Extraordinarily effective promotion by sodium in emission control catalysis: NO reduction by propene over Na-promoted Pt/γ-Al₂O₃

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Abstract

The catalytic activity and selectivity of Pt dispersed on γ-Al₂O₃, for the reduction of NO by propene is promoted extremely strongly by sodium in the temperature range 470–770 K. Remarkable and unprecedented effects on both activity and selectivity are found. Rate increases by two orders of magnitude are achievable, while the selectivity towards to N_2 is improved from ∼20% over the Na-free unpromoted Pt catalyst, to >95% over the optimally Na-promoted catalyst. The Na-free Pt is almost ineffective for the $NO + C_3H_6$ reaction over the gas composition and temperature range of this investigation. The promoting effect is due to a sodium-induced increase in the strength of Pt–NO chemisorption relative to propene on a catalyst surface predominantly covered by propene and its fragments. This is accompanied by weakening of the N–O bond, thus facilitating NO dissociation, which process is proposed as the critical reaction initiating step. ©1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Heterogeneous catalysis has 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 [1–17]. Recent reviews of the field reveal the importance of the subject and the urgency with which advances are sought [1–5].

Currently, 'three-way' catalytic converters (TWCs) are used for the simultaneous removal of all three main pollutants (NO_x, CO and hydrocarbons) from auto-motive emissions [2,3]. 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, especially under lean-burn conditions. With regard to NO_x reduction, note that Pt is relatively ineffective for the dissociative chemisorption of NO [9], whereas Palladium exhibits strong structure sensitivity for this process, which is favoured by step sites and elevated temperatures [10,11]. 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.

Considerable effort has recently been expended on enhancing the catalytic properties of Pt-group metals

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by additives (promoters) 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 ($\sim 1:15$) 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) in reactions for which Rh is the currently preferred catalyst because of its superior ability to dissociatively chemisorb NO, a process for which Pd and especially Pt are normally relatively poor catalysts [2,3].

Efforts thus far have focused on improving the catalytic properties of Pd and Pt for reactions relevant to three-way catalytic chemistry by doping the support material with additives or by using supports other than γ-Al_2O_3 (e.g. yttria-stabilised zirconia (YSZ), TiO_2, doped-TiO_2 [12,13]). These strategies have indeed improved significantly the activity and selectivity of Pd and Pt for NO reduction to N_2. Recently, Burch and Watling investigated the effects of a wide range of promoters, including Cs and K, on the Pt-catalysed reduction of NO by propene under lean-burn conditions (i.e. in the presence of 5% O_2) [14]. They found no particular benefit with these two alkalis, and concluded that the manner in which the various promoters affect reactivity is unclear. More recently, Wang et al. [15] demonstrated significantly increased catalytic activity (N_2 yield raised from 15% to 60% for NO reduction at 900 K) with supported Pd catalysts promoted by precoating the alumina support with NaOH before palladium impregnation. They concluded that strongly adsorbed NO molecules may remain on the NaOH promoted catalysts, and that the enhanced activity could be therefore, attributed to that species. At the same time Yentekakis et al. [16] reported Na-induced increases in reaction rate by up to an order of magnitude, as well as a significant enhancement in N_2 selectivity from a value of 75% over Na-free (unpromoted) Pd to values higher than 95% over optimally Na-promoted Pd, in the catalytic reduction of NO by propene over supported Pd catalysts at 520–720 K [16]. A specific model for Na promotion was proposed, which involves Na-induced increase in the strength of the Pd–NO chemisorption bond, accompanied by a weakening of the N–O bond, thus facilitating NO dissociation. This process is critical in the reaction scheme, particularly when the catalyst surface is predominantly covered by hydrocarbon species [16,17].

Although, 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 [18]. This is partly due to the difficulty of achieving in situ control of promoter concentration on the catalyst surface under reaction conditions. Most fundamental studies have addressed the role of promoters in chemisorption only under ultra-high-vacuum conditions [18,19].

Electrochemical promotion (EP) [20,21] overcomes some of these 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.

We have used EP to investigate the efficacy of Na as a promoter of Pt for reactions of environmental importance, such as CO oxidation [22] and NO reduction by CO [23] and by propene [24,25]. It was shown that Na supplied electrochemically from a ß''-Al_2O_3 solid electrolyte, a Na^+ ion conductor, strongly affects both catalytic activity and selectivity of all the above reactions [22–25].

Guided by these EP studies, we then investigated Na promotion of NO_x reduction by propene over conventional dispersed catalysts (propene is the industry standard for catalytic hydrocarbon oxidation studies). Thus, we studied the $NO + C_3H_6$ reaction over catalysts in which the active phase (Pd) was dispersed on Y_2O_3stabilised ZrO_2 (YSZ) carrier, and this catalyst was dosed by impregnation with different sodium loadings [16]. The influence of Na was thus examined in detail. Close similarities were found between electrochemically promoted catalysts [22–25] and conventionally promoted highly dispersed catalysts [16]. 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 effective catalyst formulations.

