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Regeneration of NO_x trap catalysts

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Abstract

We have investigated the regeneration of a nitrated or sulphated model Pt/Ba-based NO_x trap catalyst using different reductants. H_2 was found to be more effective at regenerating the NO_x storage activity especially at lower temperature, but more importantly over the entire temperature window after catalyst ageing. When the model NO_x storage catalyst is sulphated in SO_2 under lean conditions at 650 °C almost complete deactivation can be seen. Complete regeneration was not achieved, even under rich conditions at 800 °C in 10% H_2/He. Barium sulphate formed after the high temperature ageing was partly converted to barium sulphide on reduction. However, if the H_2 reduced sample was exposed to a rich condition in a gas mixture containing CO_2 at 650 °C, the storage activity can be recovered. Under these rich conditions the S^{2-} species becomes less stable than the ${CO_3}^{2-}$, which is active for storing NO_x. Samples which were lean aged in air containing 60 ppm SO_2 at <600 °C, after regeneration at $\lambda = 0.95$ at 650 °C, have a similar activity window to a fresh catalyst. It is, therefore, important that CO_2 is present during the rich regenerations of the sulphated model samples (as of course it would be under real conditions), as suppression of carbonate formation can lead to sulphide formation which is inactive for NO_x storage.

Keywords: NO_x trap; NO_x storage; Reduction; NO_x; After treatment; Barium

1. Introduction

NO_x storage/reduction catalysts have been under development for several years as a solution to NO_x control in lean burn engines [1]. Though first developed as a solution to NO_x emission control in lean burn gasoline engines [2–6] NO_x storage/reduction catalysts are now seen as a likely solution to NO_x control in diesel vehicles [7]. The operating mechanism of NO_x storage/reduction catalysts has attracted considerable attention (see for example [8–11]) and involves the interaction of NO_2 with an adsorber component under oxidising conditions with a periodic rich excursion to decompose and reduce the stored NO_x species. The most usual storage materials are composed of a precious metal, preferably Pt for its ability to oxidise NO and alkali or alkaline earth oxides which can readily form a nitrate. NO_x storage catalysts are unusual in the field of automotive catalysis in that the catalyst requires a highly active regeneration strategy to maintain effective operation. Precise management of this regeneration processes is essential for effective operation of NO_x storage materials in terms of both optimising catalyst life time and activity whilst maintaining high vehicle fuel economy. Regeneration takes the form of a period of rich operation to remove stored NO_x and sulphur. Regeneration of stored NO_x may occur as often as once a minute, desulphation is required far less frequently at an interval that is strongly dependent on fuel sulphur level. Several authors have demonstrated that some reductants are more effective than others at regenerating a nitrated or sulphated NO_x trap catalyst, with H_2 generally being more effective than CO which in turn is more effective than hydrocarbon [12,13]. On a vehicle the H_2 can be generated

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catalytically in situ from reactions such as water-gas shift or steam reforming of hydrocarbon. Here we present data on the effect of gas composition in the regeneration of a nitrated or sulphated model NO_x trap catalyst.

2. Experimental

The catalyst was prepared by conventional impregnation techniques with major ingredients of 2 wt.% Pt and 10 wt.% Ba relative to the alumina-based support. The material was then heated in static air at 500 °C for 2 h. For the activity measurements the material was pressed, crushed and sieved to produce a particle fraction in the range 250–355 μm. An amount of 0.6 g of catalyst was tested with a total gas flow over the sample of 2 l/min. The NO_x storage test consists of a lean/rich cycle (94 s lean, 3 s rich) with the reported NO_x storage measured on the lean portion of the fifth cycle. NO_x storage efficiency is defined as the amount of NO_x stored as a percentage of the total inlet NO_x over the lean portion of the cycle. Gas compositions unless otherwise stated are: lean—0.5% CO, 14% CO_2, 7% O_2, 5% H_2O, 400 ppm propene, 500 ppm NO; rich—11% CO or 11% H_2, 500 ppm NO, 400 ppm propene, 5% H_2O, 14% CO_2, 0.2% O_2. XRD measurements were taken using a Brucker AXS D-500 diffractometer. Temperature programmed reduction (TPR) was carried out in 10% H_2/N_2 at a ramp rate of 10 °C/min with H_2 consumption measured by TCD. The lean hydrothermally sulphur aged (LHSA) materials shown in Section 3.2 were aged in 60 ppm SO_2, 5% H_2O balance air for 60 h. Gas analysis for the temperature programmed desorption measurements was carried out with a Fisons GASLAB 300 mass spectrometer. XPS measurements were carried out using a Kratos XSAM800 with Mg Kα radiation. The samples were mounted on double sided adhesive tape for analysis. Relative concentrations quoted allow for the relative sensitivity of the instrument for different elements.

