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Strong Promotion by Na of Pt/γ-Al_2O_3 Catalysts Operated under Simulated Exhaust Conditions

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The catalytic performance of Pt dispersed on γ-Al_2O_3 is very strongly promoted by sodium in the temperature range 200–500°C under simulated exhaust conditions at the stoichiometric point. Remarkable and unprecedented effects on NO, CO, and C_3H_6 conversions, as well as enhanced selectivity towards N_2, are found. Addition of Na causes a significant decrease in the temperature of 50% conversion (T_{50}) for NO, CO, and C_3H_6. For optimally promoted Pt this temperature is ∼100° lower than for unpromoted Pt. Similar decreases are observed for the temperatures required for 100% conversion of NO, CO, and C_3H_6. The selectivity towards N_2 is improved from ∼75% over unpromoted Pt to ∼100% over the optimally Na-promoted catalyst. These effects are understandable in terms of the effects of sodium on the relative adsorption strengths of reactant species. © 2000 Academic Press

Key Words: **sodium; promotion; plantinum; simulated exhaust conditions.**

INTRODUCTION

Three-way catalytic converters (TWCs) employ a well-established technology in controlling NO_x, CO, and hydrocarbon emissions. This approach exploits the catalytic properties of Pt, Pd, and Rh (1–3). Although TWCs are very effective in oxidizing CO and hydrocarbons, they are substantially less effective in reducing the NO_x emission. In this regard, note that Pt is relatively ineffective for the dissociative chemisorption of NO (4), whereas Pd exhibits strong structure sensitivity for this process, which is favored at step sites and at elevated temperatures (5, 6). 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.

It is of interest to discover means of enhancing the catalytic properties of Pt-group metals in order to (i) reduce the noble metal loading and (ii) reduce or replace the usage of Rh because of its scarcity in comparison with Pt and Pd (∼1 : 15) (1, 2). 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 (e.g., MoO_3 or WO_3 (7–9), CeO_2, Na_2O, or K_2O (10), and La_2O_3 (11–13) or by using supports other than γ-Al_2O_3 (e.g., yttria-stabilised zirconia (YSZ), TiO_2, doped TiO_2 (14, 15). These strategies have indeed improved significantly the activity and selectivity of Pd and Pt for NO reduction to N_2.

During the last decade the promotional effect of alkalis, alkaline earths, and other metals on supported Pt and Pd metal catalysts has been a subject of considerable interest (16–24). Among other things, these studies have addressed the location and electronic state of alkali promoters and their effect on the electronic properties of the noble metal catalysts (16–19). Most have focused on catalytic reactions related to the control of NO_x, CO, and hydrocarbon emissions (20–24). Thus, Burch and Watling investigated the effects of a wide range of promoters, including K, Cs, Mg, and Ba, on the Pt-catalysed reduction of NO by propene under lean-burn conditions (20). They found no particular benefit with these promoters and concluded that the manner in which the various promoters affect reactivity is unclear. Skoglundh *et al.* investigated cobalt-promoted Pd as a three-way catalyst (21). They found that addition of cobalt to Pd caused a significant increase in the activities for oxidation of carbon monoxide and propene under stoichiometric conditions. More recently, Wang *et al.* (22) demonstrated increased activity for NO reduction 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. This formally resembles results reported by Alexandrou *et al.* (23), who demonstrated increased conversion in the CO + NO reaction over Na-promoted Pd and Pt supported catalysts. Shingoh *et al.* (24) examined the effect of Li, Na, K, Cs, Mg, Ca, Sr, and Ba on propene conversion by NO_x and O_2 under simulated exhaust conditions over Pd catalysts

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supported on γ-Al_2O_3 (24). They found that all the alkaline earths increased hydrocarbon conversion under all the conditions investigated, whereas the effect of alkalis was more complicated. Both increased and decreased conversions were observed, depending on the conditions and the identity of the alkali (24). Tanaka *et al.* (25) showed that trimetallic PtMoNa/SiO_2 catalysts exhibit improved performance for the selective reduction of NO under simulated exhaust conditions around the stoichiometric point. They concluded that this was due to Mo and Na lowering the affinity between Pt and oxygen.

Recently, we reported an extensive kinetic and spectroscopic study of well-characterised Na-promoted Pd catalysts for the reduction of NO by propene (26). These catalysts contained varying amounts of sodium, *while the Pd dispersion remained constant.* Increases in reaction rate 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 optimal Na-promoted Pd, were achieved (26). Very recently, we showed that the promotional effect of Na was even more striking in the catalytic reduction of NO by propene over highly dispersed Pt on γ-Al_2O_3 catalysts (27). In this case activity enhancement of two orders of magnitude and very large increases in N_2 selectivity were obtained (from ~15% over the unpromoted Pt to values as high as 95% over optimally promoted Pt). In effect, Pt was induced to behave like Rh for the dissociation of NO molecules (27).

