PROMOTION BY SODIUM IN EMISSION CONTROL CATALYSIS:
The difference between alkanes and alkenes in the Pd-catalysed reduction of NO by hydrocarbons

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ABSTRACT

The activity and selectivity of Pd catalysts supported on YSZ and dosed with different amounts of Na promoter has been investigated for the reduction of NO by alkenes (C_3H_6) or alkanes (CH_4). It is found that Na strongly promotes the reduction of NO by C_3H_6. Rate increases by an order of magnitude are achievable, while the N_2-selectivity is improved from ~75% over the unpromoted Pd catalyst to >95% over the optimally Na-promoted catalyst. With CH_4 as the reductant, a very different behaviour is observed: for all loadings, Na induces only poisoning. The experimental data indicate that Na increases the strength of NO chemisorption relative to the hydrocarbons. This is accompanied by weakening of the N-O bond, thus facilitating NO dissociation, which is proposed as the critical reaction-initiating step. According to this model the promoting or poisoning effect of Na depends on the interaction strength of the catalyst surface with the hydrocarbon. The different behaviour of propene and methane reflects the weaker interaction of alkanes with metal surfaces compared to that of alkenes. XPS and Auger data demonstrate that Na coverage increases monotonically with promoter loading and that there is no significant tendency for the promoter to agglomerate with increasing promoter loading. However, a very small but constant tendency to accumulate subsurface or dissolved Na was observed as the promoter loading is increased.

KEYWORDS: Sodium, NO reduction, Methane, Propene, Palladium, Promotion

INTRODUCTION

Heterogeneous catalysis has and will continue to play a major role in atmospheric pollution control. The catalytic reduction of NO_X emissions produced by both stationary and automotive combustion processes is of major environmental importance (Taylor, 1993). Automotive exhaust catalytic converters - the so-called three-way catalyst (TWC) - employ a well established technolo-

gy in controlling NO_X, CO and hydrocarbon emissions. This uses formulations based variously on Pt, Rh and Pd. With regard to NO_X reduction, Rh is highly effective for NO dissociative chemisorption and is therefore the key component responsible for NO_X reduction in conventional TWCs. On Pd this process exhibits strong structure sensitivity (Davies and Lambert, 1981), while Pt is relatively ineffective for the dissociative chemisorption of NO (Masel, 1995).

Considerable effort has been expended on finding materials for replacing or reducing the use of Rh in TWCs because of its scarcity and higher cost in comparison with Pt and Pd. For the reasons given above, Pd is particularly promising in this regard; it is also relatively inexpensive. It is therefore of interest to discover means of enhancing the catalytic performance of Pd for the reduction of NO, given that this metal is a notably effective catalyst for hydrocarbon oxidation. Efforts thus far have been focused on improving the catalytic properties of Pd by doping the support material with additives or by using supports other than Al_2O_3 (e.g. yttria-stabilised zirconia or YSZ) (Yentekakis et al., 1995; Pliangos et al., 1997). These strategies have indeed improved significantly the activity and selectivity of Pd for NO reduction to N_2. Recently, Burch and Watling (1997) 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). 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, Alexandrou et al. (1997) demonstrated significantly increased conversion in the CO+NO reaction over Na promoted Pd and Pt supported catalysts.

Here we report Na-induced increases in reaction rate *by up to an order of magnitude*, as well as a significant enhancement in N_2 selectivity, in the catalytic reduction of NO by propene over supported Pd catalysts. In contrast with this when an alkane (CH_4) was used as the reductant, we find that for all loadings Na induces only poisoning.

Previously, we used electrochemical promotion (EP) (Vayenas et al., 1992; Vayenas and Yentekakis, 1997) to investigate the efficacy of Na as a promoter for the Pt-catalysed NO reduction by CO (Palermo et al., 1996). Most recently (Yentekakis et al., 1997), the same technique was employed for Na promotion of Pt in the reduction of NO by C_3H_6. It was shown that Na supplied electrochemically from a β''-alumina solid electrolyte (a Na^+ ion conductor), strongly promoted both reactions: in effect Pt could be induced to behave like Rh. Activity enhancement of an order of magnitude and large increases in N_2 selectivity were achieved.

