The Reduction of NO by Propene over Ba-Promoted Pt/$\gamma$-Al$_2$O$_3$ Catalysts

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The performance of Ba-promoted Pt/$\gamma$-Al$_2$O$_3$ catalysts in the reduction of NO by propene has been investigated in a wide range of temperatures (ca. 200–500 $^\circ$C), reactant partial pressures, and promoter loading. The reaction follows Langmuir–Hinshelwood-type kinetics, reflecting weaker adsorption of NO on the metal surface relative to C$_3$H$_6$. Both catalytic activity and selectivity are strongly promoted by Ba, which does not however induce a change in the reaction mechanism. Rate increases by 2 orders of magnitude are achievable for N$_2$ and CO$_2$ production, while the selectivity toward N$_2$ is also significantly improved with a gain of about 50–60 percentage units exhibited by optimally Ba-promoted Pt. Barium also suppressed the formation of the undesirable by-product CO. These effects are understandable in terms of the influence of the Ba promoter on the relative adsorption strengths of reactant species. Ba promotes the adsorption (increasing coverage) of electronegative adsorbates (NO) relative to the adsorption of electropositive adsorbates (propene) on a catalyst surface predominately covered by the hydrocarbon. This is accompanied by weakening of the N=O bond, thus facilitating NO dissociation. These effects operate together to produce large increases in both activity and selectivity.

Key Words: alkaline earth; barium; platinum; TWC; promotion; NO; propene.

1. INTRODUCTION

Nitrogen oxide (NO$_x$) emissions produced primarily by combustion processes contribute significantly to a variety of environmental problems. Indeed, NO$_x$ interacts with hydrocarbons and solar radiation to produce ground-level ozone and other photochemical oxidants (smog) (1). It also contributes substantially to so-called acid rain (1–3). Moreover, N$_2$O is a powerful greenhouse gas that contributes to stratospheric ozone depletion (1). Thus, increasingly severe regulations are imposed to decrease NO$_x$ emission from vehicles since these are the primary source of such emissions. Although N$_2$O emission is not yet regulated by legislation, this is unlikely to remain the case.

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With respect to vehicles, a well-established technology for control of NO$_x$, CO, and hydrocarbons (C$_x$H$_y$) emissions is employed in the form of so-called three-way catalytic converters (TWCs) (4). TWCs employ various combinations of Pt, Pd, and Rh to catalyze efficiently reactions such as

$$\text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2 \quad [1]$$

$$\text{C}_x\text{H}_y + (x + y/4)\text{O}_2 \rightarrow x\text{CO}_2 + (y/2)\text{H}_2\text{O} \quad [2]$$

$$\text{NO} + \text{CO} \rightarrow \text{CO}_2 + \frac{1}{2}\text{N}_2 \quad (\text{N}_2\text{O}) \quad [3]$$

$$(2x + y/2)\text{NO} + \text{C}_x\text{H}_y \rightarrow x\text{CO}_2 + (x + y/4)\text{N}_2$$

$$+ (y/2)\text{H}_2\text{O} \quad (\text{N}_2\text{O}) \quad [4]$$

for the simultaneous conversion of the main pollutants, NO$_x$, CO, and unburned hydrocarbons to N$_2$, CO$_2$, and H$_2$O. Note that N$_2$O is an undesirable by-product of the last two reactions.

Although Pd and Pt are very effective in oxidizing CO and hydrocarbons, they are substantially less effective in reducing NO$_x$ emissions. Pd and Pt are relatively ineffective for the dissociative chemisorption of NO (3–6), in contrast to Rh, which is therefore a key component responsible for NO$_x$ reduction in TWCs (4). In addition, due to their low dissociation activity for NO, Pd and Pt produce a substantial amount of N$_2$O as a by-product of the last two reactions.

Considerable effort has recently been expended on enhancing the catalytic properties of Pt and Pd by additives (promoters) to increase their activity and selectivity for reactions such as [3] and [4]. The promotional effect of alkalis, alkaline earths, and other metals on supported Pt and Pd metal catalysts has been therefore the subject of considerable interest (7–16). 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 (7). 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 (8). 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. Tanaka et al. (9) showed that trimetallic
PtMoNa/SiO₂ 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. Shinjoh et al. (10) examined the effect of Li, Na, K, Cs, Mg, Ca, Sr, and Ba on propene conversion by NO₂ and O₂ under simulated exhaust conditions over Pd catalysts supported on γ-AI₂O₃ (10). They found that all the alkaline earths increased hydrocarbon conversion under all the conditions investigated, whereas the effect of alkalai was more complicated. Both increased and decreased conversions were observed, depending on the conditions and the identity of the alkali (10). More recently, they showed that the light-off temperature of NO and hydrocarbon conversions could also be improved by Ba addition on Pt under simulated automotive exhaust conditions (11). They concluded that Ba suppresses hydrocarbon chemisorption on the Pt surface, thus allowing the catalytic reaction to proceed smoothly.