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 heterogeneous catalysis is well understood only for a limited number of systems (28). This is partly due to the difficulty of achieving *in situ* control of promoter concentration on the active catalyst surface under reaction conditions. Most fundamental studies have addressed the role of promoters in chemisorption only under ultra-high-vacuum conditions (28, 29), and the transferability of this information is sometimes open to question. Electrochemical promotion (EP) (30, 31) overcomes some of these limitations and allows for a systematic study of the role and mode of action of promoters in heterogeneous catalysis. We have used EP to investigate the efficacy of Na as a promoter for reactions of environmental importance, such as CO oxidation (32) and NO reduction by CO (33) and by propene (34, 35). It was shown that Na supplied electrochemically from a β''-Al_2O_3 solid electrolyte (an Na^+ ion conductor) strongly affects both the catalytic activity and the selectivity of all the above reactions (32–35). Close similarities were found between such electrochemically promoted catalyst (32–35) and conventionally promoted highly dispersed catalysts (26, 27, 36). These findings enabled us to propose a specific model for Na promotion involving Na-induced increase in the strength of the metal–NO chemisorption bond, accompanied by a weakening of the N–O bond, thus facilitating NO dissociation (26, 27, 32–36). This process is critical in triggering the catalytic reaction, particularly when the catalyst surface is predominantly covered by hydrocarbon species (26, 27, 36). A solid basis for the present investigation has been laid.

Here we report on the promotional effect of Na for highly dispersed Pt on γ-Al_2O_3 catalysts under simulated exhaust gas under stoichiometric conditions. The results are very striking: sodium dramatically enhances the selective catalytic reduction of NO, and, more importantly, it causes large increases in N_2 selectivity from ~75% over the unpromoted Pt to values approaching 100% over optimally Na-promoted Pt at close to 100% conversion of NO. The results may be of potential technological significance.

METHODS

Materials

The basic catalyst consisted of Pt highly dispersed over a γ-Al_2O_3 carrier: this was subsequently dosed with a range of sodium loadings using conventional impregnation methods, as follows. The γ-Al_2O_3 support (Alfa products) was impregnated with a pH 3 solution of H_2PtCl_6 (Alfa products) of 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. Suspensions were initially dried at 80°C, and then overnight at 110°C. The resulting precursors were heated in flowing He (400°C/1 h/100 $cm^3\ min^{-1}$), followed by H_2 reduction (400°C/1 h/100 $cm^3\ min^{-1}$). Metal dispersions was measured by H_2 chemisorption at 25°C, and the BET surface area of the γ-Al_2O_3 support (90 $m^2\ g^{-1}$) was measured by N_2 adsorption at −196°C. Relevant data are summarised in Table 1. Five samples with different Na loadings were produced by this route.

TABLE 1

Properties of the 0.5 wt% Pt/γ-Al_2O_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
C4	4.18	0.082	29	5
C5	10.4	0.071	25	6

[a] All the above surface characterisation 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.

Apparatus

Catalyst testing was performed in a fixed-bed, single-pass, plug flow reactor, consisting of a 0.4-cm ID quartz tube. Catalyst loadings were typically 8 mg (grain size 180–250 μm), the sample being diluted further by admixture with ~80 mg 100–325 mesh α-Al_2O_3 (Alfa products). The catalyst bed was retained between plugs of quartz wool and the K-thermocouple was located in the centre of the bed.

Research-grade certified gas mixtures were supplied by MG Gases: 4.95% CO in He, 5.07% NO in He, 4.93% C_3H_6 in He, and 19.8% O_2 in He. These were further diluted in ultrapure He (99.999%) and supplied to the reactor at 1 bar. Reactant gases were fed from independent mass flow controllers (MKS type 1179A) to give a gas feed consisting 1000 ppm NO, 1067 ppm C_3H_6, 7000 ppm CO, and 7800 ppm O_2. The total gas flow rate was 80 $cm^3\ min^{-1}$.

The stoichiometric number, S, used to characterise the simulated exhaust gas mixture is defined as

$$S = \frac{2[O_2] + [NO]}{[CO] + 9[C_3H_6]}.$$

The above values of reactant gas feeds correspond to $S = 1$.

NO and NO_x concentrations at the reactor inlet and outflow were monitored by a Signal series 4000 chemiluminescence NO_x analyser. CO, CO_2, O_2, N_2, N_2O, and C_3H_6 were followed by on-line gas chromatography (Shimatzu-14B). Separation of N_2, O_2, and CO was achieved in a molecular sieve 5A column while CO_2, N_2O, and C_3H_6 were separated using a porapak-N column operated at 80°C.

Before measurements were taken, the catalysts were operated for 1 day in air and 5 days in a reactive gas mixture at 450°C to eliminate possible residue from the metal precursor and to ensure stable operation. In addition, stability tests at 500°C for up to 10 days showed no deterioration in either catalyst activity or selectivity.

Conversion performance was studied by increasing the temperature stepwise from 200 to 500°C, in each case holding the temperature flow rate and inlet composition constant for 30 min prior taking measurements. For discussion purposes it is convenient to refer to the temperature for 50% conversion for each reactant (frequently called light-off temperature), designated T_{50}. We also define T_0 as the threshold temperature for onset of conversion and X_{400} as the percentage conversion at 400°C (400°C approximates the average working temperature in autocatalyst monoliths).

