

Decomposition of Nitric Oxide over Barium Oxide Supported on Magnesium Oxide. 4. In Situ Raman Characterization of Oxide Phase Transitions and Peroxide Species by ^{18}O -Labeling

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Time-resolved in situ Raman spectroscopy was used to follow the decomposition of supported crystalline BaO_2 into defect-rich BaO . This decomposition occurred under O_2 partial pressures which were small compared to those expected from a calculated phase diagram. However, the O_2 partial pressures at which this BaO_2 decomposition takes place are much greater than those which are reached during the catalytic decomposition of NO over this material. Additionally, supported crystalline BaO_2 was never observed during the actual catalytic reaction. Therefore, it must be concluded that crystalline BaO_2 does not play a role in the catalytic reaction. In addition to crystalline BaO_2 , with a major Raman band at 848 cm^{-1} and components at 826 and 814 cm^{-1} , another peroxide species which had a band at 947 cm^{-1} was identified by ^{18}O isotopic labeling. Other bands located in this region of the spectrum may be due to peroxide ions in defect-rich BaO/BaO_2 ; however, ^{18}O isotope labeling did not provide definitive evidence for their assignment. The peroxide species with a Raman band at 947 cm^{-1} was stable only in the presence of gas-phase O_2 and responded very rapidly to changes in the O_2 partial pressure. Therefore, it is likely that these peroxide ions are located at or close to the surface of defect-rich BaO crystals. It was previously shown that the species responsible for the Raman band at 947 cm^{-1} immediately reacted with NO to form an active Ba–nitro intermediate. This peroxide species on defect-rich BaO may therefore play an important role in the catalytic decomposition of NO .

I. Introduction

Nitric oxide decomposition over Ba/MgO catalysts containing in excess of 10 mol % Ba exhibits unusual catalytic behavior in that for a given NO partial pressure a high catalytic activity is observed and a sharp reduction in the NO conversion occurs if a certain temperature is exceeded.¹ In situ Raman spectroscopy revealed that the exceptionally high activity for NO decomposition at temperatures below the threshold arises from the formation of a solid phase containing barium nitro complexes.² The discontinuity in NO decomposition is associated with a phase transition in the catalyst material from the phase containing Ba–nitro complex species to a defect-rich barium oxide phase.² This phase transition closely followed the calculated phase boundary as determined by the triple point between $\text{Ba}(\text{NO}_3)_2$, BaO_2 , and BaO .² Transient in situ Raman experiments convincingly demonstrated that the Ba–nitro complexes are intermediates in the NO decomposition reaction that occurs below the sharp falloff temperature. Although nitrates, nitrites, and Ba–nitro species were detected, they seemed not to play a direct role in the catalytic cycle.^{1,2}

In the catalytic experiments, the addition of O_2 to the NO gas feed resulted in a shift of the observed extra activity for NO decomposition to higher falloff temperatures.¹ Additionally, O_2 significantly decreased the maximum NO conversion. In the previous paper in this series, the effect of O_2 on the stability regimes of several phases and the different species observed in the active catalyst material were described.³ In the presence

of O_2 , the catalyst precursor phases were observed to form BaO_2 , but the peroxide was not observed upon decomposition of the nitrogen-containing species in pure He or in NO , where only defect-rich BaO was detected.² Moreover, in the presence of high O_2 levels, the catalytically active phase containing the Ba–nitro complex was not observed by Raman spectroscopy.³ In addition to the effect on the stability of the catalyst precursor phases, the presence of oxygen in the gas phase decreased the concentration of the active nitro complex via oxidation to nitrates.³ This reaction was found to be responsible for the inhibiting effect of O_2 on the catalytic activity.¹

Crystalline BaO_2 reacted with NO to form nitrates, nitrites, and Ba–nitro complexes, depending on the O_2 and NO partial pressures and the reaction temperature.³ It might be suggested that crystalline barium peroxide plays a role in the catalytic cycle as the species which activates gas-phase NO ; however, under catalytic conditions crystalline BaO_2 was never detected. It was not clear whether the failure to observe crystalline BaO_2 during the catalytic reaction was due to a fast reaction with NO^2 or to its inherent instability at the low O_2 partial pressures attained during catalytic NO decomposition.¹ Additional Raman bands observed in the stretching mode region of peroxides^{1–3} suggest an alternative reaction pathway for NO activation. In the absence of crystalline BaO_2 , NO activation and the formation of the Ba–nitro intermediate occurred in the presence of O_2^{2-} ions in or on defect-rich BaO . These peroxide species may play an important role in the catalytic cycle. In summary, a given O_2 partial pressure leads to catalyst deactivation by oxidation of the active Ba–nitro species to inactive nitrates, while O_2 also appears to have an enhancing effect on the

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TABLE 1: Raman Bands in the Peroxide Frequency Region

Raman bands (cm ⁻¹)	assignment	ref
844	O ₂ ²⁻	4, 5
844	O ₂ ²⁻	6, 7
793	not assigned	6, 7
821, 829, and 842	O ₂ ²⁻ in different environments in BaO ₂	8
820 and 814	not assigned	8
¹⁸ O-label: 819, 807, and 778sh	O ₂ ²⁻	8
838	O ₂ ²⁻ in pure BaO ₂	9
826, 814	O ₂ ²⁻ in BaO ₂ containing O ₂ ²⁻ defects or complex BaO ₂ ⇌ [BaO ₂ /BaO] ⇌ BaO phase diagram	9
842	O ₂ ²⁻	10
820sh, 870, and 980	not discussed	10
ca. 840 and 960	peroxide ions	11

catalytic NO decomposition reaction by replenishing O₂²⁻ which is believed to be responsible for NO activation.