Guided by these EP studies on Pt, there being no similar studies on Pd, we have chosen to investigate Na promotion of NO reduction by hydrocarbons (C_3H_6 and CH_4) over conventional dispersed Pd catalysts. (Propene is the industry standard for catalytic hydrocarbon oxidation studies and methane is relevant in the context of natural gas fuelled vehicles). Due to the very different interaction of alkanes and alkenes with metal surfaces, markedly different behaviour towards NO reduc-

Table 1[a]. Properties of the 0.5 wt % Pd/YSZ catalysts

[a] All the above surface characterisation measurements refer to used catalysts.

[b] Based on the assumption that all Na is present at the surface and distributed uniformly over the entire available area (Pd+YSZ), without any incorporation into the bulk.

[c] Calculations based on a Pd surface atom density of 1.27×10^{19} atoms/m^2

Catalyst code	Na-loading (wt %)	Nominal Na coverage[b] (%)	H_2 uptake (cm^{3}STP/g)	Dispersion (%)	Active surface area [c] (m^2/g)
C1	0	0	0.106	20	0.45
C2	0.017	5	0.105	20	0.44
C3	0.034	10	0.131	25	0.55
C4	0.068	20	0.123	23	0.52
C5	0.102	30	0.127	24	0.54

tion is expected. Thus we hope to uncover important aspects of NO/hydrocarbon catalytic chemistry. In addition, we seek to understand the mode of action of the Na promoter. The choice of support was dictated by recent studies, which show that YSZ maximizes the turnover activity of Pd for reactions of relevance to TWC chemistry (Yentekakis *et al.,* 1995; Pliangos *et al.,* 1997).

MATERIALS AND METHODS

Supported Pd catalysts used in this study were prepared by incipient wetness impregnation of the 8 mole% yttria stabilised zirconia (YSZ) support (Zirconia Sales) using a pH=3 solution of $PdCl_2$ (Alfa Products). The solution was of appropriate strength so as to yield 0.5 wt % metal loading. Sodium was added to the catalysts by subsequent impregnation with $NaNO_3$ solutions of suitable concentration. The suspensions were dried in a rotating flask by evaporation at 353 K and then overnight at 383 K. These catalyst precursors were heated in flowing He (1h/673K/100cm³min⁻¹), followed by H_2 reduction (1h/673K/100cm³min⁻¹). Five samples with different Na loadings were produced (coded as C1-C5 in Table 1).

The metal dispersion was measured via H_2 chemisorption at 333 K after reduction in H_2 at 573 K for 30 min and degassing at 673 K for 30 min. The hydrogen to metal ratio (H/M) was calculated by assuming a 1:1 hydrogen:metal stoichiometry. The H_2 uptakes were determined by back-extrapolating the high pressure "plateau" part of the adsorption isotherm to zero. The BET surface area of the YSZ support was measured by N_2 adsorption at 77 K and found to be ~7 m²g⁻¹. The catalyst characterisation data are summarised in Table 1.

For purposes of convenient comparison, a nominal percentage surface coverage by Na has been calculated for each of the catalysts C2-C5 based on the assumption that all the promoter is present at the surface and distributed uniformly over the entire available area (Pd+YSZ), without any incorporation into the bulk.

Catalyst testing was performed in a flow apparatus, which consists of a feed unit, the reactor and an analysis unit utilizing on-line gas chromatography (Shimadzu-14B) and CO_2-IR spectroscopy (Fisher-Rosemount, Binos 100 NDIR CO_2 Analyser). The fixed-bed, single-pass, plug-flow reactor,

consisting of a 0.4 cm ID quartz tube, was typically loaded with about 7.5 mg of catalyst. The total gas-flow rate was high, typically 100-600 cm³min⁻¹, in order to minimize 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 hydrocarbon conversions were always bellow 25%. 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 ensure stable operation. In addition, stability tests of Na-promoted catalysts at 723K for up to 10 days showed no deterioration in both catalyst activity and selectivity.

XPS measurements were carried out in a VG ADES 400 UHV spectrometer system. The ex-reactor catalyst samples were pressed between two discs of high-purity aluminium; separating the discs then gave two specimens from each sample consisting of compacted powder adhering to the aluminum support. XP spectra were acquired with $MgK\alpha$ radiation with the Al specimen support at ground potential; quoted binding energies are referred to the Zr $3d_{5/2}$ emission from YSZ at 182.4 eV BE. Typically, spectra were acquired by signal averaging over 10 scans.