Here 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 enhance-

ment of two orders of magnitude and large increases in N_2 selectivity from $\sim$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 molecules.

The choice of YSZ as the support for Pd (used in [16]) and of γ-Al_2O_3 for Pt (used here), was dictated by recent studies which show that YSZ and γ-Al_2O_3 maximise the turnover activity of Pd and Pt, respectively, for reactions of relevance to TWC chemistry [12,13].

2. Experimental methods

2.1. Materials and apparatus

The basic catalyst used in this study was Pt highly dispersed over a γ-Al_2O_3 carrier, subsequently dosed by several loadings of sodium modifier using conventional impregnation methods, as follows. The γ-Al_2O_3 support (Alfa products) was impregnated in a pH = 3 solution of H_2PtCl_6 (Alfa products) with appropriate concentration so as to yield 0.5 wt.% Pt metal loading. Subsequent impregnation with $NaNO_3$ was used to produce catalysts with a range of Na loadings. The suspension was initially dried at 353 K and then overnight at 383 K. The resulting precursors were heated in flowing He (673 K/1 h/100 cm^3 min^{-1}), followed by H_2 reduction (673 K/1 h/100 cm^3 min^{-1}). Metal dispersion was measured by H_2 chemisorption at 298 K and the BET surface area of the γ-Al_2O_3 support was measured by N_2 adsorption at 77 K and found to be 90 m^2 g^{-1}. Relevant data are summarised in Table 1. Seven samples with different Na loadings were produced by this route (coded as C1–C7 in Table 1).

A modified procedure involving reduction of Pt/γ-Al_2O_3 catalyst as a first step and then impregnation of this catalyst with $NaNO_3$ was also used, in order to examine possible influences of the preparation procedure on catalytic performance. Na-dosed catalysts produced in this way were found to exhibit similar activity and selectivity to those of the corresponding catalysts produced by the first route. An example of the second type of catalyst is included in Table 1, coded as C3$'$.

Reactants were Air Liquide certified standards of 8% NO in He and 10% propene in He. These were further diluted in ultrapure He (99.999%) and supplied to the reactor at 1 bar. Catalyst testing was performed in a fixed bed, single pass, plug flow reactor, consisting of a 0.4 cm ID quartz tube. The total gas flow rate was high, typically 100–300 cm^3 min^{-1}, in order to minimise conversion of reactants and to eliminate mass and heat transfer effects during acquisition of the kinetic data. The absence of intraparticle and interparticle diffusional effects was experimentally confirmed by variation of catalyst particle size and gas flow rate. NO and C_3H_6 conversions were always below 25% in experiments where kinetic data were acquired. Catalyst loadings were typically about 8 mg (grain size 180–250 μm), the sample being diluted further by admixture with $\sim$80 mg 100–325 mesh α-Al_2O_3 (Alpha products). The catalyst bed was held between plugs of quartz wool and a K-thermocouple was located in the centre of the bed. No reaction was observed over quartz wool for temperatures up to 773 K. The analysis of the reactants and products were performed by on-line gas chromatography (SHIMADZU-14B) and on-line IR spectroscopy (Fisher-Rosemount, Binos 100 NDIR CO_2 Analyzer). Separation of N_2, NO, C_3H_6 and CO was achieved in a molecular sieve 5A column at 353 K while CO_2 and N_2O were separated using a porapak-N column at the same temperature. Before measurements were taken, the catalysts were operated for 1 day in air and 5 days in a reactive gas mixture at 723 K to eliminate possible residue from the metal precursor and to ensure stable operation.

HREM studies were performed with a JEOL 2010 instrument and XRD data were acquired with a Philips PW 1710 diffractometer using Cu Kα radiation. Prior to these measurements, the samples were treated in air for 1 h at 773 K followed by 1 h H_2 flow at 723 K prior to cooling to room temperature in He.

3. Results

3.1. Catalyst characterisation

Active metal areas were measured via H_2 chemisorption at 298 K, after reduction in H_2 at 623 K for 1 h and degassing at 673 K for 1 h. The hydrogen to metal ratio (H/M) was calculated by assuming a 1 : 1

Table 1
Properties of the 0.5 wt.% Pt/γ-Al$_2$O$_3$ catalysts[a]

Catalyst code	Na-loading (wt.%)	H$_2$ uptake (cm^3 STP/g)	Dispersion (%)	Mean crystallite size[b] (nm)
C1	0	0.085	30	5
C2	0.52	0.250	87	2
C3	1.57	0.160	56	2
C3′	1.57	0.050	18	8
C4	2.60	0.101	35	4
C5	4.18	0.082	29	5
C6	5.22	0.081	28	5
C7	10.4	0.071	25	6

