Journal of Catalysis **193,** 115–122 (2000)
doi:10.1006/jcat.2000.2882, available online at http://www.idealibrary.com on

Sodium Promotion of the $NO + C_3H_6$ Reaction over Rh/γ-Al_2O_3 Catalysts

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Received December 17, 1999; revised March 8, 2000; accepted March 8, 2000

Sodium promotion strongly enhances both the activity and the nitrogen selectivity of Rh/γ-Al_2O_3 catalysts in the reduction of NO by propene. The optimally promoted catalyst (7.3% w/w Na) exhibits a ∼3 times higher TOF and 90% N_2 selectivity (at 375°C) as compared to 53% for the unpromoted catalyst under the same conditions. Na also suppressed the formation of CO and HCN. At sufficiently high Na loadings the system exhibits poisoning. The improved performance and kinetic behaviour are understandable in terms of Na-induced enhancement of NO adsorption and dissociation on the Rh surface, in competition with propene and its decomposition products. © 2000 Academic Press

Key Words: **NO; rhodium; TWC; promotion; sodium; HCN.**

1. INTRODUCTION

Current automotive catalytic converters, so-called three-way catalysts (TWCs), employ various combinations of Pt, Pd, and Rh for the simultaneous removal of NO_x, CO, and unburned hydrocarbons (1, 2). Of these metals, rhodium is the key component in relation to NO_x reduction due to its high activity for the dissociative chemisorption of NO (3).

In an effort to promote rhodium-containing catalysts, Tomishige *et al.* (4) reported that the formation of bimetallic Rh–Sn particles, synthesised by reacting a supported Rh/SiO_2 catalyst with $Sn(CH_4)_4$, significantly enhanced both NO dissociation and the reaction between $NO + H_2$. These promotional effects were attributed to the oxophilic nature of Sn metal. It was postulated that the oxygen atom of NO molecules adsorbed on rhodium sites could interact with adjacent Sn atoms, weakening the N–O bond and resulting in enhanced dissociation. More recently Chafik *et al.* (5) employed FTIR and mass spectroscopic techniques to study the adsorption and dissociation of NO over Rh supported on undoped and W^{6+}-doped TiO_2. In this case it was observed that doping of the TiO_2 carrier significantly increased the extent of transient NO decomposition and the selectivity towards N_2 formation. These effects were discussed in terms of electronic modification of the support, induced by the incorporated W^{6+} ions, which in turn modified the electronic state of surface rhodium atoms via interactions at the metal–support interface. Thus evidence exists that promoters may be used to enhance the performance of Rh as an NO_x reduction catalyst.

Electrochemical promotion (EP) (6) has recently been used to investigate the influence of alkali on the reactions of $NO + CO$ (7) and $NO + C_3H_6$ (8) over platinum. It was shown that sodium, electrochemically supplied to the metal surface, strongly influenced its catalytic properties, resulting in large increases in both activity and N_2 selectivity. Guided by these EP studies, Yentekakis *et al.* investigated the influence of sodium addition to conventional dispersed palladium (9) and platinum (10) catalyst for the reduction of NO by propene. In the case of palladium supported on yttria-stabilised zirconia (9), strong promotion by sodium was observed, accompanied by increases in nitrogen selectivity from 75% over the unpromoted catalyst to >95% over the optimally promoted catalyst. In the case of platinum supported on γ-Al_2O_3, the influence of sodium addition was even more striking (10). Rate increases by 2 orders of magnitude were obtained, again accompanied by very large increases in N_2 selectivity, from ∼20% over the unpromoted catalyst to >95% over the optimally promoted catalyst.

Here, we complete the picture by reporting on the influence of sodium promotion on the $NO + C_3H_6$ reaction over dispersed Rh/γ-Al_2O_3 catalysts. Rate increases by a factor of up to 3 were obtained, accompanied by substantial increases in N_2 selectivity over a wide range of conditions. It was also found that the presence of sodium significantly decreased the production of the undesirable by-products CO and HCN.

2. METHODS

2.1. *Materials*

The 0.5 wt% Rh/γ-Al_2O_3 catalyst which formed the basis of this study was prepared by impregnation of an alumina carrier (Aldrich, $SA = 100\ m^2\ g^{-1}$) with an aqueous solution of rhodium(III) nitrate (Alfa). Batches of this precursor were subsequently impregnated with solutions containing various concentrations of sodium nitrate. The solution concentrations were chosen so as to yield a range of sodium loadings from 0 to 12 wt%. Following impregnation the

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0021-9517/00 $35.00

TABLE 1

Properties of 0.5 wt% Rh/γ-Al_2O_3 Catalysts[a]

Na loading (wt%)	CO uptake (cm^3 STP/g)[b]	Dispersion (%)
0	1.773	36.6
1.8	1.764	36.3
3.0	1.760	36.3
7.3	1.770	36.5
11.3	1.716	35.5

[a] Calcined in air for 10 h at 450°C and reduced in H_2 for 1 h at 300°C prior to measurement.

