

Promotion by Sodium in Emission Control Catalysis: A Kinetic and Spectroscopic Study of the Pd- Catalyzed Reduction of NO by Propene

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Sodium strongly promotes the reduction of NO by propene over Pd catalysts supported on 8 mol% yttria stabilised zirconia (YSZ) in the temperature range 520–720 K. Rate increases by an order of magnitude are achievable, while the selectivity towards to N₂ is improved from ~75% over the unpromoted Pd catalyst to >95% over the optimally Na-promoted catalyst. The results indicate that promotion is due to sodium-induced increases in the 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. The XPS and Auger data are consistent with this view. These findings are in excellent accord with a recent study of the same reaction under conditions of electrochemical promotion (EP) (I. V. Yentekakis *et al.*, *J. Phys. Chem. B* 101, 3759 (1997)). © 1998 Academic Press

Key Words: promotion; sodium; NO reduction; propene; palladium; YSZ; XPS; Auger.

INTRODUCTION

The catalytic reduction of NO_x emissions produced by combustion processes is of major environmental importance (1–3). Automotive exhaust catalytic converters employ a well-established technology for control of NO_x, CO, and hydrocarbons—the so-called three-way catalyst (TWC). This uses formulations based variously on Pt, Rh, and Pd. With regard to NO_x reduction, Pt is relatively ineffective for the dissociative chemisorption of NO (3). On Pd this process exhibits strong structure sensitivity, being favoured by step sites (4–6), the extent of dissociation depending both on temperature and NO coverage. 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 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_x, 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 (e.g., MoO₃ (7) or La₂O₃ (8)), or by using supports other than Al₂O₃ (e.g. yttria-stabilised zirconia (9, 10)). These strategies have indeed improved significantly the activity and selectivity of Pd for NO reduction to N₂. 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 (11) *under lean burn conditions* (i.e., in the presence of 5% O₂). 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.* demonstrated significantly increased conversion in the CO + NO reaction over Na-promoted Pd and Pt supported catalysts (12). Here we report Na-induced increases in reaction rate *by up to an order of magnitude*, as well as a significant enhancement in N₂ selectivity in the catalytic reduction of NO by propene over supported Pd catalysts, and a specific model for Na promotion is proposed.

We have used electrochemical promotion (EP) (13) to investigate the efficacy of Na as a promoter for the Pt-catalysed NO reduction by CO (14). It was shown that Na supplied electrochemically from a β''-alumina solid electrolyte (a Na⁺ ion conductor), strongly promotes the CO + NO reaction over Pt; in effect Pt could be induced to behave like Rh. The results indicated that Na induces NO dissociation, which is thought to be the crucial reaction initiating step. Most recently (15), the same technique was employed for Na promotion of the reduction of NO by propene over a Pt film. The results were even more striking: activity enhancement of an order of magnitude and large increases in N₂ selectivity were achieved.

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Guided by these EP studies on Pt, there being no similar studies on Pd, we have chosen to investigate Na promotion of NO_x reduction by propene over conventional dispersed palladium catalysts. (Propene is the industry standard for catalytic hydrocarbon oxidation studies). We have deliberately used gas compositions close to those employed in the earlier EP work in order to permit direct comparison between the two sets of results. The motivation for choosing Pd is given above; currently, the development and application of palladium-only catalysts attracts much attention (16). The choice of support (YSZ) was dictated by recent studies which show that YSZ maximises the turnover activity of Pd for reactions of relevance to TWC chemistry (9, 10).

EXPERIMENTAL

Materials

Highly dispersed Pd catalysts were prepared by incipient wetness impregnation of the YSZ support (Zirconia Sales) using a pH 3 solution of PdCl₂ (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 NaNO₃ solutions of suitable concentration. The suspension was dried in a rotating flask by evaporation at 353 K and the impregnated support was dried overnight at 383 K. The catalyst precursors were heated in flowing He (1 h/673 K), followed by H₂ reduction (673 K/1 h/100 cm³ min⁻¹). Five samples with different Na loadings were produced (coded as C1–C5 in Table 1). Two additional Pd/YSZ catalysts were prepared, using Pd(NO₃)₂ (Alfa products) as precursor instead of PdCl₂, in order to examine possible effects of Cl⁻ ions retained on the catalysts prepared by the PdCl₂ route. The Pd(NO₃)₂ impregnated suspensions were treated as follows: (i) dried overnight and

(ii) heated in flowing He (1 h/773 K/100 cm³ min⁻¹), followed by (iii) reduction in flowing H₂ (1 h/723 K/100 cm³ min⁻¹). These two catalysts are designated as C1' and C4' 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 and C4', 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. 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.

Apparatus

Catalyst testing was performed in a flow apparatus which consists of a feed unit, the reactor, and an analysis unit utilising on-line gas chromatography (SHIMADZU-14B) and on-line IR spectroscopy (Anarad AR-500 CO₂ Analyser). Separation of N₂ and NO was achieved in a molecular sieve 5A column at 353 K while CO₂, N₂O, and propene were separated using a porapak-N column at the same temperature. No trapping of NO was ever observed on the 5A column. It was calibrated several times with certified standards containing both low (2500 ppm) and high (10%) concentrations of NO; the response was linear and the nitrogen balance during reaction closed within 5%. The fixed bed, single pass, plug flow reactor, consisting of a 0.4-cm ID quartz tube, was operated in differential mode (i.e., conversions less than 15%, for both NO and propene, during acquisition of all kinetic data). Catalyst loadings were typically about 7.5 mg, the sample being diluted further by admixture with ~70 mg 100–325 mesh α-Al₂O₃ (Alpha products). Before measurements were taken, the catalysts were operated for 5 days in a reactive gas mixture (0.5% NO + 0.5% C₃H₆) at 723 K to ensure stable operation. All catalyst characterisation

TABLE 1^a

Properties of the 0.5 wt% Pd/YSZ Catalysts

Catalyst code	Na-loading (wt%)	Nominal Na coverage ^b (%)	Pd/Na atoms/atom	H ₂ uptake cm ³ STP/g	Dispersion (%)	Active surface area ^c (m ² /g)	Crystallite size (mean) (nm)
<i>PdCl₂ precursor</i>							
C1	0	0	∞/1	0.106	20	0.45	5.2
C2	0.017	5	6/1	0.105	20	0.44	5.3
C3	0.034	10	3/1	0.131	25	0.55	4.2
C4	0.068	20	1.5/1	0.123	23	0.52	4.5
C5	0.102	30	1/1	0.127	24	0.54	4.4
<i>Pd(NO₃)₂ precursor</i>							
C1'	0	0	∞/1	0.078	15	0.33	7.1
C4'	0.068	20	1.5/1	0.058	11	0.25	9.5

^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/m².

measurements were performed on the used catalysts that had attained stable performance.