Because of this dual role played by O₂, it was of interest to investigate the phase transition between BaO₂ and BaO using in situ Raman spectroscopy. Moreover, experiments using oxygen-18 provide evidence that at least one additional Raman band observed in the peroxide stretching mode regime^{2,3} indeed arises from peroxide ions in or on defect-rich BaO. Comparable Raman bands have been reported in the literature and these are listed in Table 1. However, the referenced studies did not attempt to characterize the barium peroxide–oxide phase transition nor isolated peroxide centers, i.e., peroxide ions that are not present as crystalline BaO₂. In this contribution, we present in situ Raman spectroscopic data for the effect of temperature and O₂ pressure on the phase transition BaO₂ ⇌ BaO, as well as for additional peroxide species into which ¹⁸O has been incorporated.

II. Experimental Section

A catalyst containing 14 mol % Ba on MgO was prepared by impregnating MgO (Fisher, 38 m²/g) with the appropriate amount of Ba(NO₃)₂ (Baker). After drying in a rotary evaporator, the material was pressed at 1400 kg/cm², crushed, and sieved to 20–40 mesh size granules. All samples were stored in a desiccator over silica gel. The supported crystalline BaO₂ and BaO were generated by calcination of Ba(NO₃)₂/MgO in 10% O₂/He at elevated temperatures. In an independent series of in situ Raman experiments, the BaO-to-BaO₂ phase transition was induced by varying the O₂ partial pressure at a given temperature and the temperature at a given O₂ partial pressure. All gases used (10% O₂/He, and He) were from Matheson and were ultrahigh purity grade. The gas flow rate through the catalyst bed in the in situ Raman cell was 40 mL/min, which is identical to that used in the previously described catalytic experiments.¹ The experimental conditions included those under which the high activity for NO decomposition was observed.¹ The ¹⁸O-labeling was carried out in subsequent steps after having evacuated the in situ Raman cell to 20 Torr and refilling the cell with 1 atm of ¹⁸O₂ (Isotec, 98.0 at. %) until no changes could be observed in the high-temperature Raman spectra.

The in situ Raman spectra were recorded with a Holoprobe spectrometer (Kaiser Optical). The resolution of this instrument is 5 cm⁻¹ and the wavelength reproducibility is better than 0.5 cm⁻¹. The exciting light source was a Nd:YAG laser which was frequency doubled to 532 nm. To minimize laser heating of the sample, all spectra were recorded using a laser power of 2.5 mW, measured at the sample position. The in situ Raman cell and the optical setup are described in detail elsewhere.²

III. Results and Discussion

As outlined in the Introduction, the objective for high-temperature in situ Raman spectroscopy in this study was to answer questions concerning the stability of barium peroxide at temperatures and oxygen pressures comparable to those occurring during the catalytic decomposition of NO and questions concerning the nature of additional Raman bands observed in the peroxide stretching mode region. In the first section of this paper we will discuss the phase transition BaO₂ ⇌ BaO, and in the second section in situ Raman results of ¹⁸O-labeling experiments will be presented.

1. Effect of O₂ Pressure on the BaO₂ ⇌ BaO Phase Transition. In order to obtain information about the stability of 14 mol % BaO₂/MgO under reduced O₂ partial pressures, the catalyst was stabilized overnight at 590 °C in a 40 mL/min flow of 10% O₂/He. An additional series of experiments was conducted at 625 °C. Subsequently, the O₂ partial pressure in the feed gas was lowered stepwise to 5, 2.5, 2.25, 2.0, 1.75, 1.5, 1.25, 1.0, and 0.75% O₂/He. Time-resolved, high-temperature in situ Raman spectra were recorded at each O₂ partial pressure for a maximum of 7.5 h and a minimum of 1 h to gain information about the stability of supported BaO₂ and the rate of its decomposition into BaO. Crystalline BaO₂ on the 14 mol % BaO₂/MgO catalyst was observed to be present under all of these O₂ partial pressures.

As an example, the in situ Raman spectra obtained while decreasing O₂ partial pressures with the sample at 590 °C are shown in Figure 1. The most intense Raman band at 829 cm⁻¹, assigned to O₂²⁻ in crystalline BaO₂,^{4,5} gradually decreased, while a broad signal at 123 cm⁻¹ and its shoulder at 185 cm⁻¹ in the lattice mode regime showed some increase in intensity. In addition, the broad Raman scattering extending from 200 to 500 cm⁻¹ also slightly increased. Inset A of Figure 1 shows in detail the changes that occurred in the band of the peroxide stretching vibration. The starting material, after equilibration at 590 °C in 10% O₂/He, was characterized by a peak maximum at 829 cm⁻¹ and two shoulders at 820 and 810 cm⁻¹. This observation confirms the Raman data presented by Haller et al.,⁹ who reported three components in the Raman band of the peroxide stretching mode of crystalline BaO₂. The maximum of the band depicted in inset A of Figure 1 shifted to 833 cm⁻¹ with decreasing O₂ partial pressures, and the band broadened in the high-frequency wing.

According to the assignment of the three components in this Raman band given by Haller et al.,⁹ the band at 829 cm⁻¹ arises from a pure crystalline form of BaO₂, while the two shoulders at lower frequencies are due to peroxide ions in BaO₂ in close proximity to Ba²⁺ ions that are coordinated to one or two defect O₂²⁻ ions in BaO₂. The combined occurrence of intensity reduction, frequency shift, and broadening can be understood, if all three peroxide species identified in BaO₂ are responding to a comparable extent to a decrease in O₂ pressure. The band assigned to stoichiometric, crystalline BaO₂, however, must be affected more strongly by a general loss in long-range order induced by the release of O₂ from this material, as compared to the defect-related bands. Therefore, it is this component in the Raman band that shows considerable broadening.