[b] STP = standard temperature and pressure.

catalysts were dried in air for 4 h at 110°C and subsequently crushed/sieved to yield grain sizes in the range 255–350 μm. Metal dispersions were determined using the CO methanation technique (11, 12). Prior to this measurement the samples (100 mg) were calcined in air (60 cm^3 min^{-1}) for 10 h at 450°C followed by reduction in H_2 (60 cm^3 min^{-1}) for 1 h at 300°C. A summary of the relevant data can be found in Table 1.

2.2. Light-Off Performance and Kinetics

Catalyst testing was performed using a quartz tubular plug flow reactor (i.d. 4 mm). During light-off measurements the catalyst sample (7.5 mg, diluted in 100 mg of 255–350-μm α-Al_2O_3) was retained between plugs of quartz wool, with a K-thermocouple placed in the centre of the bed. Reactant gases (MG Gas Products) were delivered by a series of independent mass flow controllers (MKS Instruments). The feed consisted of 3000 ppm NO + 3000 ppm C_3H_6 diluted in He. The total flow was 300 cm^3 min^{-1} corresponding to a reciprocal weight time velocity, W/F = 0.0015 g s cm^{-1}. Kinetic data were obtained under differential conditions employing 1.5 mg of catalyst sample diluted in 100 mg of α-Al_2O_3 with flow rates in the range 300–600 cm^3 min^{-1}. Prior to reaction the samples were calcined in air (60 cm^3 min^{-1}) for 10 h. The reactor outflow was analysed using a Shimadzu 14B chromatograph with a TCD detector, a Signal 4000 series chemiluminescence NO/NO_2 detector, and a Hiden RC quadrupole mass spectrometer. A Poropak N column was employed for the chromatographic separation of CO_2, N_2O, and C_3H_6, and a molecular sieve 5A column for the separation of N_2, O_2, and CO. The carbon and nitrogen mass balances (based on C_3H_6, CO, CO_2, NO, N_2, N_2O, and HCN) were found to close within 1% and 2%, respectively.

3. RESULTS

3.1. Catalyst Characterisation

Active metal areas were determined by the CO methanation technique, after calcination in air at 450°C and reduction in hydrogen for 1 h at 300°C. This technique (11) makes use of a sensitive FID detector to monitor the conversion of chemisorbed CO to methane on metal sites. Prereduction was necessary in order to generate fully reduced metal sites. The metal dispersion was calculated assuming a 1:1 CO to surface metal atom ratio (Table 1); note that the measured Rh dispersion (~36.5%) is independent of initial Na loading. However, XRD analysis revealed that the reducing treatment employed prior to CO adsorption resulted in dissolution of sodium into the support, with the formation of a $NaAlO_2$ phase. Therefore the measured dispersions do not take account of site-blocking effects which may be present on calcined samples due to the presence of surface sodium compounds.

3.2. Effect of Sodium Loading on Steady-State Activity and Selectivity

Figure 1 depicts the influence of sodium loading on the CO_2, N_2, and N_2O turnover rates at 375°C for a feed containing 1000 ppm C_3H_6 and 3000 ppm NO. It is apparent from these data that Na exerts a pronounced effect. Promotion of CO_2 and N_2 occurs in the range between 0–8 wt% Na, with any further increase in loading resulting in a strong inhibition of the rates. It is interesting to note the order in which product rates maximise as a function of sodium loading, with the N_2O rate maximum occurring at the lowest Na loading, ~3 wt%, followed by CO_2 and finally N_2 at approximately 6 wt% Na.

The variation in nitrogen selectivity ($S_{N_2} = 100 \times r_{N_2}/(r_{N_2} + r_{N_2O})$) with sodium loading is illustrated in Fig. 2 for a range of NO partial pressures. First of all, it is clear that the selectivity towards nitrogen decreases significantly as the concentration of NO is increased. However, in all cases, the addition of sodium acts to strongly promote N_2 formation. For [NO] = 1000 ppm, the unpromoted Na-free

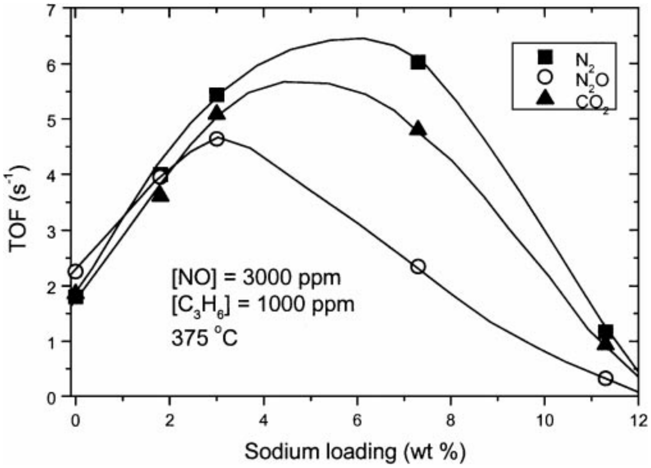

FIG. 1. Effect of sodium content on turnover formation rates of CO_2, N_2O, and N_2 for a fixed temperature and reactant concentration; $T = 375$°C, [NO] = 3000 ppm, [C_3H_6] = 1000 ppm.