XPS measurements were carried out in a VG ADES 400 UHV spectrometer system. The ex-reactor catalyst samples (cooled from 723 to 423 with ~ 100 K/min in the reaction gas mixture of 0.5% NO and 0.5% C_3H_6 and transferred under He atmosphere) 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. A particular merit of this technique is that it eliminates the use of adhesives containing organic material, thus making the C 1s spectra useful. XP spectra were acquired with MgK_{α} 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

Catalyst Characterisation

Active metal areas were measured *via* H_2 chemisorption at 333 K. The hydrogen to metal ratio (H/M) was calculated by assuming (i) a 1 : 1 hydrogen metal stoichiometry and (ii) that no H_2 uptake occurred on the support at zero pressure of H_2 . The H_2 uptakes were determined by extrapolation of the high pressure “plateau” portion of the isotherm, as described by Benson and Boudart (17). The BET surface area of the YSZ support was measured by N_2 adsorption at 77 K and found to be ~ 7 m^2 g^{-1} . The catalyst characterisation data are summarised in Table 1. It is important to note that the presence of varying amounts of Na does not significantly affect catalyst dispersion.

Effect of NO Concentration

Figures 1a, b, c show the effect of NO concentration (%) on the CO_2 , N_2 , and N_2O turnover (TOF: molecules of product per surface Pd atom per second) formation rates respectively for the seven catalysts promoted by different amounts of Na. Figure 1d illustrates the corresponding behavior 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 0.068 wt% Na (catalyst C4, 20% nominal Na coverage, Table 1) which causes up to tenfold enhancement in the turnover rate of CO_2 (Fig. 1a), and of N_2 (Fig. 1b), with respect of the unpromoted (Na-free) catalyst C1. Although the magnitude of this effect depends on NO concentration, decreasing with NO concentration beyond the optimal value, strong enhancement is present over a wide range of propene concentration (see Fig. 3). At the same time, the rate of N_2O formation remains practically unaffected (Fig. 1c). This causes a significant increase in N_2

selectivity (Fig. 1d) defined as

$$S_{N_2} = r_{N_2} / (r_{N_2} + r_{N_2O}). \quad [1]$$

It can be seen that Na promotion results in S_{N_2} values in excess of 95% (at 0.068 wt% Na; catalyst C4) compared with $\sim 75\%$ for the unpromoted catalyst C1.

Note that in Figs. 1a, b, within the experimental scatter, it is apparent that the Na-containing catalysts exhibit rate maxima within the NO concentration 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. This is made apparent in Fig. 2 which shows the CO_2 , N_2 , and N_2O turnover rates and the N_2 selectivity as a function of the Na content. The (+) and (x) data points in Figs. 1a, 1b, 1c, 1d refer to the chlorine-free 0% Na (C1') and 20% nominal Na coverage (C4') catalysts, respectively. In every case, the results are in good agreement with those obtained for catalysts C1 and C4, demonstrating that use of a chlorine-containing precursor does not substantially alter catalyst behavior.

Effect of C_3H_6 Concentration

Figures 3a, 3b, and 3c show the 653 K CO_2 , N_2 , and N_2O rates, respectively, taken for the same five catalysts (C1–C5, Table 1) as a function of propene concentration for a fixed NO concentration of 1%. 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 ($\sim 10\times$ the rate shown by the unpromoted catalyst over almost the entire range of C_3H_6 concentration). The corresponding N_2O formation rate is rather insensitive to Na loading (Fig. 3c), resulting in the N_2 selectivity behavior shown in Fig. 3d; catalyst C4 delivers up to $\sim 95\%$ N_2 selectivity compared with $\sim 80\%$ for the unpromoted system.

Arrhenius Behavior of Na-Promoted Pd; Promoter-Induced Isokinetic Effect

Figures 4a, b, c show Arrhenius plots obtained with the five catalysts. They make apparent the significant variation of catalyst turnover activity with Na promotion over the whole temperature range investigated. Increasing Na addition causes a significant increase in the apparent activation energy of the CO_2 and N_2 rates (Figs. 4a, b) from ~ 84 kJ/mol (unpromoted catalyst, C1) to ~ 160 kJ/mol (0.068 wt% optimally Na-promoted catalyst, C4) with a concomitant pronounced increase in the preexponential factor. This compensation effect (18–21) results in an isokinetic effect (Figs. 4a, b, c) with an isokinetic temperature, T_{iso} , of ~ 570 K for the N_2 , CO_2 , and N_2O rates. In the present case the compensation effect (isokinetic effect) is obtained for one reaction and one catalyst by varying the level of the