From inset B of Figure 1, a band at 977 cm⁻¹ and a shoulder at about 900 cm⁻¹ are also clearly evident. If these additional weak bands or shoulders are also attributable to peroxide ions, probably in very different environments, supported BaO₂ would contain a total of five different peroxide species. It is important to note that no additional sharp bands were detected in the lattice mode regime that could be attributed to deformation modes of

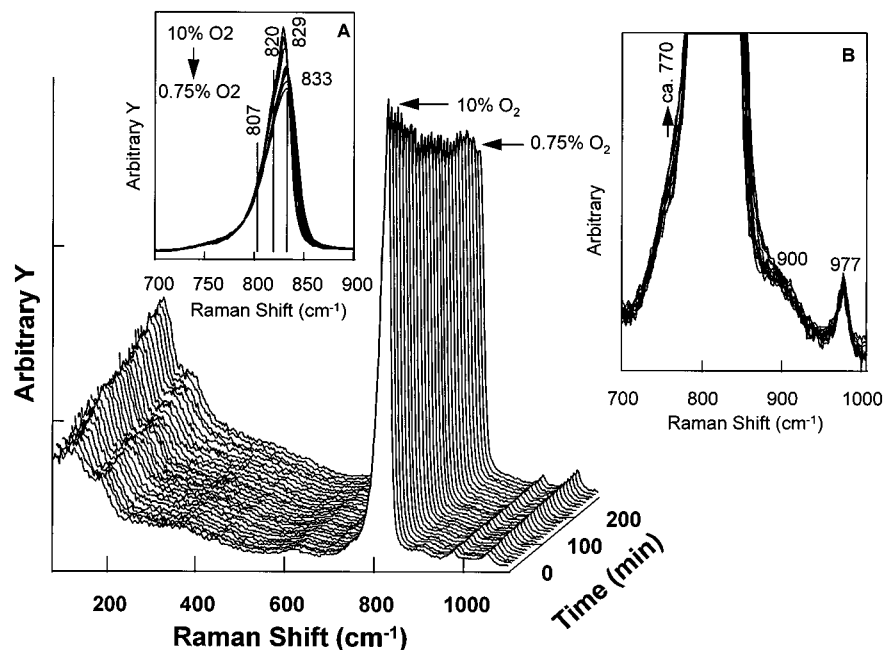


Figure 1. In situ Raman spectra of BaO₂/MgO recorded at 590 °C under decreasing O₂ partial pressures, time resolution 10 min. Inset A: Changes in the Raman band assigned to crystalline BaO₂. Inset B: Region of peroxide stretching frequencies, enlarged ordinate scale.

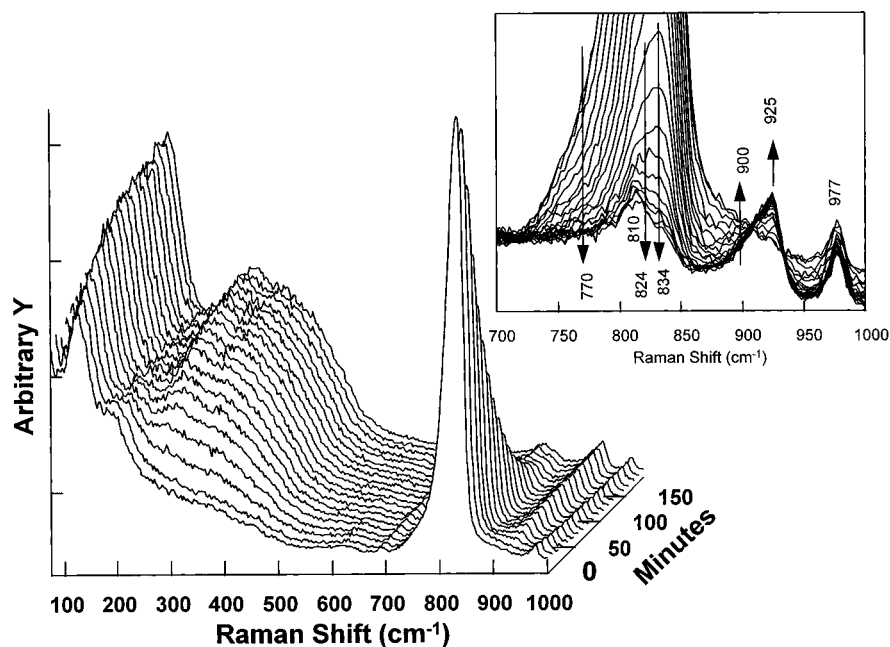


Figure 2. In situ Raman spectra of Ba/MgO recorded at 590 °C after decrease of the O₂ partial pressure from 0.75 to 0.5% O₂/He, time resolution 10 min. Inset: Region of peroxide stretching frequencies, enlarged ordinate scale.

these assumed extra O₂²⁻ species. Their local symmetry, therefore, must be reduced, and there is no crystallographically long-range ordering for these O₂²⁻ ions.

When the O₂ partial pressure was further decreased from 0.75% to 0.5% O₂/He at 590 °C, time-resolved in situ Raman spectra recorded during 150 min (Figure 2) demonstrated that crystalline BaO₂ decomposed under these conditions, as indicated by the loss of its characteristic O₂²⁻ stretching mode at 833 cm⁻¹. On the same time scale, the band at 123 cm⁻¹ increased and shifted to 112 cm⁻¹, while its shoulder at 185 cm⁻¹ showed no change in intensity. In addition, the broad Raman scattering between 200 and 500 cm⁻¹ strongly increased with the same temporal behavior as the band at 123 (or 112) cm⁻¹. The broad band shows features at 275 and 330 cm⁻¹ and an ill-defined shoulder at about 400 cm⁻¹. Barium oxide,

the decomposition product, crystallizes in the rock salt structure; therefore, first-order Raman scattering is symmetry forbidden in this material. The bands developing in the lattice mode regime are assigned to defect-induced Raman scattering in BaO. Supported barium oxide generated in this way must be crystallographically ill-defined and defect-rich. We will discuss the room temperature in situ Raman spectra of this material in more detail below.