RESULTS

Catalyst Characterisation

Active metal areas were measured by H_2 chemisorption at 25°C, after reduction in H_2 at 350°C for 1 h and degassing at 400°C for 1 h. The hydrogen to metal ratio (H/M) was calculated by assuming a 1 : 1 hydrogen metal stoichiometry. H_2 uptakes were determined by extrapolation of the "plateau" portion (~10–40 Torr) of the isotherms, as described by Benson and Boudart (37). These results are summarised in Table 1.

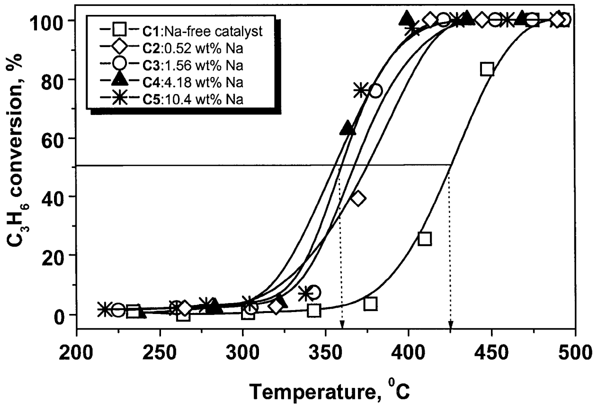

FIG. 1. Conversion of C_3H_6 as a function of temperature for Pt/γ-Al_2O_3 catalysts with different sodium loadings. Data taken under simulated exhaust conditions at the stoichiometric point (1000 ppm NO, 1067 ppm C_3H_6, 7000 ppm CO, and 7800 ppm O_2), with total flow rate 80 $cm^3\ min^{-1}$. Catalyst weight is 8 mg.

Conversion Performance of Na-Promoted Pt/γ–Al_2O_3 Catalysts

Conversion of propene. Figure 1 depicts C_3H_6 conversion as a function of catalyst temperature for the five catalysts with different sodium loadings (catalyst details given in Table 1). The reactor was fed with the simulated exhaust gas (1000 ppm NO, 1067 ppm C_3H_6, 7000 ppm CO, and 7800 ppm O_2) at a total flow rate of 80 $cm^3\ min^{-1}$ corresponding to a space velocity of 0.006 gs/cc. The conversion threshold for propene on the unpromoted catalyst was $T_0 = 370$°C with $T_{50} = 425$°C and $X_{400} = 20\%$. The conversion performance was very substantially improved by sodium promotion. The best conversion performance was achieved with catalyst C4 (4.18 wt% Na, see Table 2), for which $T_0 = 283$°C (~90° lower than the unpromoted catalyst), $T_{50} = 354$°C (~70° lower than the unpromoted catalyst), and $X_{400} = 100\%$. We designate C4 as the "optimally promoted" catalyst because it corresponds to the lowest Na loading required for maximum performance. The performance of catalysts with higher sodium loadings (>4.18 wt%) was comparable to that of catalyst C4 (4.18 wt%, see Table 1). Table 2 also lists T_0, T_{50}, and X_{400} values for CO and NO conversion; these data are considered below.

Conversion of CO. Figure 2 shows CO conversion as a function of catalyst temperature for the unpromoted and Na-promoted Pt (catalysts C1–C5, Table 1). The pronounced beneficial effect of sodium promotion is again apparent. The sodium-free catalyst is characterised by $T_0 = 310$°C,

TABLE 2

T_0, T_{50}, and X_{400} Values Obtained for CO, C_3H_6, and NO Conversion with the Pt(Na)/γ-Al_2O_3 Catalysts

	C_3H_6 conversion			CO conversion			NO conversion to N_2		
Na loading (wt%)	T_0 (°C)	T_{50} (°C)	X_{400} (%)	T_0 (°C)	T_{50} (°C)	X_{400} (%)	T_0 (°C)	T_{50} (°C)	X_{400} (%)
0	370	425	20	310	402	50	380	455	11
0.52	320	375	79	270	346	95	310	397	52
1.57	310	367	86	265	340	97	325	412	38
4.18	283	354	100	236	328	100	270	362	91
10.4	300	360	97	220	323	100	300	362	92

Note. T_0: onset temperature for conversion. T_{50}: temperature for 50% conversion. X_{400}: extent conversion at 400°C.

$T_{50} = 402$°C, and $X_{400} = 50\%$. Optimal performance is again achieved by the catalyst C4: $T_0 = 236$°C (~75° lower than the unpromoted Pt), $T_{50} = 328$°C (~70° lower than the unpromoted catalyst), and $X_{400} = 100\%$. Again, the behaviour of catalysts with higher Na loadings (e.g., catalyst C5: 10.4 wt% Na, see Table 2) is similar to that of C4.