In a series of recent kinetic and spectroscopic studies, we showed that Na can be used as a very effective promoter of Pt and Pd, enhancing very substantially both activity and N₂ selectivity of these two metals (12-15). In particular, we showed that Na-promoted Pd exhibits increased activity for the NO + C₃H₆ reaction by up to an order of magnitude in comparison to the unpromoted palladium (12). Significant improvement in N₂ selectivity relative to N₂O was also attained over this promoted catalyst (12). The beneficial effect of Na promotion was even more striking in the case of Pt-catalysed reduction of NO by propene: activity enhancement of 2 orders of magnitude and large increases in N₂ selectivity from ~15% over the unpromoted Pt to values as high as 95% over optimally Na-promoted Pt were obtained (13). We also tested these Na-promoted Pt/γ-AI₂O₃ catalysts in simulated exhaust conditions at the stoichiometric point (15). The results were very encouraging: significant increases in the conversion of all pollutants (CO, NOₓ, and hydrocarbons) were obtained, while the selectivity toward to N₂ approached ~100% at 100% conversion of NOₓ (15). Very recently, we extended these studies by investigating the promotion effect of all the remaining alkalis (Li, K, Rb and Cs) on the Pt-catalysed NO + C₃H₆ reaction (16). It was shown that all the alkalis provide a beneficial effect, the extent of which is strongly dependent on the alkali loading and identity. The best performance was exhibited by Rb promotion, where rate increases as high as 420-, 280-, and 25-fold were obtained for the formation of N₂, CO₂, and N₂O, respectively, together with large increases in N₂ selectivity (up to 70 percentage units) (16). Lambert and co-workers completed the picture of the influence of alkalis on the metal components of TWCS, reporting an about 3 times higher catalytic activity of an Rb/γ-AI₂O₃ catalyst promoted by Na for the NO + C₃H₆ reaction (17).

The progress described reflects the transfer of knowledge acquired from our application of the method of electrochemical promotion (EP) (18-20) to catalytic reactions of environmental importance (21, 22) in the design of practical catalyst formulations. That is, EP was used as a research tool for the understanding of the role and mode of action of Na promoter before applying this knowledge to the design of conventional catalyst formulations (21, 22).

Here, we show that similar benefits can be achieved by using alkaline earths as promoters. In particular, we report on the promotional effect of barium on the catalytic performance (activity and selectivity) of Pt/γ-AI₂O₃ for the reduction of NO by propene. At 450 °C, a temperature that approximates the average working temperature in autocatalyst monoliths, rate increases as high as 165- and 110-fold are obtained for the formation of N₂ and CO₂, respectively. The selectivity toward N₂ is simultaneously improved for about 50-60 percentage units, i.e., from ~45% over the unpromoted Pt to ~95% over the optimally Ba-promoted Pt, at 450 °C. It was also found that the presence of barium significantly decreased the production of the undesirable by-product CO, which at elevated temperatures is formed at a significant rate over the unpromoted Pt.

2. EXPERIMENTAL METHODS

2.1. Materials and Apparatus

The catalysts were Pt highly dispersed over a γ-AI₂O₃ carrier, loaded by various amounts of Ba promoter. The preparation procedure involved two sequential impregnation steps as follows. A powder of γ-AI₂O₃ carrier (Alfa products, surface area ~90 m²/g) was first impregnated in a solution of Pt(NH₃)₂(NO₂)₂ (Alfa products) with an appropriate concentration so as to yield 0.5 wt% Pt metal loading. After drying in air for 12 h at 110 °C, but before thermal decomposition of the active metal precursor, batches of this sample were impregnated with solutions containing various concentrations of Ba(NO₃)₂. The solution concentrations were appropriately chosen so as to yield a range of Ba loadings from 0 to ~23 wt%. This material was initially dried in air at 80 °C and then overnight at 110 °C. The resulting samples were heated for 8 h in flowing He (100 cm³/min) at 600 °C, followed by H₂ reduction for 2 h at 500 °C in a hydrogen flow of 100 cm³/min. Five Pt(Ba)/γ-AI₂O₃ catalyst samples were produced (catalysts C1-C5, Table 1). A nother sample without Pt, but containing 15 wt% barium (15 wt% Ba/γ-AI₂O₃), was also produced for control experiments.

