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The storage of nitrogen oxides on alumina-supported barium oxide

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Abstract

The storage and release of NO_2 on alumina-supported barium oxide has been studied with particular attention to the stoichiometry of the two processes. At 400 °C the storage process is characterised by a short period of complete uptake, possibly as nitrito or nitro species, followed by a slower partial uptake in which approximately one NO is released for every three NO_2 lost. The latter reaction appears to supply the oxygen necessary to store NO_2 as nitrate ions. Molecular O_2 has little direct involvement even if in large excess. The second storage reaction also occurs, but to a much lesser extent, with Al_2O_3 alone. During temperature programmed desorption, release of NO_x from Al_2O_3 peaks at ∼430 °C with evolution of NO_2 and some O_2. Release from BaO/Al_2O_3 exhibits an additional peak near 520 °C corresponding to formation of NO and a higher O_2 concentration. The NO may arise from NO_2 since BaO/Al_2O_3 has activity for NO_2 decomposition by 500 °C. Although CO_2 at low concentration is rapidly taken up by BaO/Al_2O_3 at 400 °C it is displaced by NO_2 and does not interfere with storage. Thermodynamic calculations show that the formation of $Ba(NO_3)_2$ by the reaction of NO_2 with bulk $BaCO_3$ under the conditions used here is more favourable above 380 °C if NO is evolved than if O_2 is consumed.

Keywords: NO_2 storage catalysts; Barium oxide; Barium carbonate; Aluminium oxide; Decomposition of stored nitrate

1. Introduction

Lean burn gasoline direct injection (GDI) engines can provide substantial fuel economy gains over traditional port-injected engines. However, the presence of excess air favours production of high concentrations of nitrogen oxides (NO_x), while rendering standard three-way catalysts ineffective for NO_x removal. Selective catalytic reduction using hydrocarbons is yet to prove commercially successful and current GDI vehicles rely on an intermittent storage/reduction strategy developed by Toyota and others [1–3]. During lean burn, NO is oxidised to NO_2 on platinum and stored on a basic oxide such as BaO. The stored NO_x is then released and reduced on platinum group metals by a brief period of marginally rich operation. Stored NO_x is generally described as a nitrate which can be demonstrated by XRD [4] and FTIR [2,4–9]. If nitrate ions are formed then this raises a question as to the source of the oxygen necessary to increase the oxidation state of nitrogen from +4 in NO_2 to +5 in $NO_3{}^-$. The exhaust has excess oxygen so the stoichiometric process

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

is one possibility. However, other paths in which reduced nitrogen species (e.g. NO, N_2O and N_2) are released are also allowed [8]. It is experimentally difficult to distinguish between these alternatives when Pt is present since NO and NO_2 are partially or completely interconverted under storage conditions. However, they can potentially be distinguished if Pt-free supported BaO is used alone since the $NO_2 \rightarrow NO + O_2$ equilibration can be expected to be

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much slower. The primary aim here was to determine the stoichiometries corresponding to the storage of NO_2 on BaO/Al_2O_3 and of its subsequent release.

Vehicle exhaust contains also contains CO_2 (and H_2O) in which case the expected state prior to storage may be barium carbonate rather than the oxide (or hydroxide) [4,10–12]. However, as noted recently by Rodrigues et al. [4] there are thermodynamic limitations to the storage process if it is represented as

$$BaCO_3 + 2NO_2 + \tfrac{1}{2}O_2 \rightarrow Ba(NO_3)_2 + CO_2 \qquad (2)$$

The second part of this study addresses this question, again for platinum-free BaO/Al_2O_3.

