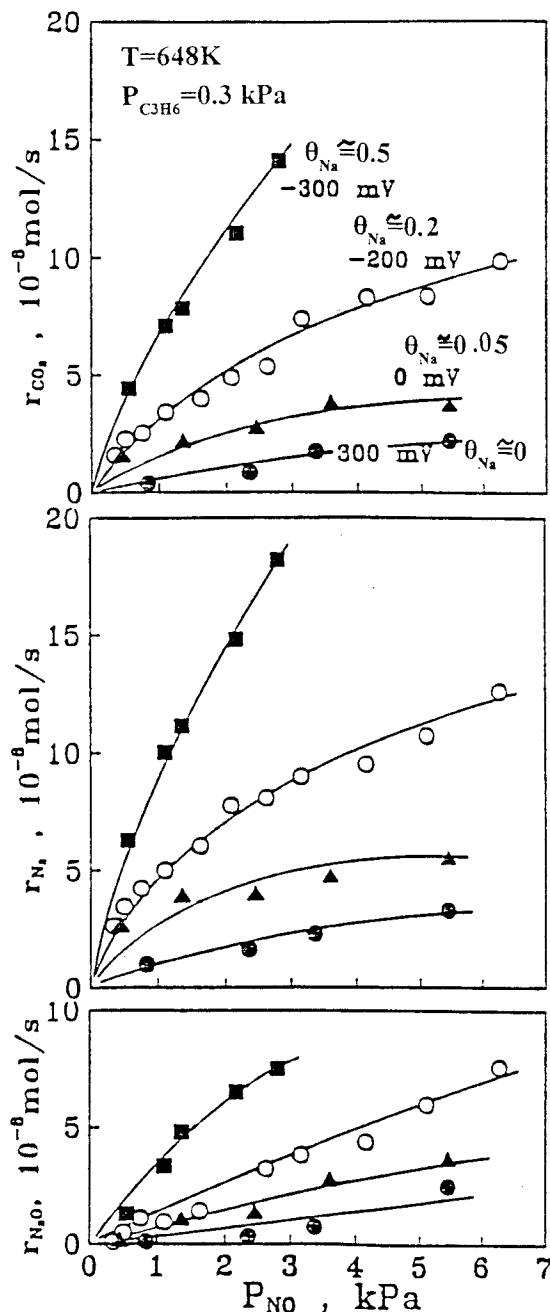


Fig. 4. Dependence of CO_2 , N_2 and N_2O production rates on P_{NO} , at several fixed values of catalyst potential V_{WR} (i.e., at different levels of Na-promoter coverage). Electrochemically promoted Pt-film catalyst.

composition, as observed previously [6-8]. The "volcano" behaviour of the rates shown in Fig. 3 is also manifested in the steady state mode [8].

3.1.3. EP Under Steady State Conditions. The dependence of the steady state CO_2 , N_2 and N_2O rates on the partial pressure of NO, P_{NO} , at constant propene partial pressure and temperature, for four different values of catalyst potential (different Na coverages), is illustrated in Fig. 4.