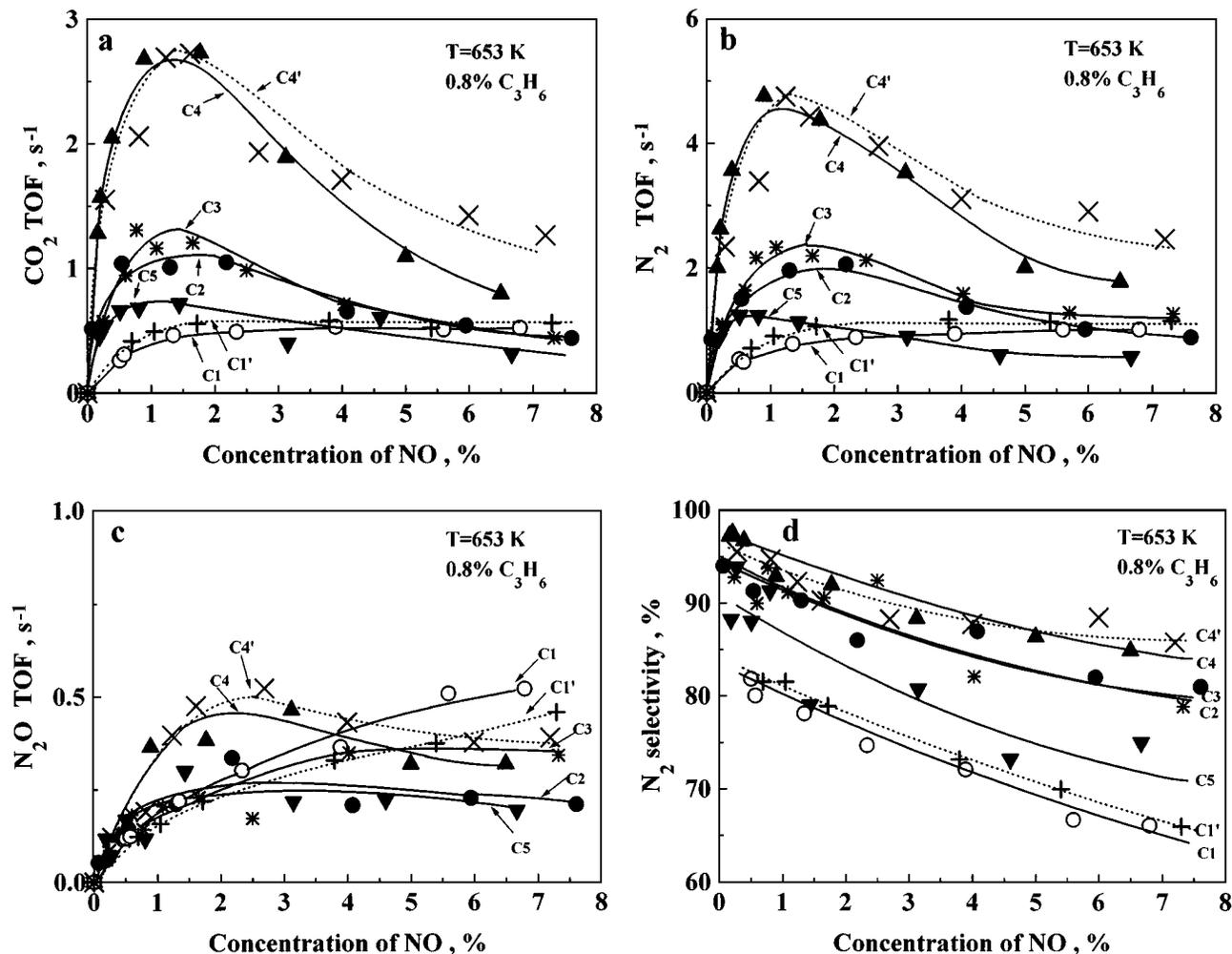


FIG. 1. The effect of NO concentration on (a) CO₂, (b) N₂, (c) N₂O TOFs, and (d) N₂ selectivity for catalysts C1–C5 and C1', C4' at 653 K and 0.8% propene concentration.

promoter. Electrochemical promotion studies (13), exhibit similar isokinetic effects as a function of catalyst potential, i.e. as a function of the catalyst work function (14, 20). In particular, it was shown (20) that the EP coefficient, α_{EP} , which is a measure of the strength of promotion (13, 20), is related to the reaction temperature relative to the isokinetic point, according to $(T/T_{iso} - 1)$. Thus the promoter-induced isokinetic effect found here provides another indication of the strong similarities between electrochemical promotion and conventional promotion. This is an important point because it highlights further the close relationship between these two methods of promotion. Obviously, the reaction exhibits the highest sensitivity to Na promotion far away from the isokinetic temperature, T_{iso} , at which temperature the effects of Na promotion are expected to disappear. That is, at temperatures above ~ 570 K, Na acts as a promoter, its effect increasing with temperature; below ~ 570 K it acts as a poison. Figure 5 shows that the logarithm of the preexponential factor, TOF^0 , depends linearly (18–23) on

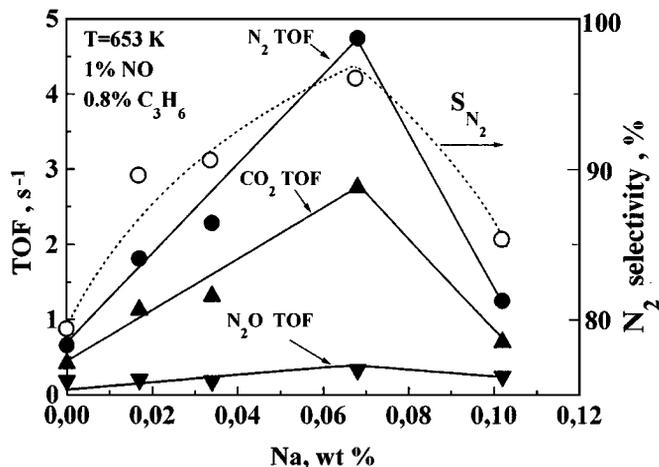


FIG. 2. The effect of sodium loading for fixed temperature and concentration of reactants on N₂, CO₂, and N₂O TOFs and on N₂ selectivity, S_{N_2} .