[a] All the above surface characterization measurements refer to used catalysts (i.e., catalysts treated for a long period of time at reaction conditions).
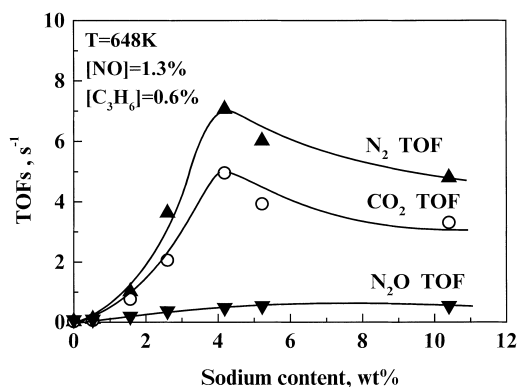[b] Calculations based on a Pt surface atom density of 1.53×10^{19} atoms/m^2.

Fig. 1. The effect of sodium for fixed temperature and reactant concentrations on the turnover (TOF) formation rates of N$_2$, CO$_2$ and N$_2$O; $T = 648$ K, [NO] = 1.3%, [C$_3$H$_6$] = 0.6%; Concentrations refer to reactor outlet.

Fig. 2. The effect of sodium loading for fixed temperature and reactant concentrations on the enhancement ratio $\rho = $ TOF/TOF^0 for the formation of N$_2$, CO$_2$ and N$_2$O; $T = 648$ K, [NO] = 1.3%, [C$_3$H$_6$] = 0.6%; TOF$^0_{N_2} = 0.024$ s^{-1}, TOF$^0_{CO_2} = 0.025$ s^{-1}, TOF$^0_{N_2O} = 0.077$ s^{-1}; Concentrations refer to reactor outlet.

hydrogen metal stoichiometry. The H$_2$ uptakes were determined by extrapolation of the 'plateau' portion ($\sim$10–40 Torr) of the isotherm, as described by Benson and Boudart [26]. These results are summarised in Table 1.

3.2. Effect of sodium loading on turnover activity of Pt

Fig. 1 depicts the effect of sodium loading on N$_2$, CO$_2$ and N$_2$O turnover rates. Promotion is maximised for a sodium content of 4.18 wt.% (Catalyst C5, Table 1). Further increase in the sodium loading (up to 10.4 wt.%) leading to a slight inhibition of the rates. In particular, all rates exhibit an exponential increase with increasing sodium loading in the interval 0–4 wt.% Na: this is made more apparent by a loga-
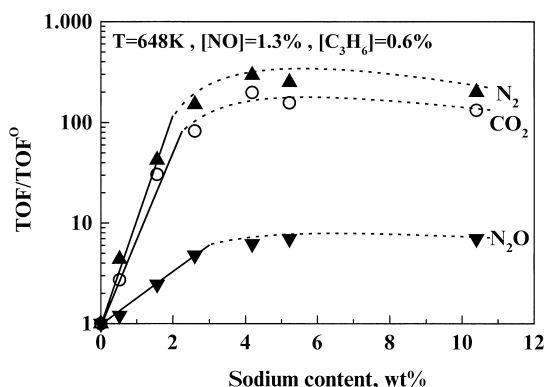
rithm plot as shown in Fig. 2. In this figure we show the effect of sodium loading on the rate enhancement ratio, ρ, defined for comparison reasons in a similar manner to that used in EP studies [20–25], i.e:

$$\rho = \frac{\text{TOF(on Na\{-\}promoted catalyst)}}{\text{TOF}^0(\text{on Na\{-\}free unpromoted catalyst})} \quad (1)$$

ρ values as high as $\rho_{N_2} \sim 300$, $\rho_{CO_2} \sim 250$, $\rho_{N_2O} \sim 7$ are found for the production of N$_2$, CO$_2$ and N$_2$O, respectively.

3.3. Effect of NO concentration on turnover rates

Fig. 3(a),(b) and (c) show the effect of NO concentration [NO], (%), on the N$_2$, CO$_2$ and N$_2$O turnover

