

# Decomposition of Nitric Oxide over Barium Oxide Supported on Magnesium Oxide. 1. Catalytic Results and *in Situ* Raman Spectroscopic Evidence for a Barium–Nitro Intermediate

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**Abstract:** Barium oxide supported on magnesium oxide (Ba/MgO) exhibits unusual behavior as a catalyst for NO decomposition at Ba loadings of 11 mol % or greater. The catalytic activity is characterized by a sharp decrease in activity when the reaction temperature exceeds a certain value that depends on the partial pressures of NO and O<sub>2</sub>. The fall-off temperatures are between 630 and 700 °C for concentrations between 1% and 4% NO in helium. At 700 °C with 4% NO, the N<sub>2</sub> formation rate was 2.5 μmol g<sup>-1</sup> s<sup>-1</sup> for a 14 mol % Ba/MgO catalyst. The discontinuity in activity is accompanied by an abrupt change in activation energy for the reaction, which suggests a change in mechanism. *In situ* Raman spectroscopy was used to follow temporal changes in the composition of the catalyst that occurred after step changes in temperature or NO concentration. A comparison of spectroscopic and catalytic results indicates that a barium–nitro phase is an intermediate in the catalytic cycle below the fall-off temperature. Nitro species at the surface apparently react with NO to form the decomposition products, N<sub>2</sub> and O<sub>2</sub>. This is believed to be the rate-limiting step in the catalytic cycle. Peroxide ions may be involved in the formation of the nitro intermediate.

## Introduction

Among the various strategies for the removal of NO formed during combustion processes, the direct catalytic decomposition to N<sub>2</sub> and O<sub>2</sub> is the most attractive.<sup>1</sup> Although the decomposition reaction is thermodynamically favorable ( $\Delta G^\circ = -20.7$  kcal/mol at 25 °C), the rate is slow, even at elevated temperatures and in the presence of a catalyst. One of the most effective catalysts is a copper-loaded ZSM-5 zeolite, which was discovered by Iwamoto and co-workers.<sup>2</sup> This material is capable of achieving NO conversions in excess of 90% at 400 °C. Li and Hall<sup>3</sup> reported 100% conversion at 500 °C. The catalyst, however, lacks sufficient activity for commercial applications.<sup>1</sup> Other catalysts that are active for NO decomposition include cobalt oxide modified with silver,<sup>4</sup> strontium–iron oxides,<sup>5</sup> and perovskite-type compounds.<sup>6–8</sup> All of the active catalysts have a common feature in that they are able to release oxygen at moderate temperatures.

Another method for the removal of NO from gas streams involves selective reduction in the presence of O<sub>2</sub>.<sup>1</sup> The reducing gas may be NH<sub>3</sub> or a hydrocarbon such as CH<sub>4</sub> or C<sub>3</sub>H<sub>6</sub>. A variety of different catalysts are effective for these reactions, including the Cu-ZSM-5 zeolite noted above with C<sub>3</sub>H<sub>6</sub> as the reductant. In addition to catalysts containing transition metal ions, it has been observed that non-reducible basic oxides, such as SrO/La<sub>2</sub>O<sub>3</sub>, also promote the selective

reduction reaction and, to a lesser extent, the direct decomposition of NO.<sup>9</sup>

While studying this class of catalysts, we observed that barium oxide supported on magnesium oxide was particularly active for NO decomposition, provided the loading of barium was large. Moreover, the catalytic conversion of NO exhibits an unusual response with respect to reaction temperature and NO pressure, which makes it an ideal system for obtaining information on surface intermediates that may be generally applicable for the decomposition reaction. It has been possible to follow the species present in the catalyst by using *in situ* Raman spectroscopy. The results indicate that a nitro species is an intermediate in the catalytic cycle and that the unusual thermal behavior can be related to the stability of this intermediate.

## Experimental Section

The Ba/MgO catalysts were prepared by adding dropwise 30 mL of a solution containing the desired amount of Ba(NO<sub>3</sub>)<sub>2</sub> (Baker, reagent grade) to a vigorously stirred 30-mL slurry containing 5.0 g of MgO (Fisher, light) and deionized water. The mixture was stirred overnight, the water was evaporated at 100 °C, and the catalyst was calcined in air for 2 h at 700 °C. The material was then pressed under 1400 kg/cm<sup>2</sup> and sieved to 20–40 mesh size. Surface areas were determined with the BET method by adsorption of N<sub>2</sub>. The surface area of the 14 mol % Ba/MgO catalyst, which was the focus of this study, was 3.2 m<sup>2</sup> g<sup>-1</sup>.

