

NO₂ Storage and Reduction in Barium Oxide Supported on Magnesium Oxide Studied by *in Situ* Raman Spectroscopy

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The mechanism for NO₂ storage in barium oxide supported on magnesium oxide (BaO/MgO) was investigated. *In situ* Raman spectroscopy and XRD were used to follow temporal changes in the composition of the storage material that occurred during the storage process, i.e., during the reaction of 14 mol % BaO with NO₂ and NO₂/O₂, and the reduction of the stored NO₂ with CO. Above 200 °C, the interaction of BaO with NO₂ leads to both the formation of nitrate and nitrite ions, which, up to 400 °C, occurs via an intermediate barium–nitro species. At lower loadings (7 mol %), a destabilization of the barium–nitro species but an enhanced rate for nitrate formation is observed. Similarly, the presence of oxygen enhances the rate for nitrate formation, but suppresses the formation of nitro species. CO reduces the stored NO₂ only above 500 °C and leads to the formation of thermally stable carbonates. In the presence of NO₂, however, they are displaced during the formation of nitrates at 400 °C.

Introduction

The need to reduce the fuel consumption of vehicles has led to the development of engines that operate under “lean”, i.e., oxygen-rich conditions.¹ Lean burn combustion can decrease the fuel consumption up to 30% compared to a stoichiometric engine.² In the presence of excess oxygen, however, conventional three-way catalysts, cannot sufficiently eliminate the nitrogen oxides in the exhaust gas emitted under these conditions. To circumvent this problem, catalysts for the selective NO_x reduction by hydrocarbons in the presence of oxygen have been studied.^{1–4} Unfortunately, these catalysts are limited with respect to the overall NO_x conversion, N₂ selectivity, and durability.

An alternative solution is to employ so-called “NO_x storage–reduction” (NSR) catalysts which are used in engines operating alternately under lean and rich conditions.⁵ Within such a cycle, NO_x is stored in the catalyst under lean conditions and subsequently converted to nitrogen by unburned hydrocarbons under rich conditions. To optimize the NSR concept, a detailed understanding of the mechanism underlying the interaction of NO_x with the storage component is of vital importance.

Typical NSR catalysts consist of a NO_x storage compound, such as an alkaline or alkaline earth metal oxide, and a noble metal for both the oxidation of NO and hydrocarbons and the reduction of the stored NO_x. Formulations developed by Toyota included BaO as the storage compound and Pt as the noble metal.⁶ Several studies have been devoted to NO_x storage on alumina-supported barium oxide.^{6–16} With such a Pt catalyst, it has been shown that the NO_x storage yield depends crucially on the amount of NO₂ produced by the NO oxidation step, a maximum being found at about 370 °C.¹² The exposure of BaO/Al₂O₃ and Pt–BaO/Al₂O₃ catalysts to NO₂ at room-temperature resulted in the formation of ionic and bidentate nitrates, as was observed by Prinetto et al.¹⁵ using FT-IR spectroscopy. According to Fridell et al.,¹⁴ exposure to NO₂ and O₂ between

100 and 400 °C led to the formation of nitrates and nitrites on Al₂O₃, as well as on BaO.

In a previous communication, the mechanism of NO₂ storage in barium oxide supported on magnesium oxide (BaO/MgO) was addressed.¹⁷ By using *in situ* Raman spectroscopy temporal changes in a storage compound containing 14 mol % BaO on MgO were monitored upon exposure to 1% NO₂ and 1% NO₂/20% O₂. At 400 °C, the reaction between nitrogen dioxide and BaO led to the formation of a Ba⁺–NO₂[–] species that transformed into nitrite ions while, simultaneously, surface or amorphous nitrates were formed. Upon further exposure, crystalline Ba(NO₃)₂ was produced. In comparison with theoretical results for the NO₂ storage on BaO(100),¹⁶ there was agreement about the initial formation of a nitro species (–NO₂) and the subsequent oxidation to nitrates, while the transformation of the Ba⁺–NO₂[–] species into nitrite ions and the formation of crystalline Ba(NO₃)₂ were not addressed theoretically. In the presence of molecular oxygen, the formation of the Ba⁺–NO₂[–] species was suppressed, and the rate of nitrate formation was increased. On the other hand, the reaction between molecular oxygen and BaO led to the formation of crystalline BaO₂, which was assumed to be responsible for the *direct* formation of nitrate ions.