Fig. 4. The effect of sodium loading for fixed temperature and reactant concentrations on the N_2 selectivity, S_{N_2}; $T = 648$ K, $[NO] = 1.3\%$, $[C_3H_6] = 0.6\%$.
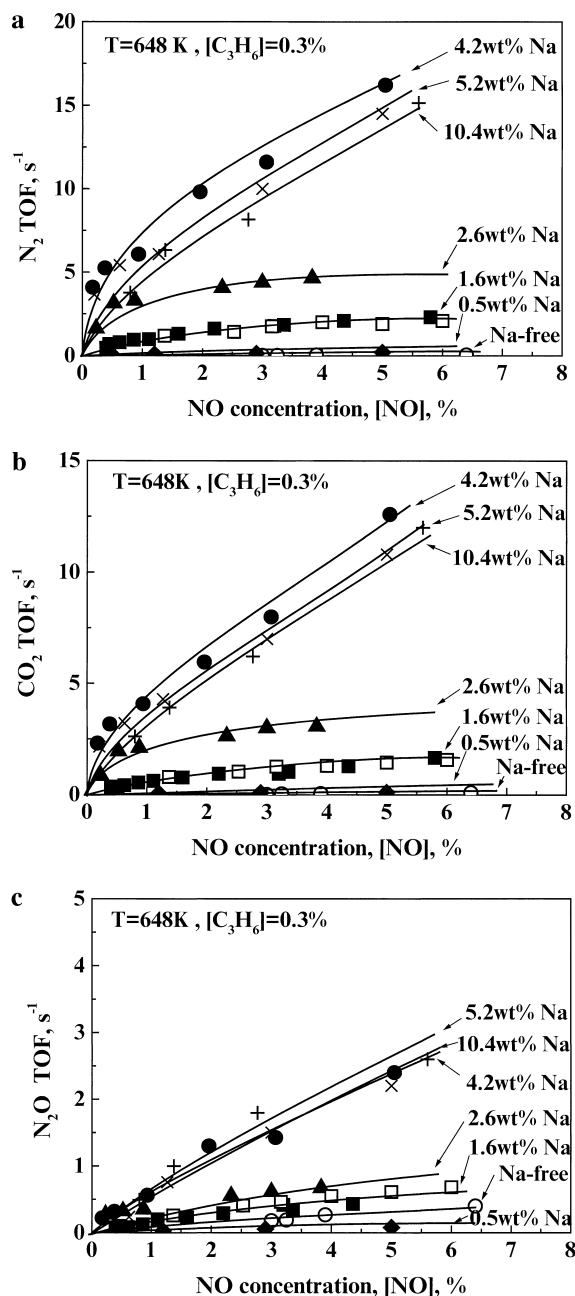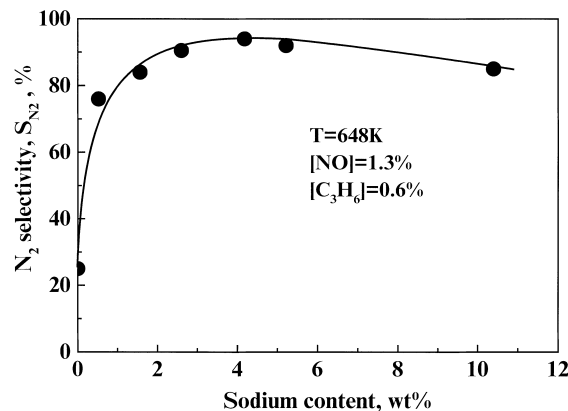

Fig. 3. The effect of NO concentration on the turnover (TOF) formation rates of (a) N_2, (b) CO_2, and (c) N_2O for catalysts C1–C7 and C3' (□) with different Na loadings at $T = 648$ K and $[C_3H_6] = 0.3\%$; Concentrations refer to reactor outlet.

rates, respectively, for the eight catalysts (C1–C7, C3') promoted by different amounts of Na. The results very clearly show a large enhancement of reaction rates induced by Na over the whole range of NO concentrations investigated. The extent of enhancement is strongly dependent on the Na loading. Under all NO concentrations, the best performance is achieved with catalyst C5 (4.18 wt.% Na, Table 1). Rate enhancement ratios of the order of 300, 250 and 10 were again achieved for the production of N_2, CO_2 and N_2O, respectively, with respect to the unpromoted (Na-free) catalyst C1.