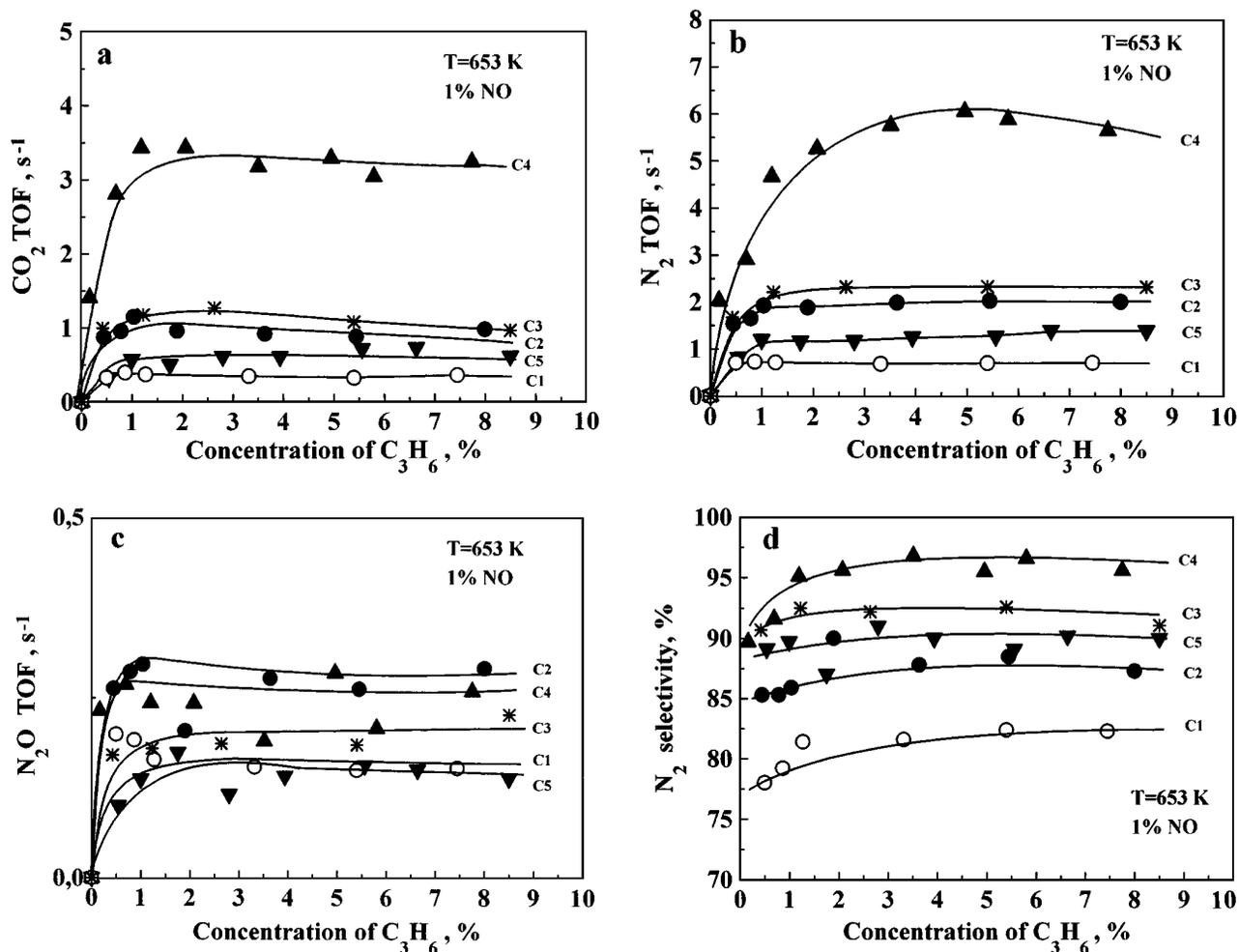


FIG. 3. The effect of propene concentration on (a) CO₂, (b) N₂, (c) N₂O TOFs, and (d) N₂ selectivity for catalysts C1–C5 at 653 K and 1% NO concentration.

E_a , i.e.,

$$\ln(\text{TOF}^0/\text{TOF}_0) = bE_a + c, \quad [2]$$

where TOF⁰ and E_a are the conventional Arrhenius parameters, with slopes b equal to ~ 0.21 mol/kJ for the formation rates of all N₂, CO₂, and N₂O products (Fig. 5). TOF₀ in Eq. [2] refers the preexponential factor of the unpromoted catalyst C1.

According to the theory of the compensation effect, Eq. [2] can define an isokinetic temperature, T_{iso} , calculated from (21–23):

$$T_{\text{iso}} = 1/bR, \quad R = 8.314 \text{ J/mol K}. \quad [3]$$

There is good agreement between the T_{iso} calculated from the slopes of Fig. 5 by using Eq. [3] (Fig. 5 $\rightarrow b = 0.21$ mol/kJ; Eq. [3] $\rightarrow T_{\text{iso}} = 573$ K) and the temperature at which the Arrhenius lines intersect (Fig. 4 $\rightarrow 1/T_{\text{iso}} = 1.75 \times 10^{-3}$ K⁻¹ $\rightarrow T_{\text{iso}} = 571$ K).

Figure 6 depicts the variation of the apparent activation energies or CO₂, N₂, and N₂O formation as a function of

added Na (note that the N₂ and CO₂ rates exhibit the same apparent activation energies to within ~ 5 kJ/mol over the whole range of Na coverages).

Effect of Na Addition on Temperature for 50% NO Conversion

Figure 7 shows the effect of catalyst temperature on NO conversion (X_{NO}) for the five catalysts C1–C5 when reactor inlet conditions were kept constant, i.e. 0.8% NO, 0.8% propene at a total flow rate of 120 cm³ STP/min. In every case, the amount of catalyst used was 7.5 (± 0.2) mg. It can be seen that the best catalyst (C4) has a 50% NO conversion temperature of ~ 635 K, i.e. about 100 K lower than that of the unpromoted catalyst.

XPS and Auger Spectra

The XP spectra obtained from samples of the five ex-reactor catalysts provide useful additional information. Figures 8a and 8b show Na KLL Auger and Na 1s photoelectron spectra, respectively, for each of the five catalysts