In this contribution, we address the temperature- and coverage-dependent behavior of the NO₂ storage in BaO/MgO, as well as the reduction of the stored NO₂ by using *in situ* Raman spectroscopy in combination with X-ray diffraction (XRD) and transmission electron microscopy (TEM). The results shown here represent part of our effort to understand, at a fundamental level, the NO_x storage chemistry in BaO/MgO that is largely unexplored. The 14 mol % BaO storage compound, which was the focus of our study, consisted of crystalline BaO containing defects, as shown by XRD and Raman spectroscopy. It is stable up to 900 °C¹⁸ and does not suffer from a decrease in storage capacity when treated above 600 °C, as has been reported for Ba/Al₂O₃ and Pt–Ba/Al₂O₃ catalysts.¹⁹ Loss of storage capacity may limit the practical application of a material.

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Experimental Section

The BaO/MgO storage compounds were prepared, as described previously,²⁰ by adding dropwise 150 mL of an aqueous solution containing the desired amount of Ba(NO₃)₂ (Baker, reagent grade) to a stirred slurry containing 5.0 g of MgO (Fisher, light) and 40 mL of deionized water. The mixture was stirred overnight at room temperature. The aqueous phase was evaporated at 100 °C, and the resulting solid was heated in air at 120 °C for 2 h. The material was then pressed under 1400 kg/cm² and sieved to 20–40 mesh size (850–425 μm).

The BaO/MgO storage compounds were characterized with XRD (Bruker D8) and TEM (JEOL 2010, 200 kV). Before and after TEM experiments, the presence of BaO/MgO was confirmed by energy-dispersive X-ray analysis (EDX).

The optical setup and the Raman cell were similar to those described previously.¹⁸ The Raman spectra were recorded using a Holoprobe spectrometer (Kaiser Optical) equipped with a Nd:YAG laser that is frequency doubled to 532 nm. The exciting laser light is coupled through a quartz fiber to the Raman probe head mounted on a xyz stage that allows one to record spatially resolved Raman spectra. The laser was operated at a low power level of 6 mW, measured at the sample position so as to minimize the effect of heating the sample. The Raman-scattered light is collected in the 180° direction. It is detected with an electrically cooled CCD camera (256 × 1022 pixels) after cutting off the laser light with a high-performance holographic notch filter. The spectral resolution of the instrument is 5 cm⁻¹, and its wavelength accuracy better than 1 cm⁻¹. The Raman cell used for the experiments consists of two parts, the cell body and a sample holder. The sample holder is a fused-quartz tube, 6 mm in diameter, that fits exactly into the cell body. At the top of the tube, approximately 50 mg of the catalyst was supported on a layer of quartz wool through which the gases were allowed to flow. A thermocouple well extended into the catalyst bed. The cell body is a fused-quartz tube with an inner diameter of 9 mm that is closed with an optical window. The tube is heated with tightly wound heating wires and thermally insulated with ceramic material.

The storage compound in the cell was heated to 900 °C for 2 h in flowing He to decompose Ba(NO₃)₂ and any BaCO₃ that might be present. The surface area of the 14 mol % BaO/MgO, which was the focus of this study, was ca. 3 m²/g, as determined with the BET method by adsorption of nitrogen. Reaction mixtures consisted of 1% NO₂ and 1% NO₂/20% O₂ in He. They were obtained by mixing 4.1% NO₂/He (Matheson, certified standard) and oxygen of ultrahigh purity (Matheson) with pure He (Praxair) so as to obtain the desired gas compositions. The CO gas (Matheson) was of 99.99% purity. The 1% NO₂/He mixture passed through the catalyst bed at 760 Torr and a flow rate of 40 mL/min, whereas, the flow rates in the cases of 1% NO₂/20% O₂/He and CO were 50 and 20 mL/min, respectively. For each of the temperatures given below, the storage material had been stable for at least 1 h, before introducing the reaction mixtures.

