Al₂O₃-based Passive NO_x Adsorbers for Low Temperature Applications

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Abstract

NO_x storage on Pt/Al₂O₃ and Pt/La-Al₂O₃ in the temperature range 80-160 °C was investigated by means of microreactor and in situ DRIFTS experiments, to ascertain their suitability for

passive NO_x adsorber applications. Addition of 1 wt% La to Al₂O₃ resulted in the creation of new NO_x storage sites and improved NO_x storage efficiency. However, according to TPD measurements, Pt/La-Al₂O₃ exhibited slightly lower NO_x desorption efficiency below 250 °C than Pt/Al₂O₃. During repeated NO_x adsorption-desorption cycles, almost no benefit of La addition was observed after five cycles, due to the inability to regenerate the strong NO_x storage sites associated with the La at 250 °C. DRIFTS measurements indicated that during NO_x-TPD, nitrites and weakly bound nitrate species were initially removed from the surface of Pt/Al₂O₃ and Pt/La-Al₂O₃. NO_x desorption at higher temperatures (>250 °C) was mainly associated with nitrate decomposition. DRIFTS measurements on Pt/Al₂O₃ revealed that NO_x was mainly stored on the Al₂O₃ surface when oxidized Pt was present, although when a reductive re-treatment was applied NO_x storage on reduced Pt sites became significant and total NO_x storage efficiency was improved. However, compared to bare Al₂O₃, NO_x desorption efficiency below 250 °C significantly dropped when Pt was present, and was even lower after pre-reduction in H₂. Overall, the Pt-Al without pre-reduction showed the highest amount of NO_x desorption below 250 °C.

Keywords: passive NO_x adsorber, alumina, lanthanum, adsorption, desorption, low temperature

1. Introduction

The control of NO_x emissions from lean-burn engines represents an on-going challenge to the automotive industry, particularly at the low exhaust temperatures associated with modern, fuel-efficient engines. While the factors limiting low temperature NO_x control by catalyst-based

aftertreatment systems are well recognized, the performance of current catalyst formulations is insufficient at the low exhaust temperatures expected for the new engines under development. For instance, the slow rate of urea decomposition limits the ability to deploy urea-based selective catalytic reduction (“urea SCR”) for NO_x reduction at low operating temperatures (<180 °C). Consequently, a system is required which combines low temperature NO_x storage with subsequent NO_x reduction. An attractive option which to date has been little explored is the use of a passive NO_x adsorber (PNA) device in combination with a urea SCR catalyst. In this system, the PNA adsorbs NO_x emitted from the engine during cold starts, and then releases the NO_x at higher temperatures, e.g., above 200 °C. At this point the SCR catalyst is sufficiently warm to function efficiently. This differs from the LNT-SCR concept, in which the LNT catalyst functions as the primary NO_x storage/reduction device, the role of the SCR catalyst being to convert NO_x slip (emitted mainly in the lean storage phase) with NH₃ which is emitted by the LNT during rich phase regenerations (and which can be stored on the SCR catalyst) [1]. Given that LNT catalysts function poorly below ca. 200 °C, in general they are unsuitable for the abatement of cold start NO_x emissions.

Cole et al. [2] reported the application of a passive NO_x adsorber to trap cold-start NO_x as early as 1997, the NO_x adsorber being used in combination with three-way catalysts. The first reference to such a concept for low-temperature lean exhaust aftertreatment appears to be a U.S. patent granted to Ford in 2001 [3]. γ -Al₂O₃ was claimed as the NO_x adsorber, promoted with a platinum group metal. In a separate study, Ford workers reported the use of an Al₂O₃-based lean NO_x trap (LNT) catalyst for low temperature applications, the high surface area alumina used exhibiting good NO_x storage performance at relatively low temperature (250 °C) [4]. A recent patent application by GM [5] claims a PNA system incorporating an external fuel injection

