

Mechanism for NO₂ Storage 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 was used to follow temporal changes in the composition of the catalyst that occurred during the reaction with NO₂. Up to catalyst temperatures of 400 °C, the formation of an intermediate barium–nitro phase precedes the formation of nitrate ions, which upon further exposure lead to the formation of bulk nitrates. In contrast, preoxidation of the catalyst or exposure to oxygen leads to the formation of peroxides that enhance the rate for nitrate formation while the formation of nitro species is suppressed above 300 °C. The spectroscopic results are in agreement with a reaction mechanism that has recently been proposed by Broquist et al. (*J. Phys. Chem. B* 2002, 106, 137) on the basis of DFT calculations.

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 The presence of excess oxygen, however, leads to the problem of eliminating the nitrogen oxides in the exhaust that are emitted under these conditions. One possible solution is to employ so-called “NO_x storage-reduction” (NSR) catalysts that are used in engines operating alternatively under lean and rich conditions.² 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.³ Several studies have been devoted to NO_x storage on alumina-supported barium oxide.^{3–13} 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.⁹ 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.¹² using FT-IR spectroscopy. According to Fridell et al.,¹¹ 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 this Letter we report on the mechanism of NO₂ storage in barium oxide at 400 °C. In situ Raman spectroscopy was used to monitor temporal changes in a model catalyst containing 14 mol % BaO on MgO upon exposure to 1% NO₂. The supported BaO that consisted of crystalline BaO containing defects, as shown by X-ray diffraction (XRD) and Raman spectroscopy, was stable up to 900 °C.¹⁴ In contrast, it has been

reported recently that Pt–BaO/Al₂O₃ catalysts show serious deactivation when exposed to high temperatures due to the reaction of Ba with alumina above 600 °C,¹⁵ which may cause problems with respect to a technical application. In addition, because NO₂ does not react with MgO under the conditions of these experiments (see below) the reactions of NO₂ with BaO can be studied in a straightforward manner, in contrast to previous studies in which Al₂O₃ was used as the support.^{9,11,12} Therefore, the results presented here allow a direct comparison with recent theoretical results by Broquist et al.¹³ dealing with the reaction of NO₂ with BaO(100). It will be shown that the present spectroscopic results are in agreement with the proposed reaction mechanism, which involves the formation of a nitro species (–NO₂) that is further oxidized to nitrates.

Experimental Section

The BaO/MgO catalysts were prepared, as described previously,¹⁶ by adding dropwise an aqueous solution containing the desired amount of Ba(NO₃)₂ (Baker, reagent grade) to a stirred slurry containing MgO (Fisher, light) and deionized water. 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 optical setup and the Raman cell were similar to those described previously.¹⁴ Briefly, the Raman spectrometer (Kaiser Optical) was equipped with a Nd:YAG laser that is frequency doubled to 532 nm. 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. 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 catalyst 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 catalyst, 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

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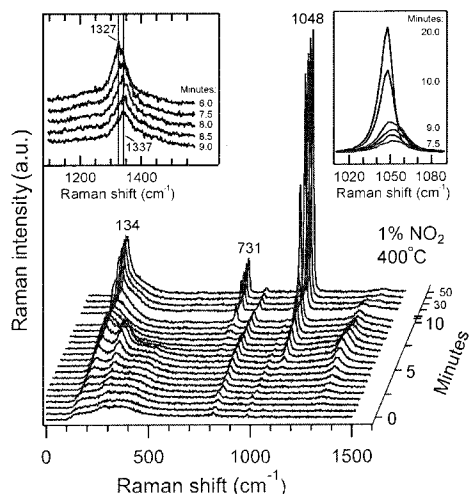


Figure 1. Raman spectra of 14 mol % BaO/MgO at 400 °C showing the temporal effect of exposure to 1% NO₂. The formation of the nitro species precedes the formation of nitrates. The insets depict the frequency shift associated with the transformation from the nitro complex to nitrite ions and the transformation of surface or amorphous nitrate ions to bulk nitrates (see text).

standard) and oxygen of ultrahigh purity (Matheson) with pure He (Praxair) so as to obtain the desired gas compositions. The mixture passed through the catalyst bed at 760 Torr at a flow rate of 40 mL/min, unless stated otherwise.