RESULTS
XPS and Auger data

The XP spectra obtained from samples of the five ex-reactor catalysts provide useful information. Inserts (a) and (b) of Figure 1 show Na KLL Auger and Na 1s photoelectron spectra, respectively, for each of the five catalysts and for the YSZ support alone. Although we cannot discriminate between Na on the metal and on the support, a notoriously difficult problem in catalyst characterisation, it is clear from both the Auger and photoelectron data that there is a monotonic increase in Na emission with increased Na loading. Additionally, this behaviour of the spectral intensities shows that there is no significant tendency for the promoter phase to agglomerate with increasing promoter loading. Background subtraction followed by quantification of these spectra shows that the ratios of the integrated Na KLL Auger and Na XP 1s intensities are as follows: C2
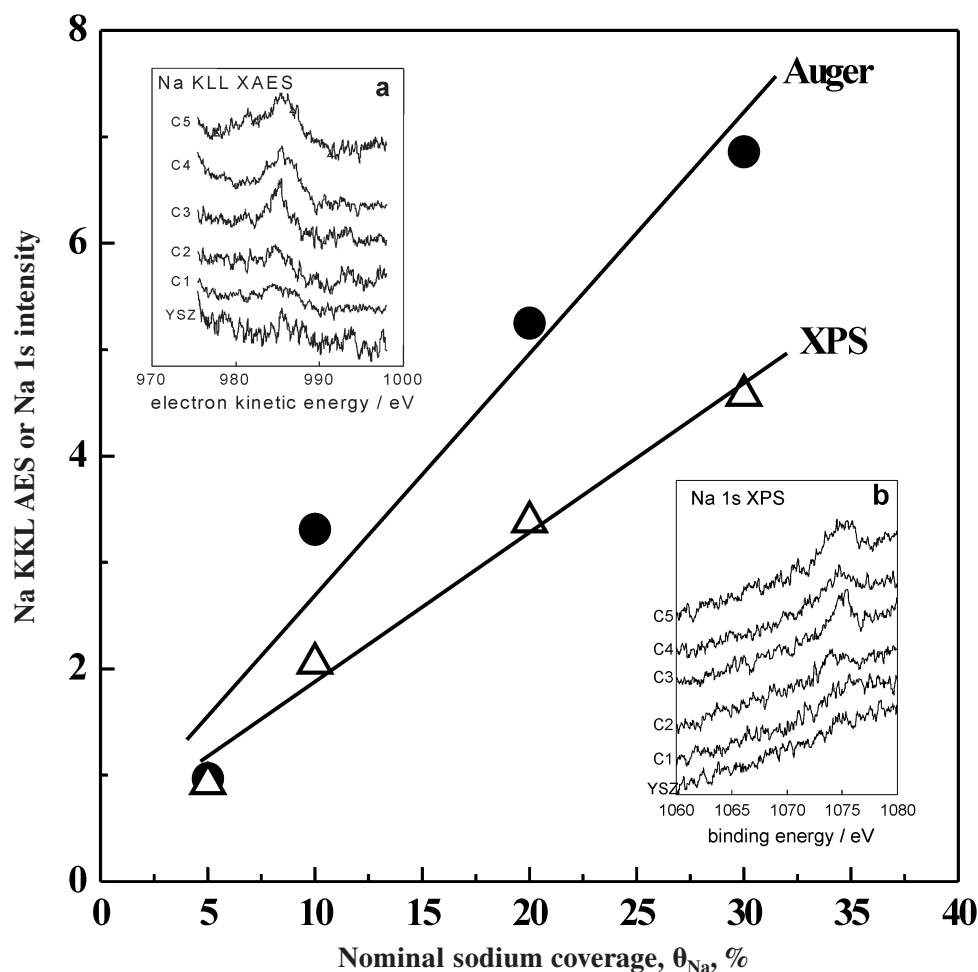
Figure 1. Dependence of integrated Na Auger and XP intensities on calculated nominal Na coverage. Insert (a): Na KLL X-ray excited Auger spectra of catalysts C1-C5 and of the YSZ support. Insert (b): Na 1s XP spectra of catalysts C1-C5 and of the YSZ support

= 1.1±0.3; C3-C5 = 1.5±0.3 (Figure 1). The very different electron kinetic energies imply different sampling depths for the Auger and XP spectra: ~10Å and ~3Å, respectively. One may therefore conclude that for the higher Na loadings (C3-C5) there is some tendency to accumulate subsurface Na relative to the lowest Na loading (C2) and that the proportion of surface to subsurface Na is the same for C3 - C5.