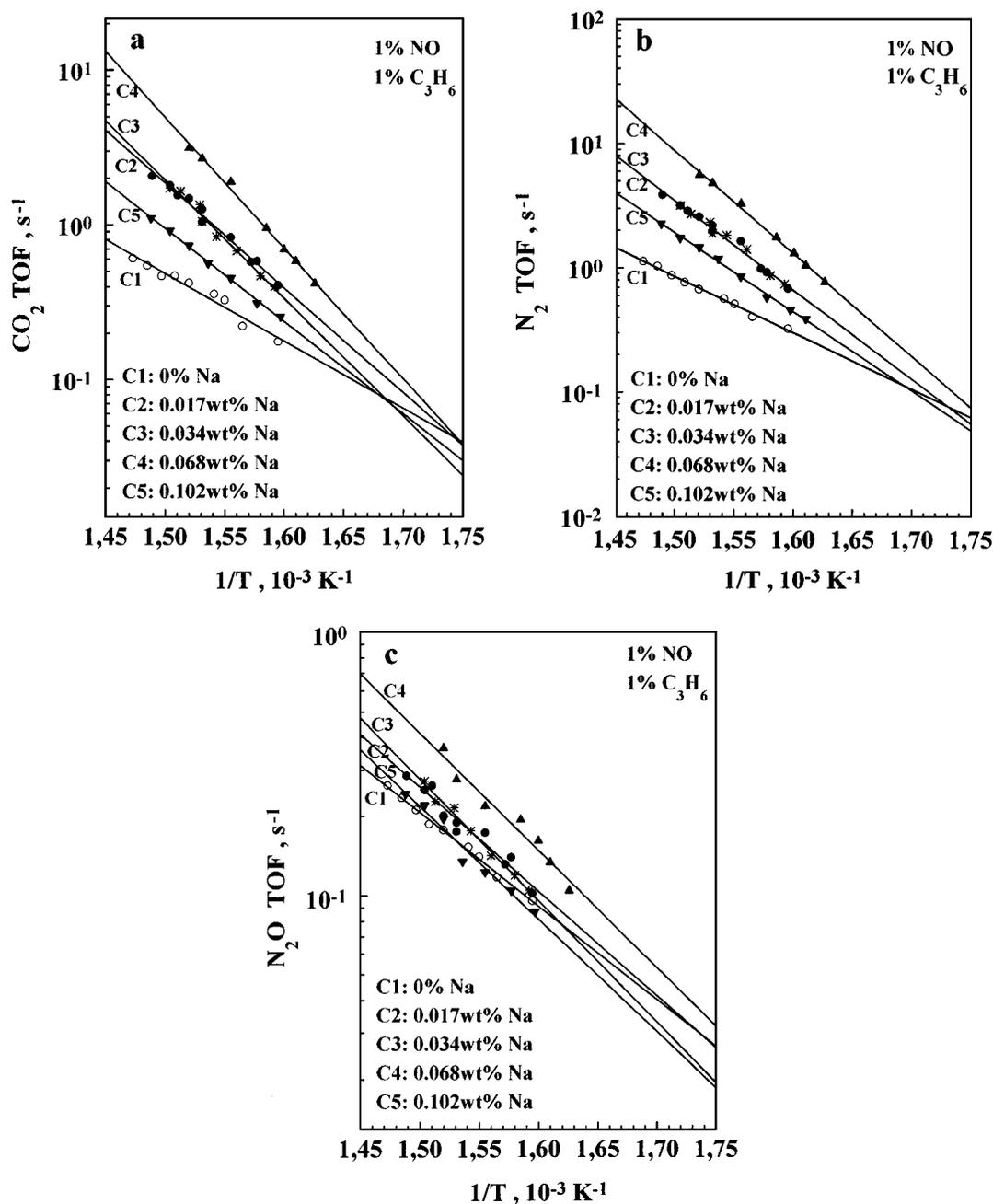


FIG. 4. Arrhenius plots obtained with catalysts C1–C5 operated at 1% NO and 1% propene concentrations for (a) CO_2 , (b) N_2 , and (c) N_2O formation rates. Observation of the isokinetic effect at $1/T \sim 1.75 \times 10^{-3} \text{ K}^{-1}$.

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 behavior 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 quantifica-

tion of these spectra shows that the ratios of the integrated Na KLL Auger and Na XP 1s intensities are as follows: C2 = 1.1 ± 0.3 ; C3–C5 = 1.5 ± 0.3 (Fig. 8c). The very different electron kinetic energies imply different sampling depths for the Auger and XP spectra: ~ 10 and ~ 3 Å, 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

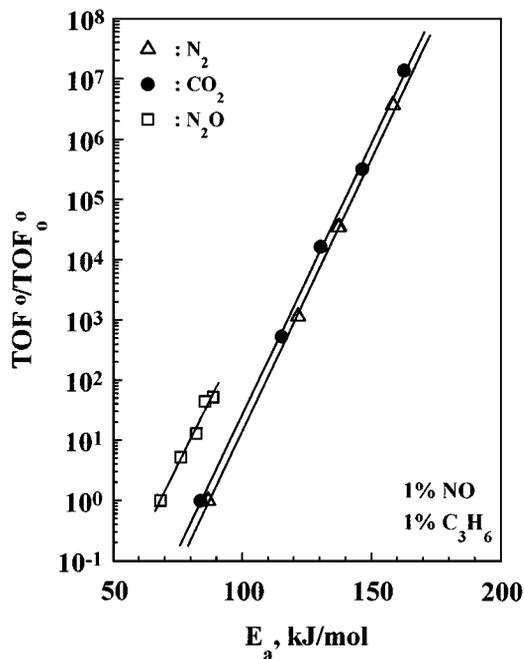


FIG. 5. Showing compensation effect for each of the three products N_2 , CO_2 , and N_2O .

for C3–C5. The Cl 2s and 2p emission from catalysts C1–C5 was undetectably low. Using the Y3d intensity arising from the 8% yttria in the support and the known photoionisation cross sections of these three core levels, we conclude that the residual chlorine content in these samples is $<0.1\%$ w/w. This shows that there was no gross contamination of these catalysts by chlorine; however the key point that effects due to chlorine are not important in influencing catalyst performance is established by comparison with the chlorine-free formulations C1' and C4' (see above and Fig. 1).

Figure 9a shows corresponding C 1s XP spectra, and Fig. 9b shows the difference spectra resulting from subtracting the contribution to the YSZ support alone. Both the raw data and the difference spectra show an interesting feature: there is emission at ~ 284.5 eV BE which is associated with the Pd component—interestingly, this feature is most intense on the optimally performing catalyst C4. A relatively weak feature at ~ 283.5 eV is apparent in the spectra from the unpromoted catalyst (C1); this could be due to some deposition of graphitic carbon on either the metal or support phases. The Pd 3d XP emission was undetectable on all samples because of (i) the low metal loading and (ii) the proximity of intense lines due to the Zr $3p_{1/2,3/2}$ emission. This is illustrated in Fig. 10, where the bottom trace shows the result of subtracting the normalised Zr intensity from pure YSZ from the XP spectrum of catalyst C1 (middle trace). Controlled vacuum deposition of an amount of Pd equivalent to ~ 2 monolayers over the whole catalyst sample exemplifies the difficulty—the Pd signal just becomes apparent (top trace). Although one does not know the