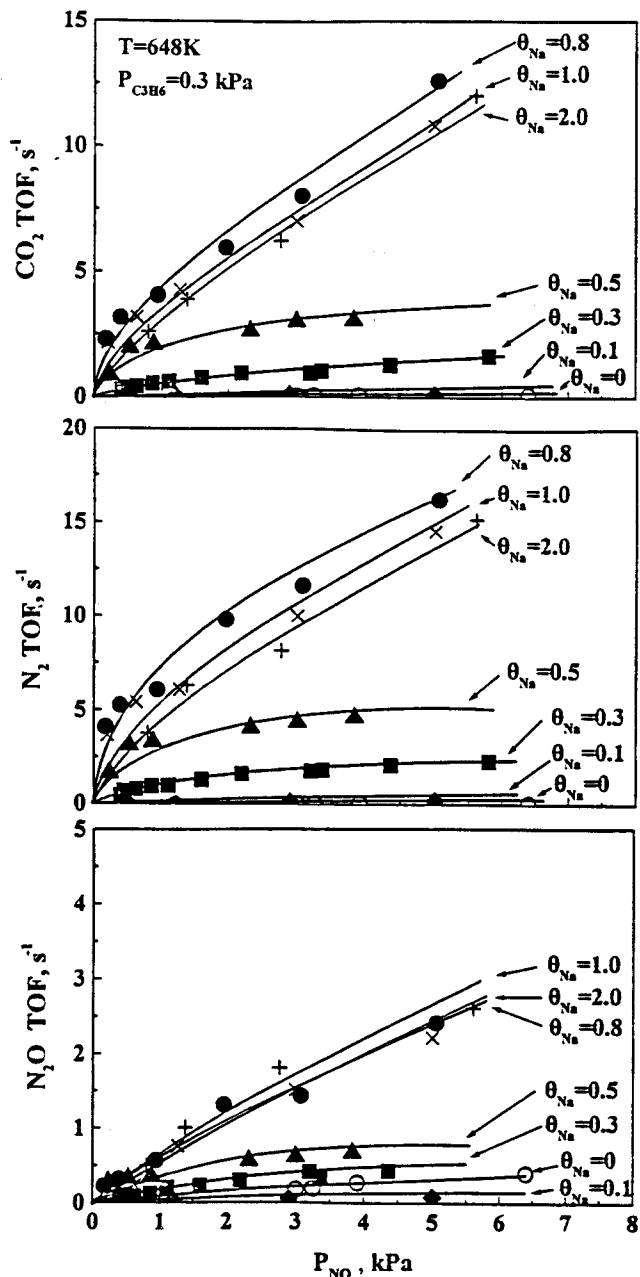


Fig. 5. Dependence of CO_2 , N_2 and N_2O production rates on P_{NO} , for catalysts C1-C7 with different promoter loading. Conventionally promoted Pt/ $\gamma\text{-Al}_2\text{O}_3$ catalysts.

For $V_{\text{WR}} = +0.3$ V the Pt surface is electrochemically cleaned from Na (*Na-free*) and the unpromoted reaction rates are low. Decreasing V_{WR} to more negative values, (supply of Na to the catalyst), causes a pronounced, about 10-fold, increase in the rates. The sodium coverage values depicted on the curves of Fig. 4 have been estimated through the galvanostatic transient behaviour of the V_{WR} (i.e., Fig. 3).

3.2. Conventional Promotion Data. Fig. 5 depicts steady state kinetic results, showing the effect of P_{NO} on the

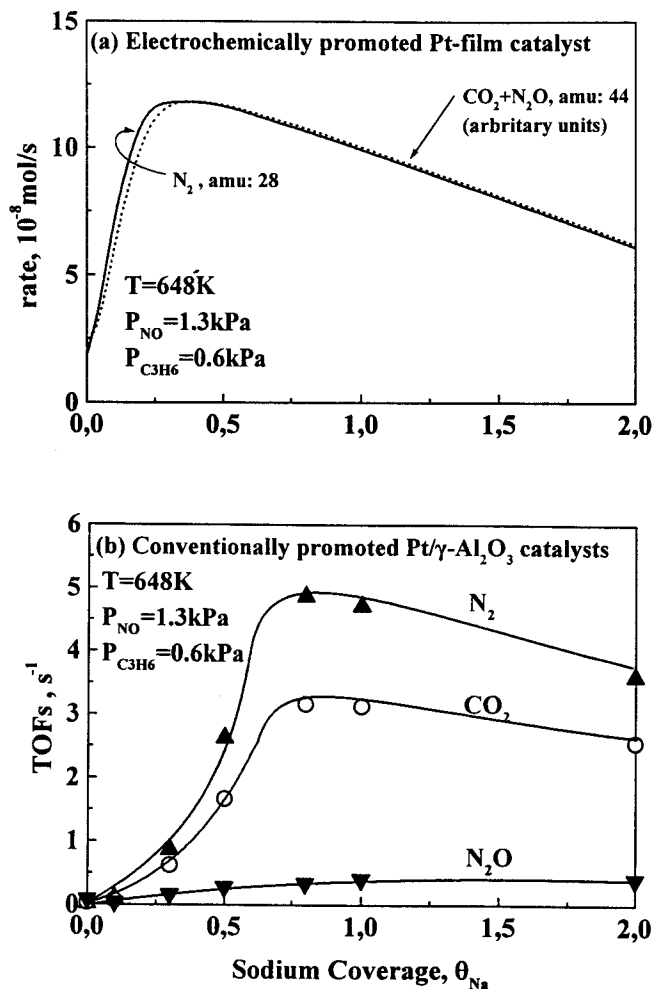


Fig. 6. Comparison of EP and conventional promotion data taken under similar conditions: $P_{\text{NO}} = 1.3$ kPa, $P_{\text{C}_3\text{H}_6} = 0.6$ kPa, $T = 648$ K; (a): Electrochemically promoted Pt-film catalyst using the transient galvanostatic mode of operation; (b) Conventionally promoted Pt/ $\gamma\text{-Al}_2\text{O}_3$ catalysts.