Conversion of NO. Figure 3a shows the effect of catalyst temperature on the total NO conversion for catalysts C1–C5 under the same conditions as those used to acquire the data shown in Figs. 1 and 2. Figures 3b and 3c show the corresponding NO conversion to N_2 and to N_2O, respectively. These results very clearly show strong promotion of NO reduction, induced by sodium, over the whole temperature range. The conversion of NO to N_2 (Fig. 3b) on the unpromoted catalyst shows $T_0 = 380$°C, $T_{50} = 455$°C, and $X_{400} \sim 11\%$. Optimum performance was again observed for catalyst C4, characterised by $T_0 = 270$°C (~110° lower than the unpromoted catalyst), $T_{50} = 362$°C (~95° lower than unpromoted Pt), and $X_{400} = 91\%$.

Figure 3c illustrates the corresponding conversion of NO to N_2O. The "volcano" type behaviour of N_2O formation as a function of temperature is in agreement with that described by Cant *et al.* for Rh, Pt, and Pd catalysts investigated under simulated exhaust conditions (38). Our results show that in the case of the unpromoted catalyst, NO conversion to N_2O is maximized at 450°C at a value of ~11%.

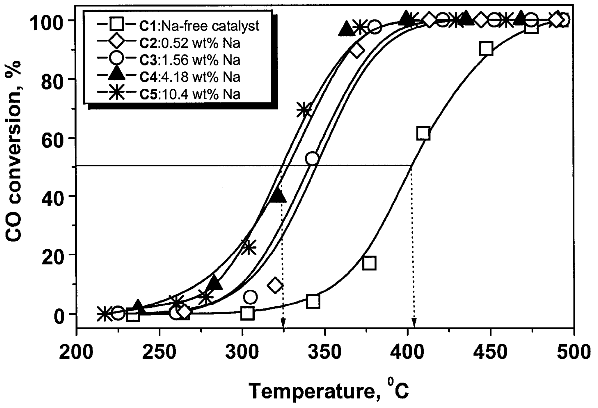

FIG. 2. Conversion of CO as a function of temperature for Pt/γ-Al_2O_3 catalysts with different sodium loadings. Data taken under simulated exhaust conditions at the stoichiometric point (1000 ppm NO, 1067 ppm C_3H_6, 7000 ppm CO, and 7800 ppm O_2), with total flow rate 80 $cm^3\,min^{-1}$. Catalyst weight is 8 mg.

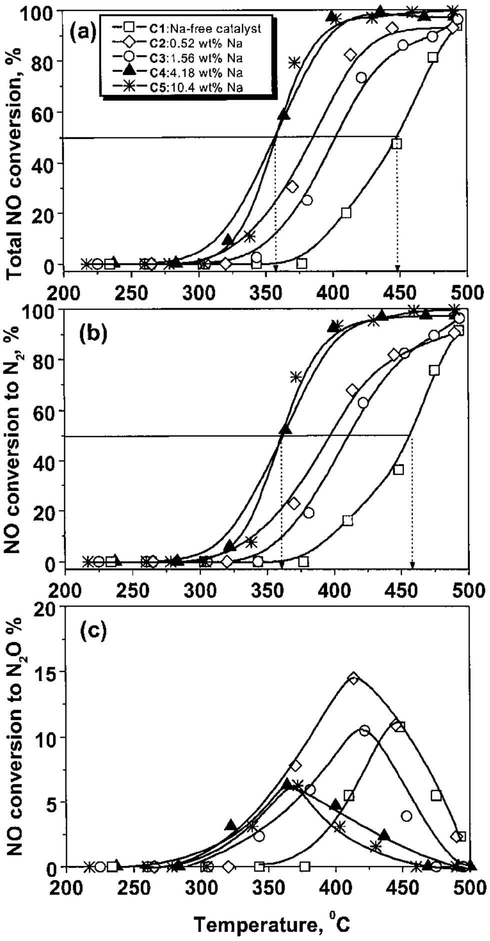

FIG. 3. The conversion of NO, (a) total, (b) to N_2, (c) to N_2O, as a function of temperature for Pt/γ-Al_2O_3 catalysts with different sodium loadings. Data taken under simulated exhaust conditions at the stoichiometric point (1000 ppm NO, 1067 ppm C_3H_6, 7000 ppm CO, and 7800 ppm O_2), with total flow rate 80 $cm^3\,min^{-1}$. Catalyst weight is 8 mg.

In contrast, the optimally promoted catalyst (catalyst C4, 4.18% Na) exhibits maximum N_2O formation at significantly lower temperature (~365°C). In addition, the extent of NO conversion to N_2O at this temperature is significantly lower (~6%) than in the unpromoted case.

Selectivity Performance of Na-Promoted Pt/γ-Al_2O_3 Catalysts

Catalyst selectivity towards N_2 formation rather than N_2O (and/or NO_2) is an important index of performance. Nitrous oxide is a powerful greenhouse gas and also contributes to stratospheric ozone depletion. Although N_2O emission is not yet regulated by legislation, this is unlikely to remain the case. Figure 4 shows selectivity data corresponding to the conversion results presented in Fig. 3. No NO_2 was detected under any experimental conditions, and we therefore define selectivity as

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

where r_{N_2} and r_{N_2O} are the formation rates of N_2 and N_2O, respectively. It can be seen that the Na-free catalyst delivers N_2 selectivity of ~70% at ~400°C. However, all levels of sodium promotion substantially improve selectivity over most of the temperature range studied, the effects being most pronounced at lower temperatures. The optimally promoted catalyst (C4) gives ~100% selectivity at 450°C, at which temperature the unpromoted catalyst is still only ~75% selective.