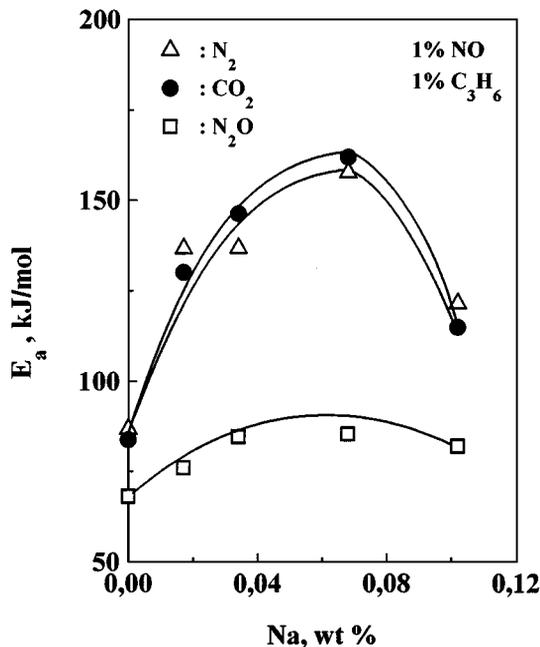


FIG. 6. Dependence of the apparent activation energy for formation of the three products N_2 , CO_2 , and N_2O on Na loading of the Pd/YSZ catalyst.

morphology of the vacuum deposited Pd, the experiment serves to indicate that, in the presence of the Zr $3p_{1/2,3/2}$ lines, only rather substantial Pd coverages are detectable, so it is unsurprising that the photoemitting Pd surface area on the catalyst samples is too small to be observed.

DISCUSSION

The present results show that the catalytic properties of Pd can be markedly affected by sodium promotion. Similar

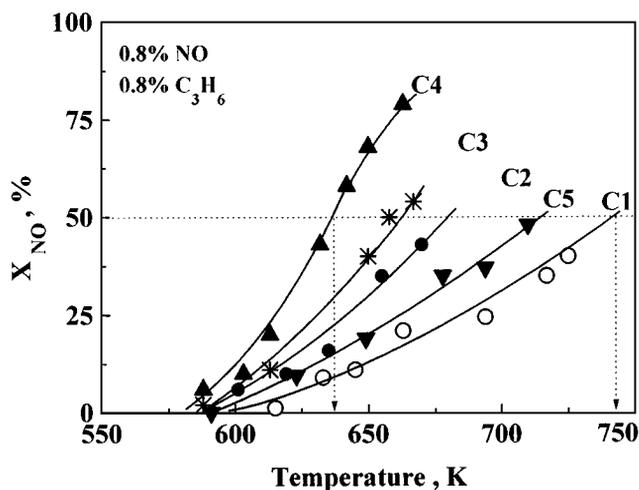


FIG. 7. NO conversion for different Na loadings as a function of temperature. Data taken with $7.5 (\pm 0.2)$ mg of catalysts C1–C5 at constant reactor inlet conditions: 0.8% NO, 0.8% propene, total flow rate $120 \text{ cm}^3 \text{ min}^{-1}$.

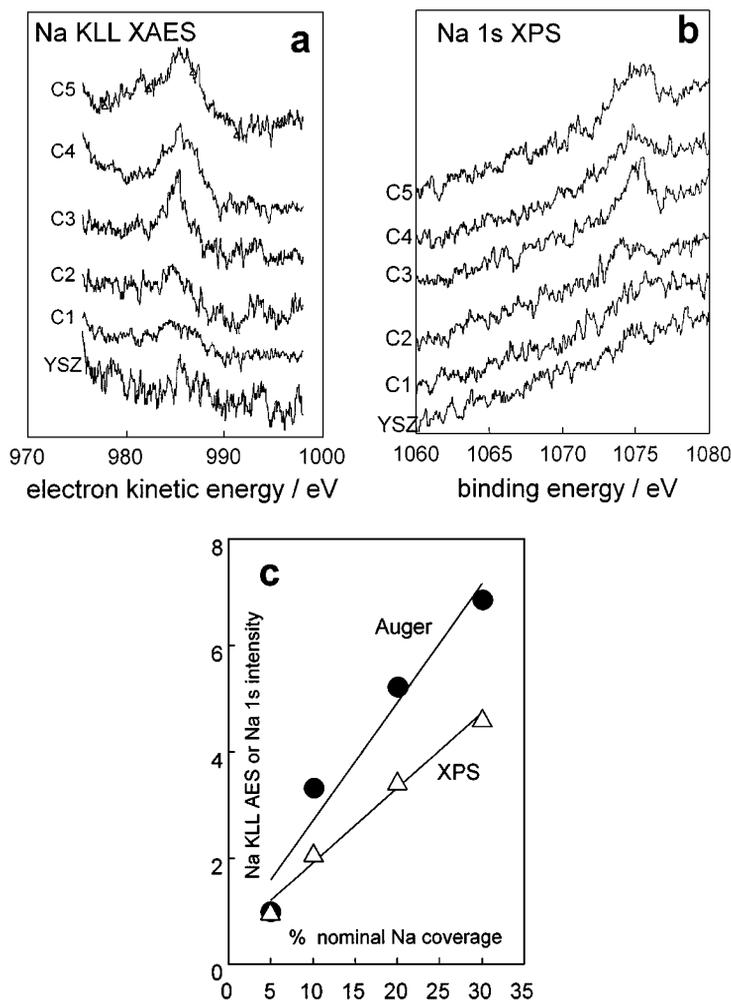


FIG. 8. (a) Na KLL X-ray excited Auger spectra of catalysts C1–C5 and of the YSZ support. (b) Na 1s XP spectra of catalysts C1–C5 and of the YSZ support. (c) Dependence of integrated Na Auger and XP intensities on calculated nominal Na coverage. Drawn lines are intended only as a guide to the eye (see text).

behavior has been reported for the CO + NO reaction over Pt and Pd catalysts (12). In the present case, NO reduction by propene, the Na-induced rate enhancements can be very large; this stands in interesting contrast with the observations of Burch *et al.* who found that Cs and K had no particular beneficial effect on the same reaction occurring over Pt/alumina catalysts (11). It may be that the identity of the support is critical, as Burch *et al.* suggest, although the amount of the promoter used may also play an important role. We have already shown that in the EP by Na of the NO reduction by propene over Pt, relatively small amounts of Na lead to very strong promotion, followed by poisoning, as the Na loading is increased. The overpromoted catalyst exhibits activity comparable to the unpromoted catalyst (15).