Results and Discussion

Figure 1 shows a series of in situ Raman spectra recorded at 40 s intervals at a catalyst temperature of 400 °C and 1% NO₂. Before the NO₂ was introduced, the catalyst had been stable at 400 °C for 4 h. The spectrum of BaO/MgO in He (the first spectrum shown) is characterized by a broad set of bands in the region of 100–600 cm⁻¹ and weak bands at 816 and 984 cm⁻¹. This spectrum has been attributed to defect-rich BaO.¹⁴ When NO₂ was introduced, new bands at 159, 259, 416, 811, 1225, and 1327 cm⁻¹ appeared within the first 3 min and increased with time. These bands are assigned to a nitro species, i.e., a ligand that is coordinated to the metal via the nitrogen atom (e.g., Ba²⁺–NO₂⁻), in agreement with previous studies.^{14,17}

After 5 min new bands appeared at 720 and 1051 cm⁻¹, which increased with time and are assigned to surface or amorphous NO₃⁻ ions. In the course of the reaction they transformed into bands at 730 and 1048 cm⁻¹, which are characteristic of bulk nitrates.¹⁴ The detection of the lattice phonon band at 134 cm⁻¹ is proof of crystallinity. In addition, the formation of crystalline Ba(NO₃)₂ was confirmed by X-ray diffraction (XRD) by taking a spectrum after exposure of the catalyst to 1% NO₂ for 10 min. Interestingly, after 5 min, while the NO₃⁻-related bands were increasing in intensity, there was a distinct shift in the maximum of the band at 1327 to 1337 cm⁻¹. At the same time the band at 254 cm⁻¹ disappeared and the intensity of a band at 822 cm⁻¹ increased. These changes are assigned to the transformation of the nitro species into NO₂⁻ ions, by comparison with a spectrum of pure Ba(NO₂)₂·H₂O.¹⁸ The nitrite-related bands reached maximum intensity at ca. 10 min and finally disappeared after ca. 45 min. The final spectrum of the series has bands at 134, 731, 1048, 1397, and 1634 cm⁻¹, which are characteristic of crystalline Ba(NO₃)₂. In a different set of experiments, the flowing gases were changed from NO₂/He to only He, as soon as the nitro species was formed (after ca. 4 min). Subsequently, within the next 15 min, the nitro species

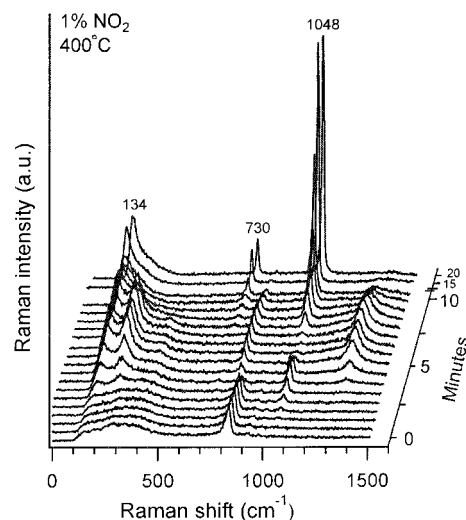


Figure 2. Raman spectra after preoxidation of a 14 mol % BaO/MgO catalyst with oxygen and the subsequent exposure to 1% NO₂ at 400 °C.

started to transform into nitrate ions, but even after 2 h the transformation was not complete.

In summary, exposure of the catalyst to NO₂ leads to the formation of a nitro species followed by the formation of nitrates. Simultaneously, the nitro species is transformed into nitrite ions. Finally, bulk nitrates are formed.

In further experiments the effect of adding O₂ before and during NO₂ exposure was studied. Figure 2 depicts a series of Raman spectra that were obtained after exposure of the catalyst to 25% O₂ in He for 4 min. Before the NO₂ was introduced, the catalyst had been stable at 400 °C for 2 h. The initial spectrum of the series is characterized by a broad set of bands in the region 100–600 cm⁻¹ (see Figure 1) and a band at 837 cm⁻¹, which can be assigned to crystalline BaO₂, as shown in previous studies.¹⁹ The minor feature at 930 cm⁻¹ is probably due to surface O₂²⁻ ions.