Effect of NO partial pressure (P_{NO})

NO+C_3H_6 reaction: Figures 2a,b,c (A) show the effect of P_{NO} on the CO_2, N_2 and N_2O turnover frequencies (TOF: molecules of product per surface Pd atom per second), respectively, for the five catalysts promoted by different amounts of Na.

Figure 2d(A) illustrates the corresponding behaviour of the selectivity towards N_2. The results very clearly show a pronounced promotion by sodium of both activity and selectivity, the extent of which is strongly dependent on the Na loading. Under our conditions, optimum performance is achieved at 0.068wt% Na (catalyst C4, 20% nominal Na coverage, Table 1), which causes up to ten-fold enhancement in the turnover rate of CO_2 (Fig. 2a(A)) and of N_2 (Fig. 2b(A)), with respect of the unpromoted (Na-free) catalyst C1.

Although the magnitude of this effect depends on P_{NO}, decreasing with P_{NO} beyond the optimal value, strong enhancement is present over a wide range of $P_{C_3H_6}$ (see below, Fig. 3). At the same time, the rate of N_2O formation remains practical-
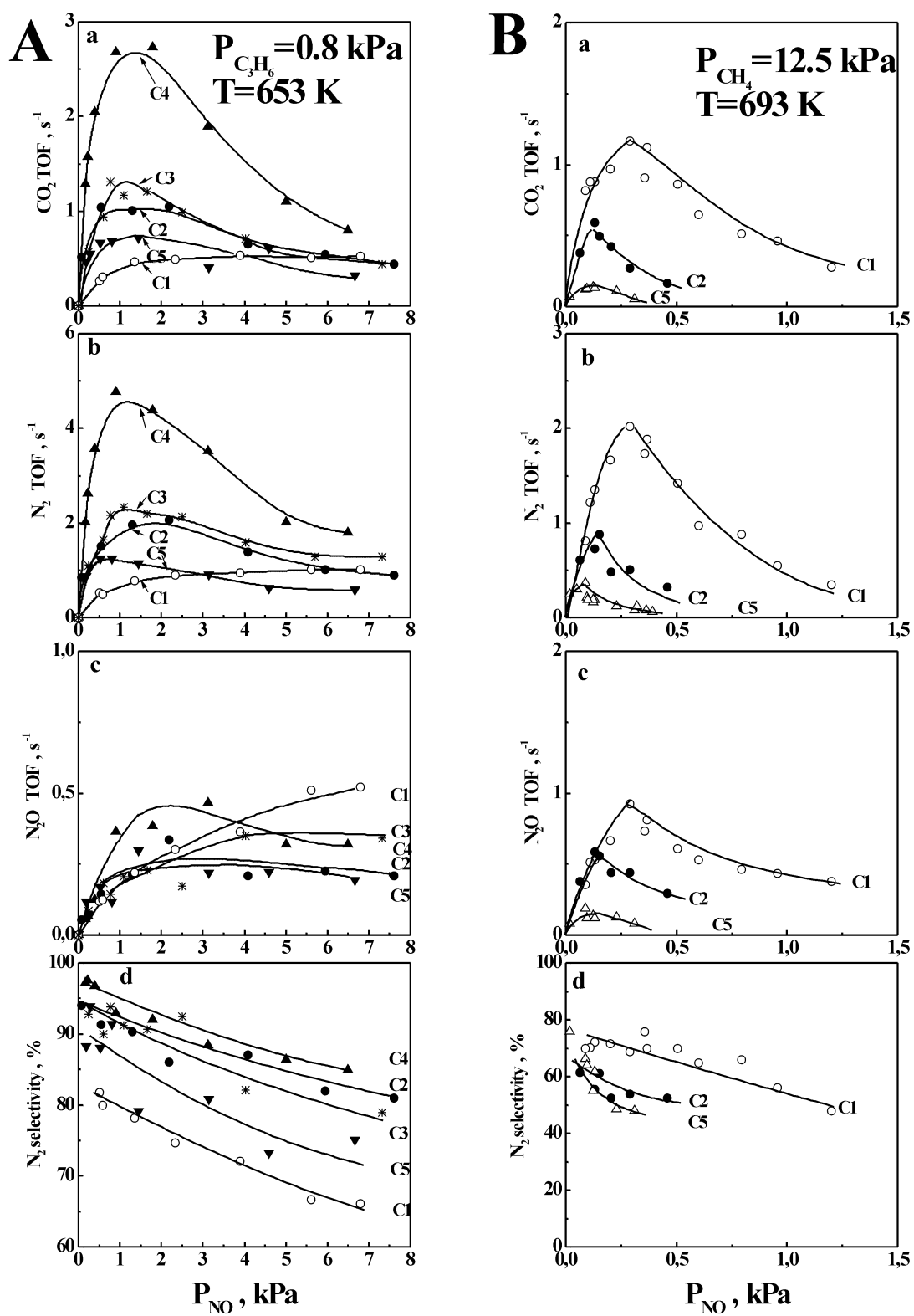
Figure 2. The effect of P_{NO} on CO_2 (a), N_2 (b), N_2O (c) TOFs and N_2 selectivity (d), for catalysts C1-C5 during the Pd-catalysed reduction of NO by C_3H_6 (A) and by CH_4 (B)