We find that the maximum observed catalytic rate enhancement, defined as the ratio between the promoted and the unpromoted catalytic rate, $\rho = r/r_0$, is of the order of 10 for both N₂ and CO₂ formation rates (Figs. 1, 2, 3, and 4).

The corresponding effect of Na addition on the rate of N₂O formation is much lower ($\rho \sim 2$). This results in a significant increase in selectivity of the system towards N₂ production, which increases from $\sim 75\%$ over the unpromoted (Na-free) catalyst C1 to $>95\%$ for catalyst C4 (Figs. 1d, 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 (15) as well as by CO (14) 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 (24) and supported by theory (25). We argued that Na increases the strength of NO chemisorption

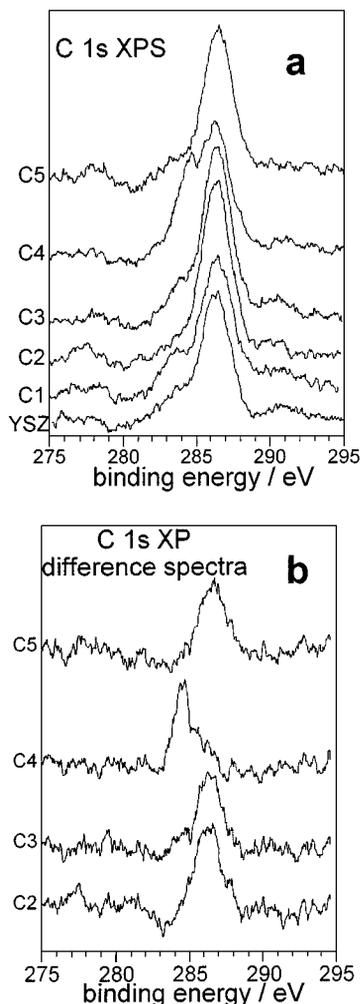


FIG. 9. (a) C 1s XP spectra of catalysts C1–C5 and of the YSZ support. (b) C 1s XP difference spectra of catalysts C1–C5 and of the YSZ support obtained by processing data in Fig. 9a (see text).

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. Since the polycrystalline Pt film consisted mainly of large crystallites ($\sim 1 \mu\text{m}$) whose external surfaces are dominated by low index planes known to be relatively ineffective for NO dissociation (3), 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 proposed as the key reaction-initiating step. Once O(a) is produced it is scavenged by adsorbed propene (or CO) accompanied by N(a) recombination or reaction with NO(a) to yield N_2 and N_2O , respectively. The observed compensation effect is in line with this. Na promotes NO dissociation, triggering the reaction, as noted above; it also increases the strength of the Pt–O and Pt–N bonds (26, 27) and, hence, the activation energy of subsequent reactions involving these species. Thus

Na appears to act by increasing the number density of surface sites active for NO dissociation whilst also increasing the activation energies of some of the ensuing reactions. It remains true that the origin and interpretation of the compensation effect are matters for debate. However, in the present case the observed temperature-dependent behavior does serve to underline the basic similarities between the present system and its electrochemically promoted analogue.

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; see Table 1). Increasing the Na content beyond this level leads to poisoning (Figs. 1, 2, 3, and 4). This is entirely analogous to the corresponding EP data for NO + propene (15) 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 blocks 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 (15) 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: promotion by low to moderate amounts of Na nitroxy compounds and poisoning due to site-blocking by these same compounds above some optimum alkali loading. Indeed our present XPS data are entirely consistent with this interpretation. They demonstrate: (i) there is no tendency to accumulate dissolved or subsurface Na as the

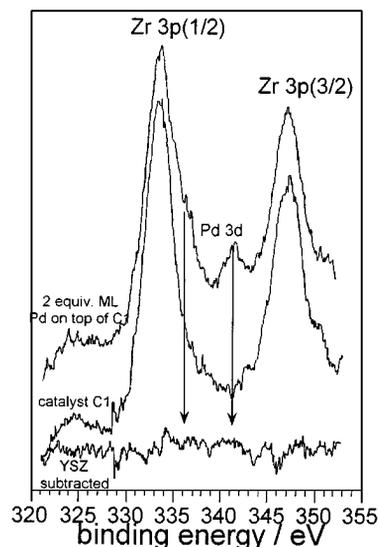
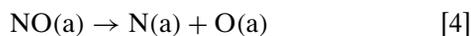


FIG. 10. Demonstrating the effect of the interference of Zr 3p lines with weak Pd 3d emission (see text).

promoter loading is varied, (ii) the actual surface coverage by Na does indeed increase linearly with promoter loading, (iii) as the surface coverage of Na increases monotonically, the catalytic activity and selectivity pass through a maximum. Furthermore, on the optimally promoted catalyst C4 there is clear evidence for maximal coverage of the Pd component by a species other than carbidic carbon. We therefore suggest that the feature at 284.5 eV BE (Figs. 9a, 9b) is due to adsorbed hydrocarbon fragments on the Pd surface. Whether these species are reaction intermediates whose population is a measure of the catalytically effective metal area (maximised on catalyst C4), or merely spectator species, cannot be determined on the basis of these data alone. At 30% nominal Na coverage catalyst C5 is “over promoted”: performance declines—due to loss of catalytically active area—and this is mirrored by the reduced 284.5 eV C 1s emission.

Figures 1 and 2 show that Na improves selectivity towards N₂ production, again paralleling the behavior of the corresponding EP system. This is readily understandable in the following terms. The rates of production of N₂ and N₂O (and, thus, N₂ selectivity, Eq. [1]) depend on the extent of NO dissociation,



which is followed by the elementary steps



The observed increase in the selectivity towards N₂ 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 N₂ selectivity.

