The effect of water and reductants on the release of nitrogen oxides stored on BaO/Al_2O_3

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The effect of water and reductants (CO and H_2) on the decomposition of NO_x stored on BaO/Al_2O_3 at 300 °C has been investigated. Water eliminates the initial rapid total uptake of NO_2 but has little effect on the subsequent formation of nitrates that is accompanied by evolution of NO. Water hinders liberation of NO_2 and NO during temperature-programmed decomposition of stored NO_x. Both CO and H_2 lower the temperatures required for decomposition through reduction of NO_2 to NO and N_2 thus restricting NO_2 readsorption. The rate of reduction is lower with H_2 than with CO.

KEY WORDS: NO_x storage catalysts; barium oxide; aluminum oxide; decomposition of stored nitrate; reduction of stored nitrate.

1. Introduction

Catalysts that operate via the sequential storage and reduction of nitrogen oxides are an effective technology for emission control of gasoline direct injection engines operating in lean-burn mode if sufficiently low sulfur fuel is available [1,2]. Platinum is used to oxidize NO during lean operation, the resulting NO_2 being stored on a basic oxide such as that of barium [3]. A subsequent period of rich operation destabilizes the stored NO_x which is then reduced to nitrogen on the platinum and/or the rhodium or palladium that is included to provide standard three-way catalysis during stoichiometric operation.

Work over the past few years has established many details of the chemistry involved in NO_x storage catalysts with the storage process proving rather complex [4]. Infrared studies confirm that NO_2 is stored more strongly than NO with surface nitrite species seen first followed by nitrates [4,5], the latter also being detectable in bulk by X-ray diffraction (XRD) [4,6,7]. The conversion of NO_2 to NO_3^- implies oxidation, with O_2 or NO_2 as the possible oxidants. In recent work using BaO/Al_2O_3 we have shown that O_2 is not used even if it is present in large excess [8]. Instead some NO_2 is converted to NO with the overall uptake stoichiometry corresponding to approximately

$$BaO(s) + 3NO_2(g) \longrightarrow Ba(NO_3)_2(s) + NO(g) \qquad (1)$$

Evolution of NO is also apparent during NO_2 uptake when Pt is present [9] but NO_2/NO equilibration on the metal is a possible complication in that case. Likewise, the presence of Pt may alter the NO_2/NO distribution during temperature-programmed decomposition of stored NO_x. With $Pt/BaO/Al_2O_3$, NO alone is seen in some studies [10] whereas BaO/Al_2O_3 yields two peaks with NO_2 evolved at ~460 °C followed by NO above 500 °C [8]. Alumina stores NO_2 to a much lesser extent, with proportionately less evolution of NO, and it is released as a single peak of NO_2 at ~430 °C [8].

Under exhaust gas conditions $Ba(OH)_2$ and $BaCO_3$ are thermodynamically favored over BaO so NO_x storage may take place with displacement of water or CO_2 rather than by simple nitrate formation. Some recent calculations indicate that conversion of bulk $BaCO_3$ to bulk $Ba(NO_3)_2$ becomes unfavorable at elevated temperature (>150 °C [7] or 340 °C [8]) during lean operation, a possible implication being that storage occurs on a dispersed surface phase rather than as a bulk one. The presence of the former has been inferred from quantitative XRD studies showing that bulk $BaCO_3$ accounts for one-half or less of the total barium present after calcination and exposure to air [7,10]. Experimentally the presence of CO_2 does not prevent storage on BaO/Al_2O_3 at 400 °C [8] although it does reduce the capacity of $Pt/BaO/Al_2O_3$ [10,11] and also enhances release of NO_x [12].

The present work had two aims. One was to determine the extent to which water might also affect NO_x storage and release processes on alumina and baria/alumina. The other was to establish if reductants, CO and H_2, influenced the desorption characteristics. In practical Pt-containing catalysts, reduction of released gaseous NO_x would be expected to be small on the oxides compared to that on the metal(s). Nonetheless it is still of interest to know if decomposition of the stored material is itself influenced by the presence of reductants and this can be followed only if the metal is absent.

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2. Experimental

The experimental procedures used here were similar to those described in detail previously [8]. In essence, BaO/Al_2O_3 containing 9 wt% Ba was made by successive impregnation of a washcoat-type alumina (Condea, $140\,m^2/g$) using a solution of barium nitrate. After drying at 110 °C, it was calcined in flowing air for 3 h at ~500 °C. Crystalline orthorhombic $BaCO_3$ (witherite) was then detectable by XRD but other studies on similar preparations indicate that this is likely to account for one-half or less of the total barium present [7,10]. The uptake and release of NO_x was studied in a flow system using 40 mg samples contained in 4 mm i.d. quartz tubes and conditioned in flowing $NO_2/O_2/He$ on a ramp to 550 °C followed by He at 550 °C.