2. Experimental

The sample referred to here as BaO/Al_2O_3 was made by five successive incipient wetness impregnations of a washcoat grade alumina (Condea, 140 m^2/g) using a near saturated solution of barium nitrate with drying in an oven at 110 °C following each impregnation. It was then calcined in flowing air for 3 h at ~550 °C. The Ba content based on the concentration of the $Ba(NO_3)_2$ solution, confirmed by X-ray fluorescence analysis, was 9 wt.%. The only phases detectable by X-ray diffraction (XRD) were transition aluminas (γ and δ) and $BaCO_3$ with a rather large particle size (>20 nm). Literature high resolution transmission electron microscopy and energy dispersive X-ray measurements on a similar type of preparation indicate that a more dispersed amorphous barium-containing phase is likely to be present as well [4].

Storage and release of nitrogen oxides was determined in a flow system with the sample contained in a 4 mm ID quartz tube with the remainder of the tubing 1 mm ID stainless steel. The main carrier stream comprising either He alone or 0.1% Ar/He with O_2 and/or CO_2 included as needed. A sidestream was added via a small volume 4-port Valco valve that could be switched between NO_2, NO, O_2, CO, CO_2 or H_2 in He or Ar/He. All streams were controlled by electronic flow meters (Brooks models 5850TR or 5850E). Additional 4-port valves before and after the reactor allowed switching between reactor and bypass with needle valves used to balance the pressures in the vent lines to the pressure upstream of the sample (~0.08 atm above ambient).

The exit stream from the system was first sampled into a quadrupole mass spectrometer (Balzers Thermostar) and then a micro-gas chromatograph (MTI model M200). It was then diluted with a known flow of N_2 and analysed by a chemiluminescent NO_x analyser (Ecotech model 9841) which determined NO and NO_x ($NO + NO_2$) alternately on a ~12 s cycle time. The NO_x analyser and mass spectrometer provided complementary information. The analyser was very accurate for NO and NO_x when values were steady but unreliable for NO_2 at low concentrations immediately following valve switches since they are calculated by difference from quantities of similar magnitude but separated slightly in time. On the other hand, the spectrometer could follow NO_2 (at m/z of 46) rapidly. However, extensive fragmentation to m/z of 30, and other effects that depended on the O_2 concentration, led to changes in sensitivity following valve switches which caused interference to the analysis of NO. The processing procedure allowed for these effects based on normalisation and observations with an empty reactor.

All experiments were carried out with a total flow rate through the reactor of ~50 cm^3 (STP)/min with the NO_2 concentration set at ~900 ppm during uptake. The samples (~40 mg in all cases) were conditioned to remove surface contaminants, such as carbon and carbonates, by a series of exposures to ~900 ppm NO_2 in 3% O_2/He at 400 °C or higher followed by ramping to 550 °C in He.

3. Results and discussion

3.1. NO_2 uptake on BaO/Al_2O_3 and Al_2O_3

The results for an experiment in which a stream containing ~900 ppm NO_2 and 1000 ppm O_2 (i.e. 0.1%) in Ar/He was switched over 40 mg of BaO/Al_2O_3 at 400 °C following pretreatment in the standard way are shown in Fig. 1. There is a short initial period (~15 s) in which neither the NO_x analyser nor the mass spectrometer shows NO or NO_2. Thus small amounts of NO_2 are completely taken up as such in a fast process. Subsequent to this NO appears, passes through a maximum and falls as NO_2 appears. Partial uptake then continues to a steadily decreasing extent as the

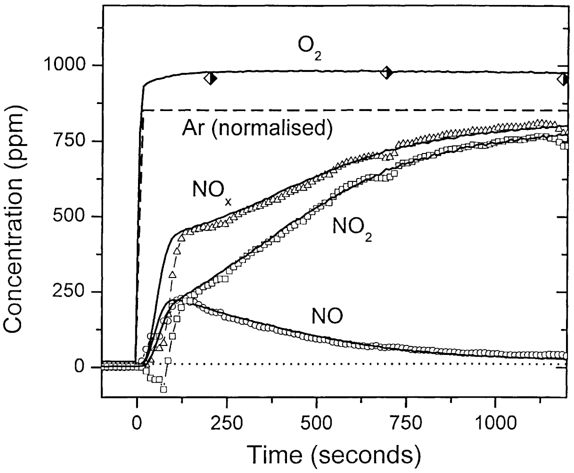

Fig. 1. Uptake of NO_2 from ~900 ppm NO_2 plus 1000 ppm O_2 in Ar/He on 40 mg BaO/Al_2O_3 at 400 °C. Chemiluminescent analyser: open symbols; gas chromatography: half-filled symbols; mass spectrometer: solid line with Ar (dashed line) normalised to match bypass NO_2 concentration.