3.4. Effect of Na loading and NO concentration on N_2 selectivity

Fig. 4 illustrates the behaviour of the selectivity towards N_2, defined as

$$S_{N_2} = \frac{r_{N_2}}{(r_{N_2} + r_{N_2O})} \qquad (2)$$

upon varying sodium loading of the catalyst. The unpromoted Na-free catalyst C1 has a very low selectivity towards N_2 of the order of 25% under these conditions. This illustrates the relatively poor activity of Pt for the dissociative chemisorption of NO. However, small additions of sodium cause extensive NO dissociation, leading to very high (~95%) N_2 selectivity values. There is an optimum Na loading of about 4.18 wt.% of Na (catalyst C5) which maximises the selectivity (Fig. 4). However, catalysts with sodium
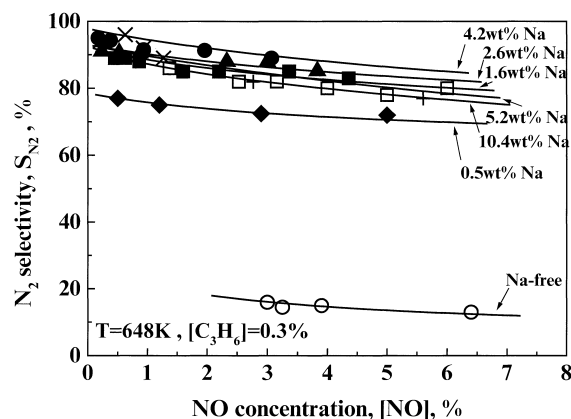
Fig. 5. The effect of NO concentration on N_2 selectivity for catalysts C1–C7 and C3' ($\square$) with different Na loadings at $T = 648\,K$ and $[C_3H_6] = 0.3\%$; Concentrations refer to reactor outlet.

loadings coverage much higher than the optimum level continue to exhibit high N_2 selectivity (>85%). Nevertheless, it is interesting to note that C5 is best in terms of both activity and selectivity.

Fig. 5 shows the selectivity behaviour of catalysts C1–C7 and C3' upon varying NO concentration at fixed temperature ($T = 648\,K$) and propene concentration ($[C_3H_6] = 0.6\%$). In accord with Fig. 4, the Na-free catalyst C1 exhibits very low selectivity (~15%), whereas all the other Na promoted catalysts operate at very high S_{N_2} values (~75–95%). The best selectivity is again observed for catalyst C5 (4.18 wt.% Na) and its superiority is maintained within the NO concentration range studied (Fig. 5). As would be expected, a small decrease in N_2 selectivity is observed upon increasing NO concentration (Fig. 5).

3.5. Effect of Na addition on temperature for 50% NO conversion

Fig. 6(a) shows the effect of catalyst temperature on NO conversion (X_{NO}) for five of the seven catalysts in Table 1 (i.e., C1, C4, C5, C6 and C7), and Fig. 6(b) illustrates the corresponding behaviour of the selectivity towards N_2. For reasons of comparison, only catalysts with similar dispersion are included in Fig. 6. The reactor inlet conditions were kept constant, i.e. 1000 ppm NO, 1000 ppm propene at a total flow rate of 80 cm³ STP/min. In every case, the amount of catalyst used was 8($\pm$0.2) mg. It can be seen that the best catalyst (C5) has a 50% NO conversion temperature
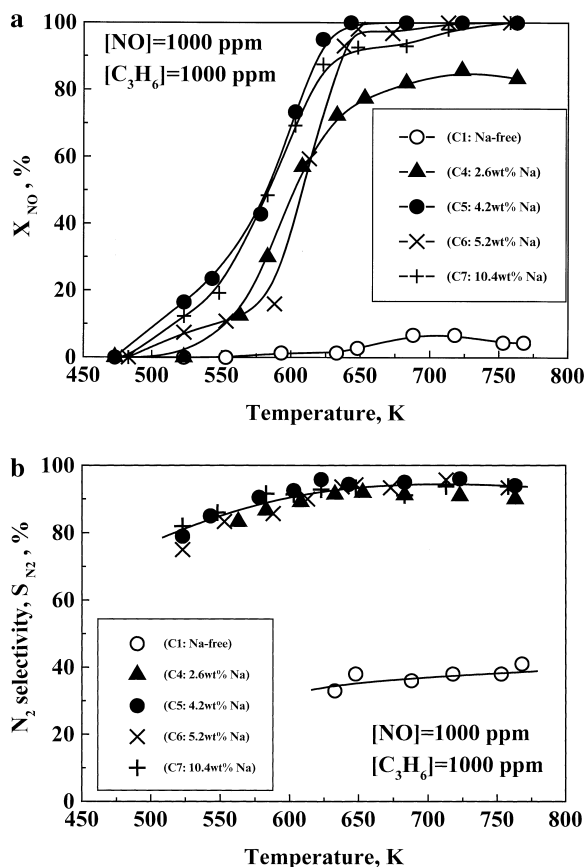

Fig. 6. (a) The conversion of NO to various products for catalysts C1, C4, C5, C6 and C7 with comparable dispersions, as a function of temperature at constant reactor inlet conditions: $[NO] = 1000$ ppm and $[C_3H_6] = 1000$ ppm; Total flowrate $F = 80\,cm^3\,min^{-1}$; Catalyst weight 8($\pm$0.2) mg. (b) The corresponding behaviour of the selectivity towards N_2.

T_{50} of ~580 K, whereas the Na-free catalyst never exceeded 5% NO conversion and was almost inactive over the whole temperature range. In accord with Figs. 4 and 5, the sodium-free catalyst C1 exhibits very low N_2 selectivity, whereas all the other Na promoted catalysts attain very high S_{N_2} over the whole temperature range studied. Optimally promoted catalyst C5 again exhibits the best selectivity.