Results and Discussion

Temperature Dependence of the NO₂ Storage. Below 300 °C, Raman spectroscopy gave no indication that a significant amount of NO₂ was stored in 14 mol % BaO/MgO.²¹ Figure 1 depicts the NO₂ storage behavior in 14 mol % BaO/MgO at 300 °C, 400 °C, and 500 °C. At each temperature, a series of in situ Raman spectra (recorded at 30–40 s intervals) shows the temporal evolution of the composition of the storage compound in the presence of 1% NO₂. In contrast, when pure

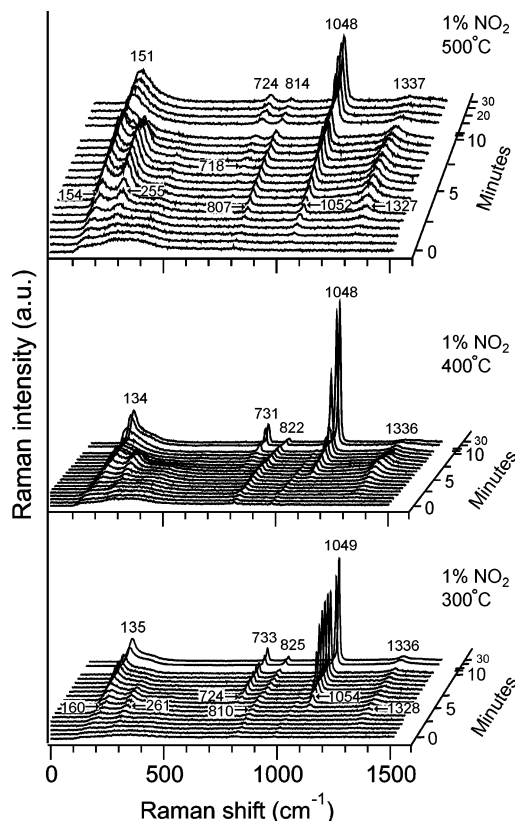


Figure 1. Raman spectra of 14 mol % BaO/MgO at 300 °C, 400 °C, and 500 °C showing the temporal effect of exposure to 1% NO₂. At 300 °C and 400 °C the formation of the nitro species precedes the formation of nitrates.

MgO was exposed to 1% NO₂, no new Raman bands were observed. Each of the first spectra shown in Figure 1 corresponds to BaO/MgO in He and is characterized by a broad set of bands in the region of 100–600 cm⁻¹ and weak bands at 816 and 986 cm⁻¹. Previously, this spectrum has been attributed to defect-rich BaO.¹⁸

At 300 °C, when NO₂ was introduced, new Raman bands at 160, 261, 810, and 1328 cm⁻¹ appeared within the first 3 min and increased with time. These bands can be assigned to a barium–nitro species, i.e., a complex in which a nitro ligand is coordinated to the metal via the nitrogen atom (e.g., Ba⁺–NO₂⁻), as described in previous studies.^{20,22} After ca. 5 min, new bands appeared at 724 and 1054 cm⁻¹ and are attributed to surface or amorphous NO₃⁻ ions. Upon further exposure to NO₂ they increased in intensity and transformed into bands at 733 and 1049 cm⁻¹ that are characteristic of bulk nitrates.¹⁸ In addition, the detection of the lattice phonon band at 135 cm⁻¹ is proof of crystallinity.¹⁸ Interestingly, after 5 min, there was an 8 cm⁻¹ blue-shift in the maximum of the stretching band at 1328 cm⁻¹ and an intensity increase of a new band at 825 cm⁻¹. In addition, the band at 261 cm⁻¹ disappeared. These changes can be assigned to the transformation of the nitro species into NO₂⁻ ions, by comparison with a spectrum of pure Ba(NO₂)₂·H₂O.²³ In addition to the nitrite-related bands at 825 and 1335 cm⁻¹, the final spectrum of the series at 300 °C has Raman bands at 135, 733, and 1049 cm⁻¹, which are characteristic of crystalline Ba(NO₃)₂.²⁴