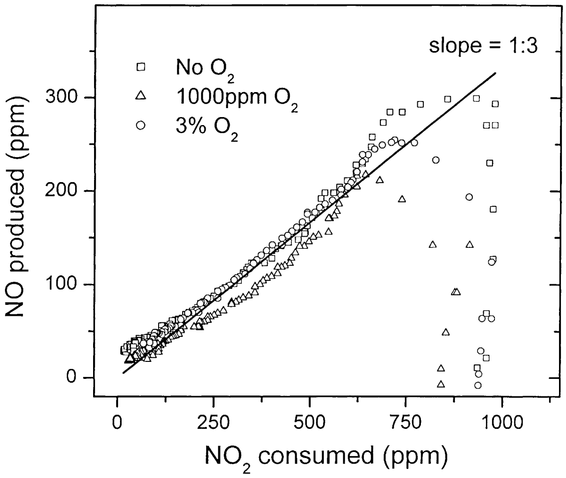

Fig. 2. Plot of NO production versus NO_2 loss during NO_2 storage on BaO/Al_2O_3 for experiments with no O_2 present, 1000 ppm O_2 present and 3% O_2 present.

NO_2 concentration trends to the bypass one (to which the Ar signal has been normalised). However, at no stage is there any take up of O_2, the curve for which follows the tracer Ar. Thus O_2 itself is not needed for storage. Even so the oxygen deposited by the conversion of NO_2 to NO must form part of the storage process since the amounts of N_2 and N_2O generated were negligible (<10 ppm). Similarly, the difference between the NO_x (i.e. NO + NO_2) and Ar signals is a measure of the amounts of NO_x stored.

Similar experiments using ~900 ppm NO_2 with other O_2 concentrations ranging from zero (i.e. NO_2 alone) to 3% O_2 (see later) gave very similar results. Storage of NO_2 was always accompanied by the generation of NO with a peak concentration of ~300 ppm. The shapes of all three curves in Fig. 1, NO, NO_2 and NO_x, are also quite similar to those shown by Fridell et al. [8] for the storage of NO_2 alone on a 2% Pt/20% BaO/Al_2O_3 sample and they state, without showing data, that BaO/Al_2O_3 behaved similarly. Thus concurrent evolution of NO seems characteristic of the uptake of NO_2 alone in both systems. Tests showed that NO itself was not stored on BaO/Al_2O_3 in the presence or absence of O_2 under the same conditions (i.e. at 400 °C with 1000 ppm NO). Thus the importance of NO oxidation for NO_x storage on vehicle catalysts is doubly clear. Not only is Pt required to oxidise the NO in the engine exhaust to NO_2 but it must also oxidise the NO evolved as NO_2 is stored.

It is of interest to know if the stoichiometry between NO formation and NO_2 consumption is fixed. Fig. 2 shows such a plot for the NO_x analyser data of Fig. 1 and other experiments with 0 and 3% O_2 present. In each system, the points beyond the maxima correspond to the initial stages where the fast complete uptake of NO_2 is likely to be still occurring to some extent. The rest of the points encompass a line with a slope of 1:3. The gradual steepening of the experimental points at low concentrations may be real although a number of experimental factors may also contribute. (It is obtained as the difference between reactor and bypass values, corrected for homogeneous decomposition in the reactor, and hence increasingly uncertain when the difference is small.) Regardless, it appears likely that the slow uptake is largely driven by a process that produces approximately one NO for every three NO_2 consumed. The various possibilities are discussed later.