ly unaffected (Fig. 2c(A)). This results in a significant increase in N_2 selectivity (Fig. 2d(A)) defined as

$$S_{N_2} = r_{N_2}/(r_{N_2} + r_{N_2O}) \qquad (1)$$

where r_{N_2} and r_{N_2O} are the production rates of N_2 and N_2O, respectively.

It is apparent that Na promotion results in S_{N_2} values in excess of 95% (at 0.068 wt% Na; catalyst C4) compared with ~75% for the unpromoted catalyst C1. Note that in Figures 2a,b(A), within the experimental scatter, it is clear that the Na-containing catalysts exhibit rate maxima within the P_{NO} range studied, whereas the Na-free catalyst does not. Note also that promotion is maximized for a sodium content of 0.068 wt% (Catalyst C4, 20% nominal Na coverage); further increase in the sodium loading leads to poisoning of the system.

NO+CH$_4$ reaction: Figure 2(B) shows the kinetics of the NO+CH$_4$ reaction upon varying P_{NO}. The results for the NO+C$_3$H$_6$ reaction are also shown (Fig. 2(A)) for comparison purposes. In contrast with the C$_3$H$_6$ case, it is clear that Na induces poisoning of Pd for NO reduction when using CH$_4$ as the reductant. This rate inhibition is accompanied by a monotonic shift of the value of the NO partial pressure corresponding to the rate maximum. This reflects a strengthening of the NO chemisorption bond as a result of Na loading of the catalyst. In a similar way, the N_2/N_2O selectivity of the Na-containing catalysts (Fig. 2d(B)) is always less than that of the Na-free catalyst C1. The characteristic rate maxima are an indication of competitive adsorption of both NO and CH$_4$ on the Pd surface. A comparison of the trends shown in Figures 2(B) and 3(B) indicates that under these conditions the adsorption of NO on Pd is significantly stronger than that of CH$_4$. In contrast with this, a similar comparison of the results in Figures 2(A) and 3(A), which depict the corresponding NO+C$_3$H$_6$ data, confirms that the adsorption strengths of NO and C$_3$H$_6$ are similar.

Effect of hydrocarbon partial pressure (P_{HC})

NO+C$_3$H$_6$ reaction: Figures 3a,b,c (A) show the CO$_2$, N$_2$ and N$_2$O rates respectively, for the same five catalysts (Table 1) as a function of $P_{C_3H_6}$,

for a fixed P_{NO} =1.0 kPa. Again, a systematic enhancement of turnover rate as a function of added Na is apparent, with the Na-promoted catalyst C4 exhibiting the highest CO$_2$ and N$_2$ rate enhancement (~10 times the rate shown by the unpromoted catalyst over almost the entire range of $P_{C_3H_6}$). The corresponding N$_2$O formation rate is rather insensitive to Na loading (Fig. 3c(A)), resulting in the N$_2$ selectivity behaviour shown in Fig. 3d(A): catalyst C4 delivers up to ~95% N$_2$ selectivity compared with ~ 80% for the unpromoted catalyst.