The apparatus consisted of a feed unit and an analysis unit utilizing a combination of on-line gas chromatography (Shimadzu-14B) with on-line CO₂/NDIR CO₂ analyzer (Fisher-Rosemount, Binos-100 NDIR CO₂ analyzer) for the analysis of reactants and products. Separation of N₂, NO, and CO was achieved in a molecular sieve 5A
2.2. Catalyst Characterization, Kinetics, and Conversion

Performance Experiments

Catalysts were characterized with respect to the exposed metallic area and metal dispersion by selective chemisorption of H₂ at 25°C in an isothermal equilibrium chemisorption and BET apparatus (A ccusorb 2100E, Micromeritics). Catalyst testing was performed in a fixed bed, single-pass, plug flow reactor, consisting of a 4-mm internal diameter quartz tube. The catalyst bed was held between plugs of quartz wool and a chromel-alumel thermocouple was located in the center of the bed. Catalyst loadings were typically ~8 mg (grain size 180–250 μm), the sample being diluted further by an admixture with ~80 mg of 100- to 325-mesh α-Al₂O₃ (A lpha products).

The reactor was operated in the differential mode; i.e., reactant conversion was kept below 10–15% during acquisition of kinetic (turnover frequency) data. To maintain conversions of reactants to this level and to eliminate mass and heat transfer effects, the total gas flow rate was high, typically f = 80–300 cm³ STP/min. The absence of intraparticle and interparticle diffusional effects was experimentally confirmed by variation of the catalyst particle size and gas flow rate. The carbon and nitrogen mass balances were found to close within 2%. No reaction was observed over quartz wool for temperatures up to 550°C. In addition, the Ba/y-Al₂O₃ control sample did not show detectable decomposition activity of N₂O up to 600°C, in accord with the literature data (23). It also showed negligible catalytic activity for the NO + C₃H₆ reaction with respect to the Pt/y-Al₂O₃ or Pt(Ba)/y-Al₂O₃ catalysts over the whole range of conditions used in this study.

In another set of experiments where the conversion performance of the catalysts was studied as a function of temperature, the temperature was increased stepwise from 200 to 500°C, with temperature, total flow, and inlet composition maintained constant for 30 min before measurements were taken. The inlet composition consisted of 1000 ppm (v) NO + 1000 ppm (v) C₃H₆ diluted in He. The inlet total gas flow was f = 80 cm³ STP/min, corresponding to a reciprocal weight time velocity w/f = 6 × 10⁻³ g s cm⁻³.

Before measurements were taken, the catalysts were operated for 1 day in air and 5 days in a reactive gas mixture, 1000 ppm (v) NO + 1000 ppm (v) C₃H₆, at 550°C to eliminate possible residue from the metal precursor and to ensure stable operation (i.e., metal crystallite stabilization resulting from reaction or thermal sintering). It should be emphasized that measurements for the determination of catalyst dispersions (Table 1) were also performed after the above pretreatment. Thus, dispersion values were stable during the acquisition of kinetic and conversion performance data.

Preliminary thermal stability tests of Ba-promoted catalysts at 550°C for 10 days showed no deterioration in either catalyst activity or selectivity.

3. Results

3.1. Catalyst Characterization

The characterization data for all catalysts tested are summarized in Table 1. Isothermal H₂ chemisorption was performed at 25°C, after reduction of the catalysts in H₂ at 300°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. The H₂ uptakes were determined by extrapolation of the “plateau” portion (~10–40 Torr) of the isotherms, as described by Benson and Boudart (24).