CO_2 , N_2 , and N_2O turnover (TOF: molecules of product per surface Pt atom per second) formation rates, respectively for the seven conventional catalysts promoted by different amounts of sodium, as listed in Table 1.

The results very clearly shows a dramatic enhancement of reaction rates induced by Na, in all the range of NO partial pressure. It is notable that the Na-free catalyst C1 is appeared to be almost ineffective for the reaction, thus leading to rate enhancement ratios (defined as: $\rho = r(\text{rate of promoted catalyst})/r_0(\text{rate of unpromoted catalyst})$) as high as ~ 300 , 150 and 10 for N_2 , CO_2 and N_2O respectively in the case of the optimally promoted catalyst C5 (4.18wt% Na, 80% nominal sodium coverage). The similarity of the results to those obtained under electrochemical promotion conditions (Fig. 4) upon varying both NO partial pressure and sodium loading is striking.

3.3. Comparison of the Two Methods of Promotion.

Fig. 6 shows in a more spectacular manner the comparison of data of Na promotion for the NO+propene reaction on Pt taken by this two ways of promotion. It depicts the effect of sodium coverage on N_2 , CO_2 and N_2O production rates. In the case of EP data (Fig. 6a), sodium coverage was calculated by the use of Faraday's law, as described earlier, while in the case of conventional catalysts the nominal sodium coverage was used. Because the EP data were taken under galvanostatic transient conditions (we remind here that similar results were taken under steady state potentiostatic conditions [8]), we was unable to separate under such transient conditions the contributions of CO_2 and N_2O at AMU 44 signal of mass spectrometer. That is why the production of these two reactants is given in arbitrary units in Fig. 6a.

Both methods of promotion provide an optimal amount of sodium coverage which leads to maximum rate enhancements. It is about 50 % and 80 % for the case of electrochemical and conventional promotion, respectively.

Similar well correlated effects were observed for the variation of N_2 selectivity of the system upon varying sodium coverage (Fig. 7) The unpromoted Na-free conventional catalyst C1 has a very low selectivity towards N_2 which can be improved up to 95 % for the optimally Na promoted catalyst C5 (80 % nominal sodium coverage).

4. Discussion

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

A detailed analysis of the electrochemical promotion data [8] in connection with our earlier works on EP of the CO+NO reaction [7], led as to infer that the promotional effect is due to enhanced NO chemisorption and dissociation on the Pt surface induced by Na addition. Recall that the polycrystalline Pt consists of crystallites of which the external surfaces are dominated by low index planes. Such low index planes of Pt are known to be relatively ineffective for NO dissociation [14]. Na-induced NO dissociation produces adsorbed atomic oxygen which is responsible for initiating the ensuing oxidation reactions of adsorbed propene and propene fragments.

The mechanism of the reaction and the way of action of Na promoter has been described in detail in recent

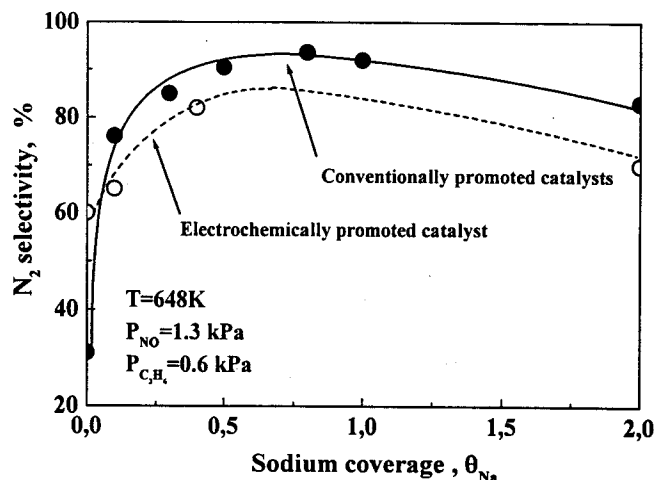


Fig. 7. Comparison of electrochemically promoted and conventionally promoted Pt with respect to N_2/N_2O selectivity during the NO+propene reaction. Experiments performed at $P_{NO} = 1.3$ kPa, $P_{C_3H_6} = 0.6$ kPa, $T = 648$ K.

communications [8,9,13]. 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 [8,13]. A study of Figs. 4 and 5, 6 and 7 shows the following similarities between the two kinds of promotion:

- (i) Both promotion methods enhance the rates of N_2 and CO_2 production with a dramatic manner, while the effect on the N_2O production rate is in both cases much less pronounced (Figs. 4, 5 and 6)
- (ii) A rapid exponential increase of the reaction rates upon sodium coverage is followed in both cases by a less pronounced inhibition (Fig. 6). Even at very high sodium coverage ($\theta_{Na} > 2$) the reaction rate is significantly higher than that of Na-free catalyst.
- (iii) In both cases the selectivity towards N_2 follows the same "volcano" behaviour passing through a maximum which corresponds to the optimally promoted catalyst.

