An Investigation of NOx Storage on Pt-BaO-Al₂O₃

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Abstract

A series of samples containing 5-wt% or 20-wt% BaO on y-Al₂O₃ with different loadings of Pt were prepared and examined for their NO₂ adsorption properties using temperature programmed desorption (TPD), temperature programmed reduction (TPR), and x-ray diffraction (XRD). For calcination at 873 K or above, BaO/Al₂O₃ formed BaAl₂O₄. While carbonates were found to be unstable on the aluminate phase, NO₂ reacted with the aluminate to form bulk $Ba(NO_3)_2$ and Al_2O_3 . even at room temperature. With BaO/Al₂O₃, reaction to form the nitrate required slightly higher temperatures because of the need to displace CO₂; however, pulsing NO₂ over pure Ba(CO₃) showed rapid reaction to form CO₂ and NO in the gas phase, along with Ba(NO₃)₂, at 673 K. The decomposition temperature for Ba(NO₃)₂ shifted by more than 100 degrees when TPD was carried out in vacuum rather than in a carrier gas, showing that re-equilibration with the gas phase is important in the decomposition process. The addition of Pt had a minimal effect on the thermal stability of the nitrates but was essential for the reduction of the nitrate in H₂. Since a relatively small amount of Pt was sufficient to cause the complete reduction of the Ba(NO₃)₂ phase at temperatures below 400 K, it appears that the nitrates must be extremely mobile within the Ba-containing phase. Finally, trapping studies of NO₂ at 573 K, with or without 10% CO₂ in the gas phase, showed no measurable difference between BaO/Al₂O₃ and BaAl₂O₄, with or without CO₂.

Keywords: NO_x; Barium Aluminate; Barium Oxide; Barium Carbonate; Temperature Programmed Desorption.

Introduction

One of the more interesting technologies for NO_x removal with lean-burn engines involves the use of NO_x traps [1,2]. The concept involves trapping NO_x that is formed while the engine is operating under lean conditions, then periodically operating the engine briefly under rich conditions to produce an exhaust that will reduce the NO_x that is present in the NO_x storage catalyst (NSC). NO_x storage catalysts are composed primarily of alkali or alkaline-earth metal oxides, often BaO, on a high-surface-area support, usually alumina. Pt is a crucial component of the traps, in part for catalyzing the formation of NO₂, since trapping involves the reaction of Ba⁺² with NO₂ to form Ba(NO₃)₂ [3-6]. The need for forming NO₂ has been demonstrated by the fact that adsorption of NO in the absence of NO₂ appears to be minimal [3-5].

However, fundamental questions remain concerning how the NO_x storage catalysts perform their function, what phases are most important for storing and releasing NO_x, and how the various components in the trapping catalyst interact. For example, Piacentini and coworkers recently reported that there are three types of BaO in Ba/Al₂O₃, with an amorphous type that forms above the monolayer BaO exhibiting the highest reactivity towards NO_x [7]. Related to this question is that BaO and Al₂O₃ will react at high temperatures to form an aluminate phase, BaAl₂O₄ [8-12]. While some have indicated that the aluminate phase can act as a trap [9-12], the majority of trapping studies reported in the literature have been performed on materials that were calcined at temperatures that suggested the aluminate phase was being avoided [3,13-19]. Certainly, the relative importance of BaO and BaAl₂O₄ phases has not been clarified. Furthermore, if BaAl₂O₄ is a good trapping material, there is the question of whether trapping occurs in the bulk or only on the surface, since bulk nitrate formation would presumably require decomposition of the aluminate phase.

Exactly how Pt interacts with the BaO phase is also unclear. Takahashi, et al [20] have reported that Pt must be present on the BaO-Al₂O₃, not simply present in an adjacent phase, indicating that Pt does more than catalyze formation of NO₂. However, the Pt loadings in most NO_x storage catalysts are low relative to the BaO content of these materials, so there cannot be direct contact between Pt and most of the BaO in the trap on a molecular scale, even if the Pt were atomically dispersed.