NO+CH$_4$ reaction: The kinetics of the NO+CH$_4$ reaction upon varying P_{CH_4} at constant P_{NO}=0.3 kPa are also shown in Fig. 3(B). A linear rate dependence on P_{CH_4} is clear. Comparison with the P_{NO} dependence (Fig. 2(B)), which exhibits well-defined rate maxima (appearing at very low ratios of P_{NO}/P_{CH_4}<0.03) strongly supports the conclusion of weak methane adsorption on the metal surface, relative to NO. Na addition causes a monotonic decrease in the rates: sodium always poisons the reduction of NO by methane. This is strikingly different from the response of the NO+C$_3$H$_6$ reaction, where strong initial promotion by sodium is observed for low to intermediate loadings (Fig. 3(A)).

A very interesting feature of Fig. 3(B) is the threshold partial pressure of methane (P_{CH_4}*), below which the activity for NO reduction vanishes. It can be seen that Na exerts a pronounced effect on the value of P_{CH_4}*. This is thought to be the partial pressure of methane, which is required to overcome O-poisoning of the surface, thus allowing in initiation of the surface reaction [NO(a) → N(a) + O(a)]. The weak interaction of CH$_4$ with the surface, as well as the shift of the P_{CH_4}* to larger values upon increasing the Na loading, are in accord with this explanation.

Although the selectivity of the Na-containing catalysts (C2-C5, Fig. 3d(B)) is always below that of the Na-free catalyst (C1), the scatter in the data precludes conclusions to be drawn about the dependence of this effect on Na content.

DISCUSSION

The present results show that the Pd-catalysed reduction of NO by hydrocarbons can be markedly affected by sodium addition to the catalyst. In the
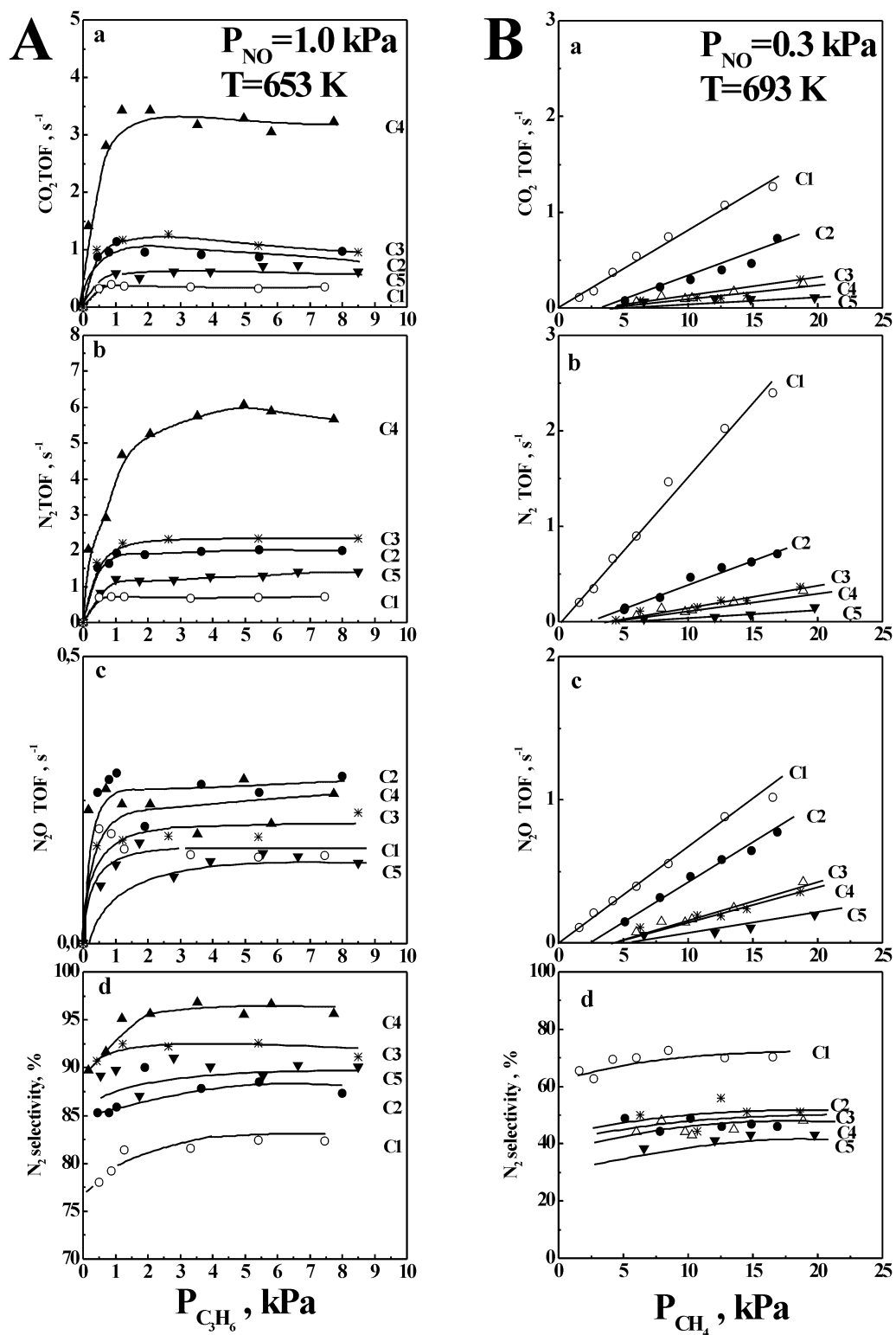
Figure 3. The effect of P_{HC} on CO_2 (a), N_2 (b), N_2O (c) TOFs and N_2 selectivity (d), for catalysts C1-C5, during the Pd-catalysed reduction of NO by C_3H_6 (A) and by CH_4 (B)