Effect of Na Loading on the Overall Conversion and Selectivity Performance of Pt/γ-Al_2O_3 at 400°C

Figures 5a and 5b provide a convenient summary of the effects of Na on performance at 400°C for a catalyst working at the stoichiometric point; as noted above, 400°C approximates the average working temperature in auto catalyst monoliths. Figure 5a shows the conversion of CO, C_3H_6, and NO (to N_2 or N_2O) as a function of Na content. It is apparent that only relatively small amounts of Na are necessary to enhance dramatically the conversions of all three pollutants. The conversions of all three reach 100% at a sodium content of 4.18 wt% (catalyst C4). Figure 5b shows the corresponding selectivity data. It is noteworthy that C4 is the optimally promoted catalyst as judged by this criterion too. Interestingly, overloading with Na (>4.18 wt%) does not adversely affect either conversion or selectivity. Under these conditions, catalysts C4 and C5 deliver almost 100% conversion of all three reactants at an N_2 selectivity of >95%.

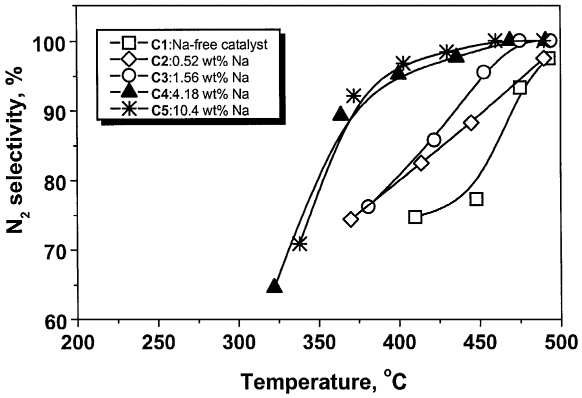

FIG. 4. Selectivity towards N_2 as a function of temperature for Pt/γ-Al_2O_3 catalysts with different sodium loadings. Data taken under simulated exhaust conditions at stoichiometric point (1000 ppm NO, 1067 ppm C_3H_6, 7000 ppm CO, and 7800 ppm O_2), with total flow rate 80 $cm^3\ min^{-1}$. Catalyst weight is 8 mg.

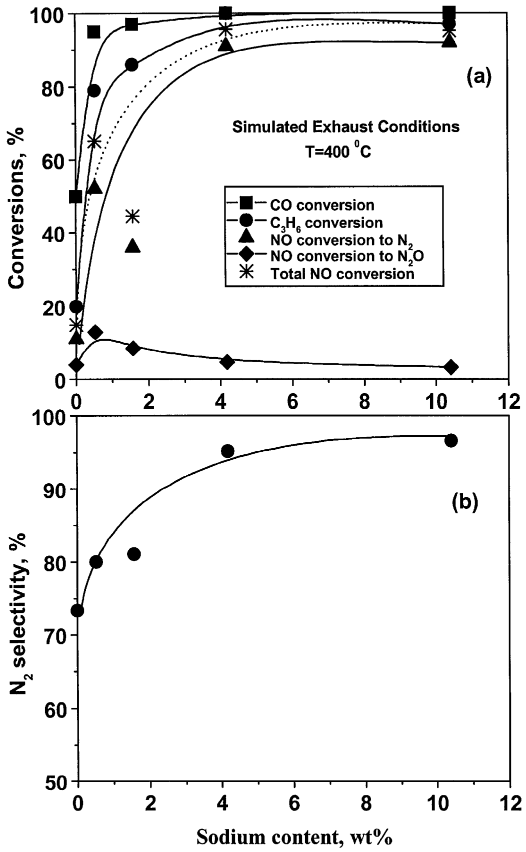

FIG. 5. The effect of sodium loading on reactant conversions (a) and selectivity towards N_2 (b) for fixed temperature and inlet conditions. Data taken at 400°C, with a catalyst weight of 8 mg under simulated exhaust conditions (1000 ppm NO, 1067 ppm C_3H_6, 7000 ppm CO, and 7800 ppm O_2). Total flow rate is 80 $cm^3\ min^{-1}$.