In an attempt to answer some of these questions, we investigated the adsorption of NO₂ on BaO and BaAl₂O₄, with different loadings of BaO and Pt, using Temperature Programmed

Desorption (TPD) and Temperature Programmed Reduction (TPR). The adsorption of NO₂ was examined, rather than NO, in order to decouple the trapping function from other parts of the system. The main conclusions based on these results are that nitrate formation is very facile and that the nitrate ions are extremely mobile, almost liquid-like within the BaO phase. Bulk nitrates formed rapidly at room temperature in the absence of carbonates, even with BaAl₂O₄; nitrates displaced carbonates so rapidly at 573 K that the carbonates seem to have negligible effect on adsorption. The main role of Pt is shown to be in the reduction of the nitrates, with relatively small amounts of Pt causing complete reduction of bulk Ba(NO₃)₂ at temperatures below 400 K. **Experimental**

The samples used in these experiments were prepared by impregnating of γ -Al₂O₃ (Alfa Aesar) with aqueous solutions of Ba(NO₃)₂ (Alfa Aesar). The BaO loadings were chosen to be 20 wt%, a value reported by Narula, et al as providing optimal storage properties [10], and 5-wt%, a value below that required to form a monolayer on the γ -Al₂O₃ [7]. After impregnation of the alumina with Ba(NO₃)₂, the samples were dried in air at 373 K for 4 h to remove excess water and then calcined in air for 5 h to various temperatures to form different phases. Some experiments were also performed on pure Ba(NO₃)₂ and pure Ba(CO₃) (Alfa Aesar) to understand the decomposition of the nitrate and the displacement of CO₂ from the carbonate. Microscopic examination of the Ba(NO₃)₂ showed that it was composed of 15 µm crystallites, consistent with the BET surface area which was determined to be less than 1 m²/g. The Ba(CO₃) crystallites were found to be between 1 and 2 µm in size.

To examine the effect of Pt, the samples having 20-wt% BaO/Al₂O₃, that had been calcined to either 823 or 873 K, were impregnated with either 0.1 or 1wt% Pt using an aqueous solution of $Pt(NH_3)_4(NO_3)_2$). These materials were then calcined again at either 823 or 873 K in air for additional 5 h.

TPD experiments were performed in vacuum and under flowing gases. The vacuum experiments were performed in a TPD-TGA (thermogravimetric analysis) system in which 5 to 40 mg of sample were placed on the sample pan of a Cahn 2000 microbalance [21]. The sample size was varied to maintain the amount of BaO in the sample as a constant. After evacuation for 1 h using a turbomolecular pump with a base pressure below 10⁻⁷ torr, the sample temperature was ramped at 10 K/min while monitoring the sample weight and the partial pressures above the

sample with an Inficon residual-gas analyzer. Because the samples could not be easily exposed to NO_2 in this system, the samples had to be exposed to NO_2 before loading them into the system.

The flow TPD experiments, along with the CO₂-displacement and TPR studies, were carried out in a flow-reactor apparatus that has a quadrupole mass spectrometer for monitoring the concentrations of the outlet gases and has been described in previous publications [22,23]. The sample sizes for TPD and TPR were between 100 and 200 mg; and the gas flow rates in both TPD and TPR were fixed at 50 cm³/min. The carrier gas in TPD was pure He and a 20% H₂-He mixture was used in TPR. The heating rate was again maintained at 10 K/min. The samples were exposed to NO₂ using a 5% NO₂-He mixture obtained from Airco. Integration of peak areas in TPD and TPR allowed adsorbate coverages to be determined quantitatively. Calibration of the NO₂ peak was accomplished by measuring desorption from a known mass of Ba(NO₃)₂. This calibration was confirmed by measuring the weight loss in TGA experiments. For the CO₂-displacement experiments, 500 mg of BaCO₃ was held at 573 K and exposed to the 5% NO₂ in He while monitoring the CO₂ in the effluent from the reactor.