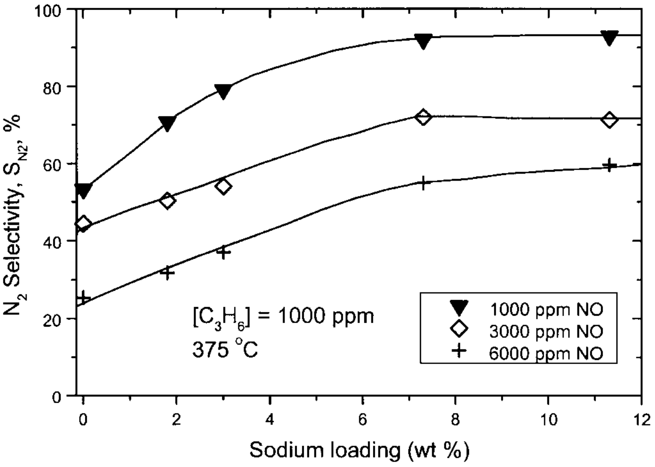

FIG. 2. Effect of sodium content on N_2 selectivity, S_{N_2}, for a fixed temperature and C_3H_6 concentration and varying NO concentrations; $T = 375°C$, $[C_3H_6] = 1000$ ppm, $[NO] = 1000$, 3000, or 6000 ppm.

catalyst exhibits a selectivity of ~53%. Addition of sodium results in a steady increase in selectivity up to a value of over 90% at 7.3 wt% Na. However, further increases in sodium loading do not significantly alter the selectivity, in contrast to the large decrease in activity that occurs at high Na loadings (Fig. 1).

To aid comparison with related studies in which Na promotion was achieved by electrochemical means (8), and with other studies on the influence of sodium on conventional dispersed catalysts (9, 10, 13) it is useful to define a rate enhancement ratio, ρ, as follows:

$$\rho = \text{TOF (on Na-promoted catalyst)}/\\ \text{TOF}^0 \text{ (on Na-free catalyst)}.$$

The ρ values obtained in the present case are plotted as a function of sodium loading in Fig. 3, from which it can be seen that the maximum rate enhancement ratios were $\rho_{CO_2} \sim 2.7$, $\rho_{N_2} \sim 3.3$, and $\rho_{N_2O} \sim 2.0$ for the production of CO_2, N_2, and N_2O respectively. (If the optimum Na coverage is calculated on the basis of total surface area—which is dominated by the support—the value obtained exceeds that determined for the optimally promoted EP catalysts by about 1 order of magnitude. This reflects strong preferential association of the Na with the support, as indeed indicated by our XRD results, see Section 3.1.)

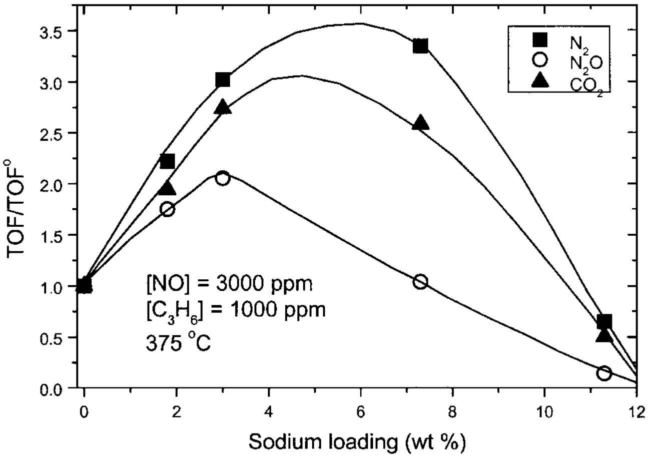

FIG. 3. Effect of sodium content on the rate enhancement ratio, $\rho = \text{TOF}/\text{TOF}^0$, for the formation of CO_2, N_2O, and N_2; $T = 375°C$, $[NO] = 3000$ ppm, $[C_3H_6] = 1000$ ppm.