A closer inspection of the peroxide stretching mode region reveals that all identified components of the spectrum associated with crystalline BaO₂ (810, 824, and 834 cm⁻¹) decreased on the same time scale. Peroxide species which gave rise to these bands were therefore not stable under these conditions. It is apparent from the inset of Figure 2, that all components of the BaO₂-related band at 833 cm⁻¹ were lost or greatly reduced in

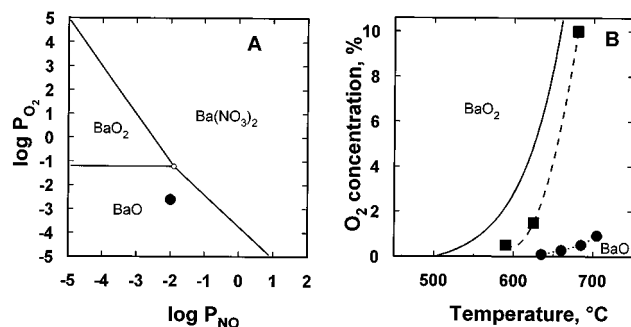


Figure 3. (A) Calculated phase diagram of BaO, BaO₂, and Ba(NO₃)₂ around the triple point at 625 °C; (filled circle), experimental conditions in the catalytic experiments under which maximum NO conversion was obtained.¹ (B) Comparison of the phase boundary between BaO₂ and BaO; (solid line), theoretical phase boundary; (filled squares), conditions for the decomposition of BaO₂ as observed by Raman spectroscopy; and (filled circles), the maximum oxygen partial pressures which are reached during the catalytic decomposition of NO.

intensity, with the exception of the remaining band at 810 cm⁻¹. Traces of the original most intense component at 833 cm⁻¹ also remained detectable as a shoulder at the same frequency. By contrast, the band at 977 cm⁻¹ was only slightly affected by this treatment.

More important is the observation that a new band evolved at 925 cm⁻¹, together with a broad shoulder at about 900 cm⁻¹. The evolution of these bands and the increase of the features in the lattice mode regime are connected with the loss in Raman intensity of the O₂²⁻ stretching modes of crystalline BaO₂ via isosbestic points at 905 and 935 cm⁻¹. This observation is indicative of a direct transition of crystalline BaO₂ into defect-rich BaO and additional O₂²⁻ species associated with certain defect sites, if we assume that the Raman structures at 900 and 925 cm⁻¹ are due to peroxide ions. Thus, a total of six different stretching frequencies in the peroxide spectral region have been observed: crystalline BaO₂ (833 cm⁻¹), two O₂²⁻ species in crystalline BaO₂ associated with O²⁻ defects (~820 and ~810 cm⁻¹), and at least three species in defect-rich BaO (900, 925, and 977 cm⁻¹). We will discuss the possibility of peroxide ions in defect-rich barium oxide in more detail below in the section on the ¹⁸O isotopic labeling experiments.

In Figure 3A, the phase diagram at 590 °C for BaO₂, BaO, and Ba(NO₃)₂ is shown. The phase boundaries present around the triple point were calculated using the software package HSC (Outokumpu Research Oy, Pori, Finland, Ver. 2.03). The filled circle represents one set of conditions at which the catalytic experiments were conducted. The calculated BaO₂ ⇌ BaO phase boundary is parallel to the NO pressure axis; thus, NO does not affect the location of this phase boundary. The O₂ partial pressures, under which the transition BaO₂ ⇌ BaO occurred, were calculated for various temperatures and are represented by the solid line in Figure 3B (see also ref 2). The filled squares in Figure 3B are the experimentally determined decomposition conditions as established by in situ Raman spectroscopy. Thus, at 590 °C, as we have already seen, decomposition occurred in 0.5% O₂. At 625 °C, the phase transition between BaO₂ and BaO was observed at a concentration of 1.5% O₂ in He; while at a concentration of 10% O₂ in He, BaO₂ was observed to decompose at 680 °C. For all reaction temperatures investigated, the 14 mol % BaO₂/MgO decomposed into defect-rich BaO at O₂ partial pressures considerably lower than the thermodynamically calculated ones. Thus, this material is to some extent more stable toward decomposition than is pure BaO₂. However, if the experimentally determined O₂ pressure which resulted in BaO₂ decom-

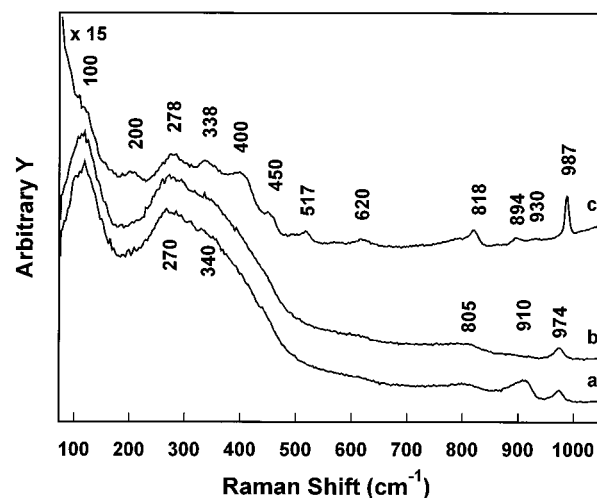


Figure 4. In situ Raman spectra of BaO/MgO: (a) under 10% O₂/He at 725 °C, (b) after 5 min in He at 725 °C (spectrum offset), (c) after cooling to 25 °C in He (spectrum amplitude multiplied by 15 and offset).

TABLE 2: Temperature Dependence of Selected Raman Bands (cm⁻¹)

assignment	25 °C	590 °C	725 °C
crystalline BaO ₂	848	829, 830	
surface O ₂ ²⁻ ion on BaO	947, 948	925	910
Bulk O ₂ ²⁻ ion in BaO ^a	987	977	974

^a Tentative assignment.

position is compared with the O₂ partial pressures that are produced at maximum NO conversions during the catalytic NO decomposition (filled circles in Figure 3B), the latter are smaller than the former by at least a factor of 10. It is, therefore, thermodynamically impossible for crystalline BaO₂ to be present under the conditions of catalytic NO decomposition. A fast reaction of NO with crystalline BaO₂ as one reaction step in a possible catalytic cycle must be excluded.