system and air pump. If the vehicle shuts down without the PNA having reached its required regeneration (i.e., thermal desorption) temperature, then air and fuel are injected so as to raise the temperature of the PNA until NO_x desorption occurs; the desorbed NO_x is reduced to N₂ by residual NH₃ stored on the downstream SCR catalyst. In a recent presentation [6], researchers from Cummins presented data which showed that a PNA/urea SCR system was able to achieve lower emissions on a light duty (V8) truck than the corresponding urea SCR-only system. A conclusion from this study was that better PNAs are required, particularly with respect to increase of the NO_x release temperature (which should not commence below 175 °C) and increased low temperature NO_x adsorption capacity (>90% storage efficiency required up to 150 °C). A recent patent by Johnson Matthey [7] has also claimed passive NO_x adsorber catalyst systems based on Al₂O₃- or CeO₂-supported Pt/Pd, the objective being to store NO_x below 200 °C; above this temperature NO_x is released and can be reduced by a suitable reductant. The use of these materials mixed with a zeolite has also been studied [8,9] as a means to abate both NO_x and hydrocarbon emissions during cold starts. Besides precious metal-based NO_x adsorbers, silver-based NO_x adsorber systems have drawn attention in both industry and academia. Indeed, the use of Al₂O₃-supported silver for this purpose has been disclosed in a US patent by GM [10]. Moreover, Olsson and co-workers [11] reported significant NO_x storage capacity achieved over an Ag/Al₂O₃ NO_x adsorber system at 200 °C.

Al₂O₃, and especially γ -Al₂O₃, has been used in a large number of chemical processes as variously an adsorbent, a catalyst and/or a catalyst support. Given its relatively high specific surface area and its thermal stability, γ -Al₂O₃ (which is often promoted with La₂O₃ to further improve its thermal stability with respect to sintering), has become an important support material in automotive catalysts. Moreover, as indicated above, the sorbent properties of Al₂O₃ render it a

promising candidate for low temperature PNA applications. However, NO_x storage on Al₂O₃ at low temperatures (<200 °C) has not been widely investigated. For this reason, we have studied NO_x storage on Pt/Al₂O₃ and Pt/La-Al₂O₃ using microreactor and in situ DRIFTS measurements in an effort to gain detailed information about the NO_x storage and desorption properties of Al₂O₃.

2. Experimental

2.1. Catalyst preparation

Two different kinds of model catalysts were used in this study, namely, Pt/ γ -Al₂O₃ and Pt/La-promoted Al₂O₃. Both catalysts were prepared by means of incipient wetness impregnation. γ -Al₂O₃ (Sasol, BET surface area of 201 m²/g) was impregnated with an aqueous solution of tetraamine platinum (II) nitrate to give a Pt loading of 1 wt%, then dried and calcined at 500 °C for 3 h. The resulting sample is hereafter denoted as Pt-Al. Pt/La-promoted Al₂O₃ was prepared in a sequential manner. γ -Al₂O₃ was first impregnated with an aqueous solution of lanthanum nitrate hexahydrate, then dried and calcined at 500 °C for 3 h. The La-promoted Al₂O₃ was subsequently impregnated with aqueous tetraamineplatinum (II) nitrate and further calcined at 500 °C for 3 h. Samples were prepared with La contents of 1 wt%, 3 wt% and 10 wt%, the Pt loading being fixed at 1 wt% in all cases. The resulting samples are denoted as Pt-1La (Pt/1wt% La-Al₂O₃), Pt-3La (Pt/3wt% La-Al₂O₃) and Pt-10La (Pt/10wt% La-Al₂O₃).

2.2. Catalyst characterization

BET surface area and pore volume measurements were performed by nitrogen adsorption at -196 °C using a Micromeritics Tri-Star 3000 system. Catalyst samples were outgassed overnight at 160 °C under vacuum prior to the measurements. Pt dispersion was determined by means of

pulsed H₂ chemisorption at dry ice temperature (-78 °C) using a Micromeritics AutoChem II Analyzer. Around 200 mg of the catalyst was loaded into the reactor. After being reduced at 300 °C in 10% H₂/Ar for 30 min, the catalyst was heated up to 400 °C (hold time 10 min) in flowing Ar to remove adsorbed H. Pulsed H₂ chemisorption was initiated using a four-way valve after the catalyst had been cooled to -78 °C. During this measurement, 0.5 ml of 10 % H₂/Ar was pulsed into the reactor every 2 min, the H₂ signal at the reactor outlet being monitored with a thermal conductivity detector (TCD). H₂ pulsing was terminated after the TCD signal had reached a constant value, i.e., the precious metal sites were saturated with H₂. Assuming a 1:1 ratio of atomic hydrogen to surface Pt, the metal dispersion was calculated based on the amount of H adsorbed.