We recall here [31] the usefulness of 'effective contact time of NO' expressed in terms of the number of available surface Pt atoms (i.e., surface Pt atoms/NO molecules fed/s) for straightforward quantitative comparisons with other literature work. This number is of the order of 1 s for the results of Fig. 6. At this contact
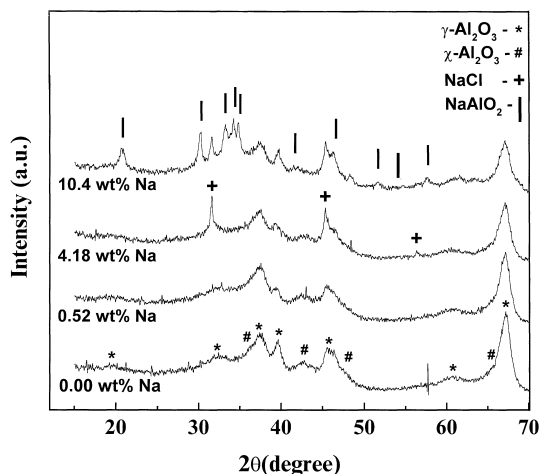
Fig. 7. XRD patterns for samples C1, C2, C5 and C7 after calcination in air at 773 K followed by reduction in hydrogen at 723 K.

time the optimally promoted catalyst C5 achieves 50% NO conversion at $T_{50} = 580$ K, while it approaches 100% NO conversion at about 650 K.

3.6. HREM and XRD studies

The XRD results (Fig. 7) show that the Na-free catalyst and the 0.52% Na catalyst contain principally γ-alumina, with some χ-alumina. At 4.18% Na (optimally promoted catalyst) reflections due to NaCl are apparent and at 10.4% Na NaAlO$_2$ also appears. HREM confirms the presence of trace NaCl as a distinct phase at high Na loadings: the material is visible as needle-like crystals of length 30–50 nm. The source of Cl is presumably the H_2PtCl_6 precursor employed. Quantification of the XRD data, by comparison with NaCl–alumina standards, shows that at 4.18 wt.% Na, the amount of Na present as NaCl is equivalent to approximately 0.6 wt.%. The HREM images also confirm the platinum dispersion, with the observed particle sizes (2–10 nm) being in accord with the metal surface areas as measured by chemisorption (Table 1).

4. Discussion

4.1. General

In agreement with Burch and Watling [27], the present results show that unpromoted Pt/γ-Al$_2$O$_3$

(Catalyst C1, Table 1) is almost ineffective for the reduction of NO by propene, presumably because surface sites are blocked by propene or propene-derived carbonaceous species that are strongly adsorbed on the catalyst surface. Indeed, in a recent detailed kinetic study of this reaction over Pt films [24] we have shown that under similar conditions, the NO + C$_3$H$_6$ reaction obeys Langmuir-Hinshelwood (LH) type kinetics with characteristic rate maxima reflecting competitive adsorption of the two reactants. These rate maxima occurred at very low [C$_3$H$_6$] : [NO] ratios, typically <0.08, i.e. very high partial pressures of NO relative to C$_3$H$_6$ are necessary in order to achieve a comparable coverage of both reactants on the Pt surface, thus maximising the rate [24]. This points to a weaker adsorption of NO on the metal surface relative to C$_3$H$_6$. As a consequence, the Pt surface is predominantly covered by propene and propene-derived species under a wide range of reaction conditions. The results presented in Fig. 3 show that for fixed [C$_3$H$_6$] = 0.3%, the reaction exhibits positive order in [NO] and no rate maxima are found within the range of accessible experimental conditions. This strongly supports the view that under all experimental conditions used in this study the adsorption of hydrocarbon on the catalyst is much stronger than that of NO.
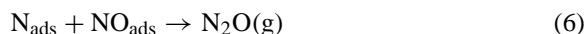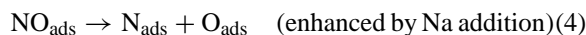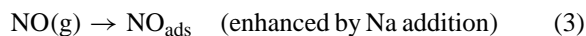
Burch and Watling [27] showed that the presence of O$_2$ eliminates the problem of site blocking by creating hydrocarbon-free sites on the catalyst surface where NO can be adsorbed, thus initiating the reaction. Here, we propose that Na plays an analogous role by enhancing the strength of the Pt–NO adsorption bond, thus increasing NO coverage of the catalyst surface. In addition, Na promotes NO dissociation, which is proposed as the critical reaction initiating step. The consequences of this are very striking: a dramatic activity enhancement by up to two orders of magnitude and a large improvement in N$_2$ selectivity from ~15% over Na-free Pt to ~95% over the optimally Na-promoted catalyst.