Uptake and release was measured from a stream containing ~1000 ppm NO_2, 3% O_2 in a carrier of 0.07% Ar in He with a combined flow rate of $50\,cm^3/min$. The exit stream was analyzed by a quadrupole mass spectrometer (Balzers Thermostar), a micro gas chromatograph (MTI model M200) and, after dilution with a known flow of N_2, by a chemiluminescent NO_x analyzer (Ecotech model 9841) that determined NO and NO_x ($NO + NO_2$) alternately on a ~12 s cycle time. The mass spectrometer signals at m/z of 30 and 46 were processed to provide NO and NO_2 using a procedure that allowed for fragmentation and changes in sensitivity (when switching from streams without NO_2 to those with NO_2) and then normalized against the chemiluminescent values. Similarly the mass spectrometer signals calculated for CO (from $m/z = 28$), O_2 (32), CO_2 (44), H_2 (2) and N_2 (28 with H_2 present, 14 with CO present) were normalized to analyses by the chromatograph which has a sensitivity in the low ppm range for all except H_2. The chromatograph enabled analysis for trace amounts of nitrous oxide. The system had a detection limit of ~10 ppm for ammonia using mass spectrometry (at $m/z = 16$) and, in one specific test, by on-line FTIR (with a resolution of $0.25\,cm^{-1}$).

Blank tests using an empty reactor showed a small uptake and release of NO_2 on metal components in the system that was somewhat greater with water present. The release plots that follow have been corrected for these effects.

3. Results and discussion

3.1. NO_2 uptake in the presence and absence of water

The present uptake measurement experiments were carried out at a lower temperature (300 °C) than the 400 °C used earlier [8] in order to minimize NO_x desorption prior to commencement of the temperature ramp during subsequent decomposition experiments. Data for uptake from ~1000 ppm NO_2 in 3% O_2/He in the absence and presence of water are shown in figures 1(A) and (B) respectively. In the dry system there is an initial period lasting ~80 s in which all NO_2 is taken up, probably as surface nitrites if infrared measurements are a guide [4,5]. Thereafter uptake is partial and accompanied by the evolution of NO which exhibits a maximum concentration of ~260 ppm after ~210 s. The stoichiometry from then on corresponds approximately to reaction (1).

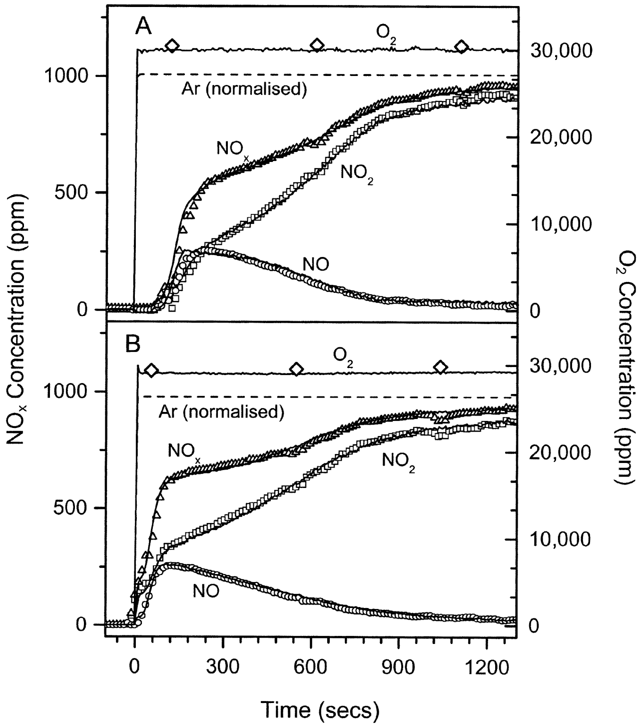

Figure 1. Uptake of NO_2 from ~1000 ppm NO_2 plus 3% O_2 in Ar/He on 40 mg BaO/Al_2O_3 at 300 °C in the absence of water (A) and in the presence of ~1% water (B). Chemiluminescent analyzer and gas chromatograph, open symbols; mass spectrometer, solid line with Ar (dashed line) normalized to match NO_2 concentration after 3600 s.