DISCUSSION

Before proceeding to a detailed discussion of alkali promotion, it is worth recalling the overall high performance obtained from our catalysts. Consider first the question of activity. The promoted catalysts exhibit high conversion at substantially lower temperatures than the unpromoted catalyst. The selectivity behaviour is no less impressive: ~100% selectivity to N_2 at 100% NO conversion at temperatures close to the operating point of real TWCs. *This superior NO_x reduction performance is achieved without the use of rhodium*. Note that although low or moderate loadings of alkali lead to some increase in Pt dispersion (Table 1), the optimal catalyst, C4, exhibits the same dispersion as the unpromoted catalyst. Therefore the principal effect of Na on performance may be attributed to modification by the promoter of the surface chemistry of the metal. (We may rule out the possibility that Na acts by "tying up" residual chlorine, based on our earlier detailed studies of this very point (26). Overpromotion did not have any adverse effect on either conversion or selectivity (Figs. 4 and 5). Catalyst C5 had ~2.5 times the Na loading of the optimally promoted catalyst C4. This suggests that the promoter is not distributed uniformly over the metal and support. Indeed it seems likely that most of it resides on the support which may act as a reservoir for the Na surface compound(s) which spillover onto the metal particles. Our post-reaction spectroscopic data (34, 39) strongly suggest that in the present case, under reaction conditions, Na is present on the Pt particles as nitrate and carbonate. The identity of the counterion is of secondary or negligible importance, for the reasons discussed below.

The principal effects of Na promotion are

(i) enhanced activity for CO and C_3H_6 oxidation, accompanied by
(ii) enhanced activity for NO reduction and
(iii) enhanced selectivity towards N_2 rather than N_2O in the presence of O_2.

We may rationalise this behaviour in terms of the effects of Na on the adsorption strength and (in the case of NO) dissociation behaviour of the reactants. Based on our kinetic and spectroscopic results for the electrochemical promotion by Na of NO reduction by CO (33) and by propene (34) over Pt catalysts, we proposed an explanation for the mechanism of Na promotion. This mechanism for promotion by Na and the supporting theoretical (40) and experimental (41) evidence have been described and discussed in detail previously (34). Briefly, adsorbed Na acts to increase the strength of NO adsorption and to weaken the N–O bond in the adsorbed molecule. This is due to the effect of the electrostatic field of the alkali cation on adjacent co-adsorbed NO molecules. It acts to lower the NO π^* orbital energy below the Fermi energy, thus populating the former with valence electrons from the metal. This results in weakening of the N–O bond and a strengthening of the metal–N bond, which effects account for the observed increases in selectivity and activity, respectively. This explanation (40) is equivalent to the more traditional "chemical" explanation presented by Blyholder, based on the Dewar–Chatt model. However the electrostatic view (essentially an example of the Stark effect) is more satisfactory in that it also provides a transparent explanation for the relative unimportance of anion effects. In principle, co-adsorbed anions should exert the opposite influence to cations. This effect should, however, be far weaker for two reasons. (1) The anions are larger than the cations, thus preventing close approach of co-adsorbates to the centre of net charge. (2) The anions have a larger radius than the cations. Both effects operate in the same direction, namely, to decrease the electrostatic field at the co-adsorbate due to the anion. Therefore, promotion by cations overwhelms poisoning by anions, and, to first approximation at least, the identity of the anion does not matter. As an example, we have shown that under different reaction conditions ($O_2 + C_3H_6$ and $NO + C_3H_6$, respectively) both $NaNO_3$ and Na_2CO_3 compounds can act as strongly promoting species (34, 39). Thus under any given conditions, the effect of alkali surface compounds is to increase the coverage and degree of dissociation of NO.

For simplicity, we illustrate this by reference to the NO + CO reaction which is generally agreed (34, and References therein) to proceed by the mechanism

$$NO_{(a)} \rightarrow N_{(a)} + O_{(a)} \qquad [1]$$

$$CO_{(a)} + O_{(a)} \rightarrow CO_2 \qquad [2]$$

$$N_{(a)} + N_{(a)} \rightarrow N_2 \qquad [3]$$

$$N_{(a)} + NO_{(a)} \rightarrow N_2O. \qquad [4]$$

Reaction [1] triggers the overall process. Since Na acts to increase both the extent of NO adsorption *and* the rate of reaction [1], a substantial enhancement in the rate of CO oxidation by NO is expected. Selectivity towards N_2 formation is determined by the competition between reactions [3] and [4]. The observed increase in selectivity is therefore understandable as a consequence of the Na-induced decrease and increase, respectively, in the amounts of molecularly adsorbed NO and atomic N on the surface, thus favouring [3] over [4]. Increased activity and selectivity in the oxidation of propene by NO may be rationalised in an analogous way. In this case, the effect on activity is even more pronounced, because in the absence of Na propene is adsorbed much more strongly than NO (42, 43).

Thus the electropositive alkali promoter decreases the chemisorption strength of propene (an electron donor) while enhancing the chemisorption of electron acceptors (NO and its dissociation products). Self-poisoning due to excessive adsorption of propene and its decomposition products is therefore counteracted. This beneficial effect on relative surface concentrations of the competing reactants is amplified by the lowering of the activation energy of reaction [1], as noted above, resulting in a large increase in activity. These effects of alkali on the competitive adsorption of the reactants have been demonstrated in detail in our earlier kinetic studies (32–34, 39).