3.2. Kinetic Measurements

3.2.1. Effect of reactant concentrations and Ba loading on turnover rates (TOFs) and selectivity. Figures 1a–1c show the kinetics of N₂, CO₂, and N₂O formation for the five catalysts C1–C5 of Table 1 with a range of Ba loadings as a function of propene concentration [C₃H₆] for fixed NO concentration ([NO] = 1.3%) and temperature (T = 375°C). The results are expressed in terms of turnover frequencies (TOF: molecules of product per surface Pt atom per second). In addition, Fig. 1d shows the corresponding behavior of the selectivity toward nitrogen, Sₐ (%) , defined as

\[ S_{N_2} (%) = \frac{\text{TOF}_{N_2}}{\text{TOF}_{N_2} + \text{TOF}_{N_2O}} \times 100. \]

It is apparent that the system exhibits characteristic rate maxima reflecting competitive adsorption of NO and propene. The rate maxima occur at very low [C₃H₆]/[NO]
molar ratios (typically <1/8), indicating weaker adsorption of NO on the metal surface relative to C₃H₆. For all catalysts C1–C5, N₂, CO₂, and N₂O production rates show essentially similar Langmuir–Hinshelwood (L-H) type behaviour as [C₃H₆] is varied, although a pronounced enhancement in catalytic activity and selectivity occurs upon Ba addition. The extent of enhancement is strongly dependent on the Ba loading. At all propene concentrations, the best TOF and selectivity performance is achieved with catalyst C4 (15.2 wt% Ba, Table 1). The data in Figs. 1a–1c suggest that the rate maxima tend to occur at higher [C₃H₆] as the Ba loading is increased (compare for example catalyst C3 and C5 data).

Figures 2a–2d depict analogous results for the dependence of N₂, CO₂, and N₂O turnover rates and N₂ selectivity at fixed [C₃H₆] = 0.3% and T = 375°C as a function of NO concentration. In this case the reaction exhibits positive-order dependence on [NO] and no rate maxima are found within the range of accessible experimental conditions. The only exception, however, is provided by catalyst C5 with the highest Ba loading (22.3 wt% Ba), which exhibits a rate maximum within the experimentally accessible range of NO concentration. Under all NO concentrations, the best performance is again achieved with catalyst C4. Comparison of the trends shown in Figs. 1 and 2 support the view that, under the conditions used in this study, the adsorption of C₃H₆ on the catalyst surface is much stronger than that of NO.

To aid comparison with related studies in which alkalis were used as promoting species (12–17) and with studies where promotion was achieved by electrochemical means (21), it is useful to define the rate enhancement ratio, ρ,

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

[6]

ρ values for N₂, CO₂, and N₂O production of up to 55, 35, and 7, respectively, were achieved with catalyst C4 (Figs. 1 and 2). At the same time large increases up to...
FIG. 2. The effect of NO concentration on the turnover (TOF) formation rates of N₂ (a), CO₂ (b), and N₂O (c) and on N₂ selectivity (d) for Ba-promoted Pt/γ-Al₂O₃ catalysts C1–C5 listed in Table 1. T = 375°C, [C₃H₆] = 0.3%. Concentrations refer to reactor outlet; w/f was varied in the range of $1.6 \times 10^{-3} - 6 \times 10^{-3}$ g cm⁻³; C₁ TOFs are “apparent TOFs,” see text.

~50–60 percentage units (Figs. 1d and 2d) in nitrogen selectivity are obtained over the whole range of NO and C₃H₆ concentrations investigated. The unpromoted Ba-free catalyst exhibits a very low selectivity toward N₂ of the order of 20–30% (Figs. 1d and 2d) under all conditions used. This illustrates the relatively poor activity of Pt for the dissociative chemisorption of NO. It is also apparent from Fig. 2d that N₂ selectivity declines significantly with NO concentration; in all cases, however, the addition of barium acts to strongly promote nitrogen selectivity.

It is also apparent from Figs. 1 and 2 that promotion of N₂ and CO₂ production occurs in the range 0–15.2 wt% Ba. A barium loading of 22.3 wt% (catalyst C5) causes inhibition of the N₂ and CO₂ rates but not that of N₂O formation (Figs. 1c and 2c). As a result, the selectivity toward N₂ of catalyst C5 is also significantly decreased (Figs. 1d and 2d).