Two observations confirm the above model for Na promotion. First, note that under reaction conditions there is clear evidence for competitive adsorption of the NO and propene on the Pd surface. This is manifest in the Langmuir–Hinshelwood kinetic behavior (Fig. 1), whereby the reaction rates over the promoted catalysts exhibit maxima as a function of NO concentration. Interestingly, the unpromoted catalysts do *not* exhibit maxima within the experimentally accessible range of NO concentration. This implies that the effect of Na is to increase the binding of NO relative to propene with increasing Na/Pd ratio, thus bringing the rate maxima into the accessible regime. That is, Na enhances NO chemisorption versus propene chemisorption on Pd catalyst. This is exactly the kind of behavior one would expect in the case of an electropositive promoter; the chemisorption strength of electron donors (propene) should be decreased, whereas the chemisorption of electron acceptors (NO and its dissociation products) should be enhanced.

Our model is also strongly supported by recent results obtained for the catalytic reduction of NO by methane (i) over Pt using electrochemical promotion by Na and (ii) using conventional supported Pd catalysts similar to those employed in the present work (28). In both cases, it is found that for all loadings Na induces *only poisoning*. This reflects the weak interaction of methane with the metal surface, relative to NO. Thus even at low concentrations of 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 behavior of Pt electrochemically promoted with Na (15) and the conventional highly dispersed catalysts investigated in the present study. These similarities include the overall kinetic behavior and the dependence of activity and selectivity on Na loading. Recall that EP is applied to thin continuous films of the catalytic material 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 (or NEMCA) phenomenon (29). 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.

CONCLUSIONS

1. For highly dispersed Pd catalysts supported on YSZ, the addition of Na strongly promotes both activity and N₂ selectivity in the reduction of NO by propene. Catalyst performance optimises at a sodium loading of 0.068 wt%, at which point the 50% NO conversion temperature is 100 K lower than that for the Na-free formulation.

2. 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.

3. The kinetic and spectroscopic data are understandable in terms of Na-induced dissociation of NO as the reaction initiating step. Over promotion leads to loss of performance due to excessive coverage of the otherwise active Pd component by surface compounds of Na; this conclusion is supported by the Na 1s and C 1s XP spectra.

4. In all respects the behavior closely resembles that observed for the same 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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REFERENCES

1. Frennet, A., and Bastin, J.-M. (Eds.), Catalysis and automotive pollution control III, Proc. Third Int. Congress (CAPOC3), in "Studies in Surface Science and Catalysis." Elsevier, Amsterdam, 1995.
2. Taylor, K. C., *Catal. Rev.-Sci. Eng.* **35**, 457 (1993).
3. Masel, R. L., *Catal. Rev.-Sci. Eng.* **28**, 335 (1986).
4. Xu, X., and Goodman, D. W., *Catal. Lett.* **24**, 31 (1994).
5. Davies, P. W., and Lambert, R. M., *Surf. Sci.* **110**, 227 (1981).
6. Ramsier, R. D., Gao, Q., Waltenburg, H. N., and Yates, J. T., Jr., *J. Chem. Phys.* **100**, 6837 (1994).
7. Gandhi, H.-S., Yao, H. C., and Stepien, H. K., *ACS Symp. Ser.* **178**, 143 (1982).
8. Muraki, H., Yokota, K., and Fujitani, Y., *Appl. Catal.* **48**, 93 (1989).
9. Yentekakis, I. V., Pliangos, C. A., Papadakis, V. G., Verykios, X. E., and Vayenas, C. G., *Stud. Surf. Sci. Catal.* **96**, 375 (1995).
10. Pliangos, C., Yentekakis, I. V., Papadakis, V. G., Vayenas, C. G., and Verykios, X. E., *Appl. Catal. B: Environmental* **14**, 161 (1997).
11. Burch, R., and Watling, T. C., *Appl. Catal. B: Environmental* **11**, 207 (1997).
12. Alexandrou, F., Papadakis, V. G., Verykios, X. E., and Vayenas, C. G., in "Studies in Surface Science and Catalysis" (N. Kruse, A. Frennet, and J.-M. Bastin, Eds.) Elsevier, Amsterdam, 1998.
13. (a) Vayenas, C. G., Bebelis, S., Yentekakis, I. V., and Lintz, H.-G., *Catal. Today* **11**, 303 (1992).
13. (b) Vayenas, C. G., Bebelis, S., Yentekakis, I. V., and Neophytides, S., in "The CRC Handbook of Solid State Electrochemistry" (P. J. Gellings and H. J. M. Bouwmeester, Eds.), pp. 445-480. CRC Press, Boca Raton, FL, 1997.
14. Palermo, A., Lambert, R. M., Harkness, I. R., Yentekakis, I. V., Marina, O., and Vayenas, C. G., *J. Catal.* **161**, 471 (1996).
15. Yentekakis, I. V., Palermo, A., Filkin, N. C., Tikhov, M. S., and Lambert, R. M., *J. Phys. Chem. B* **101**, 3759 (1997).
16. Cowley, A., in "Platinum 1997" (interim review), p. 18. Johnson Matthey, London, 1997.
17. Benson, J. E., and Boudart, M., *J. Catal.* **4**, 704 (1965).
18. Schwab, G.-M., *Advan. Catal.* **2**, 251 (1950).
19. Schwab, G.-M., *J. Catal.* **84**, 1 (1983).
20. Pliangos, C., Yentekakis, I. V., Verykios, X. E., and Vayenas, C. G., *J. Catal.* **154**, 124 (1995).
21. Karpinski, Z., and Larsson, R., *J. Catal.* **168**, 532 (1997).
22. Cremer, E., *Adv. Catal.* **7**, 75 (1955).
23. Galwey, A. K., *Adv. Catal.* **26**, 247 (1977).
24. Harkness, I. R., and Lambert, R. M., *J. Chem. Soc. Faraday Trans.* **93**, 1425 (1997).
25. Lang, N. D., Holloway, S., and Norskov, J. K., *Surf. Sci.* **24**, 150 (1985).
26. Yentekakis, I. V., Moggridge, G., Vayenas, C. G., and Lambert, R. M., *J. Catal.* **146**, 292 (1994).
27. Bertolini, J. C., Delichere, P., and Massardier, J., *Surf. Sci.* **160**, 531 (1985).
28. Yentekakis, I. V., Lambert, R. M., Konsolakis, M., and Kiousis, V., *in preparation*.
29. Vayenas, C. G., and Yentekakis, I. V., in "Handbook of Heterogeneous Catalysis" (G. Ertl, H. Knozinger, and J. Weitkamp, Eds.), Chap. 8. VCH, Weinheim/New York, 1997.