To further investigate the response of 14 mol % BaO/MgO to changes in the O₂ partial pressure, a separate experiment was performed in which the gas phase was switched from 10% O₂/He to pure He at 725 °C. In the presence of O₂, a band was observed at 910 cm⁻¹ with an asymmetry toward lower frequencies (Figure 4, spectrum a). This band was detected at 925 cm⁻¹ at 590 °C and at 947 cm⁻¹ at 25 °C (Table 2), but was completely absent in the Raman spectrum recorded after 5 min in pure He (spectrum b). Clearly, the Raman signal at 910 cm⁻¹ and its shoulder at 890 cm⁻¹ are affected by the O₂ in contact with the sample, which suggests that these bands should be assigned to peroxide ions at or close to the BaO crystallite surface. It is important that both of these suggested peroxide species which give rise to the band and the shoulder at about 900 cm⁻¹ are stable under conditions at which crystalline BaO₂ does not exist (Figure 3). In addition, it has been shown that these suggested peroxide species reacted with NO within 10 min at 600 °C to give Ba–nitro species.³ Thus, peroxide species such as these may play a role in the activation of NO.

The Raman signals at 974 and 805 cm⁻¹, on the other hand, showed very little change upon decreasing the O₂ partial pressure. If both of these Raman features arose from peroxide ions in defect-rich BaO, their stability must be high. Moreover, they must be well within the bulk of BaO crystals and probably constitute one type of an equilibrium-state lattice defect in BaO.

To gain additional information about the defect-rich supported BaO, the temperature of the catalyst was decreased to 25 °C in He, and spectrum c of Figure 4 was recorded. The spectrum

TABLE 3: Estimated Second-Order Raman Scattering in BaO

experimental fundamentals (cm^{-1})	overtones and combinations (cm^{-1})	experimental Raman bands (cm^{-1})
200	400 (200 + 200)	no overtone ^a
278	538 (200 + 338)	not observed
338	600 (200 + 400)	
400	616 (278 + 338)	620
450	650 (200 + 450)	
	676 (338 + 338)	
	678 (278 + 400)	
	717 (200 + 517)	broad scattering
	728 (278 + 450)	700–800
	738 (338 + 400)	maximum at 790
	788 (338 + 450)	
	800 (400 + 400)	
	not calculated	818
	855 (338 + 517)	not observed
	850 (400 + 450)	not observed
	900 (450 + 450)	894
	917 (400 + 517)	
	967 (450 + 517)	930
	none	987

^a The band at 400 cm^{-1} is too intense to arise from the overtone of the fundamental at 200 cm^{-1} .

shows more resolution than was obtained at high temperatures. Although first-order Raman scattering in BaO is forbidden, it has one IR-allowed vibrational mode which is split into one longitudinal optical (LO) and two degenerate transverse optical (TO) modes. The Raman spectrum (spectrum c of Figure 4) shows many more features, exhibiting bands or shoulders at 100, 200, 278, 338, 400, 450, 517, 620, 818, 894, 930, and 987 cm^{-1} . Beside a general symmetry reduction due to the presence of defects, additional processes, e.g., modes located at defects, must lead to the six bands observed in the lattice mode regime below 500 cm^{-1} . The weak intensities of the bands and shoulders observed between 400 and 700 cm^{-1} suggest that they are related to second-order Raman scattering. Table 3 compares the experimentally observed frequencies with those calculated by simply adding the assigned fundamentals, without consideration of symmetry or anharmonicity.

The band detected at 400 cm^{-1} cannot arise from an overtone ($2 \times 200\text{ cm}^{-1}$), because its intensity is comparable to that of the band at 200 cm^{-1} . When the calculated and the observed frequencies are compared, one can identify three major groups of overtones and combinations that occur between 600 and 650 cm^{-1} , between 680 and 800 cm^{-1} , and around 900 cm^{-1} , which are evident in the experimental spectrum. Thus, this simple estimate of overtone and combination frequencies suggests that the bands at 620 and 894 cm^{-1} arise from second-order scattering and are not due to stretching vibrations of peroxide ions. The very weak intensity of the band at 930 cm^{-1} and a frequency close to the calculated value of 917 cm^{-1} (Table 3) suggests that this feature also may arise from second-order scattering. The Raman bands at 818 and 987 cm^{-1} , however, are too intense to be overtones, and for the latter band there are no combinations of fundamentals which approximately match these frequencies.

The most important conclusion from this phase transition study is that crystalline BaO_2 is *not* stable at O_2 partial pressures (0.5% O_2/He at 590°C or 1.5% O_2/He at 625°C) that are at least 1 order of magnitude larger than those reached during catalytic decomposition of NO over Ba/MgO.¹ Thus, crystalline BaO_2 cannot be responsible for activating NO over this catalyst. Supported barium oxide is certainly not well crystallized, as

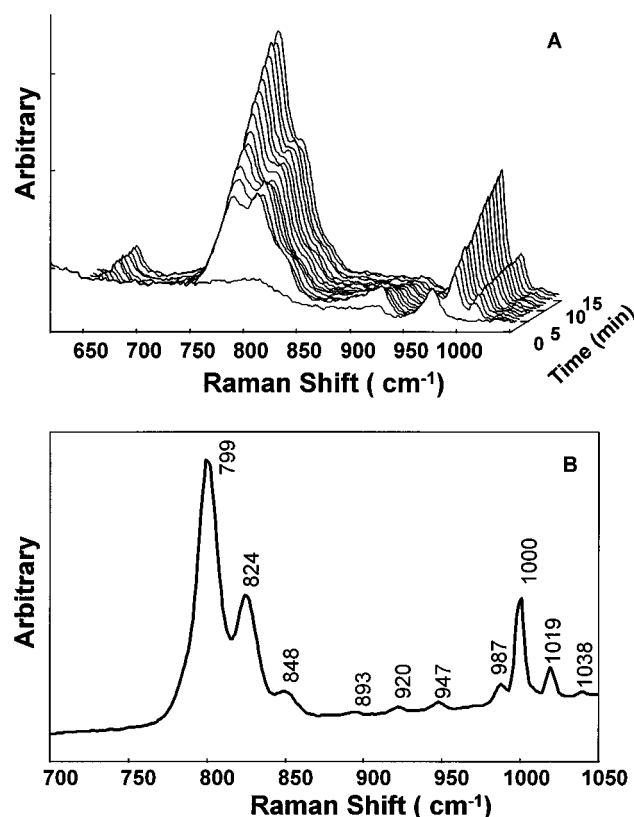


Figure 5. In situ Raman spectra of (A) Ba/MgO recorded at 500°C during 10 sequential steps of dosing 760 Torr $^{18}\text{O}_2$ into the in situ cell and (B) after cooling to 25°C in 760 Torr $^{18}\text{O}_2$.