3.2.2. Effect of temperature; apparent activation energies. It is of importance to determine whether the observed promotional effect of Ba remains effective over a wide range of temperatures, including those encountered in practical applications. Thus, Arrhenius plots for the formation of CO₂, N₂, and N₂O were obtained for the five catalysts over the temperature interval 250–500°C. Figure 3a depicts Arrhenius plots for CO₂ formation, whereas Fig. 3b shows the variation of N₂ selectivity upon 1/T. Additional information for the temperature dependence of N₂ and N₂O formation is summarized in Table 2. It is apparent that a significant variation of catalyst activity and selectivity with Ba loading was observed over the whole temperature range (Fig. 3). Catalyst C4 was again best in terms of both activity and selectivity and its superiority was maintained within the temperature range studied. We designate hereafter this catalyst as the “optimally promoted” catalyst because it maximizes both activity and selectivity over the whole range of accessible experimental conditions. Ba addition causes a significant increase in the apparent activation energies of the N₂, CO₂, and N₂O rates (Table 2) with a concomitant pronounced increase in the pre-exponential factor, thus
Fig. 3. (a) Arrhenius plots for CO₂ formation obtained with catalysts C1–C5 with different Ba loadings. Observation of the isokinetic effect at $1/T \approx 1.853 \times 10^{-3} \text{K}^{-1}$ ($\rightarrow T_{iso} = 267^\circ \text{C}$). (b) Temperature dependence of the selectivity toward N₂; constant reactor outlet conditions: $[\text{NO}] = 1.3\%$, $[\text{C}_3\text{H}_6] = 0.3\%$

providing a demonstration of the compensation effect (25, 26) with an isokinetic temperature, $T_{iso}$, of $\approx 270^\circ \text{C}$ for the N₂, CO₂, and N₂O rates. Away from the isokinetic temperature, the promotion is larger. Thus, at $450^\circ \text{C}$, rate increases by up to 2 orders of magnitude are achievable for the production of N₂ and CO₂ ($\rho_{\text{Ba}} = 165, \rho_{\text{CO}_2} = 110$), accompanied by a large increase in N₂ selectivity from $\approx 45\%$ over the unpromoted catalyst C1 to $\approx 95\%$ over the optimally promoted catalyst C4 (Table 2).

### 3.3. NO and C₃H₆ Conversion Performance of Ba-Promoted Catalysts as a Function of Temperature

Figure 4 shows the effect of catalyst temperature on NO conversion to N₂ (a), N₂ selectivity (b), and on C₃H₆ conversion to CO₂ (c) and CO (d) for catalysts C1–C5. Calculations are based on the following expressions:

\[
\text{NO conversion to N}_2(\%) = \frac{2[N_2]/[\text{NO}]^{in}}{100} \tag{7}
\]

\[
\text{C}_3\text{H}_6\text{ conversion to CO}_2(\%) = \frac{(1/3)[\text{CO}_2]/[\text{C}_3\text{H}_6]^{in}}{100} \tag{8}
\]

\[
\text{C}_3\text{H}_6\text{ conversion to CO}(\%) = \frac{(1/3)[\text{CO}]/[\text{C}_3\text{H}_6]^{in}}{100}, \tag{9}
\]

where $[\text{NO}]^{in}$ or $[\text{C}_3\text{H}_6]^{in}$ are the reactor inlet NO or C₃H₆ concentration, respectively, and $[\text{N}_2], [\text{CO}_2], [\text{CO}]$ are the concentrations of N₂, CO₂, or CO in the reactor effluent gas. For the sake of clarity the conversion of NO to N₂O is not depicted in the figure. However, since N₂ and N₂O are the only N-containing products, N₂O production is readily calculated from the data of Figs. 4a and 4b with the use of Eq. [5]). For this set of experiments the reactor inlet concentrations and total flow rate were kept constant. These concentrations were chosen to be 1000 ppm(v) NO and 1000 ppm(v) propene, which are close to those encountered in practical applications and commonly used in the literature as reference conditions. In every case, the total gas flow rate was 80 cm³ STP/min and the amount of catalyst loaded in the reactor was 8 (±0.2) mg.