3.3. *Effect of NO Concentration on Turnover Rates*

Figures 4a, 4b, and 4c show the effect of NO concentration on the N_2, N_2O, and CO_2 turnover rates, respectively, for a range of sodium loadings. These results clearly demonstrate a pronounced promotion by sodium of the N_2 and CO_2 formation rates over a wide range of NO

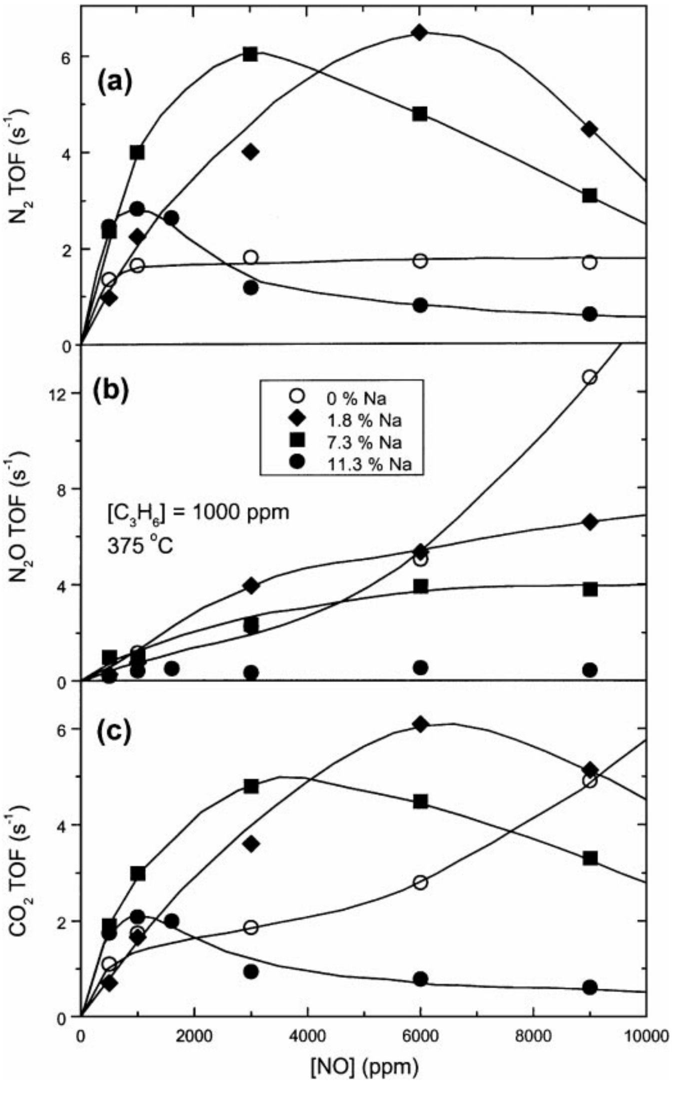

FIG. 4. Effect of NO concentration on the turnover formation rates (TOF) of (a) N_2, (b) N_2O, and (c) CO_2 for catalysts with varying sodium loadings; $T = 375°C$, $[C_3H_6] = 1000$ ppm.

concentrations. Notice that for the sodium-containing samples, the N_2 and CO_2 rates pass through a maximum, with the rates decreasing at high NO concentrations. This implies competitive adsorption of reactant NO and propene. Note also that the [NO]/[C_3H_6] ratios at which the rate maxima occur vary strongly and systematically with sodium loading, from 6/1 for 1.8% Na- to 1/1 for 11.3% Na-loaded catalyst. That is, as the Na loading is increased, the rate maxima move towards lower NO partial pressure. With the unpromoted catalyst, the rate of N_2O formation increased rapidly with NO concentration (Fig. 4b). Addition of 1.8–3 wt% Na slightly increased the rate of N_2O formation at low and medium NO concentrations. However, for high NO concentrations and/or at high sodium loadings, the effect is to significantly reduce the rate of formation of N_2O.

It will be argued below that all this behaviour receives a consistent explanation in terms of the effects of Na on adsorbed NO and adsorbed propene.

3.4. Light-Off Performance: NO Conversion and Selectivity as a Function of Temperature

Light-off performance measurements were obtained using a feed consisting of 3000 ppm NO + 3000 ppm C_3H_6 diluted in He. The total flow was 300 cm^3 min^{-1}, corresponding to a reciprocal weight time velocity, W/F = 0.0015 g s cm^{-1}.

Figure 5 shows the effect of temperature on NO conversion to N_2 for a range of sodium loadings. At low temperature there is a slight inhibition of conversion with sodium addition due to blocking of rhodium sites by the promoting sodium compounds. (Alexandrou *et al.* (14) found a moderate poisoning by Na in the reduction of NO by CO over Rh/TiO_2 at loadings up to 0.1% which differs significantly from our findings; this may reflect differences in metal–support interactions in the two cases.) In the present case, as the temperature is increased a crossover value is attained for each Na loading: above this temperature the conversion to N_2 becomes greater than that obtained over the sodium-free catalyst. Above 350°C the optimum Na loading is 7.3 wt%. This catalyst delivers 50% NO conversion to N_2 at a temperature approximately 70°C lower than that observed for the sodium-free catalyst.