demonstrated by the complex, defect-induced Raman spectrum. Consideration of possible overtone and combination frequencies suggests that the Ba/MgO may contain at least two different noncrystalline peroxide species with Raman bands at 818 and 987 cm^{-1} (room temperature values). In addition, there may be other peroxide species present on the surface of defect-rich BaO, as indicated by the rapid disappearance of the asymmetric band at about 910 cm^{-1} upon removing O_2 from the gas phase at 725°C (see Table 2). To facilitate the assignment of these bands, ^{18}O -labeling experiments were conducted.

2. ^{18}O -Labeling of Peroxide Ions in Supported 14 mol % Ba/MgO. To reach a high degree of ^{18}O -exchange, isotopic labeling was conducted after having decomposed 14 mol % BaO_2/MgO to BaO/MgO at 725°C in a flow of He (40 mL/min). Oxygen-18 labeling of the catalyst was accomplished by decreasing the pressure in the in situ Raman cell to 20 Torr for 10 min and subsequently refilling it with 750 Torr of $^{18}\text{O}_2$. The catalyst sample was exposed to the $^{18}\text{O}_2$ for 10 min at 500°C after which the gas phase was again evacuated. This procedure was repeated 10 times.

The series of in situ Raman spectra which were recorded during the 10 ^{18}O -exchange steps is depicted in Figure 5A. The starting material, 14 mol % BaO/MgO, is characterized at this temperature by bands at 810, 926, and 977 cm^{-1} in the peroxide stretching mode region. After the first exposure to 750 Torr $^{18}\text{O}_2$ and calcination for 10 min, a strong increase was observed in the intensity of peroxide-related bands at 786, 807, and 830 cm^{-1} . Simultaneously, ^{18}O -labeled CO_3^{2-} bands appeared at 999, 1020, and 1038 cm^{-1} . The assignment to CO_3^{2-} was confirmed in a subsequent series of in situ Raman experiments (spectra not shown), in which the ^{16}O -reexchange was followed by time-resolved Raman spectroscopy. These spectra show that the three bands at 999, 1020, and 1038 cm^{-1} transformed into the CO_3^{2-}

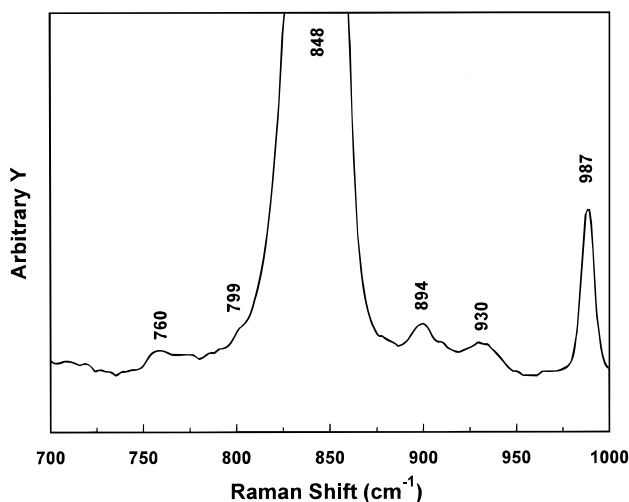


Figure 6. Raman spectrum of unlabeled BaO₂/MgO, expanded ordinate scale.

TABLE 4: ¹⁸O-Labeling of Supported BaO₂

¹⁶ O ₂ (cm ⁻¹)	calculated values (cm ⁻¹)		observed values (after ¹⁸ O-labeling) (cm ⁻¹)		
	¹⁶ O— ¹⁸ O	¹⁸ O— ¹⁸ O	¹⁶ O— ¹⁶ O	¹⁶ O— ¹⁸ O	¹⁸ O— ¹⁸ O
847	823	799	847	824	799
947	920	893	947	920	893
987	960	931	987	965	

band at 1054 cm⁻¹ accompanied by an isosbestic point. The formation of CO₃²⁻ is due to oxidation of trace amounts of organic impurities from the evacuation system.

During the process of ¹⁸O-labeling (Figure 5A), the bands due to labeled crystalline BaO₂ increased, while the band at 926 and its shoulder at 903 cm⁻¹ decayed away. We know from the phase transition studies that the band at 926 and its shoulder at about 900 cm⁻¹ are associated with the band of crystalline BaO₂ at 833 cm⁻¹ via an isosbestic point. Their decreasing intensity is thus a result of the transformation of defect-rich BaO into crystalline BaO₂.

The in situ Raman spectrum of the material after 10 steps of ¹⁸O-exchange, shown in Figure 5B, was recorded after cooling the sample to room temperature in an ¹⁸O₂-atmosphere. This spectrum showed more resolution than the high-temperature spectra, and bands were detected at 799, 824, 848, 893, 920, 947, 987, 1000, 1019, and 1038 cm⁻¹. The bands at 1000, 1019, and 1038 cm⁻¹ are again assigned to ¹⁸O-labeled CO₃²⁻. If one calculates the expected frequencies for ¹⁸O—¹⁸O- and ¹⁸O—¹⁶O-labeled peroxides using a simple harmonic oscillator model and the observed frequency of 848 cm⁻¹ for crystalline Ba¹⁶O₂, and compares these values with the experimentally observed ones, it is apparent that the strong bands at 799 and 824 cm⁻¹ arise from the doubly and singly ¹⁸O-labeled O₂²⁻ ions, respectively, in crystalline BaO₂ (Table 4). The relative intensities of these bands confirm that the crystalline BaO₂ contained a large amount of ¹⁸O₂²⁻ ions.