It is very clear that Ba addition very substantially improves NO and C₃H₆ conversion performance of Pt as well as the selectivity toward N₂ over the whole temperature range (Fig. 4). The NO and C₃H₆ conversion over Ba-free unpromoted Pt is very poor. In contrast, catalyst C4 (15.2 wt% Ba) reaches 100% NO conversion at $T_{100} > \approx 425^\circ \text{C}$ (Fig. 4a) with almost 100% selectivity (Fig 4b). This catalyst also reduces the N₂ light-off temperature, $T_{50}$, (i.e., temperature of 50% NO conversion to N₂) by $\approx 125^\circ \text{C}$ in comparison to the unpromoted case. The conversion profile of catalyst C3 (9.7 wt% Ba) is slightly better than that of the optimally promoted catalyst C4. This seems to be contradictory when comparing catalysts C3 and C4 in terms of their TOF behavior. Such anomalies in conversion relative to turnover frequency are due to the significantly different dispersions of the various catalysts depicted in Fig. 4. Indeed, catalyst C3 has twice the dispersion of catalyst C4 (Table 1). Thus, similar conversion performance of catalyst

### TABLE 2

Apparent Activation Energies for the Formation of $\text{N}_2$, CO₂, and N₂O over Ba-Promoted Pt/Al₂O₃ Catalysts; TOF and N₂ Selectivity Values at 450°C (Data Obtained at Constant Reactor Effluent Concentrations $[\text{NO}] = 1.3\%$, $[\text{C}_3\text{H}_6] = 0.3\%$)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$\text{N}_2$</th>
<th>CO₂</th>
<th>N₂O</th>
<th>N₂ TOF</th>
<th>CO₂ TOF</th>
<th>N₂O TOF</th>
<th>$S_{N2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>84</td>
<td>58</td>
<td>23</td>
<td>0.31</td>
<td>0.32</td>
<td>0.38</td>
<td>45</td>
</tr>
<tr>
<td>C2</td>
<td>133</td>
<td>118</td>
<td>54</td>
<td>4.9</td>
<td>4.0</td>
<td>0.9</td>
<td>84</td>
</tr>
<tr>
<td>C3</td>
<td>150</td>
<td>134</td>
<td>59</td>
<td>14.8</td>
<td>10.6</td>
<td>1.2</td>
<td>93</td>
</tr>
<tr>
<td>C4</td>
<td>157</td>
<td>141</td>
<td>65</td>
<td>50.3</td>
<td>34.4</td>
<td>3.4</td>
<td>94</td>
</tr>
<tr>
<td>C5</td>
<td>117</td>
<td>82</td>
<td>27</td>
<td>4.0</td>
<td>3.2</td>
<td>1.6</td>
<td>72</td>
</tr>
</tbody>
</table>
C3 relative to catalyst C4 can be attributed to the higher dispersion of the former. The data of Fig. 4 in combination with TOF data strongly support the view that the principal effect of Ba on conversion performance may be attributed to modification by the promoter of the surface chemistry of the metal.

As Fig. 4d shows, at high temperatures (\( > 400 \degree C \)) part of C3H6 is converted to CO rather than CO2. It is worth emphasizing that addition of Ba strongly suppressed the formation of this undesirable by-product: the 15.2 wt% Ba promoted catalyst (C4) produced only approximately 30 ppm(v) CO at 450 °C (i.e., \( \sim 1\% \) of propene conversion) while the Ba-free catalyst produced \( \sim 90 \) ppm(v) CO (\( \sim 3\% \) of propene conversion) at the same temperature. With respect to CO production, the optimally promoted catalyst C4 again exhibits the best behavior since it provides the lowest CO productivity (Fig. 4d).

4. DISCUSSION

The present results show that NO reduction by propene over highly dispersed Pt on \( \gamma \)-Al2O3 exhibits kinetic behavior that reflects competitive adsorption of the reactants in a manner similar to that found for polycrystalline Pt films (21). Under most conditions the Pt surface is predominantly covered by the hydrocarbon, a view that is in accord with the adsorption enthalpy of propene on Pt (27) and with the results of Burch and Watling (28), who showed (in agreement with the present results) that in the absence of oxygen unpromoted Pt/\( \gamma \)-Al2O3 is a relatively poor catalyst for the reduction of NO by propene. However, at very low \([C3H6]/[NO]\) ratios, typically \( < 1/8 \) (Fig. 1), propene adsorption is rate limiting. As the propene pressure increases, the system eventually reaches a point where NO dissociation becomes rate limiting, a condition that leads to a monotonic decline in reaction rate with a further increase in propene pressure (29). The transition between these two regimes yields the observed rate maximum as a function of propene pressure. In this connection, it is worth pointing out that Granger et al. (29) derived a rate expression based explicitly on the assumption that in NO reduction the NO!N+O surface reaction is rate determining. In our case this equation would indeed lead to a monotonically declining rate with increasing propene concentration, exactly as is observed in Fig. 1, except at the very lowest propene concentrations. At the very lowest C3H6 concentrations the equation derived by Granger et al. (29) does not hold because of course in the limit of zero C3H6 concentration the rate must fall to zero, as our experimental data indicate. At the same time, the behavior predicted (29) for the rate dependence on NO partial pressure is in accord with the results shown in Fig. 2. Ba inhibits and enhances respectively the adsorption of propene and NO. Therefore, in the presence of Ba, a higher propene partial pressure is required to reach the condition where propene adsorption is no longer rate limiting. The result should be rate maxima that shift to higher propene partial pressure with increasing Ba loading, as is indeed observed.