The temporal changes of the composition of the storage compound upon exposure of the material to 1% NO₂ exposure at 400 °C resemble very closely those reported at 300 °C. At 400 °C, slightly lower vibrational frequencies were observed. Previously, similar temperature-dependent frequency shifts have

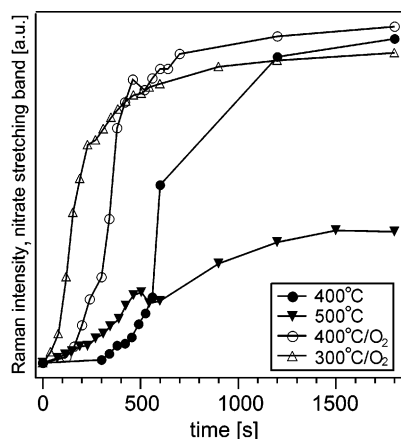
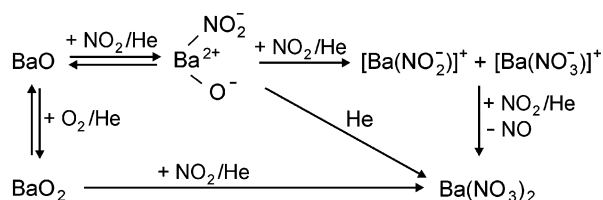


Figure 3. Temperature-dependent storage behavior of 1% NO₂ in 14 mol % BaO/MgO as measured on the basis of the intensity of the nitrate stretching band.

SCHEME 1



40% of the capacity obtained at 400 °C or in the presence of oxygen flow. In the presence of oxygen, BaO provides a similar storage capacity (as measured after 30 min) for temperatures between 200 °C and 400 °C. On the other hand, within the first 5 min the largest amount of NO₂ can be stored at 300 °C.

Mechanism for NO₂ Storage in 14 mol % BaO/MgO. On the basis of the above-mentioned results the reaction mechanism shown in Scheme 1 is proposed. Its essential features can be summarized as follows: (1) The reaction between nitrogen dioxide and BaO leads to the formation of a Ba⁺–NO₂[–] species which transforms into nitrite ions. Simultaneously, surface or amorphous nitrates are formed. Further NO₂ exposure leads to the formation of crystalline Ba(NO₃)₂. (2a) The presence of molecular oxygen increases the rate of nitrate formation at 200 °C and 300 °C, but it delays nitrate formation at 400 °C. At 400 °C, the reaction between molecular oxygen and BaO leads to the formation of crystalline BaO₂, which provides a reactive oxygen species for the direct formation of nitrates while suppressing nitro/nitrite species. (2b) At lower temperatures such as 200 °C and 300 °C, where no bulk BaO₂ is formed, the enhanced rate for nitrate formation in the presence of oxygen may result from either of two effects: First, the oxidation of Ba⁺–NO₂[–] by molecular oxygen is more effective than by NO₂, or second, *surface* peroxides, which are too small in concentration to be observed spectroscopically, but which do not delay the NO₂ storage by formation of bulk BaO₂, result in the facile formation of nitrate ions.

When the present spectroscopic results are compared with the theoretical results for the NO₂ storage on BaO(100),¹⁶ at temperatures below 500 °C, there is agreement about the initial formation of a nitro species (–NO₂) and the subsequent oxidation to nitrates. At higher temperatures (≥500 °C), however, the nitro- and nitrate-related bands appear simultaneously. Furthermore, experimentally, there is no indication for the nitrite–peroxide or nitrito complexes that were proposed to be reaction intermediates in nitrate formation. The theoretical