The FTIR spectra were recorded using a Mattson Galaxy instrument with a diffuse-reflectance attachment, Collector IITM provided by Spectra-Tech Inc.

Results

Sample Characterization

Fig. 1 shows the x-ray diffraction (XRD) patterns for γ -Al₂O₃, impregnated with Ba(NO₃)₂ to a coverage corresponding to 20 wt% BaO, following calcination to increasingly higher temperatures. (In these experiments, the identification of the peaks was accomplished using software available with the instrument, PCPDFWin v. 2.00, 1998 JCPDS-International Centre for Diffraction Data[®].) Even after heating to 673 K for 5 h, Fig. 1a), the XRD pattern shows the presence of bulk Ba(NO₃)₂. Further heating to 773 K causes the partial decomposition of the bulk nitrate, but lines associated with the nitrate ion, at approximately 19 and 38 degrees 2 θ , are still present. The nitrate features disappeared after heating to 823 K and were replaced by peaks associated with BaCO₃, Fig. 1c). While we did not intentionally expose the BaO formed by decomposition of the nitrate to CO₂, the tendency of BaO to form the carbonate was so strong that the formation of BaO was always accompanied by formation of the carbonate. Finally, XRD patterns of the samples that were heated to 873 and 1023 K, Figs. 1d) and e), showed formation of aluminate phases.

FTIR measurements demonstrate that Ba-aluminate phase does not form stable carbonates. Fig. 2 provides spectra of 20-wt% BaO/Al₂O₃ samples that had been calcined to either 873 K or 823 K, after heating in dry air to various temperatures. In these spectra, bulk carbonates are identified by the broad feature between 1300 and 1600 cm⁻¹. Fig. 2a) shows that carbonates appear to be present at room temperature on the sample calcined to 873 K; however, mild heating to 473 K, spectrum ii), and 573 K, spectrum iii), caused removal of these bands. By contrast, spectra taken on the sample that had been calcined to only 823 K, Fig. 2b), showed that carbonates were not removed by heating in CO₂-free air, even at 823 K.

The surface areas of the 20-wt% BaO/Al₂O₃ samples were determined by BET measurements of N₂ at 78 K after heating to 823, 873, and 1023 K and are shown in Table 1. The surface areas do not change significantly upon heating to form the aluminate and remain reasonably high, 88 m²/g, even after calcination to 1023 K.

$Ba(NO_3)_2$ Decomposition

To establish a starting point for understanding the decomposition of the nitrates, we first performed TPD experiments with bulk $Ba(NO_3)_2$ in vacuum (Fig. 3a)) and using the flow-reactor (Fig. 3b)) systems. Because TGA measurements were performed simultaneously with the vacuum-TPD experiments, the stoichiometry was demonstrated to correspond exactly with that expected for decomposition of $Ba(NO_3)_2$ to BaO according to reaction 1):

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

The vacuum TPD in Fig. 3a) shows decomposition in two well-defined peaks. That the primary nitrogen-containing product is NO₂ is shown by the ratio of peaks at m/e = 30 and 46, which occur in a ratio of 3:1 for NO₂. Therefore, most of the product forms between 800 and 850 K and leaves the sample as O₂ and NO₂. A second, very sharp feature is observed in the TPD curve between 850 and 870 K. Most of the products formed in this range can be assigned toNO (m/e = 30) and O₂ (m/e = 32). The relative intensity of the peak at m/e = 46 compared to the peak at m/e = 30 is greatly reduced, while the peak at m/e = 32 is greatly increased. We found no evidence for N₂O (m/e = 44) formation in any temperature range.