Fig. 3A shows data for uptake from ~900 ppm NO_2 in 3% O_2/Ar/He on Al_2O_3 alone at 400 °C. Relative to BaO/Al_2O_3 under the same conditions (Fig. 3B), the period of total uptake of NO_2 is much shorter. NO is produced almost immediately but the peak

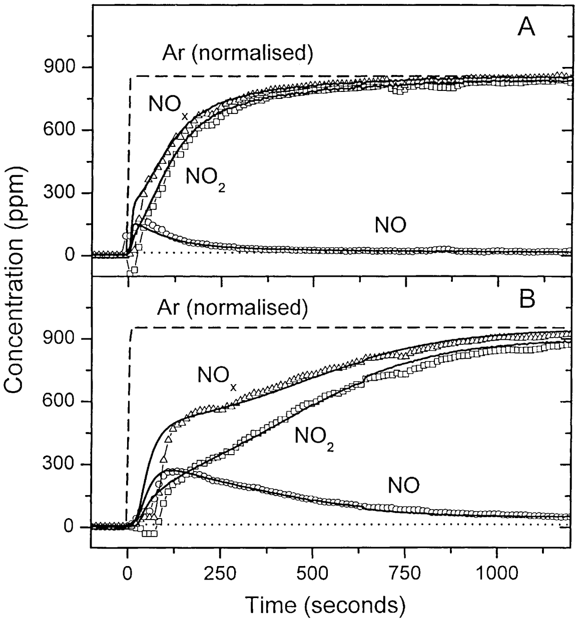

Fig. 3. Uptake of NO_2 from ~900 ppm NO_2 plus 3% O_2 in Ar/He on: (A) 40 mg Al_2O_3 at 400 °C; (B) 40 mg BaO/Al_2O_3 at 400 °C. Chemiluminescent analyser: open symbols; mass spectrometer: solid line with Ar (dashed line) normalised to match bypass NO_2 concentration.

concentration is less than for BaO/Al_2O_3 and the approach to the bypass values is faster.

Table 1 shows estimates for the amounts of NO_x stored on the two substrates after 1200 s, in total and subdivided between the initial complete uptake (much more significant with BaO/Al_2O_3) and the slower partial process that occurs on both. At 400 °C, the extent of the second process is 130% greater on BaO/Al_2O_3, and the total amount taken up is 150% greater, than on Al_2O_3. However, even for the BaO/Al_2O_3 sample the calculated NO_x/Ba ratio after 1200 s is only ~0.4 or 20% of that expected for complete conversion to $Ba(NO_3)_2$. This relatively small fraction may be a reflection of the slowness of storage on rather large barium-containing particles and the absence of Pt to facilitate spillover.

3.2. Release of NO_x

Evolution of NO_x following switches from ~900 ppm NO_2 plus 3% O_2 in Ar/He to helium alone at 400 °C and ramping at 5 °C/min to 550 °C is illustrated in Fig. 4. With Al_2O_3 (Fig. 4A) NO_2 is the predominant nitrogen oxide driven off. It is apparent from the time of the initial switch, reaches a maximum at ~430 °C and is complete below 500 °C. NO is detectable only in small amounts in the final stages of NO_2 release. The initial stages of the O_2 analyses are less reliable due to the large concentration present at the time of the switch. Nonetheless, it is clearly given off with a peak temperature that matches that of NO_2 but with less than one-half of the concentration. (It would be expected to be one-quarter for the decomposition of a bulk nitrate to NO_2 and O_2 alone.)

The behaviour of BaO/Al_2O_3 (Fig. 4B) is rather different. While there is also a peak in NO_2 production, it occurs at a slightly higher temperature (460 °C versus 430 °C with Al_2O_3) and is supplemented by a slightly larger peak of NO with a maximum at ~525 °C. This is accompanied by a peak of O_2 at a similar concentration which is probably within experimental error of the stoichiometry expected for

$$Ba(NO_3)_2 \rightarrow BaO + 2NO + 1.5O_2$$

where the O_2/NO ratio is 3:4.