X-ray powder diffraction was conducted on a Phillips X'Pert diffractometer using Cu-K α radiation ($\lambda = 1.540598 \text{ \AA}$). Diffractograms were recorded between 5° and 90° (2 θ) with a step of 0.02°.

X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo Scientific K-ALPHA spectrometer using Al-K α radiation (1486.6 eV) as the X-ray source. The beam was monochromatized by a twin crystal monochromator, yielding a focused X-ray spot with a size of 400 μm^2 , at 3 mA $\times$ 12 kV. The alpha hemi-spherical analyzer was operated in the constant energy mode with a pass energy of 50 eV. Charge compensation was achieved with a low energy electron flood gun and low energy argon ions from a single source.

2.3. NO_x storage efficiency (NSE) and temperature-programmed desorption

A microreactor loaded with ca. 150 mg of powder catalyst was employed to study the NO_x adsorption and desorption properties of the catalysts. In all the cases, a total flow rate of 120

sccm was used, corresponding to a gas hourly space velocity (GHSV) of ca. 30,000 h⁻¹. Effluent gases were analyzed using a mass spectrometer (QMS 200). Unless otherwise stated, the catalysts were first pretreated at the desired NO_x storage temperature under lean gas containing 5% O₂, 5% CO₂, 3.5% H₂O and He as the balance until the samples were saturated (based on a comparison of the feed and effluent gas concentrations); typically this required 15 min. NO_x storage was performed at three different temperatures (80, 100 and 120 °C) by adding 300 ppm NO to the lean feed gas. After NO_x storage for a specified period of time, the feed gas was switched to bypass mode and the NO flow was switched off. When the NO concentration had dropped to zero, the gas was re-directed to the reactor and temperature-programmed desorption was carried out to study NO_x desorption behavior using a ramp rate of 10 °C/min from the storage temperature up to 500 °C. In one case (Pt-Al), a reductive pretreatment was applied to the sample before NO_x storage and desorption. The sample was reduced at 450 °C for 30 min under flowing 1% H₂/Ar (120 sccm), after which the gas flow was switched to flowing Ar (120 sccm) and the temperature was raised to 500 °C and held for 30 min. After that, the catalyst was cooled down to 120 °C in flowing He for the NO_x storage measurement. In another set of experiments, the Pt-Al and Pt-1La samples were pre-treated at 500 °C in 10% O₂/He flow (120 sccm) for 30 min before cooling to 120 °C in flowing He. NO_x adsorption was then performed for 30 min using a feed gas containing 300 ppm NO, 5% O₂, and He as balance, i.e., in the absence of H₂O and CO₂. NO_x desorption was subsequently performed using 5% O₂ in He as the feed gas.

To understand the effect of multiple storage-desorption cycles, cycling experiments were also performed: first, the catalyst was exposed to NO_x storage conditions at 120 °C for 10 min, after which TPD was performed up to 250 °C using a ramp rate of 10 °C/min and the same lean feed gas but without the inclusion of NO. Subsequently, the temperature was lowered to 120 °C for

the next NO_x adsorption-desorption cycle. In total, five cycles were investigated for both Pt-Al and Pt-1La. In these experiments, H₂O and CO₂ were included in the feed gas.

NO_x storage efficiency (hereafter denoted as NSE) is defined as the percentage of NO_x fed to the reactor that is stored, while NO_x desorption efficiency (hereafter denoted as NDE) is defined as the percentage of stored NO_x that is desorbed during TPD, i.e.:

$$NSE = \left(1 - \frac{\int_0^t ([NOx]_{out}) dt}{\int_0^t ([NO]_{in}) dt} \right) \times 100\%$$

$$NDE = \frac{\int_{t(T_0)}^{t(T)} ([NOx]_{out}) dt}{NSE \times \int_0^t ([NO]_{in}) dt} \times 100\%,$$

in which t is the NO_x storage time; [NO]_{in} is the inlet NO concentration during NO_x storage; [NO_x]_{out} is the outlet NO_x concentration including NO and NO₂ during either NO_x storage or the subsequent NO_x desorption period; t(T₀) is the start time of NO_x-TPD corresponding to the NO_x storage temperature before the temperature is raised; t(T) is the end time of NO_x-TPD corresponding to the desired NO_x desorption temperature.