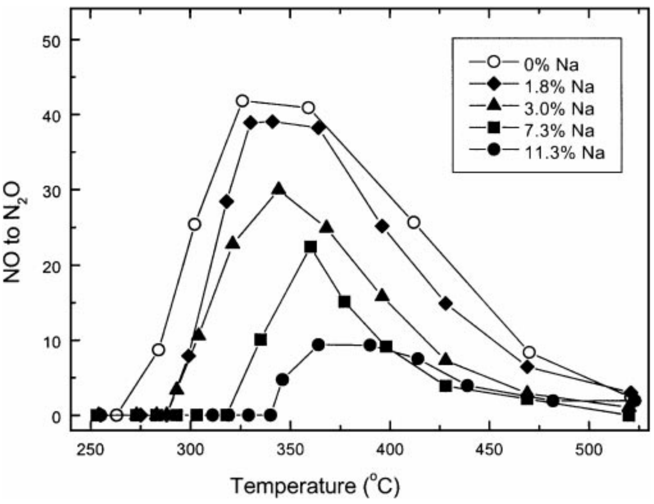

FIG. 6. Conversion of NO to N_2O as a function of temperature at constant reactor inlet conditions over catalysts with varying sodium contents; [NO] = 3000 ppm, [C_3H_6] = 3000 ppm, W/F = 0.0015 g s cm^{-3}.

The corresponding NO conversion to N_2O is shown in Fig. 6, with the nitrogen selectivity, S_{N_2}, shown in Fig. 7. It is evident that addition of sodium produces a large gain in selectivity over a wide temperature range. At 375°C, the catalyst containing 7.3% Na exhibits a selectivity of ~90% as compared to ~50% for the unpromoted sodium-free sample. It should also be noted that the N_2 selectivity

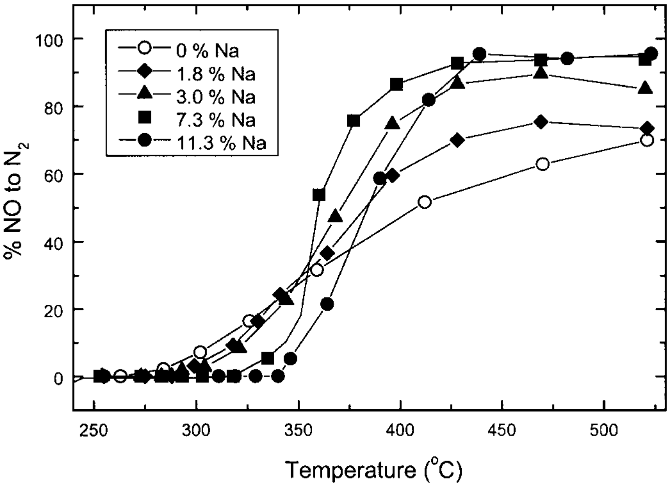

FIG. 5. Conversion of NO to N_2 as a function of temperature at constant reactor inlet conditions over catalysts with varying sodium contents; [NO] = 3000 ppm, [C_3H_6] = 3000 ppm, W/F = 0.0015 g s cm^{-3}.

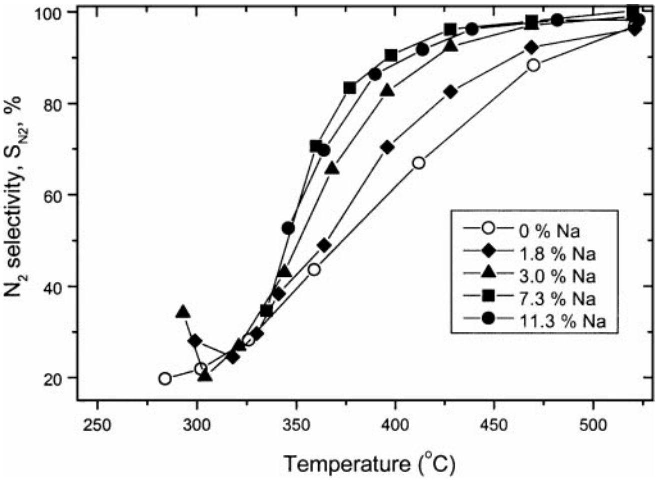

FIG. 7. N_2 selectivity, S_{N_2}, as a function of temperature over a series of catalysts with varying sodium contents; [NO] = 3000 ppm, [C_3H_6] = 3000 ppm, W/F = 0.0015 g s cm^{-3}.