Table 1
NO_2 storage and release for BaO/Al_2O_3 and Al_2O_3

Substrate	Storage in 3% O_2 (mmol/g)[a]			Release in He (mmol/g)[b]		
	Fast	Slow	Total	As NO_2	As NO	Total
BaO/Al_2O_3	0.02	0.23	0.26[c]	0.16	0.16	0.31[c]
Al_2O_3	<0.01	0.10	0.11	0.08	0.01	0.09

[a] At 400 °C from ~900 ppm NO_2 in 3% as per Fig. 3.

[b] In He alone on temperature ramp from 400 to 550 °C at 5 °C/min as per Fig. 4.

[c] Since the Ba content was 0.65 mmol/g, the apparent storage as $Ba(NO_3)_2$ is ~20 and 24% of the potential capacity on the basis of uptake and release measurements, respectively.

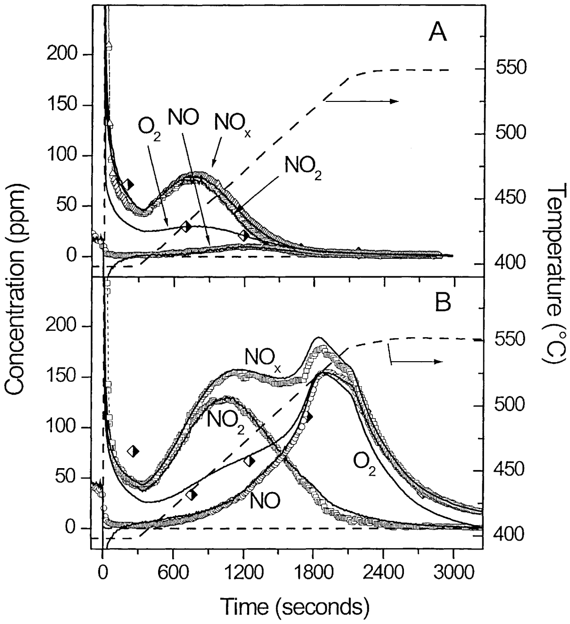

Fig. 4. Release of NO_x, stored at 400 °C as per Fig. 3B, in He alone on a ramp to 550 °C at 5 °C/min from: (A) 40 mg Al_2O_3; (B) 40 mg BaO/Al_2O_3. Chemiluminescent analyser: open symbols; gas chromatography: half-filled symbols; mass spectrometer: solid lines.

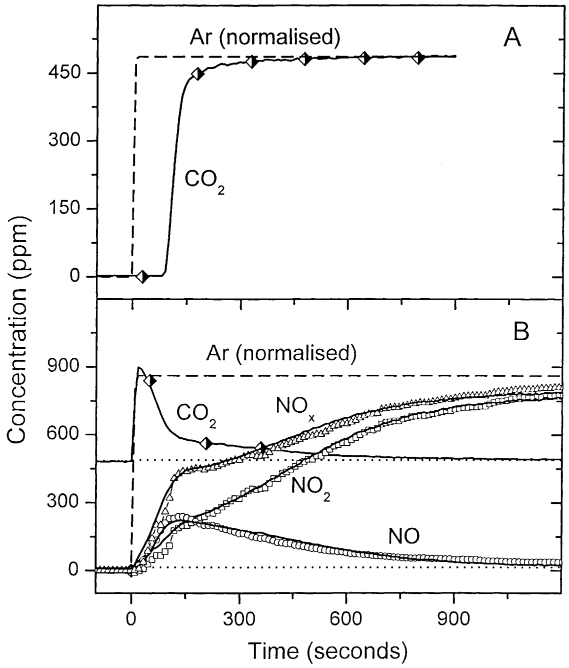

Fig. 5. Uptakes of CO_2, and NO_2 in the presence of CO_2 on 40 mg BaO/Al_2O_3 at 400 °C following switch from: (A) He to ~500 ppm CO_2 in Ar/He; (B) ~500 ppm CO_2 in He to ~900 ppm NO_2 plus ~500 ppm CO_2 in Ar/He. Chemiluminescent analyser: open symbols; gas chromatography: half-filled symbols; mass spectrometer: solid lines with Ar (dashed lines) normalised to match bypass CO_2 (A) or NO_2 (B) concentrations.