What is the significance of phases other than Pt and alumina which appear in the catalysts with higher Na loadings? It would appear that these phases (NaAlO$_2$ and NaCl) do not play an important role in determining the overall performance of promoted catalysts. The NaCl crystals present in the optimally promoted sample account for only a small amount (~0.6 wt.%) of the total sodium loading (4.18 wt.%), the remainder

being highly dispersed over the support surface. As in previous studies [16,22–25], it is this highly dispersed sodium which is responsible for the improved catalytic properties. The mode of action of the sodium modifier is discussed in detail below. The sodium aluminate phase is present only at the highest Na loading (overpromoted) and therefore, acts as a sink for excess sodium. Our spectroscopic studies [24] show that the exact chemical composition of the Na promoter phase (nitrate, carbonate ...) is dependent on the temperature and reactant partial pressures, as one would expect. In the present case, the catalysts showed no deterioration in performance after 12 days of operation at temperatures up to 723 K.

4.2. Kinetic behaviour and mode of action of the Na modifier

The formation of nitrogen containing products, and in particular the variations in N_2/N_2O selectivity may be rationalised in terms of the following reaction scheme:

$$NO(g) \rightarrow NO_{ads} \quad \text{(enhanced by Na addition)} \quad (3)$$

$$NO_{ads} \rightarrow N_{ads} + O_{ads} \quad \text{(enhanced by Na addition)} (4)$$

$$N_{ads} + N_{ads} \rightarrow N_2(g) \quad (5)$$

$$N_{ads} + NO_{ads} \rightarrow N_2O(g) \quad (6)$$

While O_{ads} reacts with the adsorbed hydrocarbonaceous species resulting from propene adsorption to yield CO_2 and H_2O.

As noted above, the kinetic behaviour of Pt catalysts for the $NO + C_3H_6$ reaction indicates LH competitive adsorption of the reactants [24], and that the chemisorption of propene is much more pronounced than that of NO under all conditions used here (Fig. 3). Thus we argue that under all our experimental conditions the surface of the Pt crystallites is covered predominately with propene and its dissociation products.

We have successfully used EP to promote the reduction of NO by CO [23] and by C_3H_6 [24] over Pt-film catalysts. It was shown that relatively small amounts of electrochemically supplied Na on the Pt surface led to very strong promotion. Recall that EP is applied to thin continuous films of the metal catalyst to which the promoting species (in this case Na) is supplied by spillover from a suitable solid electrolyte, interfaced with the catalyst film.

It is remarkable that close similarities exist between the performance of such Pt-film catalysts promoted electrochemically with Na [24] and the conventional highly dispersed Na-promoted catalysts investigated in the present study. These similarities include the overall kinetic behaviour and the dependence of activity and selectivity on Na loading, as summarised below:

1. Both promotion methods (electrochemical and conventional promotion) 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 ([24] and Figs. 1–3 of the present study).

2. A rapid exponential increase in reaction rates with sodium content is followed in both cases by a less pronounced inhibition ([24] and Figs. 1 and 2). Even at very high sodium loadings the reaction rate is significantly higher than that of Na-free catalyst.

3. In both cases the selectivity towards N_2 follows the same 'volcano' behaviour passing through a maximum which corresponds to the optimally promoted catalyst ([24] and Fig. 4).

One may also note the following differences:

(i) In the case of conventional promotion the enhancement ratio ρ (Eq. (1)) values are much more pronounced than with EP [24]. If fact, differences up to one order of magnitude are observed.

(ii) The Na-free EP catalyst exhibited an unpromoted rate significantly higher than that of the Na-free conventional Pt/γ-Al_2O_3 dispersed catalyst: the latter is practically ineffective for the $NO + C_3H_6$ reaction (Figs. 3 and 6). Both (i) and (ii) may be connected with the very different Pt particle sizes in the two cases.

All the above differences 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 [24]. Our XPS data showed that there is always a residual amount of Na on the catalyst surface due to thermal diffusion from the ß''-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 explain why the so called 'Na-free' EP catalyst appears to have a rel-

atively good activity for the reaction of NO + propene [24], whereas the true Na-free conventional catalyst used here is practically inactive, in good agreement with the literature [27].

In our earlier analysis of EP data [23–25], we argued that Na acts by increasing the strength of NO chemisorption relative to propene, an effect which is accompanied by weakening of the N–O bond, thus facilitating NO dissociation on the metal surface. Both theory [28] and experiment [29] show that ionised alkalis co-adsorbed with NO on platinum metal surfaces induce strengthening of the metal–N bond and weakening of the N–O bond by populating the NO π^*orbital. This occurs because the local electric field due to the alkali ion pulls the NO antibonding orbital below the metal Fermi level [28]. A similar effect of Na^+ on adsorbed NO is expected to occur in the presence of a counter ion (e.g. carbonate) in the case of a conventionally promoted dispersed catalyst. Interestingly, our most recent work shows that promotion of NO reduction by propene with Li, K, Rb and Cs is also effective [30].