The presence of ~1% (~10 000 ppm) water eliminates the initial complete uptake entirely (figure 1(B)). Partial uptake with NO evolution is brought forward and then proceeds as with the dry stream. This is in accord with that expected for the reaction

$$Ba(OH)_2(s) + 3NO_2(g) \longrightarrow Ba(NO_3)_2(s) + NO(g) + H_2O(g) \qquad (2)$$

Calculations carried out as described previously for the corresponding reaction involving $BaCO_3$ [8] indicated that the residual NO_2 concentration expected at equilibrium would be <1 ppm at 300 °C and that the potential extent of reaction would remain >97% until 520 °C.

NO_2 was also taken up on alumina alone at 300 °C but in smaller amounts. In the dry state the period of complete uptake was much shorter (<25 s) and, as found previously [8], the concentration of NO formed during the subsequent partial uptake was also less. The presence of water eliminated the period of complete uptake entirely. Production of NO then reached a maximum almost immediately but there was little effect on the subsequent partial uptake.

3.2. Decomposition of stored NO_x in the presence and absence of water

Water had no effect on the temperature-programmed decomposition of NO_x stored on alumina alone. In both situations, decomposition took place with concurrent peaks of NO_2 and O_2 at 430 °C. The NO_2/O_2 ratio was ~4, as expected for the stoichiometric decomposition of a metal nitrate, with the maximum concentration of NO one-tenth that of NO_2.

Results for the decomposition of NO_x stored on BaO/Al_2O_3 on a ramp at 5 °C/min in the presence and absence of water are shown in figure 2. The dry system (figure 2(A)) shows incompletely resolved peaks of first NO_2 and then NO with maximum concentrations at 435 and 520 °C respectively. Although the peak concentration of NO is less than that of NO_2, it is accompanied by more O_2 as expected if the decomposition is given by

$$Ba(NO_3)_2 \longrightarrow BaO + 2NO + 1\tfrac{1}{2}O_2 \qquad (3)$$

rather than by

$$Ba(NO_3)_2 \longrightarrow BaO + 2NO_2 + \tfrac{1}{2}O_2 \qquad (4)$$

With water present (figure 2(B)), decomposition proceeds distinctly differently. Evolution of NO_2 is delayed with an initial peak reached at 455 °C and a second smaller one at 525 °C. The peak in NO concentration also occurs at a slightly higher temperature and is more sharply defined than for the dry system. Correspondingly, evolution of O_2 proceeds more slowly to begin with than in the wet system with a subsequent well-defined maximum matching that of NO.

Overall it is apparent that water slows decomposition of NO_x stored on the barium-containing system. This is unexpected since on mass action grounds one would expect it to aid NO_x liberation via the reaction

$$Ba(NO_3)_2 + H_2O \longrightarrow Ba(OH)_2 + 2NO_2 + \tfrac{1}{2}O_2 \qquad (5)$$

There are two potential explanations. One is that adsorbed water, or hydroxyl groups derived from it, interacts with the stored NO_x in some way and increases the binding energy. This has been reported at temperatures below 300 °C but not at higher temperatures [10], and seems unlikely especially as water has little effect on desorption from alumina. The alternative is that the NO_x initially released from the surface is replaced by a crust of $Ba(OH)_2$ which impedes migration of the remaining NO_x lying underneath. The eventual onset of NO_x evolution cannot be associated with decomposition of bulk hydroxide, which has a calculated decomposition temperature of ~620 °C for the water pressure used here. However, it might reflect decomposition of a surface hydroxide that is less stable than the bulk form in the same way that dispersed carbonate appears less stable than bulk $BaCO_3$ [7]. It is also noteworthy that $Ba(OH)_2$ melts at 410 °C in which case transport of underlying NO_x to the surface may become easier at higher temperatures.