3. Results and discussion

3.1. Regeneration of nitrated NO_x trap

One of the important factors which will determine regeneration of a nitrated NO_x trap is the speciation of the gas in the rich phase. Fig. 1 shows the NO (mass 30) signal as a function of temperature for

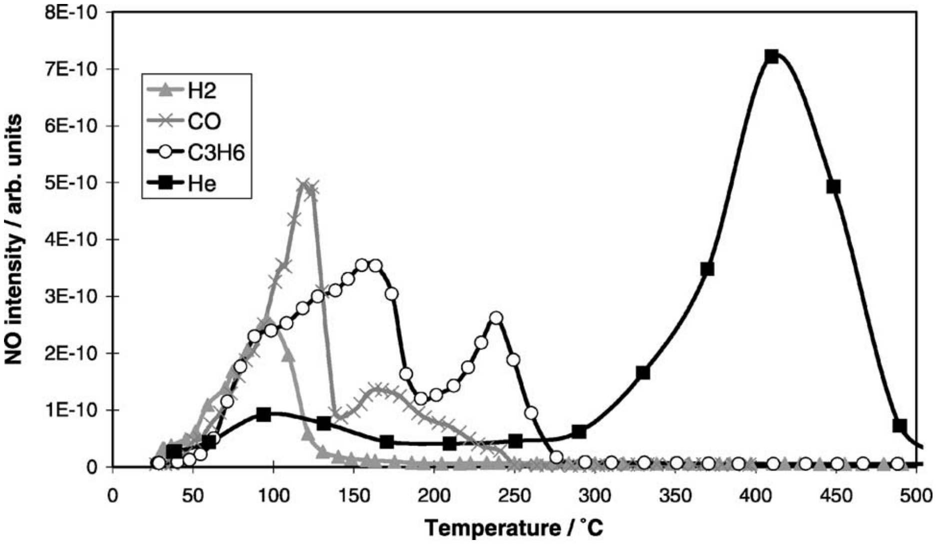

Fig. 1. Temperature programmed desorption in different gas compositions showing NO (mass 30) desorption from nitrate decomposition with a nitrated Pt/Ba-based model NO_x trap catalyst. Ramp rate of 10 °C/min; 10% of the stated gas in He or N_2 except for He which is He only. The samples were nitrated by heating in $NO/O_2/He$ at 300 °C.

decomposition of a nitrated Pt/Ba model NO_x storage catalyst in a range of different gas environments. In the presence of a reductant the decomposition temperature of the nitrate is significantly reduced. The amount of NO desorbed is also reduced compared with decomposition in He only, indicating reduction of the NO to N_2. The data show that the decomposition temperature of the nitrate increases in the order $H_2 < CO < C_3H_6, C_3H_8 < He$. It is also of note that the nitrate decomposition temperature for the Pt/Ba material is ~100 °C lower than observed for bulk $Ba(NO_3)_2$ or nitrated Ba supported on alumina, where the peak NO evolution occurs at 520 °C. This indicates that Pt reduces the decomposition temperature of the nitrate.

Fig. 2 shows a comparison of the NO_x storage efficiency of the catalyst using either CO or H_2 in the rich part of the cycle but otherwise identical conditions. For the fresh catalyst there was no significant difference between the use of CO or H_2. For samples which have been LHA at 700 °C for 60 h the data show a significant decrease in NO_x storage performance due largely to Pt sintering. However, at sample temperatures of 300 °C and less the NO_x storage efficiency is noticeably improved when H_2 rather than CO was used in the rich purge. Following LHA at 900 °C for 2 h H_2 provides an improved NO_x storage efficiency over the entire operating window. Clearly, the benefit of H_2 in the rich purge becomes more pronounced as the Pt becomes more heavily sintered with ageing.