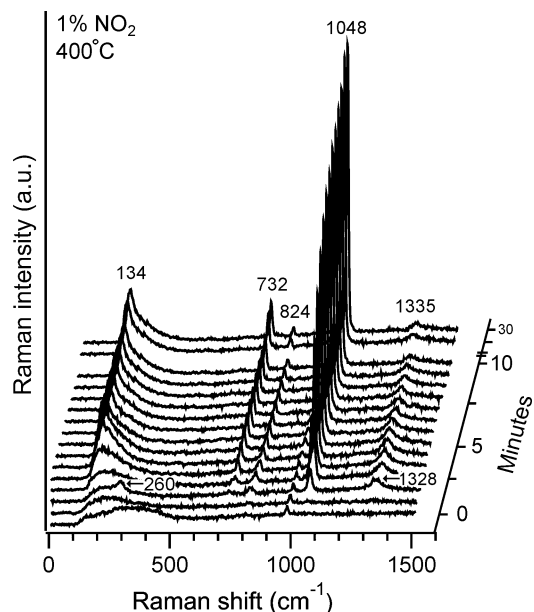


Figure 4. Raman spectra of 7 mol % BaO/MgO at 400 °C showing the temporal effect of exposure to 1% NO₂.

results do not address the transformation of the Ba⁺–NO₂[–] species into nitrite ions and the formation of crystalline Ba(NO₃)₂.

Coverage-Dependent Storage Behavior. Figure 4 depicts the storage behavior of NO₂ in 7 mol % BaO/MgO at 400 °C. In accordance with the results obtained at higher BaO loading (14 mol % BaO/MgO), both the formation of a barium–nitro species and its transformation into nitrite ions, as well as the formation of nitrates, are observed. After 30 min of exposure at both loadings, comparable amounts of NO₂ were stored. On the other hand, at the lower loading, nitrate formation sets in earlier (after only 2 min instead of 5 min at the higher loading) and simultaneously with the formation of the nitro species that transforms into nitrite ions within only 1 min after its first appearance. Obviously, the barium–nitro complex is less stable at lower loadings, in agreement with previous Raman studies on the mechanism of the NO decomposition on BaO/MgO catalysts.²⁰ Interestingly, this behavior is accompanied by a large increase in the initial rate for nitrate formation.

To correlate these differences in chemical reactivity with the structure of the used storage compounds, XRD and TEM were used. Typical TEM images of a 7 mol % (bottom) and a 14 mol % BaO/MgO sample (top) are shown in Figure 5. In addition, electron diffraction patterns were taken at the indicated areas of the samples and are shown as insets. According to the TEM image, at a loading of 14 mol %, a thick, rather homogeneous layer of BaO is formed. The electron diffraction pattern points to the formation of a bulk poly(crystalline) BaO phase which is confirmed by XRD. In contrast, at a loading of 7 mol %, the TEM image shows the formation of thin ordered layers of BaO on MgO particles having diameters of ca. 50–300 nm. At this BaO loading, no extended electron diffraction pattern can be obtained, which is in agreement with the fact that XRD gave no indication for the formation of crystalline BaO. Regarding the NO₂ storage behavior, these findings suggest that thin BaO layers destabilize the nitro species but, on the other hand, are more reactive toward NO₂ within the first minutes of exposure. On the basis of the Raman intensity of the nitrate stretching band after 30 min of exposure, the NO₂ storage capacity of BaO/MgO at the lower loading is smaller than at the higher loading. The capacity of the 7 mol % BaO