Unlabeled BaO₂ (Figure 6) showed additional weak Raman bands at 760w, 894w, 930w, and 987m cm⁻¹ at room temperature, in addition to the characteristic band of crystalline BaO₂ at 848 cm⁻¹ with its components at ~826, ~814, and ~790 cm⁻¹. The band at 930 cm⁻¹ in the room temperature spectrum was shifted from 926 cm⁻¹, the position at which it was observed at 500 °C after BaO₂ was decomposed at 725 °C (Figure 2, inset B). If one calculates the stretching frequencies under the assumption that these bands arise from peroxide ions, the band observed at 930 cm⁻¹ should give rise to ¹⁸O-labeled

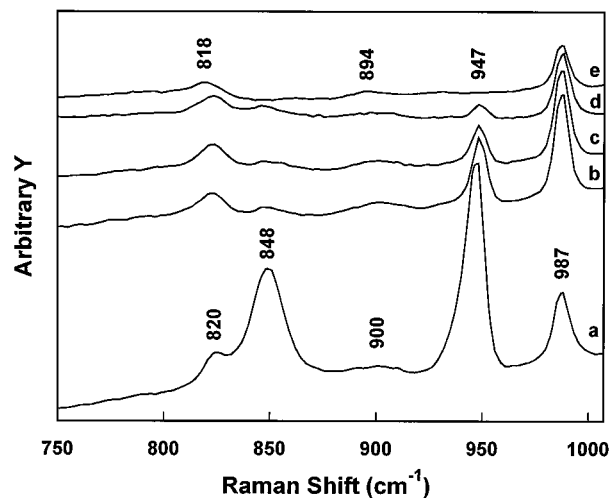


Figure 7. In situ Raman spectra of Ba/MgO: (a) after decomposing BaO₂/MgO in 10% O₂/He at 725 °C and rapidly cooling to 25 °C in 10% O₂/He; (b) after additional brief heat treatment at 725 °C and subsequent cooling to 25 °C in 10% O₂/He (this process required 10 min); (c) at 25 °C after flowing He at 25 °C for 1 h; (d) recorded at 25 °C after flowing He at 100 °C for 30 min; (e) at 25 °C after decomposing BaO₂/MgO in He at 725 °C and cooling to 25 °C in He (spectra offset).

bands at 903 and 876 cm⁻¹. The expected singly ¹⁸O-labeled band at 903 cm⁻¹ would be obscured by the band at 894 cm⁻¹ and could not be unambiguously identified. The doubly labeled band at 876 cm⁻¹ should be detectable, but no band is observed at this frequency (Figure 5B). The species giving rise to the band at 894 cm⁻¹ should generate bands at 869 and 843 cm⁻¹. The expected fully ¹⁸O-exchanged band at 843 cm⁻¹ would be strongly affected by the very intense bands arising from crystalline BaO₂ (Figure 5B). The singly ¹⁸O-labeled band at 869 cm⁻¹ should be detectable in the Raman spectra of the ¹⁸O-labeled material, but no band is apparent at this frequency in Figure 5B. The bands observed at 893 and 920 cm⁻¹ (Figure 5B) are not accounted for by any of the calculated values and, thus, cannot arise from ¹⁸O-labeled peroxide species having bands at 930 or 894 cm⁻¹.

When the Ba/MgO was calcined at 725 °C in 10% ¹⁶O₂ (conditions under which crystalline BaO₂ is not stable) and then rapidly cooled in O₂ to room temperature, the resulting Raman band at 848 cm⁻¹ (Figure 7, spectrum a) indicates the rapid formation of crystalline BaO₂ during the cooling process. In addition, the spectrum showed a broad weak structure at 900 cm⁻¹, together with bands at 820, 947, and 987 cm⁻¹. The band at 947 cm⁻¹ was the most intense feature in the spectrum. When the O₂ concentration above this material was reduced to 0.25% in He and the temperature was briefly increased to 725 °C followed by rapid cooling to room temperature (a process which required 10 min), spectrum b in Figure 7 was observed. This spectrum shows that only a small amount of the crystalline BaO₂ remained, as indicated by the weak band at 848 cm⁻¹. In addition, bands and shoulders are observed at 820, 900, 947, and 987 cm⁻¹. This treatment significantly decreased the intensity of the band at 947 cm⁻¹. The band located at 987 cm⁻¹, however, increased in intensity after this treatment. When the gas phase was switched to a flow of pure He at 25 °C for 1 h, the intensity of the band at 947 cm⁻¹ was further decreased (Figure 7, spectrum c). The Raman band at 947 cm⁻¹ is, therefore, strongly related to the O₂ partial pressure above barium oxide, and the species responsible for it is only stable in the presence of gaseous oxygen. A treatment at 100 °C in flowing He for 30 min led to further intensity reduction of the

band at 947 cm^{-1} (Figure 7, spectrum d). This was confirmed in an independent experiment in which BaO_2/MgO was decomposed at $725\text{ }^\circ\text{C}$ in flowing He, and cooled to room temperature (Figure 7, spectrum e). This in situ Raman spectrum showed no trace of the band at 947 cm^{-1} .

This series of experiments provides insight into the spectral features in the Raman spectrum of the ^{18}O -labeled material (Figure 5B) that was recorded after cooling the sample to room temperature in $^{18}\text{O}_2$. The band at 947 cm^{-1} in Figure 5B has the same origin as the one observed at this frequency in the Raman spectrum a of Figure 7 and arises from the peroxide species which was only stable in the presence of O_2 at $25\text{ }^\circ\text{C}$. If we calculate the $^{18}\text{O}-^{18}\text{O}$ and $^{18}\text{O}-^{16}\text{O}$ stretching frequencies, assuming a peroxide ion, and compare these values with the observed frequencies in the Raman spectrum of Figure 5B, it is evident that there is good agreement between these values (Table 4). Thus, this series of combined stability and ^{18}O -labeling experiments provided unambiguous identification for two different peroxide species: (a) crystalline BaO_2 and (b) an additional peroxide species which is only stable in the presence of O_2 and is characterized at $25\text{ }^\circ\text{C}$ by a Raman band at 947 cm^{-1} .

