Water-induced morphology changes in BaO/γ-Al_2O_3 NO_x storage materials

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Received (in Berkeley, CA, USA) 20th September 2006, Accepted 28th November 2006
First published as an Advance Article on the web 12th December 2006
DOI: 10.1039/b613674e

Exposure of NO_2-saturated BaO/γ-Al_2O_3 NO_x storage materials to H_2O vapour results in the conversion of surface nitrates to $Ba(NO_3)_2$ crystallites, causing dramatic morphological changes in the Ba-containing phase, demonstrating a role for water in affecting the NO_x storage/reduction properties of these materials.

The demand to develop highly fuel efficient internal combustion engines that require operational conditions of high air-to-fuel ratios (20 or higher) coincides with increasingly stringent environmental regulations on harmful exhaust gas emission levels. Under highly oxidizing (lean) conditions traditional, 3-way catalysts are unable to reduce NO_x due to their high oxidation efficiency that converts essentially all of the reducing agents present in the exhaust stream to CO_2. One of the promising technologies being considered is lean NO_x trap (LNT) systems,[1–3] that operate under cyclic fashion. NO_x is being stored on the storage component (*e.g.* BaO supported on γ-Al_2O_3) of the system primarily as nitrates in the lean cycle. Upon saturation of the NO_x storage material, a brief reducing cycle is applied in which NO_x is reduced by the precious-metal component (*e.g.* Pt) of the system, similarly to that known from 3-way automotive catalysis. Recently significant efforts have been focused on understanding the uptake of NO_x (in particular NO_2) by the Ba-containing phase. A number of spectroscopic investigations have clearly identified the presence of two different types of nitrate species present on the BaO phase upon its exposure to NO_2.[4–11] These species were identified as surface nitrates (strongly held NO_2 on the monolayer of BaO on the surface of alumina support), and bulk nitrates (nitrates that formed by the reaction of BaO particles with NO_2).[11] The thermal, chemical and spectroscopic properties of these two types of nitrate species are distinctly different. For example, surface nitrates decompose at a lower temperature than bulk nitrates and, more importantly, their desorption product is exclusively NO_2, while bulk nitrates decompose as NO + O_2 at high temperatures similarly to unsupported $Ba(NO_3)_2$ (~800 K).

Despite the extensive fundamental studies that have been conducted on these materials, key issues that strongly influence the performance of these catalytic systems still remain. One of the major concerns comes from the fact that under lean conditions the water level in the exhaust gas is very high (~10%). Previous studies have indicated a detrimental effect (although in widely varying extent) of water on the performance of these NO_x storage materials;[12–15] however no clear understanding of this effect has been developed.

Inspired by the contrasting explanations given for the effects of water on these systems, we conducted Fourier transform infrared spectroscopy (FTIR), temperature programmed desorption (TPD), and synchrotron time-resolved X-ray diffraction (TR XRD) experiments on BaO/γ-Al_2O_3 materials. The emphasis of our investigation was to follow the fate of different nitrate species formed during NO_2 adsorption (FTIR), and the corresponding changes in the morphologies of the Ba-containing phase (TR-XRD) as the samples were exposed to water.

Fig. 1 displays three FTIR spectra obtained after an 8 wt% BaO/γ-Al_2O_3 sample was first saturated with NO_2 (spectrum (a)) then exposed to H_2O at 300 K (spectrum (b)), and finally during TPD at 640 K sample temperature (spectrum (c)) . The amount of water added to the system in this experiment is very small, and the equilibrium water vapour pressure was less than 0.2 Torr after the introduction of the last H_2O dose.