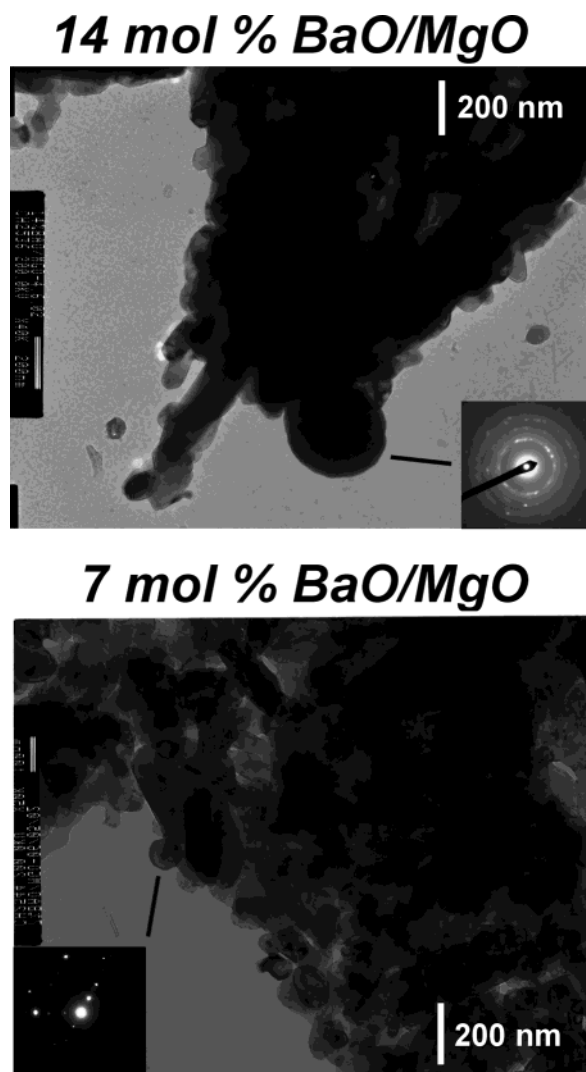


Figure 5. TEM images of 14 mol % BaO/MgO (top) and 7 mol % BaO/MgO (bottom) samples. Electron diffraction patterns from the indicated areas are shown as insets.

storage material amounts to 60% of the value at 14 mol % if absolute intensities are considered. If the corresponding Raman spectra are normalized with respect to the BaO-related peak at 986 cm^{-1} (to account for the different amounts of storage material), only 45% of the capacity at high BaO loading can be achieved.

Reduction of the Stored NO_2 . By using in situ Raman spectroscopy temporal changes of the composition of the storage material, as well as the formation of reaction products during the reduction of the stored NO_2 , were investigated. Carbon monoxide was used as the reducing agent. Prior to the reduction experiments, a significant amount of NO_2 was stored in BaO/MgO—predominantly as $\text{Ba}(\text{NO}_3)_2$ —by exposing 14 mol % BaO/MgO to 1% NO_2 for 10 min at $400\text{ }^\circ\text{C}$. Subsequently, the sample were cooled to $200\text{ }^\circ\text{C}$ and exposed to CO (at a flow rate of 20 mL/min). Up to $500\text{ }^\circ\text{C}$, no reaction was observed within 30 min of CO flow.

The top of Figure 6 depicts a series of Raman spectra upon exposure of the stored NO_2 to CO at $550\text{ }^\circ\text{C}$. Clearly, during the reaction with CO, $\text{Ba}(\text{NO}_3)_2$ was transformed completely into BaCO_3 , as confirmed by the presence of Raman bands at 694 and 1058 cm^{-1} , which can be attributed to the A_1' symmetric stretching mode and δ mode of carbonate ions, respectively.²⁹ As no Raman band around 1123 cm^{-1} was

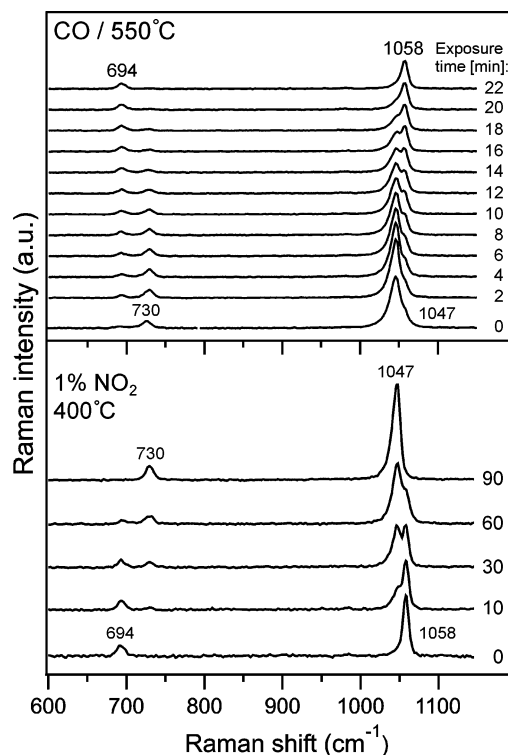


Figure 6. Raman spectra showing temporal changes of the composition of the storage compound during the reduction of stored NO_2 by CO at $550\text{ }^\circ\text{C}$ (top) and the transformation of BaCO_3 into $\text{Ba}(\text{NO}_3)_2$ at $400\text{ }^\circ\text{C}$ upon exposure to 1% NO_2 (bottom).