Additional information can be drawn from a comparison of the relative intensity ratios of the Raman bands for the labeled crystalline BaO_2 and the other peroxide species. In the most oxidized state of this material, as shown in Figure 5B, the relative ratios for the crystalline BaO_2 were $^{18}\text{O}-^{18}\text{O}; ^{18}\text{O}-^{16}\text{O}; ^{16}\text{O}-^{16}\text{O} = 1:0.5:0.12$, indicating a high level of ^{18}O incorporation. By contrast, the intensity ratios of the bands for the additional peroxide species were $^{18}\text{O}-^{18}\text{O}; ^{18}\text{O}-^{16}\text{O}; ^{16}\text{O}-^{16}\text{O} = 1:1.5:2$, which indicates that this peroxide species was labeled with ^{18}O to a much smaller extent than was the crystalline BaO_2 . We know from the phase diagram studies that crystalline BaO_2 and the peroxide species giving rise to the band at 925 cm^{-1} (the frequency at which the band at 947 cm^{-1} is observed at $590\text{ }^\circ\text{C}$ (Figure 2), see Table 2), are interconnected via an isosbestic point, and the latter peroxide species is mainly present under an oxygen-containing atmosphere when crystalline BaO_2 is essentially decomposed. This observation, together with the much lower level of ^{18}O -incorporation into the additional peroxide species as compared to the high level of ^{18}O -incorporation in crystalline BaO_2 , reflects the mutual exclusion of both peroxide species.

The assignment of the remaining bands in Figures 6 and 7 is complicated by the fact that the expected peroxide bands resulting from ^{18}O -exchange were either absent from the spectra or obscured by more intense bands. Nevertheless, because of the wavenumbers, one may expect that several of these bands may result from peroxide ions that were more difficult to exchange with $^{18}\text{O}_2$. It was shown by Haller et al.⁹ that the Raman spectrum of crystalline BaO_2 contained two additional peroxide signals which were suggested to arise from peroxide ions in the neighborhood of barium ions coordinated to one or two O^{2-} ions. A third very weak shoulder at $\sim 780\text{ cm}^{-1}$ was also detected but was not discussed by these authors.⁹ A recent X-ray diffraction single-crystal study confirmed that BaO_2 is actually a nonstoichiometric compound.¹² From the published unit cell of BaO_2 ,¹² one can deduce the maximum number of different peroxide species if one peroxide ion is replaced by an oxygen anion or a vacancy containing two electrons. One missing peroxide ion gives rise to two different lattice sites, in total two different peroxide species, i.e., two different bands in addition to the band due to fully stoichiometric BaO_2 . Two missing peroxide ions (e.g., if peroxide ions are replaced by

one O^{2-} anion and one vacancy), give rise to one or two different lattice sites and, thus to one or two additional peroxide species. Three peroxide ions missing from the unit cell give rise to one additional peroxide species. Together with the Raman band of unperturbed barium peroxide, a total of five or six different peroxide ions may occur in nonstoichiometric BaO_2 , depending on the degree of nonstoichiometry. In addition, the observed isosbestic point, which occurred in the Raman spectra of the $\text{BaO}_2 \rightleftharpoons \text{BaO}$ phase transition between the band of crystalline BaO_2 and the band related to peroxide defects in BaO , can be understood in the framework of this structural model.

If we assume that nonstoichiometry is possible not only in BaO_2 but also in defect-rich BaO , a suggestion which was made by Volnov,¹³ we can expect the additional peroxide species in or on defect-rich BaO . By assuming that comparable lattice defects are also possible in supported defect-rich BaO , one may speculate about defect geometries which would give rise to the additional peroxide Raman bands. For example, a V_k defect,¹⁴ which in this case consists of a peroxide ion and an anion vacancy containing two electrons, could have three different configurations in a body-centered lattice with a barium ion at the center. That is, the peroxide ion and the vacancy could be at crystallographic sites on a common edge of the cube, diagonally located across a face of the cube, or diagonally located at the extreme corners of the cube. Thus, when one considers the range of compositions and defects that would exist in going from pure BaO_2 to pure BaO , it is easy to conceive of a set of local environments for peroxide ions that might result in Raman bands between 780 and 987 cm^{-1} . Most of these peroxide ions, however, would be present in the bulk and would not be directly responsible for the activation of NO at the surface.

IV. Conclusions

Time-resolved in situ Raman spectroscopy was used to follow the decomposition of supported BaO_2 into defect-rich BaO . This decomposition occurred under O_2 partial pressures that were lower than those expected from a calculated phase diagram. However, the minimum O_2 partial pressures at which this phase transition takes place are at least an order of magnitude greater than those typically reached during the catalytic decomposition of NO over Ba/MgO . Additionally, supported crystalline BaO_2 was never observed during the in situ Raman characterization of the active catalyst phases.¹⁻³ Therefore, it is concluded that crystalline BaO_2 does not play a role in a catalytic cycle in which gas-phase NO is activated.

In addition to crystalline BaO_2 , having a Raman band at 848 cm^{-1} and components at 826 and 814 cm^{-1} , an additional noncrystalline peroxide species, characterized by a band at 947 cm^{-1} , was identified by its response to changes in the O_2 partial pressure and by ^{18}O isotope labeling. This peroxide species was stable at temperatures up to $725\text{ }^\circ\text{C}$ only in the presence of gas-phase O_2 and responded very rapidly to changes in the O_2 partial pressure. We suggest, therefore, that these species are located at or close to the surface of defect-rich BaO crystals. This peroxide species on defect-rich BaO could play an important role as the center which activates gas-phase NO, as suggested in the proposed catalytic cycle.¹⁻³

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