In recent studies of the Pt- or Pd-catalysed reduction of NO by propene we showed that when alkalis are used as promoters either by classical methods (12–16) or by
electrochemical means (21), very large enhancements of both catalytic activity and selectivity can result. Based on these kinetics and/or spectroscopic studies, we proposed an explanation for the mechanism of alkali-induced promotion (12–16, 21, 22). Briefly, we argued that adsorbed alkalis act to increase the strength of NO adsorption (an electronegative adsorbate) relative to propene (an electropositive adsorbate). This effect is accompanied by weakening of the N–O bond in the adsorbed molecule, thus facilitating NO dissociation on the metal surface.

In a similar manner, the present results show that Ba addition to Pt can markedly affect its catalytic properties for the NO + C₃H₆ reaction. The similarities include the overall kinetic behavior and the dependence of activity and selectivity on promoter loading. It therefore seems reasonable to infer that similar phenomena determine the promotion induced by the alkaline earth, so that the mode of action of the Ba modifier may be rationalized as proposed earlier (12–16, 21) with regard to alkali-induced promotion.

The promoting effect of Ba may be rationalized in terms of its influence on the elementary steps of the NO + C₃H₆ surface reaction:

\[
\text{NO} (g) \rightarrow \text{NO}_{\text{ads}} \quad \text{(enhanced by Ba addition)} \quad [10]
\]

\[
\text{C₃H₆} (g) \rightarrow \text{C₃H₆}_{\text{ads}} \quad \text{(inhibited by Ba addition)} \quad [11]
\]

\[
\text{NO}_{\text{ads}} \rightarrow \text{N}_{\text{ads}} + \text{O}_{\text{ads}} \quad \text{(enhanced by Ba addition)} \quad [12]
\]

Once O$_{\text{ads}}$ is produced, it is scavenged by adsorbed hydrocarbonaceous species, accompanied by N$_{\text{ads}}$ recombination or reaction with NO$_{\text{ads}}$ to yield N$_2$ and N$_2$O respectively:

\[
\text{O}_{\text{ads}} + \text{hydrocarbonaceous species}
\rightarrow \text{CO}_2 (g) + \text{CO} (g) + \text{H}_2\text{O} (g) \quad [13]
\]

\[
\text{N}_{\text{ads}} + \text{N}_{\text{ads}} \rightarrow \text{N}_2 (g) \quad [14]
\]

\[
\text{N}_{\text{ads}} + \text{NO}_{\text{ads}} \rightarrow \text{N}_2\text{O} (g) \quad [15]
\]

Based on this reaction scheme, the observed large increases in activity may be understood in terms of the following factors, which operate together. Ba addition (i) enhances NO adsorption (reaction [10]) or equivalently increases the population of NO on a catalyst surface predominately covered by propene, (ii) induces NO dissociation (reaction [12]), which is the key reaction-controlling step, and (iii) weakens the propene–Pt bond (30, 31) (reaction [11]). That is, Ba acts to increase surface coverage by NO and its dissociation products at the expense of propene adsorption.

The trend of the rate maxima to higher [C₃H₆]/[NO] ratios (Fig. 1) as the Ba loading is increased as well as the appearance of a rate maximum at relatively low NO concentration in the case of catalyst C5 with the largest amount of Ba (Fig. 2) are in line with the above view. Indeed, both observations reflect an increase in chemisorption bond strength of NO and its dissociation products relative to propene with increasing Ba loading. Such behavior is exactly what one would expect in the case of an electropositive promoter: the chemisorption strength of electron acceptors (NO and its dissociation products) should be enhanced, whereas the chemisorption of electron donors (propene) should be decreased (30, 31).