Exposure of the clean BaO/γ-Al_2O_3 sample to NO_2 resulted in the development of IR features (spectrum (a)) characteristic of both surface (1294, 1582 cm^{-1}) and bulk (1325, 1434–1480 cm^{-1}) nitrate species associated with BaO,[11] while evidence was also seen for the formation of surface nitrates on the alumina support (1270, ~1620 cm^{-1}). Upon the introduction of H_2O onto the NO_2-saturated sample, first a significant drop in the intensities of IR

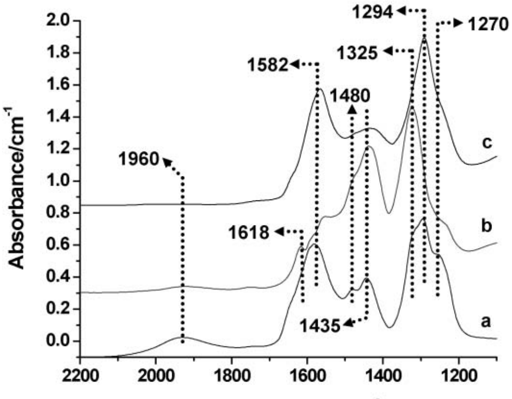

Fig. 1 FTIR spectra collected at 300 K from an 8 wt% BaO/γ-Al_2O_3 sample after NO_2 saturation (a), subsequent H_2O exposure (b), and during TPD between 640 and 670 K (c).

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features representing the vibrations of surface nitrates is observed, parallel with intensity gains of the IR bands characteristic of bulk nitrates. At the end of the water dosing experiment, no surface nitrate-related IR bands can be observed, while the intensities of the bulk nitrate features reach maxima (spectrum (b)). After the disappearance of the surface Ba-nitrate-related features, a sharpening of the alumina support-related nitrate bands (*e.g.* 1618 cm^{-1}) is clearly seen. These changes in the IR spectra as a result of H_2O exposure of an NO_2-saturated BaO/γ-Al_2O_3 sample strongly suggest the conversion of surface Ba-nitrates to bulk-like $Ba(NO_3)_2$.

TR XRD has proven to be an excellent technique to follow morphological changes in the BaO/γ-Al_2O_3 NO_x storage systems.[16] Therefore, in order to verify the proposed significant changes in the morphology of the Ba-nitrate phase on the alumina support as a result of H_2O exposure at 300 K, TR-XRD experiments were carried out. Two XRD patterns in the 9–14° 2θ range are shown in Fig. 2 that were obtained from an NO_2-saturated 20 wt% BaO/γ-Al_2O_3 NO_x storage material prior to (spectrum (a)), and following (spectrum (b)) H_2O exposure at 300 K.

The XRD pattern recorded after NO_2 saturation is identical to that we have reported previously,[16] and characteristic of nanosized $Ba(NO_3)_2$ with average particles sizes of $\sim$5 nm. Exposure of this sample to H_2O at 300 K results in intensity increases and sharpening of diffraction peaks characteristic of the $Ba(NO_3)_2$ phase (spectrum (b)). These dramatic changes in the XRD pattern suggest the formation of large $Ba(NO_3)_2$ particles on the alumina support surface caused by the exposure of the NO_2-saturated BaO/γ-Al_2O_3 sample to H_2O. The average particle size estimated from the FWHM of the (111) diffraction peak is >15 nm. The trends in the XRD results were identical for 8 wt% BaO/γ-Al_2O_3, except the intensities of the diffraction peaks were lower in accord with the lower amount of BaO initially present in that sample.

The next question we need to address is whether this morphology change reversible? To this end, we conducted TPD experiments following the NO_2/H_2O co-adsorption studies. During the TPD run, we recorded IR spectra at every 30 K, and monitored the evolving gases by a mass spectrometer. The results of the TPD experiments are summarized in Fig. 3.

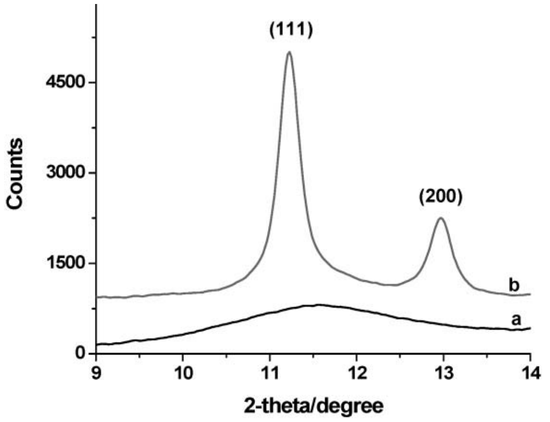


Fig. 2 TR-XRD patterns collected before (a) and after (b) H_2O exposure of an NO_2-saturated 20 wt% BaO/γ-Al_2O_3 at 300 K.