2.4. Diffuse Reflectance Infrared Fourier Transform Spectroscopy

DRIFTS measurements were performed to monitor the surface species involved in NO_x adsorption and desorption. Measurements were performed using a Nicolet 6700 IR spectrometer equipped with a Harrick Praying Mantis accessory and MCT detector. The reaction cell was sealed with a dome equipped with two ZnSe windows and one SiO₂ observation window. The temperature of the reactor cell was controlled and monitored by a K-type thermocouple placed beneath the reaction chamber. For each DRIFT spectrum an average of 115 scans was collected (requiring ca. 1 min) with a resolution of 4 cm⁻¹. The spectrometer, as well as the outside of the

reaction cell, were continuously purged with dry nitrogen to avoid diffusion of air into the system. Unless otherwise stated, catalyst samples (~50 mg) were pretreated in situ in flowing 5% O₂/Ar (120 sccm) at 500 °C for 1 h in order to remove moisture and carbonate, after which background spectra were collected (using the same feed gas) in the range 500 °C to 100 °C at intervals of 50 °C. NO_x storage was carried out at 100 °C for 30 min using a feed consisting of 5% O₂ and 300 ppm NO (120 sccm). During NO_x storage spectra were collected as a function of time. After 30 min of NO_x storage, temperature programmed desorption (TPD) was performed in flowing 5% O₂/Ar flow (120 sccm), the temperature being raised from 100 °C to 500 °C at a rate of 10 °C/min. DRIFT spectra were recorded during TPD at intervals of 50 °C. Absorbance spectra were obtained by subtracting background spectra from the spectra collected during NO_x storage and desorption.

In one case (Pt-Al), the sample was subjected to a reductive treatment prior to DRIFTS measurements. In this case, the sample was exposed to 1% H₂/Ar at 450 °C for 1 h (ca. 100 sccm), after which the feed gas was switched to Ar and the temperature raised to 500 °C for removal of adsorbed H atoms. All the subsequent background spectra (500 → 100 °C) were likewise collected in Ar (to prevent oxidation of the sample). NO_x storage was subsequently carried out at 100 °C as described above.

3. Results

3.1. Catalyst characterization

To increase the basicity of the γ -Al₂O₃ used in this study, La was added in the concentration range 1 - 10 wt%. Characterization data for the resulting four catalysts are collected in Table 1.

According to N₂ physisorption data, the specific surface areas of the samples decreased with increasing La loading, a 14% decrease being observed when the La loading increased from 0 to 10 wt%. A corresponding drop in pore volume was also observed after introduction of La, the pore volume decreasing from 0.49 cm³/g for Pt-Al to 0.42 cm³/g for Pt-10La.

According to H₂ chemisorption results, Pt was highly dispersed on the unmodified Al₂O₃ support. However, on the 1 wt% La-Al₂O₃ support the dispersion was much lower (53.0% versus 87.0%), while increase of the La loading caused a further small decrease in the Pt dispersion (Table 1). XRD analysis revealed that the La-modified samples contained nanocrystalline La₂O₃ at a loading of only 3 wt% (data not shown) - well below the supposed La₂O₃ monolayer value on the Al₂O₃ support - albeit the diffraction peak was very small. While XPS analysis indicated a significant increase in the surface La/Al atomic ratio when the La loading was increased from 1 to 3 wt% (namely, from 0.004 to 0.025), the La/Al atomic ratio increased only modestly (to 0.036) when the La loading was increased to 10 wt%. Together, these results suggest that crystalline La₂O₃ starts to form on the Al₂O₃ surface at relatively low loadings (ca. 3 wt%) and is rather poorly dispersed at the 10 wt% loading.

3.2. Effect of La addition

Fig.1 compares NO_x storage efficiency (NSE) as a function of NO_x storage time for the samples at 120 °C. All of the samples showed their highest NSE during the initial stages, NSE decreasing significantly with time. La-promoted Al₂O₃ outperformed the unpromoted analog (Pt-Al), as evidenced by the fact that NSE values for the La-promoted samples were almost double that of Pt-Al after 5 min of NO_x storage. However, with increased NO_x storage time, the promoting

effect of La became less significant, the NSE of the promoted samples showing only a marginal advantage at the end of the 30 min storage period compared to Pt-Al.