Rate enhancement is therefore, due to (i) increased coverage of NO (reaction 3) in the presence of strongly adsorbing propene and (ii) triggering of NO dissociation, which is the reaction-initiating step (reaction 4). The enhancement of NO adsorption (an electronegative adsorbate) and the inhibition of propene adsorption (an electropositive adsorbate) by Na is the key point.

These effects act to increase both the NO coverage and its degree of dissociation (reactions 3 and 4). Once O_{ads} is produced it is scavenged by adsorbed hydrocarbonaceous species, accompanied by N_{ads} recombination or reaction with NO_{ads} to yield N_2 and N_2O, respectively, (reactions 5 and 6). At sufficiently high Na loadings, both the EP and conventional Pt/γ-Al_2O_3 catalysts exhibit poisoning due to site blocking by Na surface compounds. Our XPS studies involving in situ transfer of Na promoted (and poisoned) ex-reactor EP Pt catalysts to the spectrometer analysis chamber showed [24] that the Na containing promoting (or poisoning) phase consists principally of a mixture of $NaNO_2$ and $NaNO_3$, along with some Na_2CO_3.

Further corroboration of the proposed mode of action of the Na modifier is provided by a very recent study of the Pd-catalysed reduction of NO by an alkane (CH_4) [31], where similar phenomena were at work but the consequences were very different. In regard to activity, it was found that for all loadings, Na induced only poisoning of the NO + CH_4 reaction. This reflects the weak interaction of methane with the metal surface, relative to NO [31]. Recall that alkenes show a much stronger interaction with noble metal surfaces than do alkanes [27], and that O adatoms are particularly effective in inhibiting the dissociative chemisorption of methane on Pd [32]. Thus even at low [NO], the catalyst is predominantly covered by NO. As a result, any further enhancement of the Pd–NO bond strength and NO dissociation probability due to Na addition results in poisoning. All the evidence is consistent with the view that dissociative chemisorption of CH_4 competes ineffectively with NO adsorption and dissociation [31]. Addition of Na promotes the latter but not the former. Therefore, for CH_4 + NO, poisoning by Na is observed under all conditions due to overpopulation of the surface with NO and its dissociation products [31]. However, Na promotion of the same Pd/YSZ catalysts was found [16] to substantially enhance the activity of NO reduction by propene, since a wide range of conditions can exist for which the surface is predominantly covered by the alkene, due to its much stronger interaction with the metal surface [16]. We therefore, have a consistent explanation for the response to Na of NO reduction by different types of hydrocarbons over platinum-group metal surfaces [17]. Further work is in progress to determine the effects of O_2, CO_2 and H_2O on this interesting system. Our earlier results [25] involving electrochemical promotion by Na show that the beneficial effects of alkali promotion on the reduction of NO by propene persist in the presence of oxygen.

4.3. Selectivity behaviour

The variation in N_2 selectivity upon Na loading of the catalysts can be readily understood in the following terms. The rates of production of N_2 and N_2O (and thus N_2 selectivity, Eq. (2)) depend on the extent of NO dissociation (reaction 4) which is followed by the elementary reactions (5) and (6). The observed increase in the N_2 selectivity upon sodium addition is a consequence of increased NO dissociation (due to Na) i.e., a decreased amount of molecular NO, and an increased amount of atomic N on the surface. Both

factors favour reaction (5) over reaction (6), leading to higher N_2 selectivity.

Finally, we note that although catalysts C3 and C3′ differ significantly in regard to metal dispersion, their behaviour with respect to N_2 selectivity is not very different. Close inspection of Fig. 5 (compare open and filled squares) does however, show that the more highly dispersed catalyst (C3) does exhibit measurably higher selectivity than C3′. This may be understood as follows. The low index planes of Pt are ineffective for NO dissociation; however, high index planes are effective (see [24] and references therein). Therefore, with unpromoted Pt one would expect some increase in N_2 selectivity with dispersion. The effect of Na is to induce NO dissociation on the low index planes, hence reducing the effects of particle size on selectivity.

5. Conclusions

1. The catalytic reduction of NO by propene over Pt exhibits strong promotion by Na. Rate increases by two-orders of magnitude are achievable, while the selectivity towards N_2 is improved from 15% over the Na-free unpromoted Pt to >95% over a 4.18 wt.% Na-promoted Pt.
2. A specific model for Na promotion is proposed which explains all the experimental observations and is consistent with our previous electrochemical promotion studies. 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 characterised by competitive adsorption of the reactants.
3. Close similarities exist between the performance of Pt-film catalysts promoted electrochemically and highly dispersed 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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