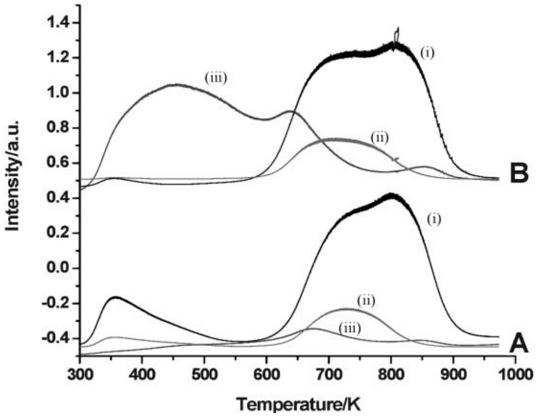
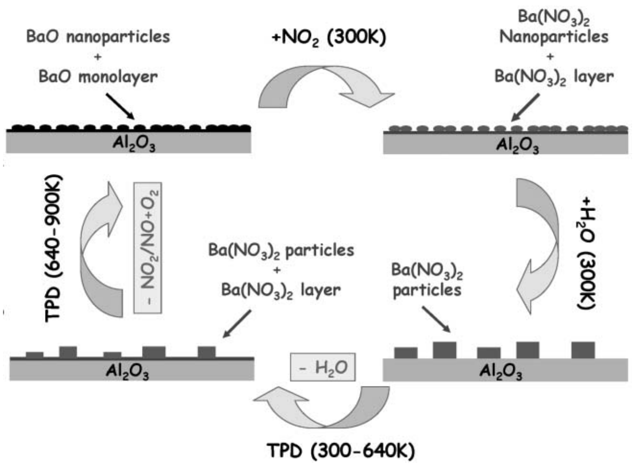


Fig. 3 TPD spectra obtained from a 20 wt% BaO/γ-Al_2O_3 sample after NO_2 saturation (A), and following H_2O exposure of the NO_2-saturated sample (B). (m/z = 30 (i), 46 (ii) and 18 (iii); heating rate: 12 K min^{-1}.)

Two sets of TPD data (intensities of the *m*/*z* 18, 30 and 46 signals) are displayed for an NO_2-saturated 20 wt% BaO/γ-Al_2O_3 sample prior to (spectra A), and following (spectra B) H_2O exposure. Comparing the NO_x desorption features (*m*/*z* 30 and 46) from these two samples, the shape and also the intensities (and intensity ratios of the *m*/*z* 30/46 signals) of these features are strikingly similar. (Here we consider only the high-temperature desorption features (>550 K), since the low-temperature features, arising primarily from weakly adsorbed N_2O_3, are easily removed by adsorbed H_2O. Therefore, these features are absent in the TPD spectrum of the sample that was exposed to water prior to the TPD run.) We have shown previously[11] that the relative intensities of the high-temperature NO_x desorption features (NO_2 at $\sim$730 K, and NO + O_2 at $\sim$805 K) are dependent on the amount of bulk nitrates present; *i.e.* from NO_2-saturated 8 wt% BaO/γ-Al_2O_3 sample the majority of the NO_x stored desorbs as NO_2, since most of the BaO present on the alumina surface prior to NO_2 exposure is in the form of a monolayer uniformly covering the support oxide. On the other hand, for the 20 wt% BaO/γ-Al_2O_3 material we observed a large amount on NO desorption at high temperature (accompanied by O_2 desorption) in accord with the thermal decomposition of bulk nitrates (the amount of BaO present in the starting material is higher than that needed for the completion of a monolayer). Just considering the IR and XRD data obtained after H_2O exposure of the NO_2-saturated samples discussed above, one might have expected to observe desorption only from the bulk nitrate state (NO + O_2) at the expense of the desorption from the surface state (NO_2 desorption). The results, however, suggest that, during the temperature ramp of the TPD experiment as water desorbs the surface nitrate layer re-forms on the alumina surface. Consequently, the intensities of TPD traces of NO_x species are very similar from the two samples, regardless of the absence or presence of H_2O on the samples after NO_2 saturation. The results of FTIR measurements conducted during the TPD experiments also support the re-formation of the surface nitrate layer as water is desorbing from the sample. Spectrum (c) in Fig. 1, collected during the TPD experiment at 640–670 K temperature range, reveals that the intensities of the IR signatures of surface nitrates are very close to those recorded prior to H_2O exposure, while those of the bulk nitrates decreased significantly (compare spectrum (c) to spectrum (a)). In the 300–670 K temperature range most of the water desorbs from the catalyst, and the initial surface-to-bulk nitrate ratio is re-established. In the