Another interesting feature arising from the use of H_2 to regenerate a nitrated NO_x trap occurs when CO/hydrocarbon/CO_2 are excluded from the feed gas and H_2 is used as the reductant in the rich regeneration. In this condition barium carbonate formation is prevented so nitrate decomposition must occur to the oxide and not the carbonate. The result is a widening of the NO_x storage efficiency window to much higher temperature, as shown in Fig. 3. It is clear that barium nitrate is far more stable with respect to the oxide than the carbonate.

3.2. Sulphur deactivation and regeneration

Lean sulphur ageing is well known to deactivate NO_x storage materials due to sulphate formation [14,15]. The sulphate is more stable than the nitrate

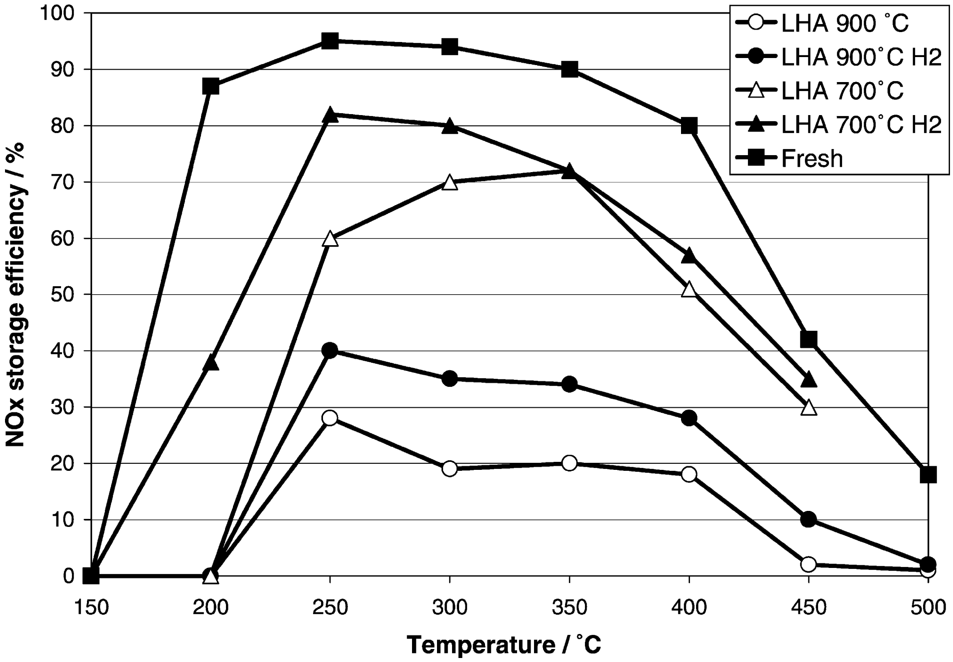

Fig. 2. NO_x storage efficiency window for 2 wt.% Pt/10 wt.% Ba-based catalyst fresh and lean hydrothermally aged (LHA), 5% H_2O in air, at different temperatures using CO or H_2 in the rich phase.

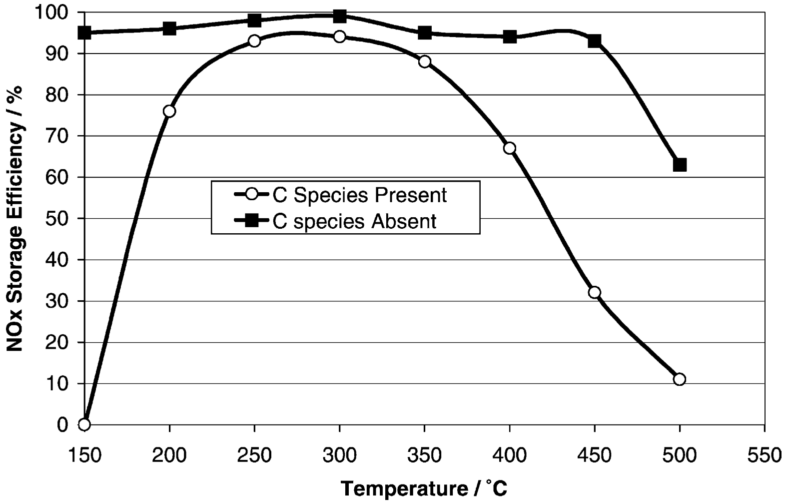

Fig. 3. NO_x storage efficiency window with normal gas feed (CO in rich phase), C species present, and in the absence of CO, hydrocarbon and CO with H_2 in the rich phase, C species absent.