Within the first 4 min following the introduction of 1% NO₂, the peroxide band at 837 cm⁻¹ disappeared. Surprisingly, while this band was decreasing in intensity, NO₃⁻ was formed, as indicated by the growth of the band at 1053 cm⁻¹. This behavior is in contrast to the results presented above (see Figure 1), which showed that the formation of nitrates followed that of the nitro species when no oxygen was added. Moreover, after an initial increase in intensity, the NO₃⁻-related band suddenly disappeared after 4 min. At the same time, the bands related to the nitro species at 159, 259, 416, 811, and 1327 cm⁻¹ increased in intensity. Upon further NO₂ exposure, the nitro species transformed into nitrite ions, and nitrate ions were again formed. The latter resemble, although delayed, the behavior observed without oxygen treatment (see Figure 1).

As can be seen in Figure 3, exposure of the BaO/MgO catalyst simultaneously to 1% NO₂ and 20% O₂ at 400 °C and a flow rate of 50 mL/min resulted in the transient formation of the peroxide band and the direct formation of nitrates, even after about 2 min. Bands due to the nitro species were not detected; therefore, the presence of oxygen suppresses the formation of nitro-related bands and increases the rate of nitrate formation.

For catalyst temperatures between 300 and 400 °C, exposure to 1% NO₂ led to a similar sequence of spectra as described above, i.e., the formation of a nitro species followed by the formation of nitrates. The presence of oxygen favored the formation of nitrate ions. In contrast to the results obtained with the sample at 400 °C, the formation of nitro species was not

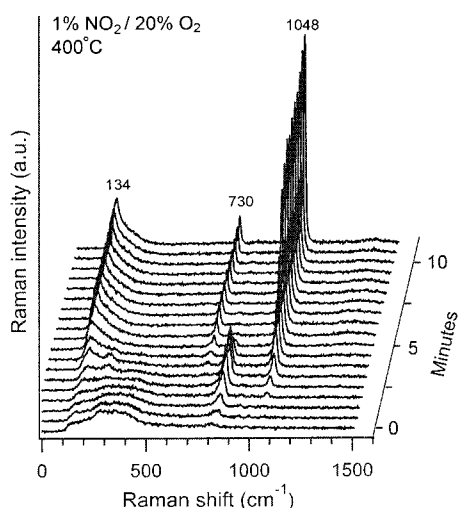
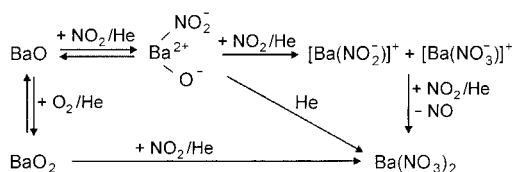


Figure 3. Raman spectra of 14 mol % BaO/MgO at 400 °C showing the temporal effect of exposure to 1% NO₂/20% O₂.

SCHEME 1



completely suppressed at lower temperatures. Details of the temperature-dependent behavior of the NO₂ storage will be described in a subsequent publication.

Conclusions

On the basis of these observations the reaction mechanism shown in Scheme 1 is proposed. Its essential features are as follows: (1) The reaction between nitrogen dioxide and BaO leads to the formation of a Ba²⁺–NO₂[–] species, which transforms into nitrite ions. At the same time surface or amorphous nitrates are formed and, upon further exposure, crystalline Ba(NO₃)₂ is produced. (2) The presence of molecular oxygen suppresses the formation of the Ba²⁺–NO₂[–] species and increases the rate of nitrate formation. (3) At higher temperatures (e.g., 400 °C) the reaction between molecular oxygen and BaO leads to the formation of crystalline BaO₂, which transforms nitro species into nitrate ions. As indicated in Scheme 1, nitro species can transform into nitrates at 400 °C without further exposure to NO₂. The oxidation may

either involve adjacent substrate oxygen ions or NO₂ obtained as a result of the reversible decomposition of Ba²⁺–NO₂[–].

When the present spectroscopic results are compared with the theoretical results for the NO₂ storage on BaO(100),¹³ it is evident that there is agreement about the initial formation of a nitro species (–NO₂) and the subsequent oxidation to nitrates. On the other hand, experimentally, there is no indication for nitrite–peroxide or nitrito complexes that were proposed to be reaction intermediates in nitrate formation. The theoretical results do not address the transformation of the Ba²⁺–NO₂[–] species into nitrite ions and the formation of crystalline Ba(NO₃)₂.

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