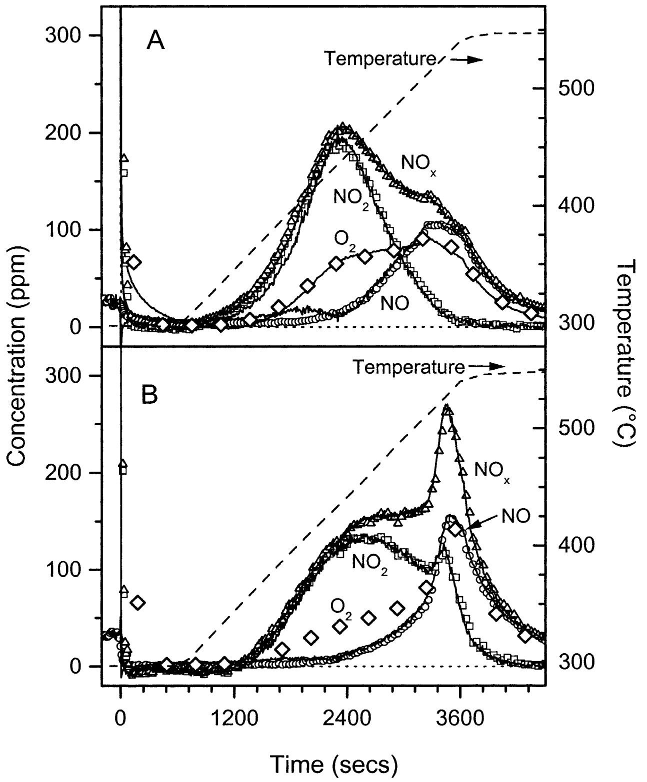

Figure 2. Decomposition of NO_x stored on 40 mg of BaO/Al_2O_3 on a ramp to 550 °C at 5 °C/min: (A) into He alone after uptake as per figure 1(A); (B) into ~1% H_2O/He after uptake as per figure 1(B). Chemiluminescent analyzer and gas chromatograph, open symbols; mass spectrometer, solid lines with Ar dashed.

3.3. Decomposition of stored NO_x in the presence of CO and H_2

Decomposition of stored NO_x in the presence of reductants was carried out under dry conditions. The behavior with 5000 ppm CO present, shown in figure 3, is distinctly different from that in He (figure 2(A)). NO_2 is observed in low concentrations only and confined to a narrow range of temperatures, 380–400 °C. In compensation, the peak concentration of NO is much higher and reached at a much lower temperature, 410 °C compared to 520 °C using helium alone. It is clear that CO is reducing NO_2 according to

$$NO_2 + CO \longrightarrow NO + CO_2 \qquad (6)$$

with some reaction at temperatures as low as 300 °C. It is also apparent from figure 3 that the fall-off in NO concentration above the maximum is associated with the production of N_2 by further reduction

$$NO + CO \longrightarrow \tfrac{1}{2}N_2 + CO_2 \qquad (7)$$

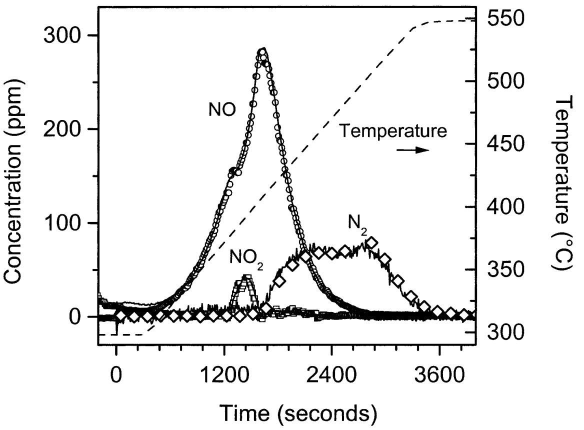

Figure 3. Decomposition of NO_x stored on 40 mg of BaO/Al_2O_3 at 300 °C as per figure 1(A) into a stream of 5000 ppm CO in He on a ramp to 550 °C at 5 °C/min after 5 min of flushing in He. Chemiluminescent analyzer and gas chromatograph, open symbols; mass spectrometer, solid lines.

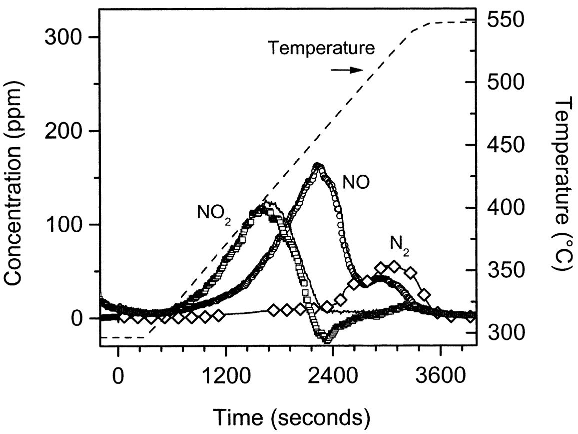

Figure 4. Decomposition of NO_x stored on 40 mg of BaO/Al_2O_3 at 300 °C as per figure 1(A) into a stream of 2500 ppm H_2 in He on a ramp to 550 °C at 5 °C/min after 5 min of flushing in He. Chemiluminescent analyzer and gas chromatograph, open symbols; mass spectrometer, solid lines.

Very little (<5 ppm) N_2O was formed and no O_2 was detectable.