and under normal operating conditions, the sulphate accumulates leading to a loss in NO_x storage capacity. The catalyst is therefore periodically regenerated at a rich condition at high temperature (750–850 °C) to remove the sulphur. To further understand this process we have looked at the regeneration of the sulphur aged model catalyst under different conditions starting from a simple regeneration in H_2/He or CO/He and then in a more complex gas mixture.

Fig. 4 shows the NO_x storage efficiency windows for several samples following lean sulphur ageing (10 h, 600 °C, 60 ppm SO_2) and reduced in H_2 or CO at 700 or 800 °C. For comparison the fresh activity window is also shown as is the NO_x storage efficiency of samples calcined in air (600 °C, 5 h) and then reduced in H_2 at 700 or 800 °C. The initial sulphur ageing severely deactivates the sample and though some activity is recovered following subsequent reduction the original activity is not recovered. The sample which was reduced in CO was even less active than the corresponding H_2 regenerated sample. Calcination and reduction of the fresh sample (without sulphur ageing) has a relatively small effect on the activity.

Fig. 5 shows TPR profile for the sulphur aged model catalyst. The samples were reoxidised by temperature programmed oxidation (TPO) to 600 °C in 10% O_2/He and retested, the resulting TPR profile is also shown. If the process is repeated a third time the reduction peaks are almost unchanged. A sample which has been oxidised at 600 °C, reduced then reoxidised is also shown. Comparison of this with the S aged sample indicates that the H_2 consumption from ∼350 °C is due to sulphate reduction as no equivalent reduction peaks were observed without sulphur ageing. Analysis of the gas desorbed from the sample shows release of SO_2 and H_2S and chemical analysis before and after the first reduction shows significant reduction of the sulphur loading, Table 1. However, it is clear that some species remain that can be reoxidised and reduced. A combination of XRD, XPS and XRF was therefore used to identify this species. XRD analysis of the fresh sample shows the presence of barium carbonate and the LHSA sample barium sulphate. On reduction in H_2 of the sulphur aged sample the barium sulphate decreases and a new phase also appears which can be assigned to barium sulphide ($2\theta = 24.1°$). The XPS data in Table 1 provides further confirmation of barium sulphide formation. Reported binding energies for $BaCO_3$ and $BaSO_4$ are 779.9 and 780.8 eV, respectively, which correspond almost exactly with the Ba binding energies reported for the fresh and LHSA samples. The sulphation procedure clearly produces a well sulphated surface, though significant levels of sulphur are still detected following reduction at 800 °C in both the XPS and XRF measurement indicating substantial amounts of sulphur remain on the catalyst surface and