A key difference between the present work and our earlier work on Na-promoted NO reduction is the *presence of gaseous oxygen* in the reactant feed ($O_2:NO \sim 8:1$). The interpretation offered above must also account for Na-induced promotion in the presence of oxygen. Our work (39) on the EP by Na of Pt-catalysed propene combustion is highly relevant here. This showed that the positive effects of Na promotion on the combustion rate decreased on going from fuel-rich, through stoichiometric, to oxygen-rich gas compositions. At the stoichiometric point (zero order in propene, positive order in oxygen), optimal Na promotion more than doubled the combustion rate (39) due to enhancement of oxygen adsorption. Those experiments were carried out in a CST reactor at low conversions, in contrast with the plug flow reactor data presented here. The oxygen partial pressure used here was very similar to those used in the CST reactor experiments (39). However, in the present case there is a substantial oxygen concentration gradient along the reactor, whereas in the EP CST reactor the gas composition was constant throughout the reaction volume. The net effect is that the average oxygen coverage in the present case is lower than in the CSTR experiments. Therefore, in the present case, under stoichiometric conditions, one expects even higher promotion by sodium of the $O_2 +$ propene reaction.

Our interpretation of Na promotion in simulated exhaust gas under stoichometric conditions is then as follows. Propene and its decomposition fragments are strongly adsorbed, reducing the number of catalytically active sites. This is in accord with the known adsorption enthalpy of propene on Pt (44), the EP data mentioned above (39), and the views of Burch *et al.* (45, 46). Na promotes the adsorption of electronegative adsorbates (oxygen, NO) (32, 41) and inhibits the adsorption of electropositive adsorbates (propene) (42). Adsorption of the former is therefore enhanced at the expense of the latter, “cleaning off” the metal surface and increasing the overall oxidation activity of both oxygen and NO. That is, the effects of self-poisoning by propene and its decomposition products are strongly reduced.

There are a number of issues still to be addressed in relation to the possible application of alkali promoters in TWC catalysts. First of all, the influence of a large concentration of water vapour on both the activity and the stability of these systems is still unclear. It is also likely that the influence of sodium on light-off temperatures will vary considerably with the nature of the hydrocarbon, being significantly less pronounced in the presence of weekly adsorbed hydrocarbons such as alkanes. Indeed, our previous study of the $NO + CH_4$ reaction over palladium-based catalysts (47) found poisoning only on addition of Na due to over-promotion of the adsorption of NO. However, in the presence of strongly adsorbed hydrocarbons such as alkenes and aromatics, significant promotional effects on both activity and selectivity are expected.

CONCLUSIONS

1. Na promotion yields large improvements in the performance of $Pt/\gamma\text{-}Al_2O_3$ catalysts in the conversion of NO, CO, and propene in simulated exhaust gas, under stoichiometric conditions.
2. Very substantial increases in both conversion and N_2 selectivity can be achieved, the optimally promoted catalyst corresponding to a sodium loading of 4.18 wt%. At 400°C the best catalyst delivers almost 100% conversion of all three reactants at an N_2 selectivity of >95%.
3. Promotion is due to the effects of sodium on the relative adsorption strengths and (in the case of NO) dissociation behaviour of the reactants.

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REFERENCES

1. Taylor, K. C., *Catal. Rev. Sci. Eng.* **35**, 457 (1993).
2. Fritz, A., and Pitchon, V., *Appl. Catal. B* **13**, 1 (1997).
3. Armor, J. N., *Appl. Catal. B* **1**, 221 (1992).
4. Masel, R. I., *Catal. Rev. Sci. Eng.* **28**, 335 (1986).
5. Davies, P. W., and Lambert, R. M., *Surf. Sci.* **110**, 227 (1981).
6. Sharpe, R. G., and Bowker, M., *Surf. Sci.* **360**, 21 (1996).
7. Gandhi, H.-S., Yao, H. C., and Stepien, H. K., *ACS Symp. Ser.* **178**, 143 (1982).
8. Adams, K. M., and Gandhi, H. S., *Ind. Eng. Chem. Prod. Res. Dev.* **22**, 207 (1983).
9. Williamson, W. B., Lewis, D., Perry, J., and Gandhi, H. S., *Ind. Eng. Chem. Prod. Res. Dev.* **23**, 531 (1984).
10. Lee, C.-H., and Chen, Y-W., *Ind Eng. Chem. Res.* **36**, 1498 (1997).
11. Muraki, H., Yokota, K., and Fujitani, Y., *Appl. Catal.* **48**, 93 (1989).
12. Muraki, H., Fujitani, Y., and Shinjoh, H., *Appl. Catal.* **22**, 325 (1986).
13. Muraki, H., Shinjoh, H., Sobukawa, H., Yokota, K., and Fujitani, Y., *Ind. Eng. Chem. Prod. Res. Dev.* **25**, 202 (1986).
14. Yentekakis, I. V., Pliangos, C. A., Papadakis, V. G., Verykios, X. E., and Vayenas, C. G., *Stud. Surf. Sci. Catal.* **96**, 375 (1995).
15. Papadakis, V. G., Pliangos, C. A., Yentekakis, I. V., Verykios, X. E., and Vayenas, C. G., *Catal. Today* **29**, 71 (1996).
16. Pitchon, V., Guenin, and Praliaud, H., *Appl. Catal.* **63**, 333 (1990).
17. Liotta, L. F., Deganello, G., Delichere, P., Leclercq, Ch., and Martin, G. A., *J. Catal.* **164**, 334 (1996).
18. de Miguel, S. R., Castro, A. A., Scelza, O. A., and Soria, J., *Catal. Lett.* **32**, 281 (1995).
19. Venezia, A. M., Rossi, A., Liotta, L. F., Martorana, A., and Deganello, G., *Appl. Catal. A Gen.* **147**, 81 (1996).