case of using CH_4 as the reductant, sodium behaves as a strong poison at all Na loadings. In marked contrast, very pronounced promotional effects of Na were observed when an alkene (C_3H_6) was used as the reductant. In this case the Na-induced rate enhancements were very large. Thus, with propene the maximum observed catalytic rate enhancement ϱ, defined as the ratio between the promoted r and the un-promoted r_o catalytic rate,

$$\varrho = r/r_o \qquad (2),$$

is of the order of 10 for both N_2 and CO_2 formation rates (Figs. 2 and 3). The corresponding effect of Na addition on the rate of N_2O formation is much lower ($\varrho \sim 2$). This results in a significant increase in S_{N_2} of the system, which increases from ~75% over the unpromoted (Na-free) catalyst C1 to > 95% for catalyst C4 (Figs. 2d and 3d).

These data bear a close and very interesting resemblance to those obtained by electrochemical promotion (EP) of a Pt catalyst film supplied with Na from a solid electrolyte. Indeed, it was this EP work which prompted the present investigation. Thus, we have shown that the reduction of NO by propene (Yentekakis et al., 1997) as well as by CO (Palermo et al., 1996) over a Pt catalyst film in contact with β″-alumina (a Na$^+$ ion conductor) exhibits large increases in rate and selectivity when Na is supplied to the metal surface. Our EP findings led us to conclude that Na promotion is due to enhanced metal-NO interaction mediated by the sodium, as verified by experiments on Pt{111}/Na+NO (Harkness and Lambert, 1997) and supported by theory (Lang et al., 1985). We argued that Na increases the strength of NO chemisorption relative to propene (or CO), an effect which is accompanied by weakening of the N-O bond, thus facilitating NO dissociation on the metal surface. Given that the polycrystalline Pt film consisted mainly of large crystallites (~1 μm) whose external surfaces are dominated by low index planes known to be relatively ineffective for NO dissociation, the effect of Na is to activate previously inactive crystal planes. Thus Na promotion is due to (i) increased coverage of NO in the presence of strongly adsorbing propene (or CO), (ii) triggering of NO dissociation, which is the key reaction-initiating step. Once O(a) is produced it is consumed by

adsorbed propene (or CO) accompanied by N(a) recombination or reaction with NO(a) to yield N_2 and N_2O, respectively.

In the present case the promotional effect of Na exhibits a maximum as a function of Na content at a sodium loading of 0.068 wt% (20% nominal Na coverage). Increasing the Na content beyond this level leads to poisoning (Figs. 2 and 3). This is entirely analogous to the corresponding EP data for NO + propene (Yentekakis et al., 1997) and reflects two opposing effects, namely (i) the Na-induced activation of previously inactive metal sites as described above, and (ii) the accumulation of Na surface compounds, which progressively block the surface to adsorption of the reactants. XPS studies involving in situ transfer of promoted and poisoned ex-reactor EP catalysts to the spectrometer analysis chamber show (Yentekakis et al., 1997) that in the case of NO+propene the Na-containing promoting (or poisoning) phase consists principally of a mixture of $NaNO_2$ and $NaNO_3$, along with some Na_2CO_3. It therefore seems reasonable to propose that similar phenomena occur at the surface of our Na-promoted Pd catalysts. In other words, there is a promotion by low to moderate amounts of Na nitroxy compounds and a poisoning due to site blocking by these same compounds above some optimum alkali loading. Our XPS data are entirely consistent with this interpretation. They demonstrate that there is no tendency to accumulate dissolved or subsurface Na as the promoter loading is varied. The surface coverage by Na does indeed increase with promoter loading, and the catalytic activity and selectivity pass through a maximum.