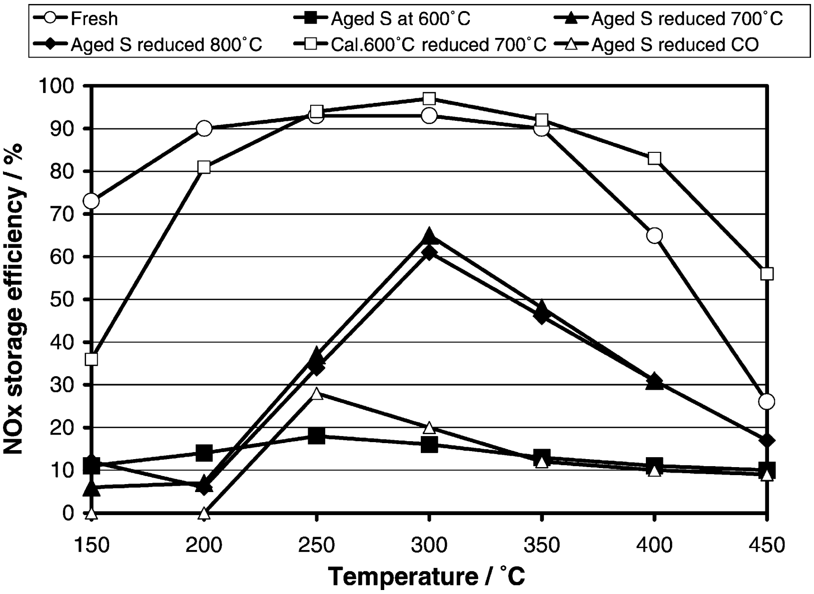

Fig. 4. NO_x storage efficiency window of sulphated and reduced samples compared with the fresh sample and following similar oxidation and reduction treatments in the absence of sulphur. Samples reduced in H_2 unless stated.

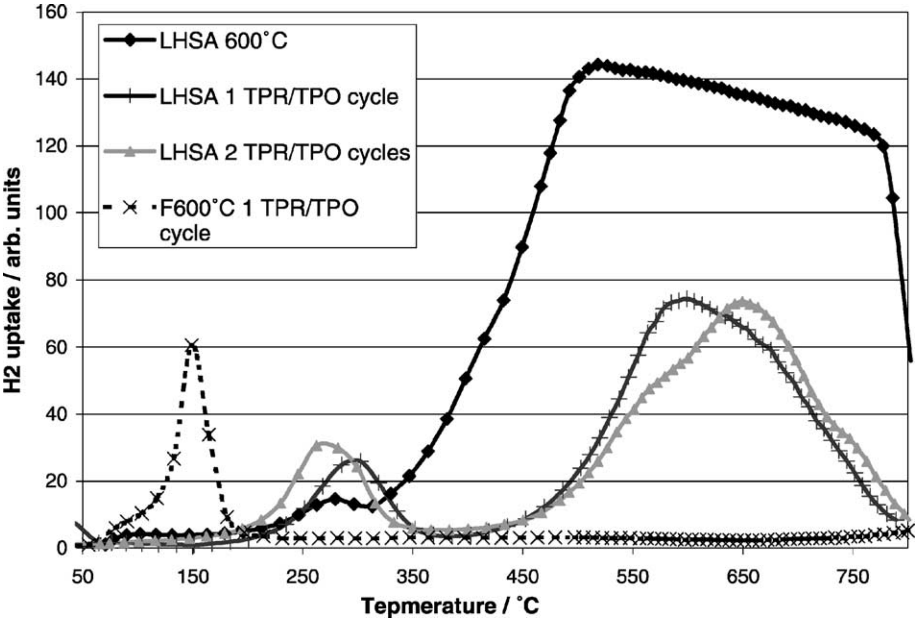

Fig. 5. TPR profiles comparing the model catalyst sample after: (A) LHSA at 600 °C; (B) LHSA/TPR/TPO; (C) LHSA/TPR/TPO/TPR/TPO; (D) calcined 600 °C/TPR/TPO/TPR.

Table 1
XPS binding energies and atomic concentrations for sulphur and barium in different samples[a]

Sample	Ba 3d—XPS		S 2p—XPS		S/Ba ratio	
	BE (eV)	Relative concentration	BE (eV)	Relative concentration	XPS	XRF
Fresh	779.9	1.3	n.a.	n.a.	n.a.	n.a.
LHSA 600 °C	780.9	1.1	169.8	2.3	2.09	0.209
LHSA 600 °C red. 700 °C	780.3	1.1	169.1	0.3	0.27	0.088
LHSA 600 °C red. 800 °C	779.9	1.2	169.2/166.9	0.3/0.1	0.33	0.074
F 600 °C	780.2	1.2	n.a.	n.a.	n.a.	n.a.