Scheme 1

XRD patterns no obvious changes were observed during the TPD process up to 640 K, although the IR results clearly show the re-formation of surface nitrates (XRD is only able to detect crystalline phases). Scheme 1 (below) clearly indicates, that the average crystallite size after NO_2 adsorption is very different from that after heating to 640 K of a water-saturated, NO_2-dosed sample (bulk, but nano-sized *vs.* large $Ba(NO_3)_2$ crystallites).

The last issue we need to discuss is how these findings may contribute to the understanding of the effect of H_2O on the performance of NO_x storage materials. Several previous reports have addressed the adverse effect of water on BaO/γ-Al_2O_3-based NO_x storage materials.[12–15] Water was shown to negatively influence the NO_x uptake properties primarily at low operating temperatures.[12,14] Epling *et al.*[12] reported that the presence of water shortened the time period before NO_x slip occurred. Toops *et al.*[14] attributed the effect of water to the reduction of NO_x uptake by the alumina support, as it eliminates NO_x adsorption sites where nitrates can form. Cant and Patterson[13] observed a significant change in the NO_x TPD profiles when they used a 1% H_2O/He purge gas mixture, instead of pure He. The intensity of the low-temperature desorption feature (desorption of NO_2) decreased, while that of the high-temperature one ($NO + O_2$) increased accordingly. The common feature of all of these findings is that they were primarily observed at low operating temperatures ($<$550 K).

The changes in the morphology of the Ba-containing phase in the presence of water discussed in this communication can account for most of the variations in the NO_x uptake properties reported previously. In the NO_x uptake process in the presence of water, large $Ba(NO_3)_2$ particles form. This has two consequences on the NO_x storage: (1) it slows down the NO_x uptake as it decreases the contact between the active storage phase (BaO) and the Pt particles where NO_2 is being formed; (2) by forming large Ba-nitrate particles the diffusion of NO_2 into the bulk is also slowed. However, it does not affect the total amount of NO_x stored, rather it slows down the rate towards NO_x saturation. The TPD results of Cant and Patterson[13] can also be explained by our data: since water is present in the He flow which is used during the TPD experiment, water remains on the surface up to fairly high temperatures, thus preventing the reformation of surface nitrates. As a consequence, the low-temperature TPD feature that originates from NO_2 desorption from surface nitrates loses intensity, while the high-temperature feature coming from the decomposition of bulk nitrates gains intensity in the presence of water. The suppression of NO_2 adsorption on the alumina surface by the competitive adsorption of water[14] is inconsistent with our recent results on the effect of water on NO_2 adsorption on γ-Al_2O_3.[17] In this latter work we show that the amount of NO_x stored as surface nitrates on alumina is unaffected by the presence of water, although the ratio of differently coordinated nitrate species changes significantly when an NO_2 saturated γ-Al_2O_3 sample was exposed to water.

The conclusion of our results is summarized in Scheme 1. It depicts the formation of surface and nano-sized Ba-nitrate species upon the exposure of a BaO/γ-Al_2O_3 sample to NO_2 at 300 K.[16] When this NO_2-saturated sample is subjected to water vapour, surface nitrates are converted to bulk nitrates. Removing the water (*e.g.* by temperature ramping) results in the re-formation of the surface nitrate layer. The presence of water can influence the surface/bulk nitrate ratio; however, the total amount of stored NO_x remains unaffected by H_2O.

We wish to acknowledge the financial support of this work by the US DOE, Office of Freedom Car and Vehicles Technology and Basic Energy Sciences.

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