observed, the formation of significant amounts of MgCO_3 can be excluded. Unfortunately, during the reduction of $\text{Ba}(\text{NO}_3)_2$, the product of the oxidation reaction, CO_2 , reacts to undesirable carbonates due its high affinity toward BaO. In principle, the decomposition of BaCO_3 requires temperatures as high as $900\text{ }^\circ\text{C}$; however, as shown at the bottom of Figure 6, BaCO_3 can be transformed completely into $\text{Ba}(\text{NO}_3)_2$ at $400\text{ }^\circ\text{C}$ upon exposure to 1% NO_2 for a period of 90 min.

Conclusions

Using in situ Raman spectroscopy the NO_2 storage in BaO, a crucial and largely unexplored step in the NO_x storage-reduction cycle, could be studied in detail. Up to $400\text{ }^\circ\text{C}$, the NO_2 storage behavior in 14 mol % BaO/MgO is characterized by the formation of a barium–nitro species which transforms into nitrite ions while, simultaneously, nitrates are formed. Above $400\text{ }^\circ\text{C}$, although initially larger amounts of nitrates are formed, the overall storage capacities are substantially smaller than at lower temperatures. The presence of oxygen increases the rate for nitrate formation while largely suppressing nitro species/nitrite ions. At temperatures of $300\text{ }^\circ\text{C}/400\text{ }^\circ\text{C}$, the maximum rate and capacity for the NO_2 storage in 14 mol % BaO/MgO was found. At $400\text{ }^\circ\text{C}$, the formation of crystalline BaO_2 provides a direct pathway for the formation of nitrates.³⁰ At lower temperatures, the enhanced rate for nitrate formation may be due to surface peroxides or more facile oxidation of the barium–nitro complex by oxygen compared to NO_2 .

The reduction of the stored NO_2 by CO leads to the formation of CO_2 that limits the NO_2 storage process by forming thermally stable BaCO_3 . However, as BaCO_3 can be transformed into $\text{Ba}(\text{NO}_3)_2$ in the presence of NO_2 at $400\text{ }^\circ\text{C}$, this seems not to be a major limitation.