The results of subsequent NO_x-TPD are compared in Figure 2. As shown in Fig. 2a, in general two NO_x desorption events were observed during TPD, the first one occurring below 250 °C (low-temperature NO_x desorption) and the second one between 250 and 500 °C (high-temperature NO_x desorption). For La loadings between 0 and 3%, the second desorption maximum occurred around 400 °C. A noticeable increase of ca. 40 °C in the position of the desorption maximum was observed for Pt-10La, implying stronger NO_x interaction with storage sites at the high La loading.

NO_x desorption efficiency (NDE) is compared in Fig. 2b. For TPD up to 500 °C, total NO_x desorption efficiency ranks as follows: Pt-1La>Pt-3La>Pt-10La>Pt-Al. Among these four catalysts, Pt-1La displayed a NDE of 98%, indicative of nearly complete NO_x desorption. In contrast, the value for Pt-Al was 88%, indicating that ~12% of the stored NO_x remained on Pt-Al even when the temperature was raised to 500 °C. A further comparison was made on the basis of the two individual NO_x desorption events (i.e., below 250 °C and between 250 and 500 °C). As seen in Fig. 2b, the NO_x desorption efficiency below 250 °C follows the order Pt-Al>Pt-10La~Pt-1La>Pt-3La. Ca. 55% of NO_x stored on Pt-Al was desorbed below 250 °C, while the La-promoted catalysts achieved values of ca. 40%, indicating that ~60% of the NO_x stored at 120 °C required a temperature greater than 250 °C for thermal desorption. Similar to NO_x storage behavior, increasing the La loading failed to significantly impact NO_x desorption behavior. Therefore, Pt-Al and Pt-1La were chosen for further study.

3.3. Effect of NO_x storage temperature

Three different NO_x storage temperatures were investigated in this study: 80, 120 and 160 °C. The selection of 80 °C as the minimum storage temperature was based on published data from Ford Motor Co. [12]; specifically, it was shown that the exhaust gas temperature behind the diesel oxidation catalyst of a 4.4 L diesel engine (upstream of the SCR catalyst) reached a value of ~60 °C after about 10 s of the cold start. Consequently, there is little value in studying NO_x storage at very low temperatures (e.g., 20 °C). The effect of NO_x storage temperature on NSE for Pt-Al and Pt-1La is shown in Fig. 3. For Pt-Al, NSE increased with storage temperature. For example, the 1 min NO_x storage efficiency increased by 30% when the temperature was raised from 80 to 160 °C. However, at 160 °C the NSE decreased with storage time more sharply relative to storage at 80 and 120 °C, such that after 30 min of storage there was little difference between the NSE values for the three temperatures. In the case of Pt-1La, increasing the storage temperature from 80 to 120 °C likewise improved the NSE. Increase of the temperature to 160 °C negatively impacted NO_x storage capability as shown in Fig. 3b, although at long storage times NSE values were again similar.

The effect of NO_x storage temperature on NO_x desorption behavior is shown in Fig. 4. As shown in Fig. 4a, the catalysts displayed a common trend, namely, that low temperature NDE (below 250 °C) decreased with increasing NO_x storage temperature, implying stronger interaction of NO_x with adsorption sites at high NO_x storage temperatures. Moreover, Pt-Al showed higher low-temperature NDE than Pt-1La at the three temperatures investigated. It can be concluded that increasing the NO_x storage temperature exerts a positive effect on NO_x storage efficiency but a negative effect on NO_x desorption efficiency. The combined impact of these two effects is reflected in the amount of NO_x desorbed below 250 °C (Fig. 4c). Pt-1La displayed the highest amount of NO_x desorbed below 250 °C, corresponding to a storage

temperature of 80 °C ($36.6 \mu\text{mol NOx/g}_{\text{cat}}$), while Pt-Al exhibited its highest value after NOx storage at 120 °C ($29.1 \mu\text{mol NOx/g}_{\text{cat}}$). Overall, Pt-1La exhibited better low temperature desorption capability than Pt-Al after NOx storage at 80 °C, whereas after storage at 160 °C the situation was reversed, Pt-1La failing to show any NOx release below 250 °C. After storage at 120 °C, the two catalysts showed similar low temperature NOx release.