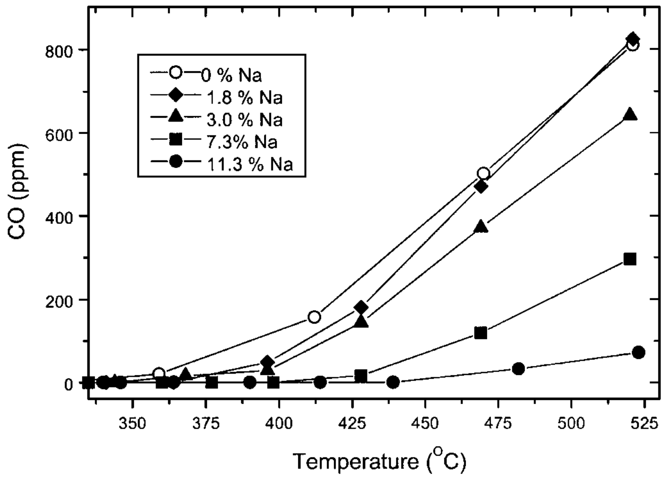

FIG. 8. Influence of sodium content on C_3H_6 conversion to CO as a function of temperature; [NO] = 3000 ppm, $[C_3H_6]$ = 3000 ppm, W/F = 0.0015 g s cm^{-3}.

increases with sodium loading only in the range 0–7.3% Na, as observed in Fig. 2, with further addition having little or no effect on this parameter.

3.5. *Light-Off Performance: C_3H_6 Combustion to CO and CO_2*

Under our conditions (3000 ppm NO + 3000 ppm C_3H_6), propene combustion produced significant quantities of CO at high temperatures (Fig. 8). At 525°C the sodium-free catalyst produced 810 ppm CO. However, as is also clear from Fig. 8, addition of sodium strongly suppressed CO production: the 11 wt% Na sample produced only approximately 80 ppm CO at 525°C. This is due to promotion of the complete oxidation of C_3H_6 to CO_2, as shown in Fig. 9. Therefore Na promotes complete combustion of propene at temperatures >375°C.

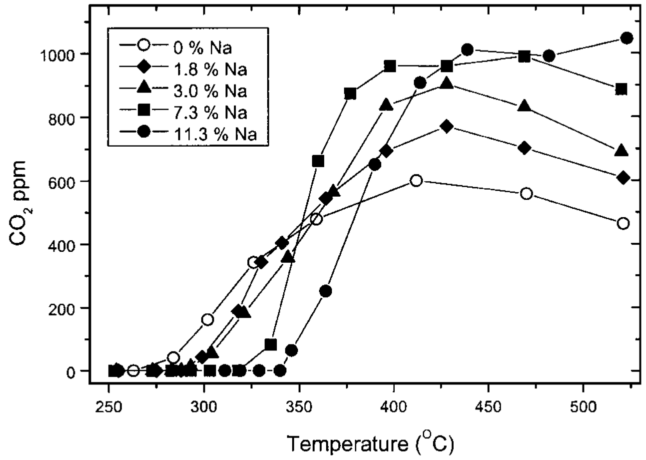

FIG. 9. Influence of sodium content on C_3H_6 conversion to CO_2 as a function of temperature; [NO] = 3000 ppm, $[C_3H_6]$ = 3000 ppm, W/F = 0.0015 g s cm^{-3}.

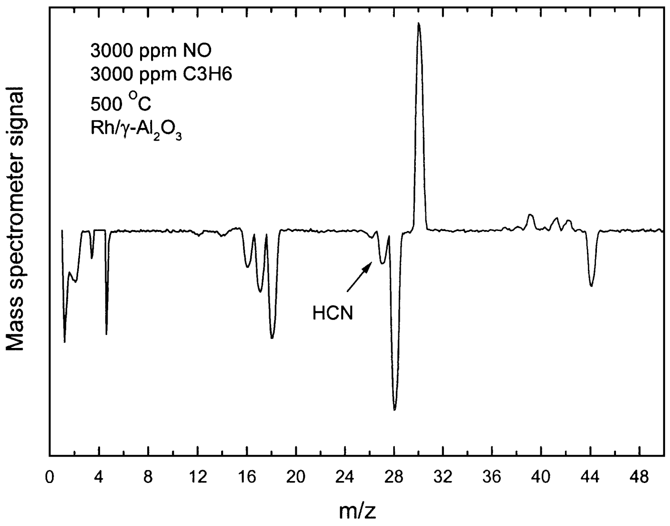

FIG. 10. MS difference spectrum (reactor inlet (bypass) − reactor outlet) revealing HCN formation; 0.5 wt% Rh/γ-Al_2O_3 catalyst, T = 500°C, [NO] = 3000 ppm, $[C_3H_6]$ = 3000 ppm.

3.6. *Light-Off Performance: HCN Formation*

HCN formation was observed over 0%, 1.8%, and 3.0% Na samples at temperatures above ~375°C. This product was evident in the GC trace as a peak eluting approximately 2 min after H_2O. Its identity was confirmed as HCN by mass spectrometry. Mass spectral analysis of HCN was complicated in this case due to the presence of the reactant C_3H_6, which yields major cracking peaks at the m/z values of interest (26 and 27). However, the difference spectrum shown in Fig. 10 (reactor inlet (bypass) − reactor outlet), in which products of the reaction appear as negative peaks, clearly reveals the formation of HCN.