There is no obvious reason for the second desorption feature in Fig. 3a). That the two nitrate ions associated with each Ba^{+2} might be inequivalent is not consistent with the relative areas of the two TPD peaks. Furthermore, the TPD results on the bulk $Ba(NO_3)_2$ cannot be explained in terms of surface and bulk nitrates since the fraction of nitrate ions at the surface of

the 15-µm crystallites is clearly negligible compared to the amount in the bulk. Therefore, we suggest that the reaction to NO is strictly associated with the temperature at which the nitrate decomposes.

The TPD result for Ba(NO₃)₂ in the flow reactor, shown in Fig. 3b), exhibits an important difference from that in Fig. 3a). The peak is shifted to significantly higher temperatures, more than 100 degrees. Since the presence of an inert gas like He cannot affect the intrinsic desorption process, the increased desorption peak temperature must be associated with readsorption of NO₂ in the gas phase above the sample [24,25]. Based on the carrier-gas flow rates and Ba(NO₃)₂ sample size, we estimate that the NO_x pressure above the sample in the peak desorption region was less than 10⁻³ torr in the vacuum experiments and ~10 torr in the flow experiments [26]. For this partial pressure to have an effect on peak temperature, the rate of readsorption from the gas phase, back onto the catalyst, must be significant. The product ratio for NO and NO₂ is probably not meaningful in this experiment because, unlike the vacuum experiment, the products are not immediately detected after leaving the sample. It appears that the composition detected in the mass spectrometer is due to equilibrium between NO, NO₂, O₂ in the lines leading from the flow reactor to the mass spectrometer.

CO₂ Displacement

In order to understand the adsorption of NO₂ onto BaO, it is instructive to examine the products formed upon exposure of 0.5 g of Ba(CO₃) to NO₂. Fig. 4 shows the reactor effluent during a step change in the gas phase from pure He to 5% NO₂ in He at a flow rate of 10 cm³/min at 573 K. During the entire time of this NO₂ exposure, the only products are CO₂ (m/e=44) and NO (m/e=30), with a complete absence of NO₂ (m/e=30 and 46). This demonstrates that NO₂ causes the rapid displacement of CO₂ and formation of NO (m/e = 30), consistent with Reaction 2).

$$Ba(CO_3) + 3NO_2 \rightarrow Ba(NO_3)_2 + CO_2 + NO$$
 2)

Since there was no O_2 in the gas phase, nitrate formation requires formation NO. It is also interesting to notice that the sample did not become saturated during the duration of this experiment, even though the NO₂ exposure was more than sufficient to saturate the external surface of the Ba(CO₃). For purposes of this study, the data indicate that one should expect to form Ba(NO₃)₂ readily upon exposure of samples to NO₂, even if Ba(CO₃) is produced during exposure to the air.

TPD Following NO₂ Adsorption

Fig. 5 shows representative TPD results, using the flow-reactor system, for samples containing 20-wt% BaO following saturation exposures to NO₂. The NO₂ exposures were calculated to be sufficient to saturate the BaO phase by a factor of four times. The samples that were examined here were the 20-wt% BaO/Al₂O₃ sample calcined at 823 K to avoid aluminate formation, the same sample calcined to 873 K to intentionally form the aluminate, and the sample calcined to 873 K but having 1 wt% Pt. The data in Fig. 5 show the mass-spectrum signals at m/e = 44 (CO₂) and 30 (NO and NO₂) only; however, in each of these measurements, the signal at m/e = 46 followed the signal at m/e = 30. As discussed earlier in the section on Ba(NO₃)₂ decomposition, NO, O₂, and NO₂ appeared to undergo equilibration prior to reaching the mass spectrometer in this flow system, making it impossible to determine whether the desorbing product was NO₂ or a mixture of NO and O₂. Under the conditions of these measurements, the exposure of Al₂O₃ to NO₂ resulted in uptakes that were less than 10% of that on the BaO-containing samples, so that the adsorption is primarily associated with the Ba-containing phases.