[a] Also the S/Ba ratio obtained from XPS and XRF measurements. BE: binding energy; red.: reduced; F: calcined in static air.

in the bulk. Following sulphation and 800 °C reduction, the Ba binding energy shifts back to the original value suggesting some of the Ba is converted back to the carbonate. A second S 2p peak also appears at 166.9 eV consistent with sulphide formation. The essentially constant concentration of Ba suggests there is no substantial barium sintering. The peak at 600 °C in the reduced/reoxidised TPR therefore represents conversion of barium sulphate to these more reduced barium phases, the process being reversible on oxidation at 600 °C. This explains the reappearance of the peak after oxidation. In the original sulphur aged sample the reduction peak is broader and so may indicate other processes are occurring leading to the removal of some of the sulphur from the catalyst. This would be consistent with the loss of some but not all of the sulphur on reduction indicated by XPS, XRF (Table 1) and the reduction in the H_2 consumption for the repeat TPR following reoxidation.

It is known that Ba can exist as the carbonate in the presence of CO_2 [16]. According to thermodynamic calculations, the $CO_3{}^{2-}$ phase should be the most stable phase under all reaction conditions rich of stoichiometry. In order to determine the effect of CO_2 a H_2 reduced sample (sulphated at 500 °C) which contains BaS was exposed to a rich reaction gas mixture ($\lambda = 0.95$ with 15% CO_2) at 650 °C. Fig. 6 shows the NO_x storage activity of these reactivated samples. It is evident that the sample exposed to the CO_2 rich mixture was significantly more active than the sample which had only undergone the H_2 reduction. Postreactor analysis of these samples shows no barium sulphide and a significant reduction in the barium sulphate level compared with the LHSA sample. Fig. 6 also shows a sample sulphated at 500 °C and then reactivated only at $\lambda = 0.95$ at 650 °C without the H_2 pretreatment. The sample had a similar activity pattern to the pre-H_2 reduced sample. These results agree with thermodynamic predictions that $CO_3{}^{2-}$ can displace S^{2-} from Ba under rich conditions. They also clearly demonstrate the importance of forming $BaCO_3$ and not BaS during the rich regenerations of sulphated samples for NO_x storage activity. Any BaS formed is stable even at 800 °C in H_2/N_2 and therefore significant S remains on the surface leading to a reduction in the NO_x storage capacity and subsequent lower activity. However, in the presence of CO_2 the conversion of barium sulphate or sulphide to the carbonate occurs at high temperature allowing more facile removal of sulphur from the sample.

We have similarly studied the regeneration of samples sulphated at different temperatures but regenerated using the same conditions ($\lambda = 0.95$ at 650 °C with 15% CO_2). The NO_x storage capacity of the catalysts regenerated in this way is shown in Fig. 7. The NO_x storage performance is significantly better than the samples reduced in H_2/N_2, Fig. 4. In fact for the sample LHSA at 350 °C the activity following regeneration was identical to that of the fresh catalyst. As the ageing temperature increases the activity drops though this is simply due to additional Pt sintering at these higher temperatures. Comparison of the activity with samples LHA at the same temperature showed that the sulphur had a negligible effect on the activity following regeneration at 650 °C.

It is of note that in the literature there are reports of rich regenerations in the absence of CO_2 so it is clear that dramatically different results can be obtained depending on the gas composition during the test. In order to determine if formation of BaS is confined to ageing in the absence of CO_2 we have also a rich hydrothermally sulphur aged (RHSA) Pt/Ba-based