One may also notice the following small differences:

- (a) In the case of conventional promotion the enhancement ratio ρ (r/r_0) values are much more pronounced than with EP. In fact, differences up to one order of magnitude can be observed (Figs. 4, 5 and 6).
- (b) The sodium free EP catalyst has an unpromoted Na-free rate significantly higher than that of Na-free conventional Pt/ γ - Al_2O_3 catalyst, which is practically ineffective for the NO+ C_3H_6 reaction (Figs. 4, 5 and 6). Actually, observation (a) is a result of the above (b).

(c) The optimal promoter loading was found to be somewhat lower ($\theta_{\text{Na}} \sim 50\%$) for EP than that of conventional promotion ($\theta_{\text{Na}} \sim 80\%$) (Fig. 6).

All the above differences can easily explained on the following basis: As the XPS data show (Fig. 2) there is always a residual amount of Na on the catalyst surface due to thermal diffusion. It is also important that a significant area of the porous Pt electrode interfaced with $\beta''\text{-Al}_2\text{O}_3$ is influenced by Na from the substrate. This is the area at the vicinity of the *tpb* (three phase boundary) between the solid electrolyte, the Pt catalyst and the gas phase. That is, the electrochemically cleaned Pt is not entirely Na-free so that its catalytic properties are already affected to some extent by Na adatoms. On the other hand, the calculation of the nominal sodium coverage of conventionally supported catalysts is based on the assumption that there is no tendency for Na agglomeration or subsurface accumulation. If either of these two assumptions is not satisfied, the estimated Na coverage will be higher than the true value.

Consequently one expects an overestimation of the Na coverage for the conventional catalyst and an underestimation of its value for the EP catalysts. This explains why the so called "Na-free" EP catalyst appears to have good activity for the reaction of NO+propene, while the true Na-free conventional catalyst is practically ineffective, in good comparison with literature [15].

It is notable that Pt/ $\gamma\text{-Al}_2\text{O}_3$ is an ineffective catalyst for the reduction of NO by propene, presumably because surface sites are blocked by propene derived carbonaceous species which are strongly adsorbed on catalyst surface [15]. The presence of O_2 eliminates this problem by creating hydrocarbon free sites on the catalyst surface where NO can be adsorbed for the initiation of the reaction [15]. Here we propose that Na can play a similar role by enhancing the strength of the NO adsorption bond, thus enhancing NO population on catalyst surface, as well as enhancing NO dissociation, which is proposed as the critical reaction initiating step.

The above analysis of the estimation of sodium coverage for the two methods of promotion implies that in the case of EP the term "electrochemically clean catalyst" is more appropriate than the term "Na-free catalyst". The same analysis explains the phenomenologically observed lower Na coverage of 50 % which optimizes EP catalyst performance in contrast to the value of 80 % which optimizes the conventional catalyst.

5. Conclusions

The catalytic reduction of NO by propene over Pt exhibits strong electrochemical promotion when Na from a $\beta''\text{-Al}_2\text{O}_3$ solid electrolyte is supplied to the catalyst surface. A detailed kinetic study under EP conditions leads us to propose a specific model for Na promotion. According to this model promotion is due to 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 process is proposed as the critical reaction initiating step. In addition, the population of NO is increased in a surface predominantly covered by the strongly adsorbed hydrocarbon, thus increasing the probability of surface reaction in the reaction under consideration which is characterized by competitive adsorption of the reactants.

XPS data confirm that the mode of operation of the electrochemically promoted Pt film does indeed involve reversible pumping of Na to or from Pt from or to the solid electrolyte. This electropumped Na is indistinguishable from Na put down by vacuum deposition.

Close similarities exists between the performance of Pt-film catalyst promoted electrochemically with highly dispersed on high surface area supporting materials (e.g., $\gamma\text{-Al}_2\text{O}_3$) Pt promoted by conventional means. These similarities include the overall kinetic behaviour and the dependence of activity and selectivity on Na loading. Among other things, they demonstrate that the insight obtained from EP studies can be used to design successfully effective catalyst formulations that were previously untried, thus opening up new areas for the investigation in the frontiers between catalysis and electrochemistry.

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