Figure 11 illustrates the influence of sodium loading on HCN formation as a function of temperature. Over the

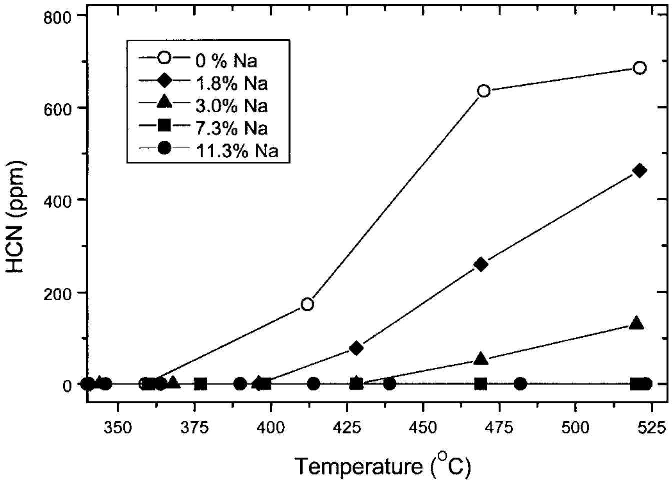

FIG. 11. Influence of sodium content on HCN as a function of temperature; [NO] = 3000 ppm, $[C_3H_6]$ = 3000 ppm, W/F = 0.0015 g s cm^{-3}.

sodium-free catalyst formation of this product reached 680 ppm at 525°C. Addition of sodium strongly suppressed HCN production, with both 7.3 and 11.3 wt% Na catalysts producing no HCN over the range of temperatures investigated.

4. DISCUSSION

4.1. Kinetic Behaviour and Mode of Action of Na

NO reduction by propene exhibits pronounced promotion by Na with regard to activity (Figs. 1 and 3) accompanied by a marked improvement in selectivity (Fig. 2). The rate gains and selectivity enhancements observed here ($\rho(N_2) = 3.3$, $\Delta S = 53\% \rightarrow 90\%$) are comparable with those found for the (Na) electrochemically promoted (EP) reaction on Rh films (15): $\rho(N_2) = 2.3$, $\Delta S = 45\% \rightarrow 82\%$. In the EP case there is direct spectroscopic evidence that the effects on catalytic performance are due to supply of Na *to the metal surface* (9). Therefore in the present case we infer that the promotional effects are also due to enhanced NO chemisorption and dissociation on the Rh surface induced by Na. It is proposed that co-adsorbed ionic sodium enhances NO adsorption and induces NO dissociation, producing the O_a species which are then responsible for initiating the ensuing oxidation reactions of adsorbed propene and propene fragments. Specifically, the electronic effects of the sodium promoter are to strengthen the Rh–N bond (increasing NO coverage) and weaken the N–O bond (facilitating NO dissociation). The increased activity may therefore be understood. Theoretical support for this view is provided by the work of Lang *et al.* (16) who have discussed in detail the dissociation of chemisorbed diatomic molecules on metal surfaces induced by the electrostatic field of co-adsorbed alkali cations. More recently, we have experimentally demonstrated the Na-induced dissociation of NO on Pt{111} (17). The rate inhibition that occurs at the highest Na loadings may be rationalised in terms of (i) active site blocking by the promoter and (ii) self-poisoning of propene adsorption due to "overpromotion" of NO adsorption and dissociation.

The enhanced selectivity towards N_2 formation may be rationalised as follows. This quantity is determined by competition between the following reactions that occur on the Rh surface:

$$N_a + N_a \rightarrow N_2 \qquad [1]$$

$$N_a + NO \rightarrow N_2O. \qquad [2]$$

The increase in N_2O formation with NO partial pressure observed in Fig. 2 can therefore be attributed to increasing coverage of NO_{ads}. The observed behaviour on addition of sodium is a consequence of the Na-induced decrease and increase, respectively, in the amounts of molecularly adsorbed NO and atomic N on the surface. This favours the first reaction over the second. Note that the rate data in Figs. 4a, 4b, and 4c are consistent with this interpretation.

The systematic effect of Na loading on the reaction kinetics (Fig. 4) is understandable in terms of the effects of the promoter on the adsorption strength of the reactants. The CO_2 and N_2 rate data in Fig. 4 indicate that the reaction obeys Langmuir–Hinshelwood type kinetics with the characteristic rate maxima reflecting competitive adsorption of the two reactants. What is interesting is that as the Na loading *increases*, there is a systematic shift of the CO_2 and N_2 rate maxima to *lower* NO partial pressure. This behaviour reflects an increase in chemisorption bond strength of NO relative to propene with increasing Na coverage. Such behaviour is exactly what 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.