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References and Notes

- (1) Shelef, M. *Chem. Rev.* **1995**, *95*, 209.
- (2) Heck, R. M.; Farrauto, R. J. *Catalytic Air Pollution Control*; Van Nostrand-Reinhold: New York, 1995.
- (3) Iwamoto, M.; Hamada, H. *Catal. Today* **1991**, *10*, 51.
- (4) Burch, R.; Millington, P. J.; Walker, A. P. *Appl. Catal. B: Environ.* **1994**, *4*, 65.
- (5) Shinjoh, H.; Takahashi, N.; Yokota, K.; Sugiura, M. *Appl. Catal. B: Environ.* **1998**, *15*, 189.
- (6) Takahashi, N.; Shinjoh, H.; Iijima, T.; Szuki, T.; Yamazaki, K.; Yokota, K.; Suzuki, H.; Miyoshi, N.; Matsumoto, S.; Tanizawa, T.; Tanaka, T.; Tateishi, S.; Kasahara, K. *Catal. Today* **1996**, *27*, 63.
- (7) Bögnér, W.; Krämer, M.; Krutsch, B.; Pischinger, S.; Voigtländer, D.; Wenninger, G.; Wirbeleit, F.; Brogan, M.; Brisley, R.; Webster, D. E. *Appl. Catal. B* **1995**, *7*, 153.
- (8) Fridell, E.; Skoglundh, M.; Johansson, S.; Westerberg, B.; Törn-crona, A.; Smedler, G. *Stud. Surf. Sci. Catal.* **1998**, *116*, 537.
- (9) Fridell, E.; Skoglundh, M.; Westerberg, B.; Johansson, S.; Smedler, G. *J. Catal.* **1999**, *183*, 196.
- (10) Fridell, E.; Persson, H.; Olsson, L.; Westerberg, B.; Amberntsson, A.; Skoglundh, M. *Top. Catal.* **2001**, *16/17*, 133.
- (11) Olsson, L.; Persson, H.; Fridell, E.; Skoglundh, M.; Andersson, B. *J. Phys. Chem. B* **2001**, *105*, 6895.
- (12) Fridell, E.; Persson, H.; Westerberg, B.; Olsson, L.; Skoglundh, M. *Catal. Lett.* **2000**, *66*, 71.
- (13) Rodrigues, F.; Juste, L.; Potvin, C.; Tempè, J. F.; Blanchard, G.; Djéga-Mariadassou, G. *Catal. Lett.* **2001**, *72*, 59.
- (14) Westerberg, B.; Fridell, E. *J. Mol. Catal. A: Chemical* **2001**, *165*, 249.
- (15) Prinetto, F.; Ghiotti, G.; Nova, I.; Lietti, L.; Tronconi, E.; Forzatti, P. *J. Phys. Chem. B* **2001**, *105*, 12732.
- (16) Broquist, P.; Panas, I.; Fridell, E.; Persson, H. *J. Phys. Chem. B* **2002**, *106*, 137.
- (17) Hess, Ch.; Lunsford, J. H. *J. Phys. Chem. B* **2002**, *106*, 6358.
- (18) Mestl, G.; Rosynek, M. P.; Lunsford, J. H. *J. Phys. Chem. B* **1997**, *101*, 9321.
- (19) Jang, B.-H.; Yeon, T.-H.; Han, H.-S.; Park, Y.-K.; Yie, J.-E. *Catal. Lett.* **2001**, *77*, 21.
- (20) Xie, S.; Mestl, G.; Rosynek, M. P.; Lunsford, J. H. *J. Am. Chem. Soc.* **1997**, *119*, 10186.
- (21) At 200 °C, the introduction of NO₂ led to the formation of a small nitrate-related Raman peak at 1051 cm⁻¹ within the first 3 min. Once formed, it was constant in intensity, even after 20 min of NO₂/He flow.
- (22) Nolan, M. J.; James, D. W. *Aust. J. Chem.* **1970**, *23*, 1043.
- (23) The Raman spectrum of Ba(NO₃)₂·H₂O at 25 °C is characterized by two prominent bands at 829 and 1333 cm⁻¹.
- (24) Besides the nitrite-related bands, the shoulder at 220 cm⁻¹ indicates deviations from a Raman spectrum obtained for pure Ba(NO₃)₂ on MgO.
- (25) Ishii, Y.; Nagasaki, T.; Igawa, N.; Watanabe, H.; Ohno, H. *J. Am. Ceram. Soc.* **1991**, *74*, 2324.
- (26) This decrease in storage capacity is in agreement with a decrease in the nitrate-related Raman bands when Ba(NO₃)₂/MgO is heated from 400 °C to 500 °C or higher temperatures in He flow. Cooling the sample back to 400 °C did not result in a significant increase in band intensity; thus, the phenomenon is not a Raman effect.
- (27) In the second spectrum of this series a band at 1055 cm⁻¹ was observed which indicates a contribution from CO₃²⁻ ions, in agreement with previous findings for BaO/MgO at 300 °C (29).
- (28) Mestl, G.; Rosynek, M. P.; Lunsford, J. H. *J. Phys. Chem. B* **1998**, *102*, 154.
- (29) Lunsford, J. H.; Yang, X.; Haller, K.; Laane, J.; Mestl, G.; Knözinger, H. *J. Phys. Chem. B* **1993**, *97*, 13810.
- (30) Previous results demonstrated that nitrate ions were formed directly, even in the absence of gas-phase O₂, provided BaO₂ was present.¹⁷