The corresponding result for the decomposition of stored NO_x in H_2 is shown in figure 4, the pattern being intermediate between that observed with the other systems. The concentration of NO_2 is higher than when using CO (figure 3) but less than in helium (figure 2(A)). Thus reduction of NO_2 to NO by H_2

$$NO_2 + H_2 \longrightarrow NO + H_2O \qquad (8)$$

is slower that the corresponding reduction by CO, reaction (6). Similarly, it is apparent that the further reduction of NO to N_2 by H_2

$$NO + H_2 \longrightarrow \tfrac{1}{2}N_2 + H_2O \qquad (9)$$

is also slower than that by CO, reaction (7), since the fall-off in NO concentration associated with the onset of N_2 production occurs at a higher temperature. Mole balance calculations indicated that hydrogen consumption was significantly greater than that which could be accounted for by reduction of NO_2 to NO and N_2, suggesting that some ammonia might also be forming. However, none could be detected in the product stream by mass spectrometry or FTIR to the detection limit of ~10 ppm.

It may be noted that the NO_2 concentrations registered by the chemiluminescent analyzer (open squares in figure 4) deviate from the mass spectrometer trace (continuous line) and become negative at temperatures above 450 °C. This behavior is the result of an instrumental artifact arising because some NO undergoes reduction by H_2 within the chemiluminescent analyzer prior to the determination of total NO_x (i.e. $NO + NO_2$). Ammonia, if present, might contribute to production of the same artifact but none was observed by mass spectrometry or FTIR as noted above.

If the decompositions of stored NO_x in He, CO and H_2 are compared in terms of the total N being evolved, then it is apparent that the two reductants do facilitate the liberation process with maximum rates at 435, 414 and 429 °C respectively. The operative mechanism is probably through a reduction in the rate of readsorption, which is usually substantial during desorption from packed beds of porous particles [13,14]. With helium alone as the carrier, evolved NO_2 molecules are likely to strike sites being vacated by other NO_2 molecules during transport out of the system and hence be readsorbed. If they are reduced to NO and N_2 then readsorption in the same form cannot occur and transport out of the system is facilitated.

Table 1 summarizes the quantities of NO_x stored in the experiments illustrated in figures 1–4 based on uptake and release measurements. The latter are likely to be more accurate since the slow approach to the plateau during uptake makes it difficult to determine when this process is complete. (The present calculations use the NO_x concentration after ~1 h as the cut-off point.) As may be seen, alumina appears responsible

Table 1
Uptake and release of NO_2 for BaO/Al_2O_3 and Al_2O_3 at 300 °C

Substrate	H_2O (%)	Reductant	Uptake (mmol/g) [a]	Release (mmol/g)
Al_2O_3	0	–	0.22	0.18 [b]
Al_2O_3	~1	–	0.17	0.09 [b]
BaO/Al_2O_3	0	–	0.35	0.34 [b]
BaO/Al_2O_3	~1	–	0.25	0.33 [b]
BaO/Al_2O_3	0	CO	0.33	0.43 [c]
BaO/Al_2O_3	0	H_2	0.37	0.38 [d]

[a] At 300 °C from ~1000 ppm NO_2 in 3% O_2.
[b] In He alone on temperature ramp from 300 to 550 °C at 5 °C/min.
[c] Calculated from sum of NO_2, NO and N_2 produced (as shown in figure 3).
[d] Calculated from sum of NO_2, NO and N_2 produced (as shown in figure 4).

for approximately one-half the amount stored on BaO/Al_2O_3 in the dry state while water reduces the uptake by up to 50%. Since the amount of barium in the sample is 0.59 mmol/g, the proportion converted to $Ba(NO_3)_2$ in the dry state (~0.18 mmol(NO_x)/g) is 15% of the potential capacity. This is somewhat less than reported for $Pt/BaO/Al_2O_3$ (e.g. 0.58 mmol(NO_x)/g for a sample with 16.5 wt% Ba which corresponds to 24% of the potential capacity [10]).

4. Conclusions

Water reduces storage of NO_2 on BaO/Al_2O_3, largely by eliminating the initial uptake that has been attributed to nitrite formation with little effect on the subsequent partial uptake that is accompanied by NO evolution and nitrate formation. Water has little effect on the temperature-programmed decomposition of any NO_x stored on alumina which takes place with evolution of NO_2 and O_2 and minimal NO. However, it does impede the decomposition of the more stable NO_x stored on barium which liberates NO as well as NO_2. Carbon monoxide and hydrogen enhance decomposition of stored NO_2 under dry conditions by reducing NO_2 to NO and N_2, with hydrogen being a less effective reductant than CO.

Acknowledgment

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