4.2. Light-Off Performance

The influence of sodium on NO conversion was found to be strongly temperature dependent (Fig. 5). At low temperatures a small rate inhibition was observed. The is attributed to blocking of active sites by the promoting sodium compound. This interpretation is consistent with the observation that as the Na loading increased, the temperature required to initiate the reaction also increased. It is interesting to note that in similar studies on Pd- (9) and Pt- (10) containing catalysts no such inhibition by sodium was observed. This may reflect the strong structure sensitivity of NO adsorption and dissociation over these two metals (2, 18–21) on which sodium activates previously inactive low-index planes (10). On polycrystalline Rh, for which the low-index planes are already active for NO dissociation (22–24), the effects of Na promotion are correspondingly less pronounced so that site blocking effects of Na become apparent at sufficiently low temperatures. At temperatures above ~340°C sodium strongly promoted NO conversion and substantially improved N_2 selectivity (Figs. 5, 6, 7). For example, at 375°C the catalyst containing 7.3% Na exhibited N_2 selectivity of ~90%, compared to ~50% for sodium-free sample. This is understandable in terms of the interpretation offered above, involving Na-induced enhancement of the adsorption and dissociation of NO.

The formation of significant amounts of CO over the Na-free catalyst and the progressive suppression of this product by Na, accompanied by increased CO_2 production, also deserve comment (Figs. 8 and 9). Promotion of deep oxidation (CO_2) is understandable in terms of the overall rise in oxidation activity due to increased O_a coverage resulting from both increased NO adsorption relative to propene and also Na-induced NO dissociation.

4.3. HCN Formation and Influence of Sodium

The formation of hydrogen cyanide under simulated exhaust conditions has been reported in a number of studies, both under lean burn conditions over various catalysts (25–27), and on metal-honeycomb-supported three-way catalysts (28). In recent single-crystal studies by van Hardeveld *et al.*, employing temperature-programmed reaction spectroscopy (TPRS) and secondary ion mass spectroscopy (SIMS) (29, 30), the formation of HCN was observed on a Rh{111} surface during reaction of ethylene with both NO (29) and *atomic nitrogen* (30). This suggests that cyanide formation occurs via the reaction of N_{ads}, formed via dissociation of NO, with surface carbon,

$$C_{ads} + N_{ads} \rightarrow CN_{ads}, \qquad [3]$$

with subsequent formation and desorption of HCN taking place via

$$CN_{ads} + CH_{x,ads} \rightarrow HCN\uparrow + CH_{x-1,ads}. \qquad [4]$$

Another possibility is the direct reaction between adsorbed nitrogen and hydrocarbon fragments,

$$N_{ads} + CH_{ads} \rightarrow HCN\uparrow. \qquad [5]$$

Although van Hardeveld *et al.* could not exclude possible contributions from reaction [5], clear evidence for the occurrence of reaction [4] was obtained; the surface coverage of CN was observed to decrease during evolution of HCN in the gas phase. The authors also reported that the selectivity of the reaction towards HCN formation varied strongly with ethylene coverage, being favoured at high C_2H_4 coverages. The influence of sodium addition on HCN formation (Fig. 11) may therefore be rationalised as follows: Fig. 4 clearly illustrates the dramatic change in surface coverages of NO and C_3H_6 brought about by addition of sodium. As the Na loading increases, NO adsorption is strongly promoted relative to propene, thereby reducing the concentrations of C_{ads} and HC_{ads} on the metal surface, which subsequently reduces the formation of CN via reaction [3] and HCN via reaction [4].

We now know that Na promotion of NO reduction by propene *in the absence of oxygen* is very effective in the case of dispersed Pt (10), Pd (9), and Rh catalysts (present work). Guided by these encouraging results, very recent investigations show that the beneficial effects of alkali promotion persist under simulated three-way exhaust conditions and under lean burn conditions (31).

5. CONCLUSIONS

(1) Sodium promotion enhances the performance of Rh/γ-Al_2O_3 catalysts in the reduction of NO by propene. Pronounced activity enhancement is accompanied by marked improvement in nitrogen selectivity. Na also strongly suppresses CO and HCN formation.

(2) The kinetic behaviour parallels that exhibited by the corresponding electrochemically Na-promoted catalysts—Rh films on Na-β'' alumina. Therefore the effects observed here are ascribed to Na-induced changes in the surface chemistry of Rh.

(3) Sodium promotes Rh by enhancing the adsorption strength and extent of dissociation of NO. This provides a straightforward explanation for the observed gains in both activity and selectivity.

ACKNOWLEDGMENTS

Financial support from the UK Engineering and Physical Sciences Research Council and from the European Union is gratefully acknowledged under grants GR/M76706 and BRPR-CT97-0460, respectively. J.I. acknowledges additional financial support from Johnson Matthey plc, under a CASE studentship.

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