20. Burch, R., and Watling, T. C., *Appl. Catal. B Env.* **11**, 207 (1997).
21. Skoglundh, M., Johansson, H., Lowendahl, L., Jansson, K., Dahl, L., and Hirschauer, B., *Appl. Catal. B* **7**, 299 (1996).
22. Wang, C.-B., Chang, Wu, R.-C., and Yeh, C.-T., *Appl. Catal. B* **17**, 51 (1998).
23. Alexandrou, F. A., Papadakis, V. G., Verykios, X. E., and Vayenas, C. G., *in* "Proceedings, 4th International Congress on Catalysis and Automotive Pollution Control, Brussels," Vol. 2, pp. 7–12, 1997.
24. Shinjoh, H., Isomura, N., Sobukawa, H., and Sugiura, M., *in* "Proceedings, 4th International Congress on Catalysis and Automotive Pollution Control, Brussels," Vol. 1. pp. 29–38, 1997; Shinjoh, H., Isomura, N., Sobukawa, H., and Sugiura, M., *in* "Studies in Surface Science and Catalysis" (N. Kruse, A. Frennet, and J.-M. Bastin, Eds.), Vol. 116, p. 83. Elsevier, Amsterdam/New York, 1998.
25. Tanaka, T., Yokota, K., Isomura, N., Doi, H., and Sugiura, M., *Appl. Catal. B* **16**, 199 (1998).
26. Yentekakis, I. V., Lambert, R. M., Tikhov, M. S., Konsolakis, M., and Kiousis, V., *J. Catal.* **176**, 82 (1998).
27. Yentekakis, I. V., Konsolakis, M., Lambert, R. M., Macleod, N., and Nalbantian, L., *Appl. Catal. B* **22**, 123 (1999).
28. Kiskinova, M., *Stud. Surf. Sci. Catal.* **70**, 1 (1992).
29. Cambell, J. M., "Catalysis at Surfaces." Chapman & Hall, New York, 1998.
30. Vayenas, C. G., Bebelis, S., Yentekakis, I. V., and Lintz, H.-G., *Catal. Today* **11**, 303 (1992).
31. Vayenas, C. G., and Yentekakis, I. V., *in* "Handbook of Heterogeneous Catalysis" (G. Ertl *et al.*, Eds.), VCH, Weinheim/New York, 1997.
32. Yentekakis, I. V., Moggridge, G., Vayenas, C. G., and Lambert, R. M., *J. Catal.* **146**, 292 (1994).
33. Palermo, A., Lambert, R. M., Harkness, I. R., Yentekakis, I. V., Marina, O., and Vayenas, C. G., *J. Catal.* **161**, 471 (1996).
34. Yentekakis, I. V., Palermo, A., Filkin, N. C., Tikhov, M. S., and Lambert, R. M., *J. Phys. Chem. B* **101**, 3759 (1997).
35. Yentekakis, I. V., Palermo, A., Filkin, N. C., Tikhov, M. S., and Lambert, R. M., *Stud. Surf. Sci. Catal.* **116**, 255 (1998).
36. Yentekakis, I. V., Konsolakis, M., Kiousis, V., Lambert, R. M., and Tikhov, M. S., *Global Nest Int. J.* **1**(2), 121 (1999).
37. Benson, J. E., and Boudart, M., *J. Catal.* **4**, 704 (1965).
38. Cant, N. W., Angore, D. E., and Chambers, D. C., *Appl. Catal. B* **17**, 63 (1998).
39. Filkin, N. C., Tikhov, M. S., Palermo, A., and Lambert, R. M., *J. Phys. Chem. B* **103**, 2680 (1999).
40. Lang, N. D., Holloway, S., and Norskov, J. K., *Surf. Sci.* **150**, 24 (1985).
41. Harkness, I. R., and Lambert, R. M., *J. Chem. Soc. Faraday Trans.* **93**, 1425 (1997).
42. Cassuto, A., Mane, M., Tourillou, P., Parent, P., and Jupille, J., *Surf. Sci.* **287/288**, 460 (1993).
43. Ge, Q., Brown, W. A., Sharma, R. K., and King, D. A., *J. Chem. Phys.* **110**, 12082 (1999).
44. Brown, W. A., Kose, R., and King, D. A., *Surf. Sci.* **440**, 271 (1999).
45. Burch, R., and Millington, P. J., *Catal. Today* **26**, 185 (1995).
46. Burch, R., Millington, P. J., and Walker, A. P., *Appl. Catal. B* **4**, 65 (1994).
47. Yentekakis, I. V., Lambert, R. M., Konsolakis, M., and Kiousis, V., *Appl. Catal. B* **18**, 293 (1998).