The Ba-induced enhancement in N$_2$ selectivity can be readily understood in the following terms. The rates of production of N$_2$ and N$_2$O (and thus N$_2$ selectivity, Eq. [5]) depend on the extent of NO dissociation and the competition between the surface reactions [14] and [15]. The observed increase in the N$_2$ selectivity is therefore a consequence of the Ba-induced increase of N$_{\text{ads}}$ on the surface, together with a decrease of molecularly adsorbed NO (reaction [12]). Both factors favor reaction [14] over reaction [15], leading to higher N$_2$ selectivity. The decline in N$_2$ selectivity with [NO] depicted in Fig. 2d can be attributed to increasing coverage of NO$_{\text{ads}}$ as the gas phase NO concentration rises.

CO$_2$ and N$_2$O rate inhibition at very high Ba loading (Figs. 1 and 2; catalyst C5) is probably the result of more than one effect. First, excessive accumulation of NO dissociation products and surface compounds formed by the Ba promoter (e.g., nitrate or carbonate) reduces the number of active sites available to the reactants. Earlier XPS work has shown that such surface compounds do indeed form on the metal surface under conditions of alkali overpromotion (21, 32, 33). Second, on such a densely populated surface, NO dissociation is inhibited by the decreasing availability of nearest neighbor vacant sites. This further suppresses the N$_2$ and CO$_2$ rates, resulting in the observed strong poisoning. However, the N$_2$O rate continues to increase until it approaches or overcomes the N$_2$ rate. Note that these rates depend on [N$_{\text{ads}}$] and [N$_{\text{ads}}$]$^2$, respectively. Under our conditions the net result is an increase in the N$_2$O rate because reaction [15] gains at the expense of reaction [14]. This reflects the opposing (favorable/unfavorable) effects of decreased NO dissociation on reaction [15] in contrast to the strong quenching effect of decreased NO dissociation on reaction [14]. (In this connection we note that strictly speaking it is not correct to make reference to TOF values under conditions of strong site blocking (catalyst C5) since we are normalising the measured rates with respect to the unpoisoned metal area. Such values, used for convenience, are only apparent TOF values; their use does not affect our reasoning or our conclusions).

Theoretical support for our model of promoter action is provided by the work of Lang et al. (34), who have discussed in detail the dissociation of chemisorbed diatomic molecules on metal surfaces induced by the electrostatic field of co-adsorbed electropositive cations (e.g., alkalis). Moreover, experimental demonstration of the K and
N$_2$-induced dissociation of NO on Pt(111) model catalysts has been provided by Kiskinova et al. (35) and by Harkness and Lambert (36), respectively.

It is of interest to note that TWCs washcoat contains several metal oxide additives (e.g., CeO$_2$, La$_2$O$_3$, BaO) that contribute to catalyst durability and/or activity performance (37, 38). In particular, BaO is commonly used at a content of approximately 2–3 wt% in TWC supports and is usually considered as a stabiliser rather than as a promoter. The amount of Ba used in TWCs corresponds to far less than the optimal loading found in this study, even assuming that all the Ba was associated with the Pt metal component. Thus, although the beneficial effect of Ba in real TWCs might be expected, it is unlikely that such effects are at work in current TWC systems.

5. CONCLUSIONS

1. The NO + C$_3$H$_6$ reaction over Pt(111) model catalysts exhibits kinetic behavior that reflects competitive adsorption of the reactants. Rate maxima occurring at very low [C$_3$H$_6$]/[NO] molar ratios (<1:8) reflect weaker adsorption of NO on the metal surface relative to C$_3$H$_6$. The addition of Ba does not result in any change of the reaction mechanism.

2. Pt exhibits strong promotion by barium. Rate enhancements as high as 165- and 110-fold for the formation of N$_2$ and CO$_2$, respectively, are achievable at 450°C. Rate promotion is accompanied by a substantial increase in selectivity toward N$_2$, which is improved typically by about 50–60 percentage units relative to unpromoted Pt, yielding values S$_{N_2} > 95\%$ at T > ~400°C. Barium addition also suppresses the formation of the undesirable by-product CO.

3. Promotion is due to the effect of Ba on the relative adsorption strengths of reactant species. Barium addition to the catalyst strengthens the Pt–NO bond (thus increasing NO coverage) and weakens the N–O bond (thus promoting NO dissociation). It also inhibits the adsorption of propene on a catalyst surface predominantly covered by propene and its fragments. These factors work together to generate the observed major improvements in activity and selectivity.

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