Separate tests in which ~900 ppm NO_2 in 3% O_2 was passed over BaO/Al_2O_3 at 500 °C showed a conversion to NO of approximately 50% in the steady state which is similar to that apparent at the same temperature in Fig. 4B. Thus the substrate has substantial activity for NO_2 decomposition at the temperatures where NO_x is evolved. As a result it is impossible to decide if NO is evolved directly during the ramp or whether NO_2 is released first and then decomposes subsequently to NO and O_2.

Table 1 includes data for the release of NO, NO_2 and total NO_x from BaO/Al_2O_3 and from Al_2O_3. In both cases the total NO_x released agrees with total NO_x stored within experimental error so release is complete. It is clear that the peaks for NO_2 and NO evolution from BaO/Al_2O_3 do not correspond to the fast and slow stages during uptake since the quantities do not match. Likewise, it would be unreasonable to attribute the NO peak to release from BaO, and the NO_2 one to release from Al_2O_3, as the amount of NO_2 released is much larger for the barium-containing sample. The more likely explanation is that evolution from BaO/Al_2O_3 occurs as NO_2 alone from the three sources in overlapping fashion but NO becomes more important at higher temperature due to the increasing activity of the sample for NO_2 decomposition.

3.3. Uptake in CO_2-containing systems

Tests with Al_2O_3 showed that it adsorbed negligible amounts of CO_2 at 400 °C. Fig. 5A shows data for CO_2 storage on BaO/Al_2O_3 that had been pretreated by exposure to ~900 ppm NO_2 in 3% O_2/He (at 400 °C increasing to 550 °C) and then to He at 550 °C. Uptake of CO_2 is total for ~100 s after which time the CO_2 concentration rises steeply with little of the second stage slower process seen for NO_2. Integrating the difference between the Ar and CO_2 curves indicates a CO_2 uptake of ~0.05 mmol/g. This corresponds to a CO_3:Ba ratio of ~0.08 or 8% of saturation. In experiments using 1200 ppm CO_2 the amount taken up was slightly greater (~0.08 mmol/g) of which 40% could be removed by flushing at 400 °C and a further 35% on a ramp to 550 °C. The relative ease of removal indicates that the form of the stored CO_2 is unlike bulk $BaCO_3$ which is much more stable with a calculated decomposition pressure of $<10^{-8}$ atm at 550 °C.

Fig. 5B shows data obtained when ~900 ppm NO_2 was added to the stream of ~500 ppm CO_2 in He passing over BaO/Al_2O_3 at 400 °C as in Fig. 5A. As may be seen, uptake of NO_2 proceeds with NO evolution in similar fashion to that in part (B) of Figs. 1 and 3. This displaces CO_2 as a initial sharp peak and then more slowly as uptake of NO_2 continues. Other experiments showed that storage of NO_2 proceeded in the same way when the CO_2 concentration during storage was increased to 8000 ppm. Thus CO_2 does not impede storage of NO_2 at the concentration used here. The data of Kobayashi et al. [10] for a $Pt/BaO/Al_2O_3$ do show some fall-off in NO_x uptake at much higher concentrations but it was relatively small—less than 20% with a CO_2 concentration of 150,000 ppm (i.e. almost 20 times the maximum concentration used here).

3.4. Thermodynamics of NO_2 uptake

The data in Fig. 1 indicates that the small complete uptake of NO_2 that occurs initially on BaO/Al_2O_3 does not require oxygen and hence is likely to be as a coordinately bound surface species, e.g. a nitro or nitrito group. Subsequent uptake on BaO/Al_2O_3 is accompanied by the consumption of oxygen generated by the conversion of NO_2 to NO rather than through using O_2, even when the latter is in large excess. Consumption of oxygen is indicative of nitrate formation. If the starting states were regarded as bulk species the possible stoichiometric equations for NO_2 uptake on BaO/Al_2O_3 and its carbonated counterpart would be as follows:

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

$$BaCO_3 + 2NO_2 + \tfrac{1}{2}O_2 \rightarrow Ba(NO_3)_2 + CO_2 \qquad (2)$$

$$BaO + 3NO_2 \rightarrow Ba(NO_3)_2 + NO \qquad (3)$$

$$BaCO_3 + 3NO_2 \rightarrow Ba(NO_3)_2 + NO + CO_2 \qquad (4)$$

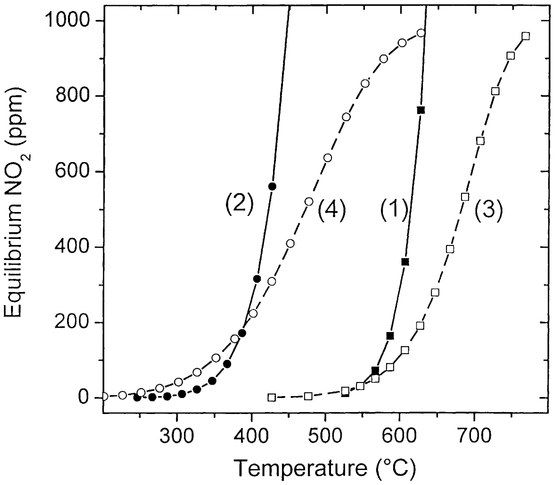

Fig. 6. Calculated equilibrium NO_2 concentration (expressed as ppm in diluent at 1 bar total pressure) versus temperature for reactions (1)–(4) with CO_2 set at 0.0005 bar, O_2 set at 0.03 bar and with NO_2 initially at 0.001 bar for (3) and (4), see text.

Eqs. (3) and (4) have the ratio of 1 NO produced for 3 NO_2 consumed implied by the plot in Fig. 2 and it is of interest to compare their thermodynamic favourability with those of the O_2 consuming counterparts, Eqs. (1) and (2).

Fig. 6 shows the results of calculations for the conditions of interest here, namely 1000 ppm NO_2 in He initially (equivalent to ~0.001 bar), O_2 set at 3% in He (0.03 bar) and CO_2 set at 500 ppm in He (0.0005 bar) in a static system. The estimates use the thermochemical data of Barin [13] and are plotted as the equilibrium NO_2 pressure (expressed as ppm in diluent at 1 bar) assuming that NO_2 decomposition (i.e. $NO_2 \rightarrow NO + \tfrac{1}{2}O_2$) does not occur, as is true at 400 °C for the conditions used here. The lower the NO_2 pressure the more favoured is the process. It is apparent that uptake on the bulk carbonate, reactions (2) and (4), can go to completion only below ~250 °C. By ~380 °C the potential removal of NO_2 is restricted to about 80%. Above that the potential removal falls steeply but the reaction generating NO, reaction (4), can reduce the NO_2 concentration further than the O_2 consuming one, reaction (2). Thus the experimental observation of NO evolution during NO_2 storage is not unexpected. In practical terms any distinction between the two reactions is meaningless by 500 °C since, based on the earlier discussion of the data in Fig. 4, the assumption of no equilibration between NO and NO_2 is probably invalid. Likewise, although it is also clear from Fig. 6 that uptake on BaO is clearly more favourable than on $BaCO_3$, any distinction between the two possible uptake reactions (1) and (3), based on data above 550 °C is meaningless for the same reason. It should be noted that the calculations here are useful only in indicating the direction in which a reaction can proceed for a given set of starting concentrations. If the reaction is feasible, then there is no limit to the extent of $Ba(NO_3)_2$ formation in a flow system since the products (CO_2 and/or NO) are continuously removed.

With higher CO_2 concentrations both reactions (2) and (4) become less favourable and closer together. It may also be noted here that the present calculations for reaction (2) are not in complete conformity with the recent ones of Rodrigues et al. [4]. Their estimates indicate that the temperature at which the equilibrium NO_2 pressure is 340×10^{-6} bar when $CO_2 = 0.1$ bar and $O_2 = 0.08$ bar is ∼420 K. With the same pressures our program gives ∼610 K.

The steps through which the overall processes represented by Eqs. (3) and (4) might be achieved are uncertain. One possibility, suggested by Fridell et al. [8], is that barium oxide is first oxidised to barium peroxide which is then able to store NO_2 as nitrate without need for additional oxygen, i.e.

$$BaO + NO_2 \rightarrow BaO_2 + NO \quad (5)$$

$$BaO_2 + 2NO_2 \rightarrow Ba(NO_3)_2 \quad (6)$$

Calculations for bulk compounds show that reaction (5) is, in isolation, thermodynamically feasible under present conditions (1000 ppm NO_2), somewhat more so than the corresponding reaction with O_2 at 3% in He, i.e.

$$BaO + \tfrac{1}{2}O_2 \rightarrow BaO_2 \quad (7)$$

Reaction (5) should also be favoured kinetically on the grounds that breaking a bond in NO_2 is much easier than that in O_2 (or moving ions in a lattice) as required for (7).

Two possible objections may be raised against peroxide formation. One is that although production of BaO_2 by reactions (5) or (7) is thermodynamically allowed under storage conditions the corresponding reactions starting with bulk $BaCO_3$ are highly unfavourable. As described previously, the surface carbonate on BaO/Al_2O_3 appears less stable than bulk $BaCO_3$ itself but whether it is sufficiently so to allow peroxide formation is yet to be established. The second possible objection is that the uptake of NO_2 on Al_2O_3 itself generates NO, suggesting a similarity in mechanism, and yet peroxide formation is not an issue with Al_2O_3. Hence, although attractive, peroxide formation is not unproblematic.

The alternative, also mentioned by Fridell et al. [8], is that NO_2 is first adsorbed as a nitrite (or some other species with oxidation state below +5) and then oxidised to nitrate by the strong oxidant, NO_2. The oxidation is necessarily complex since a single oxygen atom needs to oxidise two adsorbed NO_2 molecules. Either a single adsorbed NO_2 is first oxidised to a higher oxidation state which facilitates oxidation of the second NO_2, or two adsorbed NO_2 are oxidised together in a concerted process. There is no obvious way to distinguish between these possibilities.

4. Conclusions

The present results show that the uptake of NO_2 on alumina-supported barium oxide at ∼400 °C under dry conditions has two stages, a small complete uptake followed by a larger, slower process that generates approximately one NO for every three NO_2 lost. The second stage also occurs, but to a lesser extent, on Al_2O_3 alone. Desorption of NO_2 from Al_2O_3 occurs in a single step below 500 °C with liberation of NO_2 and some O_2 but very little NO. NO_2 is retained more strongly when barium is present. Decomposition still yields NO_2 below 500 °C but a similar amount of NO, accompanied by additional O_2, is given off with a peak temperature of 520 °C. It is impossible to decide if NO is generated as such or from NO_2 after release, since BaO/Al_2O_3 has considerable activity for the $NO_2 \rightarrow NO + \frac{1}{2}O_2$ reaction at the temperature where NO is seen. Carbon dioxide, in the gas phase or pre-equilibrated, does not prevent NO_2 uptake on BaO/Al_2O_3. Thermodynamic calculations indicate that the uptake of NO_2 on bulk $BaCO_3$ as nitrate is more favourable above 380 °C if the oxygen needed is obtained from additional NO_2 via release of NO than through use of molecular O_2 even if the latter is in large excess.

Acknowledgements

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