Catalytic results were obtained with the use of a 4 mm i.d. fused-quartz, single-pass flow reactor at atmospheric pressure. Typically, a 100-mg sample of the catalyst was contained between two layers of quartz wool, and the space upstream from the catalyst bed was filled with fused-quartz chips. The catalysts were pretreated for 1 h at 800 °C in a 5.4% mixture of O<sub>2</sub> in He at a flow rate of 20 mL min<sup>-1</sup> and cooled to 25 °C in this gas mixture. Then the catalysts were heated to the reaction temperature in a mixture of flowing NO and He. Before obtaining data, reactions were run for a period of 50 min at each

<sup>⊗</sup> Abstract published in *Advance ACS Abstracts*, October 1, 1997.

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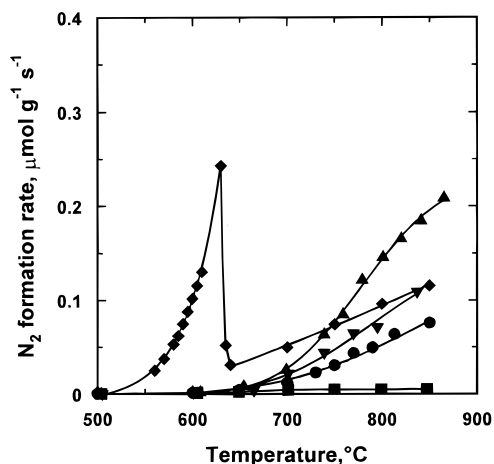
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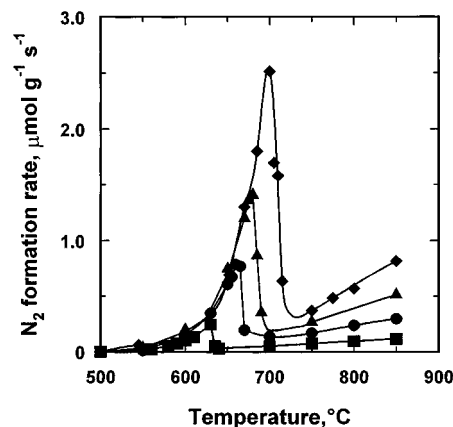
**Figure 1.** Effect of Ba loading level on decomposition of 1% NO/He over Ba/MgO catalysts: ■, MgO; ●, 1 mol % Ba/MgO; ▲, 4 mol % Ba/MgO; ▼, 7 mol % Ba/MgO; ◆, 14 mol % Ba/MgO.

temperature to ensure steady state conditions. Reaction mixtures were obtained by mixing 4.1% NO/He, and in a few cases 5.4% O<sub>2</sub>/He, with pure He so as to obtain the desired gas compositions. The total flow rate was 40 mL min<sup>-1</sup>. All gas mixtures and the pure He were obtained from Matheson. Analyses of the gases after reaction were performed with an HP5890 gas chromatograph, equipped with a 9 m HayeSep DB column (Alltech). The NO conversion was obtained from the relationship  $2([N_2] + [N_2O])/[NO]_0$ , where  $[NO]_0$  is the concentration of nitric oxide in the feed gas mixture.

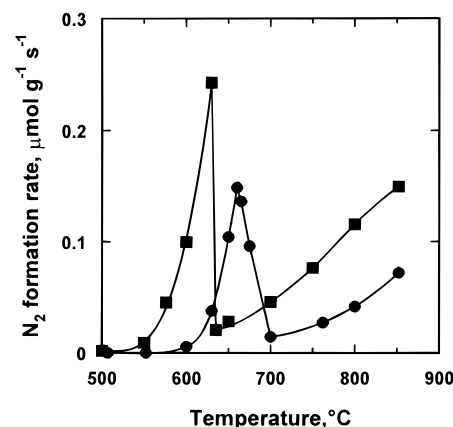
The Raman spectrometer (Kaiser Optical) was equipped with a NdYAG laser that is frequency doubled to 532 nm. The laser was operated at a low power level of 2.5 mW, measured at the sample position, so as to minimize heating of the sample. The effect of laser heating was estimated by exposing a small thermocouple, 0.25 mm in diameter, to the focused laser beam. In one case the thermocouple was covered with a thin layer of MgO and in another case the thermocouple was bare. Under ambient conditions (*i.e.*, in air at 25 °C) the temperature of the MgO-covered thermocouple increased 2 °C and that of the bare thermocouple increased 3 °C. We estimate that under reaction conditions the temperature increase due to laser heating was ≤ 5 °C. The optical setup and the *in situ* Raman cell will be described in detail elsewhere.<sup>10</sup> Briefly, 50 mg of catalyst was supported on a fused-quartz frit through which the gases flowed. The volume of the system was small so that the time required to change the gas composition in the cell was *ca.* 20 s. During a temperature change, approximately 3 min were required to reach a new value.

## Results

**Kinetic Behavior of the Ba/MgO Catalysts.** The specific activities for pure MgO and representative Ba/MgO catalysts as a function of temperature are shown in Figure 1. The pure MgO sample showed very little activity for NO decomposition, even at 850 °C. The catalysts containing from 1 to 7 mol % Ba exhibited the expected monotonic increase in activity with respect to increasing temperature. (The specific activity of the 7 mol % catalyst is lower than that of the 4 mol % catalyst because of its lower surface area.) These catalysts will be discussed in more detail in a separate publication.<sup>11</sup> The 14 mol % Ba/MgO catalyst, by contrast, was characterized by a sharp decrease in activity that occurred at temperatures above 630 °C for a 1% NO/He mixture. The maximum activity corresponded to 17% NO conversion with 100 mg of catalyst. With 2 g of 14 mol % Ba/MgO and at a flow rate of 40 mL min<sup>-1</sup> for a 1% NO mixture, it was possible to obtain 96% NO conversion at 630 °C to stoichiometric amounts of N<sub>2</sub> and O<sub>2</sub>. Provided that the reaction temperature was not greater than 630



**Figure 2.** Effect of NO concentration on decomposition of NO over a 14 mol % Ba/MgO catalyst: ■, 1% NO; ●, 2% NO; ▲, 3% NO; ◆, 4% NO.



**Figure 3.** Effects of added O<sub>2</sub> on the activity of a 14 mol % Ba/MgO catalyst for 1% NO decomposition: ■, 1% NO; ●, 1% NO + 0.5% O<sub>2</sub>.

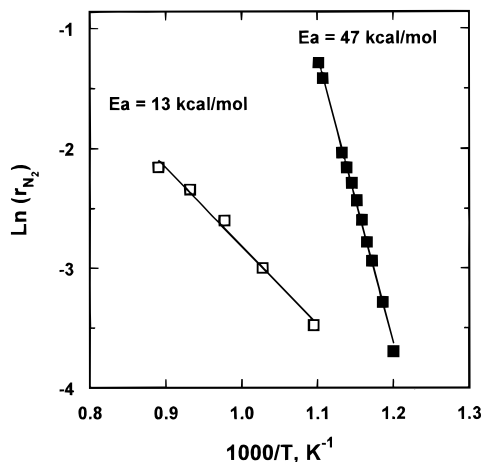
°C, the activity of the 14 mol % Ba/MgO catalyst was stable for many hours. This unusual kinetic behavior also was observed for 11 and 25 mol % Ba/MgO, as well as for pure BaO. The NO concentration also has an effect on the fall-off temperature, as shown in Figure 2. Here, the fall-off temperature is defined as the temperature of maximum activity. As the NO concentration was increased from 1% to 4%, the fall-off temperature increased from 630 °C to 700 °C. Correspondingly, the maximum steady state rate of N<sub>2</sub> formation increased from 0.24 μmol g<sup>-1</sup> s<sup>-1</sup> to 2.5 μmol g<sup>-1</sup> s<sup>-1</sup>. The decrease in activity above the fall-off temperature was reversible in that the low-temperature activity could be recovered by decreasing the temperature to a point below the fall-off temperature.

The addition of O<sub>2</sub> to the NO/He mixture likewise increased the fall-off temperature, as shown in Figure 3. (At temperatures in excess of 600 °C the thermodynamic equilibrium concentration of NO<sub>2</sub> is very small.) The addition of 0.5% O<sub>2</sub> to the 1% NO reagent gas increased the fall-off temperature from 630 °C to 660 °C, but the maximum rate of N<sub>2</sub> formation decreased from 0.24 μmol g<sup>-1</sup> s<sup>-1</sup> to 0.15 μmol g<sup>-1</sup> s<sup>-1</sup>. It should be noted that the amount of O<sub>2</sub> added at the 0.5% level is approximately 10 times larger than the amount of O<sub>2</sub> produced during the decomposition of NO.

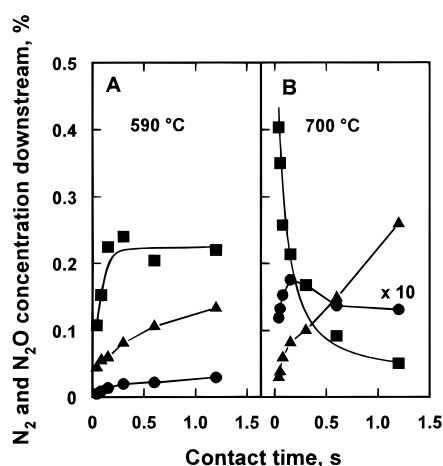
The overall activation energies for NO decomposition over the 14 mol % Ba/MgO catalyst, above and below the fall-off temperature, were obtained from the Arrhenius plots shown in Figure 4. With 1% NO, the activation energies were 47 and 13 kcal/mol at temperatures below and above 630 °C, respec-

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**Figure 4.** Arrhenius plots for decomposition of 1% NO over a 14 mol % Ba/MgO catalyst: ■, reaction temperatures lower than 630 °C; □, reaction temperatures higher than 635 °C.

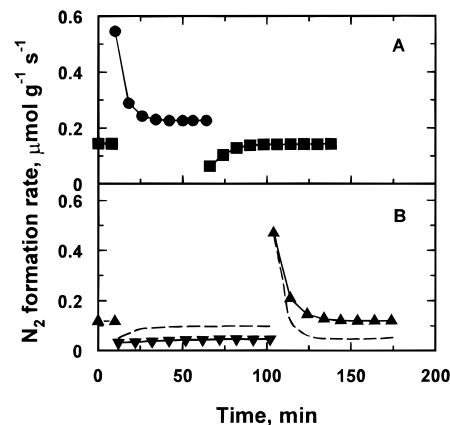


**Figure 5.** Distribution of products from decomposition of NO over a 14 mol % Ba/MgO catalyst: (A) 4% NO at 590 °C; ●, [N<sub>2</sub>O]; ▲, [N<sub>2</sub>]; ■, [N<sub>2</sub>O]/[N<sub>2</sub>]; (B) 2% NO at 700 °C; ●, [N<sub>2</sub>O]; ▲, [N<sub>2</sub>]; ■, [N<sub>2</sub>O]/[N<sub>2</sub>].

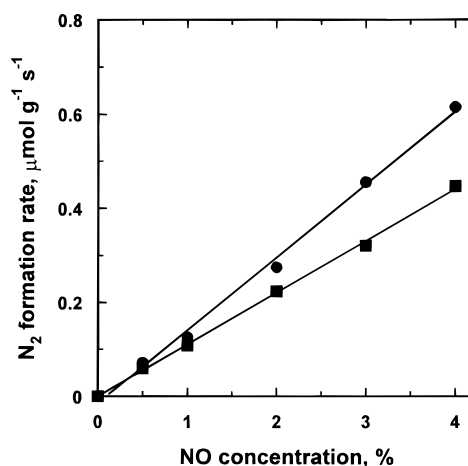
tively. These results suggest that there is an abrupt change in the reaction mechanism at the fall-off temperature.

The change in mechanism also is indicated by the presence or absence of N<sub>2</sub>O as an intermediate. Nitrous oxide has been suggested as a gas-phase intermediate during NO decomposition over certain transition metal oxides.<sup>12</sup> To investigate the possible role of N<sub>2</sub>O as an intermediate over the 14 mol % Ba/MgO catalyst, the product distribution was determined as a function of contact time at temperatures below (590 °C) and above (700 °C) the fall-off temperature. The results at 590 °C (Figure 5A) show that the N<sub>2</sub>O/N<sub>2</sub> ratio either increased or remained nearly constant as the contact time increased. This behavior suggests that N<sub>2</sub>O was not an intermediate. By contrast, at 700 °C the N<sub>2</sub>O/N<sub>2</sub> ratio continuously decreased with increasing contact time (Figure 5B), which is the typical behavior expected for a reaction in which N<sub>2</sub>O is an intermediate in the formation of N<sub>2</sub>.

An interesting transient result was obtained when the NO concentration was abruptly changed at temperatures *below* the fall-off temperatures. The phenomenon was observed, for example, when the NO concentration was switched between 1% and 4%, with the catalyst at 600 °C. The results are shown in Figure 6A. When the NO concentration was abruptly



**Figure 6.** Transient behavior of 14 mol % Ba/MgO catalyst when the NO concentration in the feed gas was changed: (A) 600 °C; ■, 1% NO; ●, 4% NO; (B) 590 °C; ▲, 4% NO; ▼, 0.5% NO. The dashed lines in B describe the relative changes in the Raman band at 244 cm<sup>-1</sup> (Figure 9B).



**Figure 7.** Initial activities of a 14 mol % Ba/MgO catalyst at 600 °C following changes in NO concentration: ■, catalyst was previously at steady state in 1% NO; ●, catalyst was previously at steady state in 0.5% NO.

changed from 1% to 4%, with the catalyst at steady state, the N<sub>2</sub> formation rate immediately increased 4-fold and then decayed over 30 min to a new steady state value. After the activity was stabilized in 4% NO, the NO concentration was switched back to 1% NO. The activity immediately decreased 4-fold, and then increased to the original steady state activity in 1% NO. The volumes of the system and the flow rates were such that it required less than 2 min for the gas phase to reach a new value after the flow rates were changed to vary the NO concentration.

Similar results were obtained at 590 °C; however, in this case the NO concentration was first switched from 4% to 0.5%. Again, the N<sub>2</sub> formation rate first decreased and then slowly increased to a new steady state value. When the concentration was switched from 0.5% back to 4%, the N<sub>2</sub> formation rate rapidly increased to a level that was substantially greater than the steady state level and then decreased over a 30-min period to the original steady state level.

These results imply that the surface of the catalyst is modified by the presence of gas-phase NO through reactions which occur on the time scale of minutes. To determine the order of the decomposition reaction, apart from the complications introduced by these longer term surface transformations, the rate of N<sub>2</sub> formation was determined 2 min after the NO concentration was changed and the results are reported in Figure 7. In the two cases, the catalyst was allowed to reach steady state in 0.5%

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NO and 1% NO, respectively, before increasing or decreasing the NO concentration. The reaction rate varied linearly with NO concentration, indicating that the reaction is first order with respect to the gas-phase NO concentration. Moreover, the rates were greater following changes from a steady state in 0.5% NO, which suggests that surface intermediates involved in the decomposition reaction (see below) have a larger concentration in 0.5% NO than in 1% NO. As a consequence of the opposite effects of NO (*i.e.*, gas phase versus surface species) the *steady state* rate of N<sub>2</sub> formation is not a linear function of the NO concentration. These results may be understood by considering the rate equation

$$d[\text{NO}]/dt = -k[\text{NO}][\text{I}] \quad (1)$$

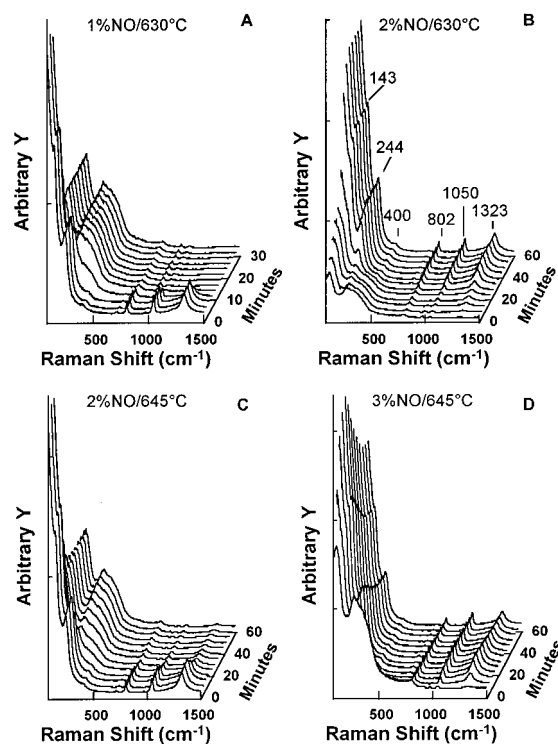
where [NO] is the concentration of NO in the gas phase and [I] is the concentration of an intermediate on the surface. The concentration of the intermediate, which will be identified in the subsequent section, is inversely proportional to the concentration of NO over the range from 0.5% to 4% NO.

**Characterization by *in Situ* Raman Spectroscopy.** To obtain more information about the surface chemistry of the 14 mol % Ba/MgO catalyst under reaction conditions, *in situ* Raman spectroscopy was employed to follow transformations in the material, particularly under transient conditions. For the Raman experiments, the same Ba(NO<sub>3</sub>)<sub>2</sub>/MgO precursor material was used, but the catalyst was not calcined and stored in air so as to prevent the formation of BaCO<sub>3</sub>. The CO<sub>3</sub><sup>2-</sup> bands interfered with those of NO<sub>3</sub><sup>-</sup> ions in the Raman spectra. It was demonstrated that the same catalytic behavior was observed for the calcined and the uncalcined samples. In addition, independent Raman results demonstrated that the same spectral features were present for catalysts prepared by both activation methods; *i.e.*, with or without calcination.

A series of transient experiments was carried out in which the temperature was increased so as to move from conditions of high activity to those of low activity, and the NO concentration was increased so as to move from conditions of low activity to those of high activity. The spectroscopic results presented in Figure 8 should be compared with the catalytic results of Figure 2.

In series A of Figure 8, Raman spectra were recorded at 2.5-min intervals after the temperature of the catalyst was increased from 625 °C to 630 °C. (The sample in the laser beam may have been as much as 5 °C higher than the remainder of the sample, thus causing a slight discrepancy in fall-off temperature determined in the catalytic reaction and the temperature of the Raman experiment.) The catalyst was in 1% NO and had been stable at 625 °C for 18 h. The increase in temperature at this NO concentration would have transformed the catalyst from the more active to the less active state (Figure 2). The first spectrum of this series, which also is the spectrum of the initial steady state catalyst, had bands at 711, 1050, and 1644 cm<sup>-1</sup> that are assigned to NO<sub>3</sub><sup>-</sup> ions and bands at 143, 244, 400, 802, 1230, and 1323 cm<sup>-1</sup> that are assigned to a nitro species, in agreement with literature values.<sup>13</sup> In the nitro group (-NO<sub>2</sub>) the ligand is coordinated to the metal ion via the nitrogen atom *e.g.*, as Ba-NO<sub>2</sub>.<sup>10</sup>

Following the increase in temperature to 630 °C, the nitro species and the nitrate ions decomposed within 10 min into a defect form of BaO. After the NO concentration was increased to 2% with the sample still at 630 °C (a condition that resulted in the more active catalytic state), the nitrate ions and nitro complexes reformed over a period of 40 min and reached a new steady state concentration as shown in Figure 8B.



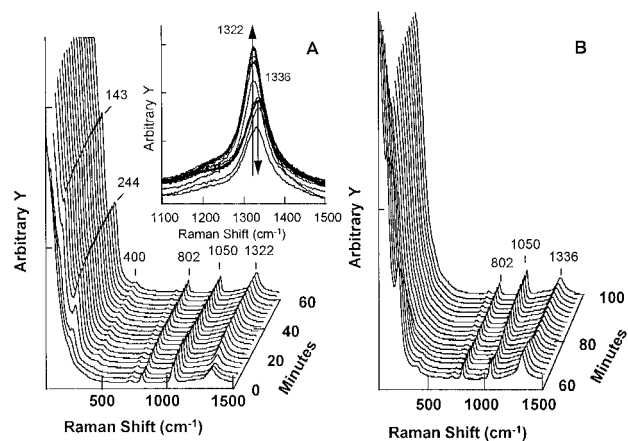
**Figure 8.** Raman spectra showing the effect of NO concentration and temperature on the formation of nitro and nitrate species: (A) after increasing temperature from 625 °C to 630 °C in 1% NO; (B) after increasing NO concentration from 1% to 2% at 630 °C; (C) after increasing temperature from 630 °C to 645 °C in 2% NO; (D) after increasing NO concentration from 2% to 3% at 645 °C.

Prior to obtaining the spectra shown in series C, the temperature was increased in 5 °C increments, remaining at each temperature for 1 h. The NO concentration remained at 2%. Both the nitrate and nitro species were stable at 635 and 640 °C; however, at 645 °C decomposition occurred within 20 min. Here, there is again a minor discrepancy between the catalytic and the spectroscopic results in that the fall-off temperature in 2% NO was 660 °C. The difference, in part, may be related to laser heating of the sample at the point where the Raman scattering occurs as mentioned above, and also to the effect of O<sub>2</sub> on the fall-off temperature as shown in Figure 3. The residence time was less over the catalyst in the Raman cell than in the conventional reactor. As a consequence, a larger percentage of NO decomposition occurred in the conventional reactor, and the resulting O<sub>2</sub> increased the fall-off temperature. This phenomenon would be greater in 2% NO than in 1% NO. Finally, in series D the NO concentration was increased to 3% and the nitrate ions and nitro complexes reformed, again corresponding to conditions of high catalytic activity.

Apart from small differences that can be attributed to inaccuracy in the measurement of sample temperatures and the effects of O<sub>2</sub>, there is a good correlation between the presence of nitrate and nitro species and activity for NO decomposition. On the basis of the results presented to this point, however, it is not possible to distinguish between NO<sub>3</sub><sup>-</sup> ions and Ba-NO<sub>2</sub> complexes as possible reaction intermediates. But the distinction can be made when one considers the results of transient experiments carried out at 590 °C.

Under steady state conditions at 590 °C with 4% NO, a new set of bands at 807 and 1336 cm<sup>-1</sup> is present. These bands, depicted in the initial spectrum of Figure 9, series A, are tentatively assigned to nitrito complexes in which the NO<sub>2</sub> ligand is coordinated to Ba *via* one oxygen atom.<sup>14</sup> On the 14 mol %

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**Figure 9.** Raman spectra showing the temporal effect of NO concentration with 14 mol % Ba/MgO at 590 °C: (A) at  $t = 0$  the NO concentration was switched from 4% to 0.5% NO; (B) at  $t = 0$  the NO concentration was switched from 0.5% to 4% NO.

Ba/MgO catalyst in 4% NO, the nitrito species is present below the fall-off temperature.

When the NO concentration was switched from 4% to 0.5%, the typical bands of the nitro species appeared at 143, 244, 400, 802, 1230 (sh), and 1325  $\text{cm}^{-1}$ . As shown in the insert, there was a distinct shift in the maximum from 1336  $\text{cm}^{-1}$  for the nitrito species to 1322  $\text{cm}^{-1}$  for the nitro species. The growth in the bands of the nitro species increased over a period of *ca.* 30 min. Meanwhile, the bands due to the nitrate ions first increased in amplitude and then decreased to a new steady state level. As shown in series B, the phenomena were reversed when the NO concentration was switched from 0.5% back to 4% NO. In this case, the time needed to attain the new steady state was about 15 min. The relative increase or decrease in the Raman band at 244  $\text{cm}^{-1}$  is plotted as the dashed line in Figure 6B.

The transient spectroscopic results of Figure 9 should be compared with the transient catalytic results of Figure 6B, keeping in mind that the rate of  $\text{N}_2$  formation may depend both on the gas-phase concentration of NO and on the presence of a reactive intermediate on the surface. The most dramatic effect in Figure 6B is the large initial increase in  $\text{N}_2$  formation rate when the NO concentration was increased from 0.5 to 4%. The  $\text{N}_2$  formation was considerably greater than the steady state rate, either at the outset of the experiment or 150 min into the experiment. These results can be explained by the larger concentration of nitro species that occurred when the NO concentration was 0.5%, if one assumes that surface nitro species are indeed intermediates in the NO decomposition reaction. After an increase in the NO concentration from 0.5% to 4% one would initially have high concentrations of *both* NO in the gas phase *and* the surface nitro species. With increasing time, the concentration of the nitro species would decrease as well as the rate of NO dissociation. The time scale for these two phenomena was approximately the same. The other results depicted in Figure 6 could be interpreted by analogous changes in the gas-phase NO and surface nitro concentrations. It is important to note from the results of Figures 6 and 9 that there was no correlation between the temporal changes in the concentrations of nitrate or nitrito ions and the rate of  $\text{N}_2$  formation.

The effect of added  $\text{O}_2$  on catalytic properties of 14 mol % Ba/MgO, as shown in Figure 3, can likewise be interpreted in

light of the Raman results.<sup>15</sup> In one experiment, the catalyst was allowed to reach steady state at 600 °C in 1% NO, and then 1%  $\text{O}_2$  was introduced to the gas feed. The presence of  $\text{O}_2$  caused the nitro species to disappear (spectra not shown) within about 15 min. The concentration of nitrate ions at first increased and subsequently decreased after about 10 min on stream. Meanwhile, crystalline barium peroxide appeared on the surface, as indicated by the growth of a new band at 830  $\text{cm}^{-1}$ .<sup>16</sup> These results indicate that the transformation of nitro species into nitrate ions may be responsible for the sharp decrease in  $\text{N}_2$  formation rate when  $\text{O}_2$  is added to the reagent gas (Figure 3).

Although  $\text{O}_2$  is capable of destroying nitro species when present in excessive amounts, it also may be responsible for the formation of nitro species, which could account for the shift in the temperature of maximum activity from 630 °C to 660 °C upon the addition of  $\text{O}_2$ . Again, Raman results provide insight into the possible role of  $\text{O}_2^{2-}$  ions in the formation of nitro species.<sup>15</sup> Following the formation of  $\text{BaO}_2$  by treating a 14 mol % Ba/MgO catalyst with a 10%  $\text{O}_2/\text{He}$  mixture, the flowing gas was switched to 0.5% NO/He with the catalyst at only 450 °C. After 5 min, the spectrum of the peroxide ions was greatly reduced and that of the nitro species dominated the spectrum (not shown). In the absence of the initial crystalline barium peroxide ions, the growth of the nitro bands required 500 min at 500 °C.

Finally, Raman spectroscopy has been used to determine differences between the 4 mol % Ba/MgO and the 14 mol % Ba/MgO materials that might provide insight into the variations in catalytic behavior depicted in Figure 1. On the basis of calculations, monolayer coverage could be achieved when the Ba loading is about 2.5 mol %, which is consistent with the XPS results obtained by Dissanayake *et al.*<sup>17</sup> Thus, monolayer coverage probably already had been reached for the 4 and 7 mol % Ba/MgO catalysts, for which no unusual catalytic behavior was observed. *In situ* Raman results were obtained for 10 different 14 mol % catalyst samples and at many locations on the surface. In all cases, comparable spectra were obtained, with a maximum variation in the  $\text{NO}_3^-$  band at 1045  $\text{cm}^{-1}$  of about 50%. This variation is attributed to differences in crystallite size. By contrast, when a similar Raman experiment was conducted on a 4 mol % Ba/MgO catalyst, it was found that the surface was very inhomogeneous. The catalyst had been exposed to 1% NO up to 750 °C and cooled in NO to 500 °C. As shown by the Raman spectra displayed in Figure 10, only one spot of the ten randomly chosen sites showed a large concentration of nitro complexes and nitrate ions. The remaining sites had either smaller concentrations or no detectable concentrations at all. The estimated lateral resolution was 1  $\mu\text{m}$ . These results, together with the fact that unsupported BaO was active and showed the large maximum with respect to temperature, suggest that moderately large crystallites of BaO are needed to stabilize the nitro species.

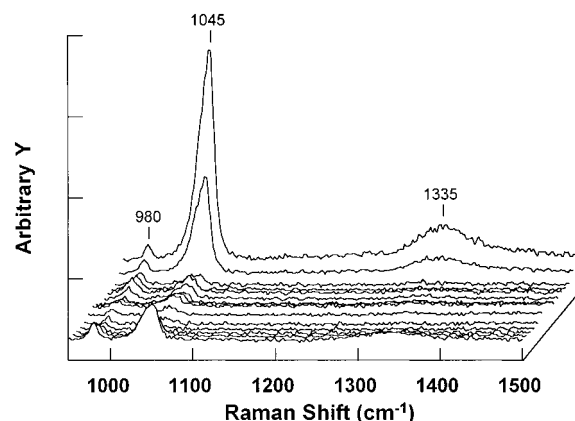
It has been previously demonstrated that the support may modify the character of the barium oxide so as to affect its properties with respect to the stabilization of carbonate ions and the activation of methane.<sup>17</sup> In the case of methane oxidative coupling reactions, large Ba loadings were unfavorable because  $\text{CO}_2$ , a side product of the coupling reaction, strongly poisoned the active centers. Such a problem does not occur during the

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**Figure 10.** Laterally resolved Raman spectra of a 4 mol % Ba/MgO catalyst.

decomposition of pure NO in a NO/He mixture; however, in the practical utilization of a Ba/MgO catalyst to remove NO from the effluent of a combustion process, the effect of CO<sub>2</sub> on catalytic activity would become important. In fact, CO<sub>2</sub> strongly poisons the 14 mol % Ba/MgO catalyst for NO decomposition. In 1% NO with the catalyst at 625 °C, the N<sub>2</sub> formation rate decreased from 0.19 μmol g<sup>-1</sup> s<sup>-1</sup> to 0.02 μmol g<sup>-1</sup> s<sup>-1</sup> when 1.2% CO<sub>2</sub> was added to the reagents. At larger CO<sub>2</sub> concentrations the rate of N<sub>2</sub> formation remained constant.

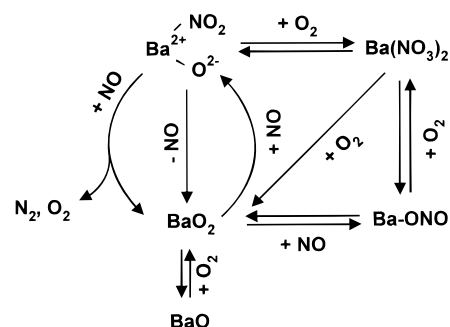
### Discussion

A comparison between the catalytic and *in situ* Raman results supports the role of a Ba-NO<sub>2</sub> surface intermediate in the decomposition of NO. The stability of this nitro intermediate appears to be responsible for unusual maxima in activity which occur at different temperatures, depending on the partial pressure of NO. Oxygen, which is a product of the reaction, converts the nitro complexes to nitrate ions, but peroxide ions, derived from O<sub>2</sub>, also may be responsible for the formation of the nitro intermediates. The sharp decrease in nitro complex concentration, and consequently the activity, at a particular temperature is reminiscent of a phase transformation, and is difficult to rationalize in terms of the usual effects of temperature on rates of reaction. In a subsequent publication, it will be demonstrated that the presence of the nitro species can be empirically related to the thermodynamic phase boundary between BaO, BaO<sub>2</sub>, and Ba(NO<sub>3</sub>)<sub>2</sub>.

The mechanism for the decomposition reaction clearly changes as one moves through the activity maximum. This is evident from the marked change in activation energy and, to a lesser extent, the presence or absence of N<sub>2</sub>O as a gas-phase intermediate.

On the basis of these observations the reaction mechanism shown in Scheme 1 is proposed. The essential features of this mechanism are as follows: (i) nitric oxide, either from the gas phase or weakly adsorbed on the surface, reacts with a Ba-NO<sub>2</sub> surface intermediate to form N<sub>2</sub> and O<sub>2</sub>, (ii) the nitro species are regenerated by the reaction of NO with the surface, perhaps via peroxide ions, and (iii) molecular oxygen transforms nitro species into nitrate ions, but it may also be required to generate

### Scheme 1



the nitro intermediate. Assuming that the rate limiting step is the reaction of NO with the Ba-NO<sub>2</sub> species, the rate law should depend on the concentration of both species. By obtaining the rates soon after a step change in the gas-phase NO concentration it was possible to show that the reaction was first order with respect to NO. With increasing time on stream, however, the concentration of the Ba-NO<sub>2</sub> intermediate actually decreased with increasing NO concentration. This unusual behavior may be attributed not to NO itself but to O<sub>2</sub> that was produced during the decomposition reaction since oxygen is capable of converting the nitro species to nitrate ions. Thus, oxygen is believed to be responsible not only for the formation of the nitro species but also for its depletion.

It is significant that the relative rates of the several steps in the catalytic cycle are such that a probable reaction intermediate can be detected under reaction conditions. Moreover, other transformations are sufficiently slow so that they can be followed with use of the available methodology. In most catalytic studies the opposite is true; therefore, it is usually not possible to characterize surface intermediates, even with *in situ* spectroscopy.

### Conclusions

The unusual behavior for NO decomposition exhibited by Ba/MgO catalysts that contained a large amount of barium has provided an opportunity to explore the relationship between a probable intermediate and the rate of reaction. Nitro species, formed by the reaction of NO with peroxide ions at the surface, are believed to react with NO to form N<sub>2</sub> and O<sub>2</sub>. The decomposition of these nitro species is responsible for the sharp fall off in catalytic activity when the temperature is increased beyond a certain value for a given NO partial pressure. Although oxygen, produced during the NO decomposition reaction, decreases the nitro concentration, the fall off in activity appears to be associated with a type of phase transition that involves BaO, BaO<sub>2</sub>, and Ba(NO<sub>3</sub>)<sub>2</sub> in relatively large crystallites on the MgO surface.

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