Two observations confirm the proposed model for Na promotion:

(i) Under reaction conditions there is clear evidence for competitive adsorption of the NO and hydrocarbon (C_3H_6 or CH_4) on the Pd surface. This is manifested by the Langmuir-Hinshelwood kinetic behaviour (Fig. 2), whereby the reaction rates exhibit maxima as a function of P_{NO}. Interestingly, in both cases these rate maxima shift to lower NO partial pressures as the sodium content of the catalyst is increased, reflecting an increase in the binding of NO relative to C_3H_6 or CH_4 with increasing Na/Pd ratio, i.e., Na enhances NO chemisorption versus hydrocarbon chemisorption on Pd. This is exactly the kind of behaviour one would expect in

the case of an electropositive promoter, i.e., the chemisorption strength of electron donors (hydrocarbon in the present case) should be decreased whereas the chemisorption of electron acceptors (NO and its dissociation products) should be enhanced.

(ii) The model is also strongly supported by the behaviour observed in the catalytic reduction of NO by CH_4. As is clear from Figs. 2 and 3, sodium induces only poisoning at all Na loadings. This reflects the weak interaction of CH_4 with the metal surface, relative to NO. Thus even at low P_{NO}, the catalyst is predominantly covered by NO. As a result, any further enhancement of the Pd-NO bond strength induced by sodium addition results in poisoning. With alkenes, however, due to their much stronger interaction with the metal surface, a wide range of conditions exist for which the surface is predominantly covered by hydrocarbon. Na addition then results in promotion as discussed above.

It is remarkable that such close similarities exist between the behaviour of Pt electrochemically promoted with Na (Yentekakis *et al.,* 1997) and the conventional highly dispersed catalysts investigated in the present study. These similarities include the overall kinetic behaviour and the dependence of activity and selectivity on Na loading. Recall that EP is applied to thin continuous films of the catalytic metal to which the promoting species (in this case Na) is supplied by spillover from a suitable solid electrolyte. Among other things, our results serve to validate further the interpretation offered for the EP phenomenon (Vayenas *et al.,* 1992; Vayenas and Yentekakis, 1997). More importantly, they demonstrate that the insight obtained from EP studies can be used to design successfully effective catalyst formulations, which were previously untried, thus opening up new areas for investigation (Yentekakis *et al.,* 1998; Konsolakis *et al.,* 1998).

A comment concerning the effect of temperature is in order. One might expect a degree of temperature dependence of the promotion effect. This could be due to (a) possible redistribution of the Na surface compounds, (b) in the propene/NO case

one might predict that higher temperatures should tend to reduce the strength of the promotion effect, since NO dissociation on unpromoted sites should also become significant. However, it is likely that other temperature-dependent effects would also contribute to the overall behaviour so that predictions cannot be made with certainty. Equally, a detailed study of the high-temperature stability of these catalysts is called for in order to evaluate their potential practical utility. This is being addressed by current work in our laboratory.

CONCLUSIONS

For highly dispersed Pd catalysts supported on YSZ, addition of Na strongly promotes both activity and N_2 selectivity in the reduction of NO by propene. Catalyst performance becomes optimal at a sodium loading of 0.068 wt%, 20% nominal Na coverage. With CH_4 as the reductant, all Na loadings induce only poisoning. In both cases the kinetic data are understandable in terms of Na-induced dissociation of NO as the reaction-initiating step.

Electron spectroscopic data show that coverage of the catalyst by Na increases monotonically with promoter loading, and that there is no tendency towards promoter agglomeration at the higher loadings. Additionally, they demonstrate a small but constant tendency to accumulate subsurface or dissolved Na as the promoter loading is increased above 5% nominal Na coverage.

In all respects the behaviour closely resembles that observed for the $NO+C_3H_6$ reaction under conditions of electrochemical promotion by Na. The present results therefore validate the interpretation offered for the EP system. They also show how insight gained from the latter may guide the formulation of new types of conventional catalysts.

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