3.4. Effect of NOx storage time

The effect of NOx storage time on NOx-TPD was investigated using a NOx storage temperature of 120 °C. Three different storage times were employed: 5 min, 10 min and 30 min. NOx desorption behavior for the different storage times is compared in Fig. 5, from which several trends emerge. First, Pt-1La shows slightly higher total NDE than Pt-Al in all the three cases, while Pt-Al possesses higher low-temperature NDE than Pt-1La. Moreover, low-temperature NDE increased with storage time for both catalysts, implying that at longer storage times NOx is stored on weaker adsorption sites. The total amount of NOx desorbed below 250 °C is compared in Fig. 5c. For both Pt-Al and Pt-1La, the total amount of NOx desorbed below 250 °C increased with storage time, and significant increase was observed in the first 10 minutes for both catalysts, again implying that at longer storage times NOx is increasingly stored on weak sites. As shown in Fig. 5c, comparison of the two catalysts indicates that the benefit of La addition mainly occurs at short storage times. This can be attributed to the fact that while the low-temperature NDE of Pt-1La is consistently inferior to that of Pt-Al, the NSE of Pt-1La is significantly higher than that of Pt-Al at short to moderate storage times (Fig. 1), resulting in higher overall NOx release. At long NOx storage times (e.g., 30 min) the NSE values of Pt-1La and Pt-Al are similar, and hence the superior low-temperature NDE of Pt-Al causes it to display superior overall low-temperature NOx release.

3.5. Effect of CO₂ and H₂O

Although not of relevance for real world applications, NO_x storage and desorption data were collected in the absence of CO₂ and H₂O with the goal of facilitating a more realistic comparison between microreactor data and DRIFTS data (these also being collected in the absence of these components, see section 3.7). Prior to NO_x storage, samples were treated at 500 °C to remove surface carbonates and adsorbed water. As expected, in the absence of CO₂ and H₂O (which can compete with NO_x for storage sites), high NSE was obtained for Pt-Al for the first minute, as evidenced by a NSE of 96.8 % (relative to 46.7% obtained in the presence of CO₂ and H₂O; see Fig. S1). At the end of 30 min storage, NSE values of 70.9% and 51.9% were achieved for Pt-Al and Pt-1La, respectively (compared to 16.3% and 19.0% under regular conditions). During subsequent NO_x-TPD (Fig. S2), two well defined desorption events were observed for both samples, i.e., one in the low temperature range (<250 °C) and one at higher temperature (ca. 250-400 °C). These TPD data are qualitatively similar to those obtained in the presence of CO₂ and H₂O, albeit that in the absence of CO₂ and H₂O the low temperature NO_x desorption peak shifted to slightly higher temperature (by ~35 °C) and the high temperature peak shifted to lower temperature (~70 °C). In terms of the NDE, a decrease was found for both samples compared to the measurements with CO₂ and H₂O present (Figure S3), NDE falling for Pt-Al from 55.5% to 44.5% and for Pt-1La from 38.6% to 10%. Despite this, the amount of NO_x desorbed below 250 °C for Pt-Al was almost three times higher in the absence of CO₂ and H₂O, due to the high NSE (see Table S1). In the case of Pt-1La, the low NDE resulted in a slight decrease in the amount of NO_x desorbed below 250 °C. This difference in NO_x desorption behavior for Pt-Al and Pt-1La can be ascribed to the occupancy of weak NO_x adsorption sites by La during catalyst preparation, as discussed below (section 4).

3.6. Adsorption-desorption cycling study

In a real world application, a PNA would be cycled between ambient temperature (cold start) and an operating temperature at which some degree of NO_x desorption would be achieved; for a light duty diesel engine, typical operating temperatures are likely to lie in the range ~180-350 °C. To simulate this, a cycling experiment was performed in which NO_x was stored at 120 °C for 10 min (in the presence of CO₂ and H₂O), after which the catalyst was heated to 250 °C to promote thermal release of the stored NO_x; in total, this process was repeated five times. Fig. 6 displays the measured NSE for Pt-Al and Pt-1La as a function of cycle number. In the case of Pt-1La, a continuous decrease in NSE was observed for each cycle, the decrease being most marked for the first 3 cycles. After five cycles, