

Decomposition of Nitric Oxide over Barium Oxide Supported on Magnesium Oxide. 3. In Situ Raman Characterization of the Role of Oxygen

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Received: June 23, 1997[⊗]

Time-resolved high-temperature in situ Raman spectroscopy was successfully used to study details of the complex reaction network between gas phase oxygen and the species present in highly loaded Ba/MgO catalysts. The decomposition of the catalyst precursor $\text{Ba}(\text{NO}_3)_2$ to an amorphous phase containing nitrate and nitrite ions (phase II') occurs at higher temperatures in the presence of O_2 than in He. Thus, the presence of O_2 stabilizes the precursor $\text{Ba}(\text{NO}_3)_2$. In the presence of O_2 , phase III, containing the Ba–nitro complex, is not observed, and the decomposition of the amorphous phase II' directly reacts to BaO_2 . Defect-rich BaO rather than BaO_2 is formed when the decomposition is in pure He. Gas-phase oxygen, therefore, exerts a strong effect on the stability of the phases present on the catalyst. In addition, it was shown that oxygen, added to the gas feed during catalytic NO decomposition, reduces the number of active Ba–nitro complex species via oxidation to nitrates. This reaction is identified with the inhibiting effect of oxygen on the catalytic activity. Crystalline BaO_2 reacts with NO to form nitrates, nitrites, and Ba–nitro complexes, depending on the O_2 and NO partial pressures and reaction temperatures. At lower temperatures, phase II' is formed, while at elevated temperatures, the reaction results in phase III containing Ba–nitro complexes. The formation of these phases from BaO_2 and their interconversions confirms the previously established phase diagram and suggests the role of BaO_2 in the activation of NO. Crystalline BaO_2 , however, was never detected under catalytic conditions. It has been shown that, in the absence of crystalline BaO_2 , NO activation occurs on O_2^{2-} ions that are present in or on defect-rich BaO. Peroxide species, therefore, may play an important role in the catalytic cycle. A catalytic cycle is proposed in which the intermediate Ba–nitro species are formed from the reaction of NO with O_2^{2-} ions in or on defect-rich BaO. In the rate-determining step, the intermediate Ba–nitro species react with a second gas phase, or weakly adsorbed, NO molecule to produce N_2 and O_2 . Oxygen reforms the activating peroxide species.

I. Introduction

As outlined in our preceding paper,¹ environmental and, in particular, human health considerations require the removal of nitric oxide (DeNO_x) from offgases of stationary power plants and automotive exhausts. The need for highly efficient automotive DeNO_x catalysts that operate in the lean-burn region has stimulated research in this field. The direct decomposition of NO is the most desirable method; however, the catalytic reduction of NO with hydrocarbons could be effectively employed.

In a recent publication, Xie et al.² reported on the catalytic reduction of NO with CH_4 over Ba/MgO catalysts. The same materials were also observed to be active in the direct decomposition as well,³ especially when the barium loading was 11 mol % or greater. In addition, the highly loaded Ba/MgO catalysts exhibited a very interesting behavior as described in detail in the preceding paper.¹ For a given NO partial pressure, these highly loaded catalysts exhibited a sharp decrease in the NO conversion, when a certain temperature was exceeded. This discontinuity in NO decomposition was attributed to a phase transition in the material at the falloff temperature.¹ Transient in situ Raman experiments indicate that a Ba–nitro complex is an intermediate in the direct NO decomposition below the falloff temperature.^{1,2}

These same Ba/MgO catalysts were previously shown to be active and selective for the oxidative coupling of methane

(OCM). In this reaction, methane, together with an oxidant such as O_2 or N_2O , is converted to ethane and ethylene.⁴ The catalyst initiates the reaction by forming CH_3^\bullet radicals. Peroxide surface groups are believed to be responsible for the abstraction of hydrogen atoms from methane.⁵ High temperature in situ Raman spectroscopy^{6–8} has been used to show that peroxide ions are present on Ba/MgO catalysts under OCM conditions, and the Raman intensities of the O_2^{2-} bands respond to changes in the CH_4 partial pressure in a manner which suggests their role as a radical initiator. It was of interest to determine the possible role of surface peroxide ions in the catalytic decomposition of NO.

This paper is the third in a series which describes the use of in situ Raman spectroscopy to characterize highly loaded Ba/MgO catalysts. The series focuses on a 14 mol % Ba/MgO catalyst as representative of the materials that exhibit the unique behavior in catalytic decomposition of NO.² In this contribution, the effect of O_2 on the stability of the catalyst phases and the different species observed in the active catalyst material are described. The fourth contribution⁹ will provide results of an in situ Raman ^{18}O -isotope study on the different peroxide species which were observed in these materials.

II. Experimental Section

As described in the preceding paper,¹ the 14 mol % Ba/MgO catalysts were made by impregnating MgO (Fisher light, 38 m^2/g) with the required amount of $\text{Ba}(\text{NO}_3)_2$ (Baker). After drying in a rotary evaporator, the material was pressed under 400 kg/cm^2 and crushed and sieved to 20–40 mesh size. Changes in the in situ Raman spectra were induced by varying the partial

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[⊗] Abstract published in *Advance ACS Abstracts*, October 15, 1997.

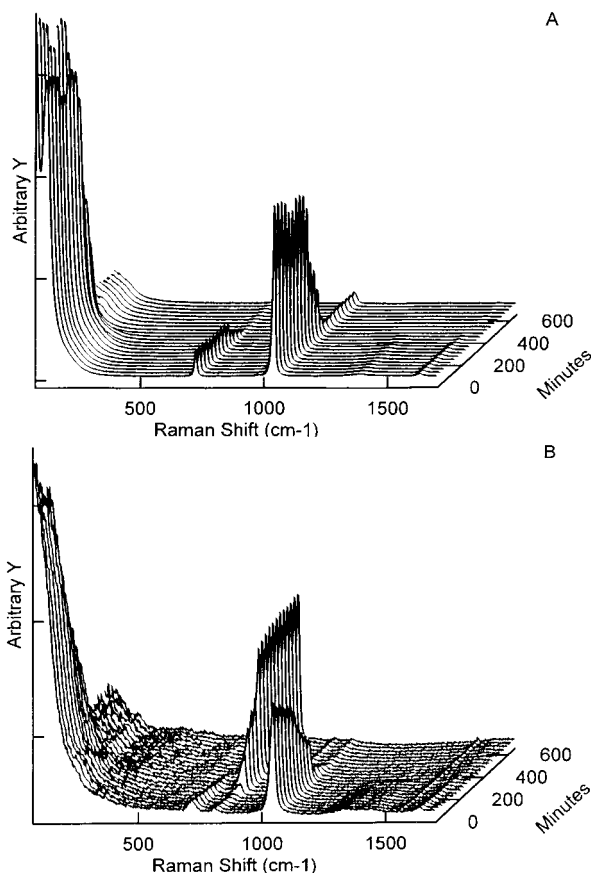


Figure 1. In situ Raman spectra obtained during the decomposition of 14 mol % $\text{Ba}(\text{NO}_3)_2/\text{MgO}$ in the presence of O_2 : (A) Decomposition in 10% O_2/He at 500 °C, time resolution 30 min. (B) Decomposition in 10% O_2/He at 550 °C, time resolution 30 min.

pressures of NO (4.1% NO/He, UHP, Matheson) and/or O_2 (10% O_2/He , UHP, Matheson). This was achieved by mixing pure He (UHP, Matheson) with the other gases before they were allowed to flow through the catalyst bed. The total gas flow was kept constant at 40 mL/min. The response of the catalyst material upon changes in the gas phase was also investigated as a function of temperature.

The Raman spectra were recorded with the Holoprobe spectrometer (Kaiser Optical) described in detail in the previous paper.¹ All Raman spectra were recorded with an excitation wavelength of 532 nm and a laser power of 2.5 mW, measured at the sample position. The in situ Raman cell was designed so that rapid changes in temperature and gas-phase composition could be achieved.¹

III. Results and Discussion

1. Stability of Catalyst Phases in the Presence of O_2 . *Ba- $(\text{NO}_3)_2/\text{MgO}$ Decomposition in 10% O_2/He .* At 25 °C, the starting material, 14 mol % $\text{Ba}(\text{NO}_3)_2/\text{MgO}$, was characterized by Raman bands of crystalline $\text{Ba}(\text{NO}_3)_2$.¹ When the sample was heated in the presence of O_2 , no specific spectral changes were observed up to 450 °C, apart from the decomposition of $\text{Mg}(\text{OH})_2$ that occurred at 300 °C. This is in contrast to the decomposition of 14 mol % $\text{Ba}(\text{NO}_3)_2/\text{MgO}$ in pure He, which began to occur at 450 °C.¹ Oxygen present in the gas phase obviously stabilizes the barium nitrate precursor phase.

In Figure 1A, the Raman spectra which were recorded over a period of 600 min at 500 °C in 10% O_2 are displayed. The lattice mode of crystalline $\text{Ba}(\text{NO}_3)_2$ at 118 cm^{-1} was completely lost after 5 h on stream. The bending, as well as the symmetric and antisymmetric stretching modes of NO_3^- ions at 729, 1044,

and 1400 cm^{-1} , however, did not completely disappear but were stabilized at a considerably lower intensity. With the loss in intensity, the bending mode shifted to 721 cm^{-1} while the symmetric stretching mode was located at 1046 cm^{-1} . The shifts in wavenumber indicate a change in the environment of the nitrate ions. In addition to these spectral changes of the nitrate-related bands, new, very weak signals appeared at about 810 and 1335 cm^{-1} (more evident on an expanded ordinate scale), which can be assigned to traces of NO_2^- ions. Raman spectra of this type are characteristic of the amorphous phase II',¹ which contains nitrate and nitrite ions. In pure He, the formation of this amorphous phase II' was observed after ca. 3 h at only 450 °C.¹ In summary, nitrate decomposition in 10% O_2 occurs at higher temperatures than in pure He, but in both cases the reaction proceeds to the amorphous phase II'. Thus, the presence of O_2 stabilizes phase I, i.e., crystalline $\text{Ba}(\text{NO}_3)_2$, and the first decomposition step leads to the amorphous phase II'.

At 550 °C in 10% O_2/He , the Raman bands of the NO_3^- ions and the very weak bands of the NO_2^- ions (phase II') disappeared after 200 min on stream, while a strong band developed at 830 cm^{-1} (Figure 1B). In a separate experiment, the same process required 400 min under a lower O_2 partial pressure corresponding to 5% O_2/He (spectra not shown). The signal position of the newly formed band at 830 cm^{-1} is in agreement with the Raman band of crystalline BaO_2 .¹⁰⁻¹² Obviously, the presence of O_2 has a strong influence upon the stability of the amorphous phase II' which contains NO_3^- and NO_2^- ions. In the presence of O_2 , the decomposition of the amorphous phase II' directly results in the formation of BaO_2 . Phase III containing the Ba-nitro complex^{1,3} was not observed. The O_2 partial pressures above the catalyst material, thus, play a critical role in the formation and stability of the catalytically active phase III.

Reaction of O_2 with the Ba-Nitro Species. Catalytic results clearly revealed that the addition of O_2 to the gas feed had a negative effect on the NO decomposition rate.³ Therefore, O_2 has to play an active role in the reaction network in addition to the stabilizing effect on the precursor phases I and II'. The experiments described in the preceding contribution¹ suggested that the oxidation of Ba-nitro complexes to nitrates might occur. This possible reaction was examined in an independent series of experiments.

The time-resolved in situ Raman spectra, shown in Figure 2A, provide additional evidence for the oxidation of Ba-nitro complexes to nitrate ions. For this experiment, the catalyst was stabilized in 1% NO/He at 600 °C overnight, bringing about the formation of phase III. This catalyst was characterized by the nitrate stretching mode at 1047 cm^{-1} and the band related to the Ba-nitro complex at 1323 cm^{-1} . Subsequently, the flow of NO was stopped, and the gas mixture was changed to 1.25% O_2/He . Under these conditions, the Ba-nitro intermediates reacted rapidly (within 10 min) with O_2 to give nitrates, as indicated by the complete loss of the characteristic Ba-nitro complex bands and the growth of the nitrate band. Even the Ba-nitrito species of phase II'' were not stable under this higher O_2 partial pressure as demonstrated by the absence of the band at 1333 cm^{-1} . The intensity of the nitrate-related Raman band at 1047 cm^{-1} reached its maximum 10 min after adding 1.25% O_2 and subsequently vanished. Thus, nitrates were unstable under these conditions and almost could not be detected after 20 min on stream. During the same time period, a band at 830 cm^{-1} developed, which is characteristic of crystalline BaO_2 .¹¹⁻¹³

The time-resolved in situ Raman spectra which were recorded when this experiment was repeated with 1% NO and the addition

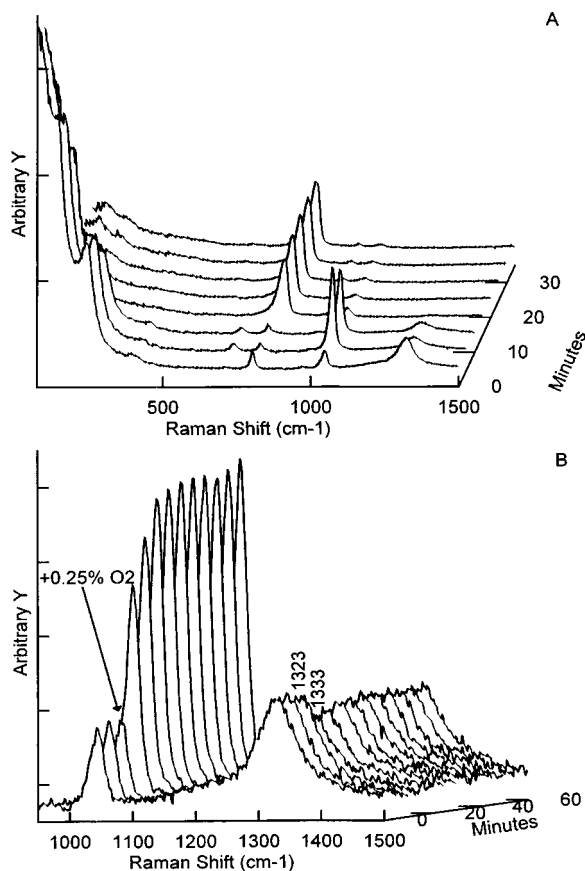


Figure 2. In situ Raman spectra obtained during (A) the reaction of phase III with 1.25% O_2 in He at 600 °C, time resolution 5 min, and (B) the reaction of phase III with 0.25% O_2 plus 1% NO in He at 600 °C, time resolution 4 min.

of 0.25% O_2 are shown in Figure 2B. The nitrate band strongly increased in intensity during 15 min after adding O_2 , while the band due to the Ba–nitro species at 1323 cm^{-1} disappeared, and a new band grew in at the higher frequency of 1333 cm^{-1} . The new band is characteristic of a Ba–nitrito complex.¹ This indicates that Ba–nitro species were not stable in the presence of O_2 but were oxidized under these conditions to nitrates, and at the same time the phase transition occurred from phase III to phase II'', which contained Ba–nitrito species. Under this lower O_2 partial pressure, the stability regime of nitrates was not exceeded, thus the formation of BaO_2 was not observed.

The changes in the Raman bands related to nitrates and Ba–nitro species observed in these two experiments are in agreement with the decrease in activity when the catalyst was exposed to a gas stream containing O_2 .³ Oxygen present in the gas phase reduces the number of active Ba–nitro species by oxidation to nitrates and thus exerts an inhibiting effect on the catalytic activity. In addition, at relatively high O_2 levels nitrogen-containing compounds are replaced by crystalline BaO_2 .

2. Role of Peroxide Groups. Reaction of BaO_2 with 1%NO/He. The starting material, 14 mol % Ba/MgO after in situ calcination in 5% O_2 /He at 720 °C for 1 h and cooling to room temperature, was characterized by Raman bands (spectrum not shown) at 128w, 200, 388br w, 454w, 630vw, 846vs, and 1682 cm^{-1} , which can be assigned to crystalline BaO_2 .^{10–12} A weak band at 1056 cm^{-1} is due to small amounts of remaining carbonates. No spectral changes were observed when the catalyst was exposed to 1% NO/He for 1 h at room temperature; however, after 1 h at 100 °C, a very weak shoulder at 1047 cm^{-1} had developed near the weak carbonate band. This shoulder may indicate some nitrate formation.

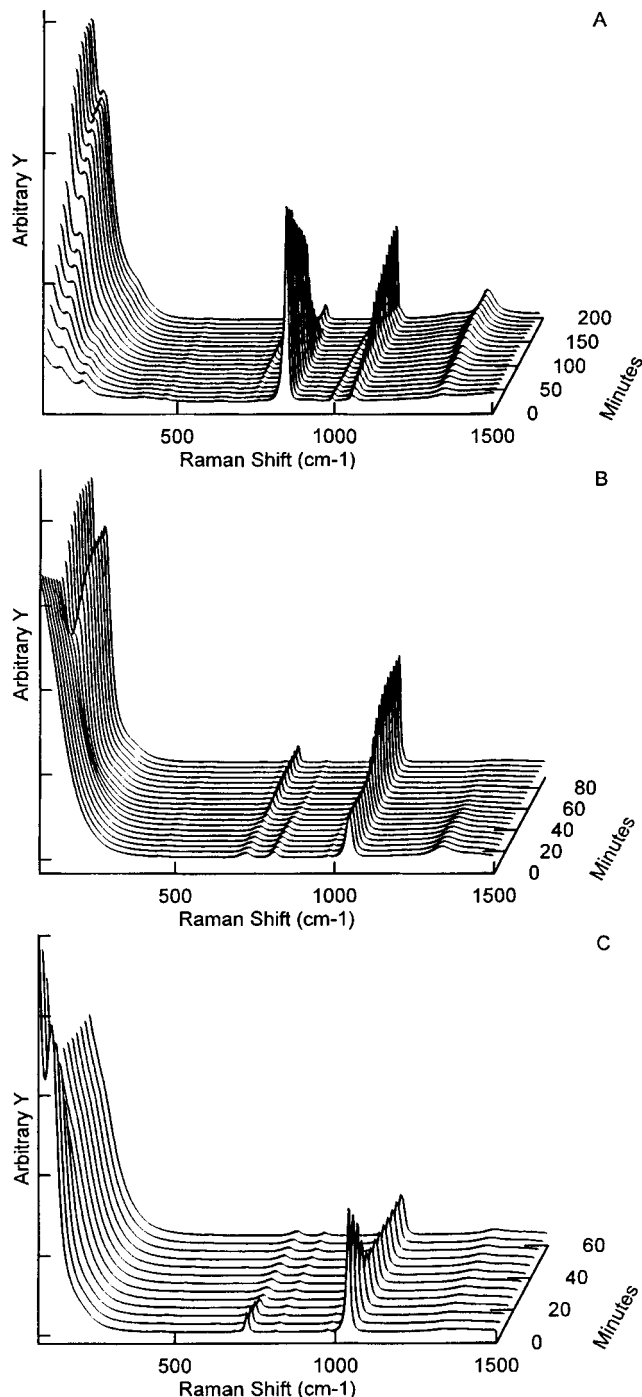


Figure 3. In situ Raman spectra obtained during the reaction of 14 mol % BaO_2 /MgO with 1% NO (A) at 200 °C, time resolution 11 min; (B) at 400 °C; (C) at 500 °C, time resolution 5 min.

After the initial reaction at 100 °C, the catalyst was studied by time-resolved in situ Raman spectroscopy at 200 °C, and the results are shown in Figure 3A. At this temperature, crystalline barium peroxide reacted with 1% NO/He within 180 min to form nitrates and traces of nitrites. This reaction is indicated by the disappearance of the characteristic peroxide bands at 122, 194, 382, 840, and an overtone at 1671 cm^{-1} (not shown) of the band at 840 cm^{-1} . At the same time, nitrate bands developed at 732 and 1047 cm^{-1} . In addition, Raman bands at 820, 1235 and 1335 cm^{-1} due to barium nitrite increased with time. When the temperature was subsequently increased to 400 °C in 1% NO/He, the NO_3^- bands increased and the NO_2^- ion bands decreased (Figure 3B). The growth of the lattice mode at 126 cm^{-1} indicates that crystallization

and defect healing occurred in $\text{Ba}(\text{NO}_3)_2$. At 500 °C in 1% NO/He, the crystalline $\text{Ba}(\text{NO}_3)_2$ (phase I) was not stable, and the amorphous phase II' containing nitrate and nitrite ions was formed within 50 min. This is revealed in the series of Raman spectra displayed in Figure 3C, which show the loss of the characteristic $\text{Ba}(\text{NO}_3)_2$ lattice mode at 126 cm^{-1} and the growth of nitrite-related bands at 810 and 1335 cm^{-1} .

These experiments demonstrate that NO reacts with crystalline BaO_2 at relatively low temperatures to form nitrates and traces of nitrites. As the temperature is increased above the Tammann temperature of $\text{Ba}(\text{NO}_3)_2$, 300 °C, recrystallization and defect healing in $\text{Ba}(\text{NO}_3)_2$ occurs, and at still higher temperatures the amorphous intermediate phase II' is formed. All of these observations are in agreement with the established phase diagram.¹

However, when the BaO_2/MgO material was initially reacted with 1% NO/He at 300 °C, the in situ Raman spectra (Figure 4A) establish that new species are formed. The characteristic bands of BaO_2 at 130, 200, and 837 cm^{-1} almost disappeared within 5 min on stream. New bands appeared at 1059 and 718 cm^{-1} which again can be assigned to the formation of NO_3^- ions. But at the same time, bands were observed at 160, 263, 420, 807, 1235sh w, and 1329 cm^{-1} . This spectrum is characteristic of the Ba–nitro complexes observed under catalytic conditions.^{1,2} Thus, in contrast to the reaction of BaO_2 with NO at temperatures below 200 °C, the reaction at 300 °C leads to the formation of the Ba–nitro species. Of course, these Ba–nitro complexes are not stable under this NO partial pressure, as one expects from the phase diagram,¹ and after an additional 5 min on stream, the Raman spectrum was characteristic of the amorphous phase II' containing NO_3^- and Ba–nitrito complexes, as indicated by the bands and shoulders at 333, 456, 822, and 1335 cm^{-1} .

In another set of experiments, in situ Raman spectra were recorded during the reaction of BaO_2/MgO with 0.5% NO at 450 °C. The lower NO partial pressure in this experiment, as compared to the one described above, was used in an attempt to stabilize the Ba–nitro species. The initial Raman spectrum of crystalline BaO_2 (Figure 4B) completely vanished after 5 min reaction time. In its place, the Raman spectrum of phase III, which contained the catalytically active Ba–nitro complexes was observed. Despite the lower NO partial pressure, the Ba–nitro species was not stable under these conditions, and phase III transformed into the amorphous phase II' containing nitrates and Ba–nitrito species. When the temperature was further increased to 550 °C under 0.5% NO/He, the reformation of phase III, containing the catalytically active Ba–nitro species, was observed (Figure 4C), as expected from our previous study.¹

From the observed fast reaction of BaO_2 with NO to form Ba–nitro complexes, the question arises as to whether crystalline BaO_2 , present in the catalyst, is essential for NO activation. To gain additional information about the role of crystalline BaO_2 in the catalytic decomposition of NO, 14 mol % $\text{Ba}(\text{NO}_3)_2/\text{MgO}$ was decomposed in 10% O_2/He at 600 °C to give supported BaO_2 . Subsequently, the gas-phase composition was switched to 0.5% NO/He. The initial Raman spectrum of crystalline BaO_2 vanished after 5 min reaction time, as shown in Figure 5A. The band at 1050 cm^{-1} related to nitrates went through a maximum after 6 min, while the Raman band at 1324 cm^{-1} related to the Ba–nitro complex reached its maximum after 12 min on stream. Nitrate ions and the Ba–nitro complex are not stable under this low NO partial pressure, as known from the phase diagram,¹ and decomposition into BaO occurred. Thus, after equilibration, only weak signals due to both nitrogen-containing species were observed, and mainly defect-rich BaO

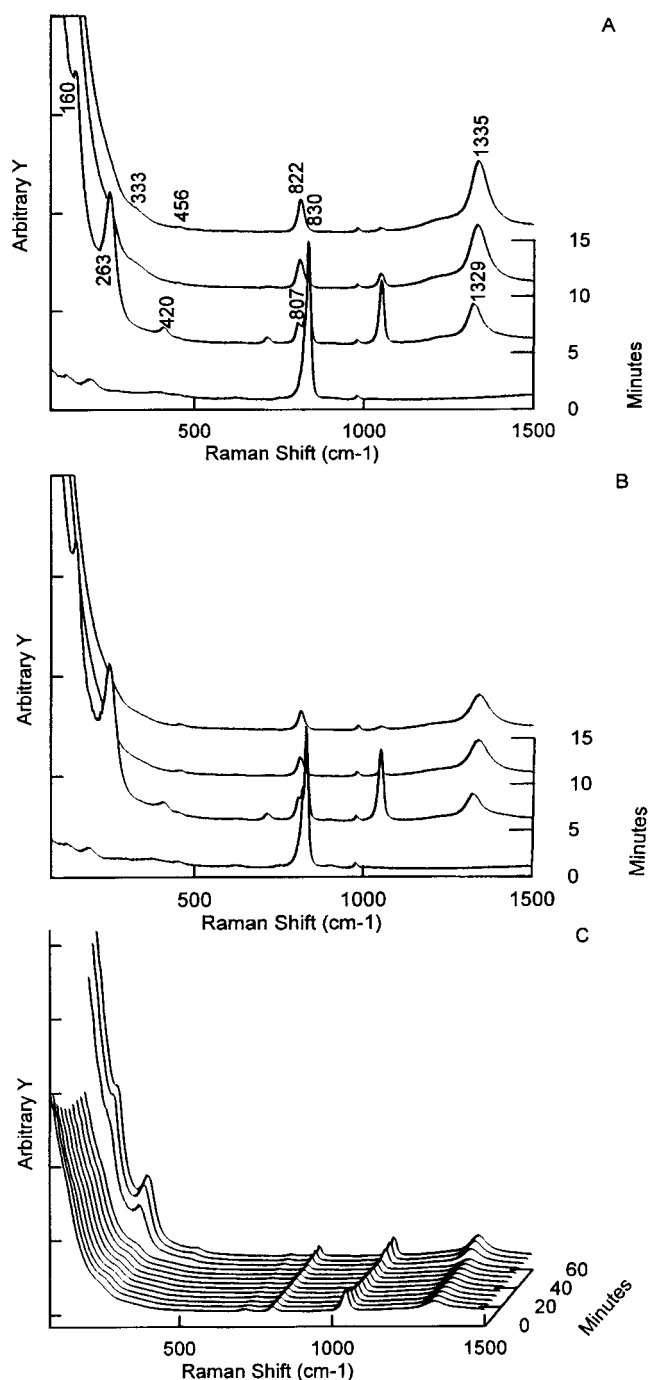


Figure 4. In situ Raman spectra obtained during the reaction of 14 mol % BaO_2/MgO with (A) 1% NO at 300 °C, time resolution 5 min; (B) 0.5% NO at 450 °C, time resolution 5 min; (C) 1% NO at 550 °C, time resolution 5 min.

was present, as indicated by the broad low-frequency Raman bands.⁹ An increase of the NO pressure to 1% NO/He (Figure 5B) resulted in the formation of phase III containing the Ba–nitro complex.

Under catalytic conditions, Raman bands due to crystalline BaO_2 were never observed,¹ which may be due to the observed fast reaction of BaO_2 with NO. However, there may also be pathways for NO activation which do not require the presence of crystalline BaO_2 . To explore this possibility, we have investigated the phase boundary between BaO and phase III containing the Ba–nitro species.

The decomposition of crystalline BaO_2 into defect-rich BaO results in an isosbestic point in the Raman spectra.⁹ The same observation is made when phase III decomposes into defect-

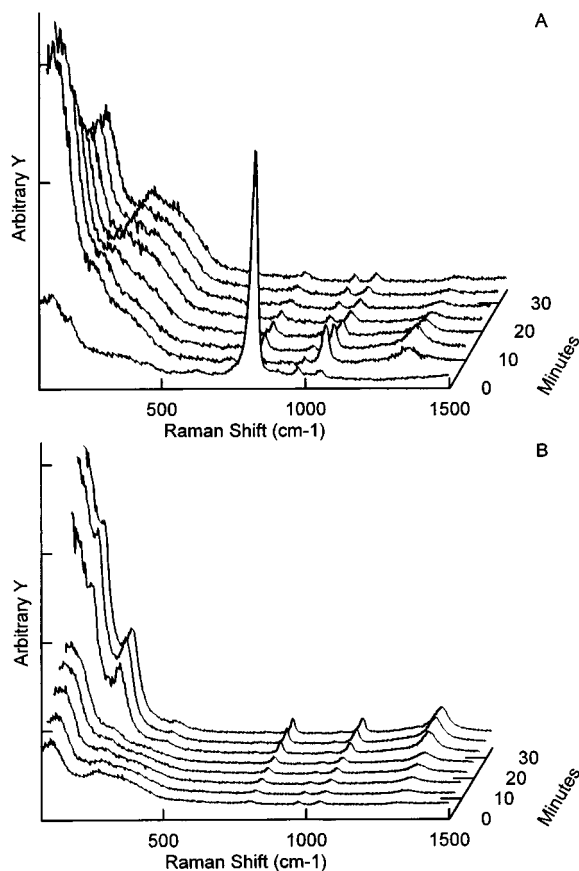


Figure 5. In situ Raman spectra obtained during the reaction of 14 mol % BaO_2/MgO : (A) with 0.5% NO at 600 °C, time resolution 4 min; (B) reaction of phase IV in 1% NO at 600 °C, time resolution 4 min.

rich BaO .¹ Thus, the three compounds, i.e. the Ba–nitro complex, BaO and BaO_2 , are directly transformed into each other. The Raman spectra of defect-rich BaO , formed via both pathways, exhibit a series of bands in the frequency regime between 800 and 1000 cm^{-1} , which is characteristic of peroxide ions.⁹ Because crystalline BaO_2 was never observed during the transient experiments,^{1,2} peroxide ions in or on defect-rich BaO may actually be the species which are responsible for NO activation.

As described above, NO reacts with crystalline BaO_2 within 5 min at the low temperatures of 300 and 450 °C to give Ba–nitro complexes; however, a reaction between NO and defect-rich BaO may also occur at low temperatures. To examine this possible activation step, supported BaO/MgO was reacted with 0.5% NO at 500 °C. The series of time-resolved in situ Raman spectra is displayed in Figure 6. While the reaction of 0.5% NO with supported, crystalline BaO_2 at the lower temperature of 450 °C required only 5 min, the reaction between 0.5% NO and supported BaO needed more than 500 min on stream for the intensity of the Raman bands of the Ba–nitro complex to reach steady state. Although it is evident from this experiment that crystalline BaO_2 is not essential for the activation of gas-phase NO to form Ba–nitro complexes, the results do not distinguish between the role of BaO itself and peroxide ions on defect-rich BaO . The peroxide ions could have been formed by the reaction of BaO with O_2 that was produced during the decomposition of NO.

The reaction of these noncrystalline peroxide ions with NO was studied at a more realistic catalytic temperature of 600 °C. The catalyst was prepared by decomposing $\text{Ba}(\text{NO}_3)_2$ in a sufficiently low partial pressure of O_2 (0.25%), such that

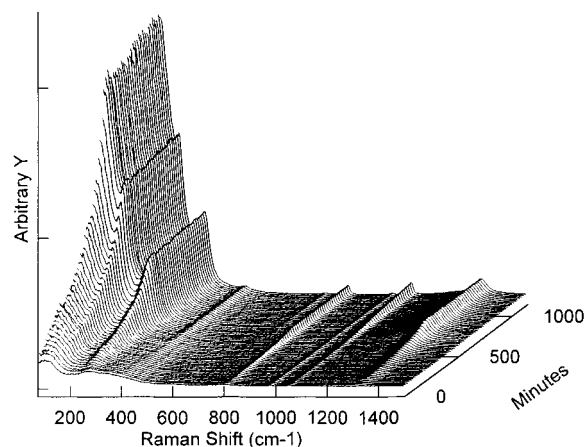


Figure 6. In situ Raman spectra obtained during the reaction of 14 mol % BaO/MgO with 0.5% NO at 500 °C, time resolution 15 min.

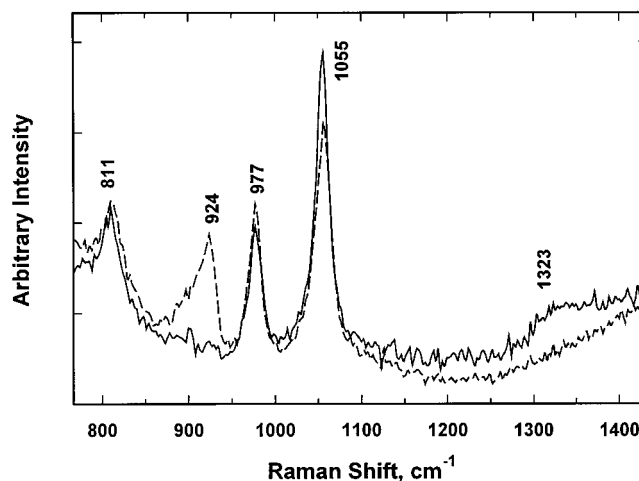


Figure 7. In situ Raman spectra of 14 mol % BaO/MgO at 600 °C (dashed line) after reaction with 0.25% O_2 ; (solid line) after reaction in 0.5% NO for 10 min.

crystalline BaO_2 was not formed.⁹ As shown in Figure 7, this material is characterized by Raman bands (dashed line of Figure 7) at 811, 924, and 977 cm^{-1} , in addition to the low frequency, defect-induced Raman scattering (not shown), and a band at 1055 cm^{-1} due to some remaining NO_3^- ions. If the phase diagram of the catalyst material is considered,¹ a switch of the gas phase from 0.25% O_2/He to 0.5% NO/He should generate a state close to the phase boundary for the formation of phase III, containing the active Ba–nitro species. Such an experiment, thus, may be able to show the initial interaction of peroxide ions on defect-rich BaO with NO during the generation of the catalytically active state. Within 10 min after adding 0.5% NO to the gas feed, the Raman spectrum (solid line) showed a weak band at 1323 cm^{-1} , which is characteristic of the symmetric stretching mode of the Ba–nitro complex.^{1,2} From the phase diagram¹ we know that Ba–nitrito species, or ionic nitrites are only stable at much higher NO pressures, and, moreover, their stretching modes occur above 1330 cm^{-1} . Therefore, we attribute the detection of the band at 1323 cm^{-1} to the generation of the first traces of the Ba–nitro complex on the surface of defect-rich BaO .

The Raman band at 924 cm^{-1} , which arises from peroxide ions in or on BaO ,⁹ completely disappeared. This observation may indicate that peroxide defects in or on BaO react with NO to give the Ba–nitro complex, comparable to the reaction of crystalline BaO_2 with NO. This experiment further confirms that the presence of crystalline BaO_2 is not required to activate

NO and to form the Ba–nitro species. We suggest that this reaction occurs under catalytic conditions on O_2^{2-} ions that are in or on defect-rich BaO. The peroxide ions on BaO, therefore, may play an important role in the catalytic cycle as the centers which activate gas-phase NO to form Ba–nitro complexes. The nature of these Ba peroxide ions will be discussed in the follow-up paper,⁹ in which we report on ^{18}O isotope labeling methods to confirm their identity.

IV. Summary and Speculation about a Reaction Mechanism

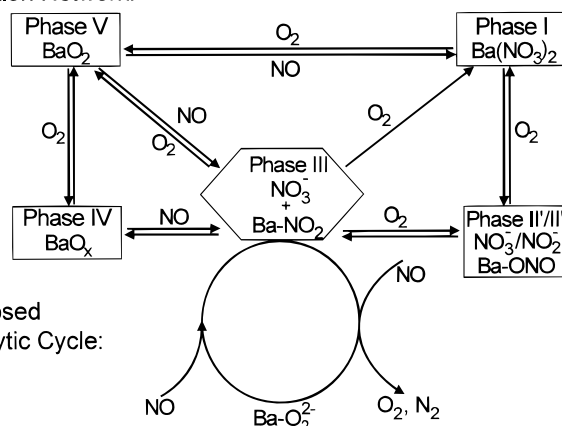
In the preceding paper,¹ we provided evidence for a complex phase behavior in highly loaded Ba/MgO catalysts under reaction conditions. Raman results strongly suggested that the enhanced activity of highly loaded Ba/MgO catalysts for the direct NO decomposition arises from the formation of a phase containing Ba–nitro species. The sharp falloff in the N_2 formation rate, which was observed in the catalytic reaction,^{1,3} could be related to a transition in the catalyst between this active phase and a defect-rich BaO phase. The knowledge of these phase relationships was necessary to develop a consistent picture of the processes which occur under the catalytic reaction conditions. Transient *in situ* Raman experiments across the phase boundaries demonstrated that these Ba–nitro complexes are taking part in the catalytic cycle as reaction intermediates. The intensity variations of the Raman bands related to nitrates or Ba–nitrito species, on the other hand, were in disagreement with the variations in catalytic activity during the transient experiments.^{1,3} The observed changes in the nitrate bands were explained by an oxidation of the active Ba–nitro species to NO_3^- .

In this contribution, it has been established that O_2 present in the gas phase not only affects the stability of catalyst phases, but also is responsible for the oxidation of Ba–nitro species to nitrates. The inhibiting effect of O_2 on the catalytic NO decomposition,³ therefore, is due to this oxidation reaction.

Moreover, BaO_2 reacts readily with NO to form the intermediate Ba–nitro species at a relatively low temperature; however, under catalytic conditions, crystalline BaO_2 was never detected.^{1,3} It appears that the presence of crystalline BaO_2 is not required for NO activation and the formation of Ba–nitro species. Rather, the formation of Ba–nitro species probably occurs via the reaction of NO with surface peroxide ions on defect-rich BaO. In addition, the time scale of the phase transformation from defect-rich BaO to the catalytically active phase was comparable with the time periods needed for catalyst reactivation.^{1,3} Oxygen, thus, exerts two opposing effects on the catalytic NO decomposition reaction: (1) It is responsible for the formation of surface peroxide ions that react with NO to produce the Ba–nitro intermediate, and (2) it reacts with these nitro species to produce inactive nitrate ions. The O_2 may be derived from the decomposition of NO or it may be purposely added to the reagent. The net effect of the oxygen is determined by the relative rates of the Ba–nitro formation and destruction reactions. These relative rates, in turn, depend on the temper-

SCHEME 1

Reaction Network:



Proposed Catalytic Cycle:

ature of the reaction, the extent of NO decomposition, and the amount of O_2 added to the reagent.

On the basis of the catalytic and spectroscopic results, one can propose a network of reactions and a possible catalytic cycle for the decomposition of NO over highly loaded Ba/MgO catalysts (Scheme 1). In the catalytic cycle, surface peroxide ions on defect-rich BaO react with gas phase NO to form the Ba–nitro reaction intermediate. This Ba–nitro complex is suggested to react in the rate-limiting step with a second gas phase, or weakly adsorbed, NO molecule to give N_2 and O_2 . Gas phase or weakly adsorbed oxygen replenishes the surface peroxide ions, but because of their rapid reaction with NO, they are not detected under catalytic conditions.

Acknowledgment. This research was supported by the National Science Foundation under Grant No. CHE-9520806. G. Mestl had a Feodor-Lynen-Research Fellowship provided by the Alexander von Humboldt Foundation.

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