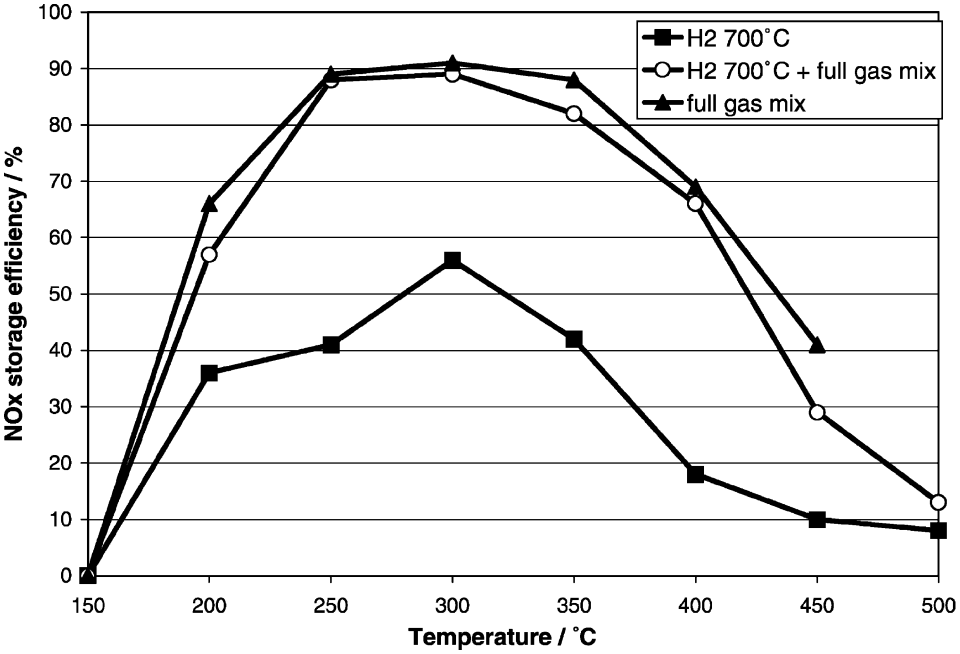

Fig. 6. NO_x storage efficiency window for 2 wt.% Pt/10 wt.% Ba-based model catalyst LHSA at 500 °C for 60 h then regenerated in different ways as described in the text.

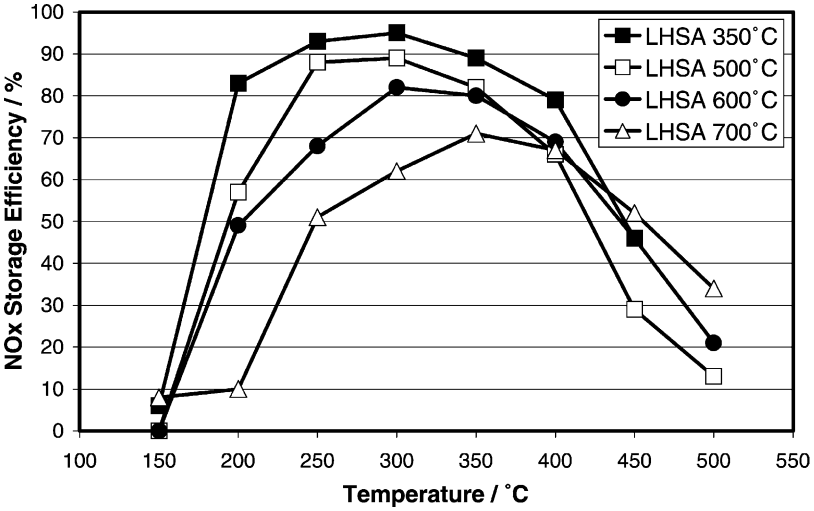

Fig. 7. NO_x storage efficiency window for 2 wt.% Pt/10 wt.% Ba-based model catalyst LHSA at different temperatures for ~60 h then regenerated in the normal rich condition for 30 min at 650 °C.

model catalyst at 830 °C for 16 h in the presence of 10% CO_2, 3% CO, 1% H_2 and 5% H_2O. XRD analysis of this sample again showed BaS formation highlighting that BaS can be extremely thermally stable under rich conditions and that prevention of BaS formation may be an important consideration for NO_x trap desulphation.

4. Conclusions

The nitrate stability for a nitrated Pt/Ba-based model NO_x storage catalyst decreases in a reducing environment when the reductant is changed from propene to CO to H_2. This leads to more effective regeneration and so higher NO_x storage efficiency when H_2 rather than CO was used in the rich regeneration stage of a lean/rich test cycle, especially for an aged catalyst where the Pt was sintered. The use of hydrogen to regenerate sulphated Pt/Ba-based model NO_x storage materials has been demonstrated. In the presence of 10% H_2 in N_2 complete regeneration was not observed even at 800 °C due to the formation of barium sulphide which was stable at this condition. In the presence of a more representative rich exhaust mix, in particular containing CO_2, better regeneration was observed. For a sample LHSA at 350 °C the NO_x storage activity following regeneration was identical to the fresh activity. For samples aged at higher temperatures some activity was lost due to Pt sintering but his was no more than observed in the absence of sulphur in the ageing.

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