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Fig. 5a) was the result obtained on the sample calcined to 823 K following exposure to NO₂ at room temperature. Only a relatively small amount (0.8 mmol/g) of NO_x left the sample after this exposure; and decomposition occurred at a high temperature, ~1073 K. All of the desorption below this temperature was CO₂, ~0.8 mmol/g, presumably formed by decomposition of the carbonate. It is not clear why the CO₂ leaves the sample over such a wide temperature range or why the nitrate decomposes at a temperature higher than that observed for pure Ba(NO₃)₂; however, we suggest that the nature of the sample must be changing during the temperature ramp and that the nitrate-decomposition chemistry may be affected by the presence of neighboring carbonate ions. When a sample calcined at 823 K was exposed to NO₂ at 573 K, Fig. 5b), the TPD result was almost identical to what we obtained with pure Ba(NO₃)₂ powder, Fig. 3b). Only a small amount of CO₂ is observed in the TPD, near the leading edge of the NO_x-desorption peak; and the peak temperature for NO_x shifted downward to approximately 923 K. The amount of NO_x desorbing from the sample, 2.2 mmol/g, also correspond closely to what would be expected following the complete transformation of BaO to Ba(NO₃)₂. For 20-wt% BaO, a nitrate stoichiometry of 2:1 would lead to 2.6 mmol/g of NO₂.

The TPD results obtained following NO₂ exposure to the sample calcined at 873 K, Fig. 5c) and d), were quite different. The room-temperature exposure led to a large uptake in NO_x, 2.1 mmol/g, with the uptake at 573 K being slightly less, 1.8 mmol/g. In both cases, desorption occurred in two features, between 673 and 773 K and between 773 and 873 K. It is also noteworthy that negligible amounts of CO₂ were observed leaving the sample, consistent with the FTIR result showing that carbonates were not stable on samples that had been calcined to temperatures high enough to form BaAl₂O₄. Finally, the addition of 1-wt% Pt to this sample had no effect on the room-temperature uptake of NO₂ on this sample. Although the addition of Pt led to a slight shift in the peak desorption temperature, it is unlikely that the shift is due to destabilization of nitrate ions; most of the nitrate ions are not in contact with Pt, given that the Ba:Pt ratio in this sample is 25. Since the data from Fig. 3 demonstrate that readsorption from the gas-phase can influence the TPD peak temperature, the role of Pt could simply be to react NO₂ to NO and O₂, potentially changing the peak temperature by decreasing the rate of readsorption.

A surprising implication of the data in Fig. 5c) is that exposing $BaAl_2O_4$ to NO_2 at room temperature is sufficient to decompose the aluminate and form what is essentially the bulk $Ba(NO_3)_2$. On a surface-area basis, the uptake of 2.1 mmol/g corresponds to $1.2x10^{19}$ (NO_3)⁻ ions/m², a coverage that is too high for simple monolayer adsorption and is close to the value expected for formation of bulk $Ba(NO_3)_2$, 2.6 mmol/g. That the $BaAl_2O_4$ phase decomposes readily to form nitrates is also demonstrated by the XRD patterns in Fig. 6. Fig. 6 shows the patterns of the 20 wt% BaO/Al_2O_3 sample, calcined to 873 K, before (i) and after (ii) room-temperature exposure to excess 5% NO_2 in He. The patterns show that the intensity of the lines associated with $BaAl_2O_4$ decrease significantly together with an appearance of lines associated with $Ba(NO_3)_2$.

Because it has been reported that the properties of NSC change with BaO loading [28], we compared results for adsorption on samples with high and low BaO loadings. Fig. 7 shows a comparison of TPD results following saturation exposures of NO₂ on BaO/Al₂O₃ samples with 20-wt% BaO, Fig. 7a), and 5-wt% BaO, Fig. 7b), performed in vacuum in the TPD-TGA apparatus. Both samples were calcined to 873 K to form the aluminate phase and then given saturation exposures of NO₂ in the flow reactor before being transferred to the TPD-TGA unit. On both samples, the mass change between 600 and 900 K corresponded closely to two nitrate

ions per Ba⁺². As discussed earlier, the 20-wt% BaO sample exhibits two desorption features, and the feature at the higher temperature occurs at the same temperature as that observed with Ba(NO₃)₂ powder, Fig. 3a). On the NO₂-exposed BaO/Al₂O₃ sample, a higher fraction of the NO₂ reacts to NO and O₂ below 800 K; however, the very sharp feature just below 850 K, composed of strictly NO and O₂, has an appearance that is virtually identical in both samples, although a larger fraction of the NO_x desorbs from this feature on BaO/Al₂O₃. In agreement with the earlier study that showed there are different types of BaO depending on the sample loading [28], only the low-temperature desorption feature is observed on the 5-wt% sample and the high-temperature desorption peak is completely absent. We suggest that the low-temperature feature corresponds to that nitrate that is in essential contact with the Al₂O₃ and is influenced by the Al₂O₃.

TPR in H_2

The requirement that Pt be in intimate contact with the BaO phase is clearly observed in the TPR results in Fig. 8. Starting with 20-wt% BaO/Al₂O₃ that had been calcined at 873 K to form the aluminate, samples with Pt loadings of 0, 0.1, and 1.0 wt% were prepared. Each sample was then given a saturation exposure to NO₂ at room temperature before performing a TPR experiment while monitoring m/e = 28 (N₂) and 30 (NO). For the sample without Pt, Fig. 8a) shows that most of the nitrate desorbs as NO at a temperature only 100 K lower than that observed in TPD carried out in He. By contrast, the main nitrogen-containing product on the sample with 1 w% Pt, Fig. 8c), was N₂ and essentially all of the N₂ formed in a very sharp spike below 400 K. Even with only 0.1 wt% Pt, Fig. 8b), most of the nitrogen left the sample as N₂, although the reaction occurred at higher temperatures.

It is interesting to consider that the Ba:Pt atomic ratio is 25 for the 1 wt% Pt sample and 250 for the 0.1 wt% sample. Even if the Pt were atomically dispersed, which is almost certainly not the case for samples that had been calcined to 873 K following the addition of Pt, much of the Ba(NO₃)₂ in the sample must be spatially separated from the Pt particles by a distance that is very long on a molecular scale. For all of the nitrate ions to be reduced by H₂ below 400 K on the 1-wt% Pt sample, there must be significant movement of species at low temperatures. One possibility is that H₂ spills over from the Pt onto the Ba(NO₃)₂ phase, but this would require that the nitrate ion can be reduced by hydrogen atoms without requiring contact with a catalyst. In our view, a more realistic interpretation is that the nitrate ions are completely mobile within the

Ba-containing phase, with reaction occurring rapidly at the interface with the Pt particles. A high mobility of nitrate ions is also consistent with the observation that, in the absence of carbonates, one can produce bulk nitrates by exposing BaO-containing samples to NO₂ at room temperature.

Effect of Calcination Temperature on NO₂ Adsorption Rates

Several observations in this paper have demonstrated that the tendency of BaO to form carbonates is strongly suppressed when BaO/Al₂O₃ is calcined above 873 K to form the aluminate. While the carbonate is easily displaced by nitrate ions, it is important to consider whether the aluminate could be a better storage material, especially if there is CO₂ in the gas phase. To test for this, we measured the adsorption uptakes as a function of NO₂ exposures on samples that contained 1-wt% Pt and 20-wt% BaO and that had been calcined to either 823 K or 873 K. The uptake measurements were performed in the flow-reactor system at 573 K, exposing the samples to NO₂ in He, with or without CO₂, for varying lengths of time. The amount of nitrate stored on the sample was then determined by exposing it to 10% H₂ in He and measuring the amount of N₂ produced. The results are summarized in Fig. 9 and show that, for these experimental conditions, there is no significant difference between the storage properties of the two samples. Furthermore, the presence of dry CO₂ had no effect on the ability of these materials to form the nitrates. This suggests that the tendency to form nitrates is so strong as to overwhelm the affinity for CO₂.

Discussion

Perhaps the most interesting observation in this study is the observation that the nitrate ions are extremely mobile in the BaO phases. With $BaAl_2O_4$, nitrates rapidly form even at room temperature and modest exposures to NO_2 . Somewhat higher temperatures are required for rapid displacement of carbonates; but, even in this case, displacement occurs at room temperature. Since $(NO_3)^-$:Ba⁺² stoichiometries of nearly two are achieved with materials containing 20 wt% BaO, this mobility extends to the bulk, not just surfaces phases. Finally, in TPR with H₂, all of the nitrate ions are able to migrate to Pt particles at temperatures below 400 K. Therefore, the picture that emerges suggests that the nitrate ions are almost liquid-like within the Ba-containing phase.

This has important implications for spectroscopic studies. As in the case with sulfates [22], one should expect that infrared bands for bulk species will be different from that of surface species. However, if surface and bulk nitrates can convert rapidly from one to the other at room

temperature, as our results suggest, one must question how significant the distinction between surface and bulk species is. Furthermore, the complexity of the desorption process, as evidenced by the large differences in the peak temperatures when desorption is carried out into a carrier gas or in vacuum, suggest that one must be careful assigning TPD features to particular types of species.

The comparison between BaO on Al_2O_3 and $BaAl_2O_4$ is also of interest. Certainly, all the evidence from our study suggests that the aluminate is at least as effective for NO_x storage as the BaO phase, so that aluminate formation should not be thought of as a deactivation process. The aluminate phase is quite different from BaO in that carbonates are destabilized significantly. Pure BaCO₃ is reported to be thermally stable up to 1700 K [27], while our FTIR data suggests that any carbonates present on BaAl₂O₄ can be removed by heating to 473 K. On the other hand, our results suggest that aluminate formation has very little effect on storage of nitrates. The nitrates decompose the aluminate readily, just as they readily displace carbonates. The ease with which nitrates decompose carbonates and aluminates can be understood from the reaction energetics. Energetically, the reaction to form nitrates from aluminates is highly favorable, as shown by reaction 3):

 $Ba(Al_2O_4) + 2NO_2 + \frac{1}{2}O_2 \rightarrow Ba(NO_3)_2 + Al_2O_3$ $\Delta H_o = -409.4 \text{ kJ/mol}$ 3) However, energetic arguments suggest that formation of carbonates from aluminates should also be favorable:

 $Ba(Al_2O_4) + CO_2 \rightarrow BaCO_3 + Al_2O_3 \qquad \Delta H_0 = -174 \text{ kJ/mol} \qquad 4)$

Since the peak temperature in TPD experiments for an adsorbate with a heat of adsorption equal to 174 kJ/mol should be above 500 K, even ignoring the influence of readsorption and diffusion processes that tend to shift peaks to higher temperatures [24,25], it would appear that reaction 4) does not adequately describe carbonate formation from the aluminate. Finally, displacing the CO_2 from BaCO₃ with NO₂, reaction 5), is also predicted to occur readily:

$$BaCO_3 + 2NO_2 + \frac{1}{2}O_2 \rightarrow Ba(NO_3)_2 + CO_2$$
 $\Delta H_0 = -225.2 \text{ kJ/mol}$ 5)

The addition of Pt and changes in Pt loading clearly gave rise to the largest changes we observed. The role of Pt, other than catalyzing the formation of NO₂, is primarily in the reduction of the nitrate, since Pt addition gave rise to only minor changes the nitrate decomposition features in TPD. In the absence of Pt, Ba(NO₃)₂ is rather unreactive with H₂. That the nitrates can be reduced to N₂ below 400 K when Pt is present indicates that there must be in physical contact

with the Ba-containing phase. It seems apparent that loss of Pt dispersion could lead to regions where the Ba-containing phase would not be in contact with Pt and would then be unutilized.

As with all adsorption studies for all reactions, there is the question concerning the effect of the other gases in the reaction mixture. Having CO_2 in the gas-phase did not have a significant effect on the NO₂ adsorption in our study but water might well be more important. Even if the surface coverage of water remains low on the surface of the trapping material, it can cause changes in the material itself. A better understanding of how these changes affect the storage properties is clearly needed.

Conclusions

We have found that BaO and $BaAl_2O_4$ appear to be equally effective as NO_x storage materials. Bulk nitrates are formed readily by reaction with NO_2 in both materials, although nitrate formation on $BaCO_3$ requires higher temperatures due to the need to displace CO_2 . Pt plays a crucial role in the reduction of the nitrates, requiring intimate contact with the Ba-containing phase. The nitrates on both BaO and $BaAl_2O_4$ appear to be highly mobile, allowing bulk formation of nitrates at room temperature and allowing all of the bulk nitrate to come in contact with the Pt during the reduction phase.

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Table 1

BET surface areas of the 20wt% BaO/Al_2O_3 samples used in this study.

Calcination T (K)	823	873	1023
Surface Area(m ² /g)	113	109	88

Figure Captions

- Fig. 1 XRD patterns for 20 wt% BaO on γ-Al₂O₃ samples prepared by aqueous impregnation of Ba(NO₃)₂ and calcination for 5 h at the following temperatures: a) 673 K; b) 773 K; c)
 823 K; d) 873 K; e) 1023 K
- Fig. 2 FTIR spectra of 20 wt% BaO/Al₂O₃ samples, measured in flowing dry air at various temperatures. a) The sample was calcined at 873 K and the spectra recorded at: i) room temperature; ii) 473 K; and iii) 573 K; b) The sample was calcined at 823 K and the spectra recorded at: i) room temperature; ii) 573 K; and iii) 823 K.
- Fig. 3 TPD results obtained from: a) 5mg pure Ba(NO₃)₂ in a vacuum system; b) 100 mg pure Ba(NO₃)₂ in the pulse-reactor apparatus using a carrier gas.
- Fig. 4 The effluent from the reactor while exposing BaCO₃ to an NO₂ pulse for 30 minutes at 573 K.
- Fig.5 TPD results for a 20 wt% BaO/Al₂O₃ that had been calcined at 823 K and exposed to NO₂ at room temperature, a), and 573 K, b). TPD results for a 20 wt% BaO/Al₂O₃ that had been calcined at 873 K and exposed to NO₂ at room temperature, c), and 573 K, d). e) TPD result after NO₂ exposure at room temperature obtained from 1-wt% Pt, 20 wt% BaO/Al₂O₃ that had been calcined at 873 K.
- Fig. 6 X-ray diffraction patterns for the BaO/Al₂O₃ samples that had been calcined to 873 K to form the aluminate, before (i) and after (ii) exposure to NO₂ at room temperature.
- Fig. 7 TPD results using the vacuum system following NO₂ exposure at room temperature to BaO/Al₂O₃ that had been calcined at 873 K: a) 20 mg of 20 wt% BaO/γ-Al₂O₃; b) 40 mg 5 wt% BaO/γ-Al₂O₃.
- Fig. 8 TPR results obtained following NO₂ exposure at room temperature to 20 wt% BaO/Al₂O₃ that had been calcined at 873 K with a) 0 wt% Pt loading; b) 0.1 wt% Pt loading; c) 1 wt% Pt loading.
- Fig. 9 NO₂ adsorption (mmol/g) at 573 K vs. time: NO₂ adsorption of 1 wt% Pt, 20 wt%
 BaO/Al₂O₃ that had been calcined in 823 K without CO₂ and ◆ with CO₂; ▲NO₂ adsorption of 1 wt% Pt, 20 wt% BaO/Al₂O₃ that had been calcined in 873 K without CO₂.







Fig. 2



Fig. 3



Fig. 4





Fig. 6



Fig. 7



Fig. 8



Fig. 9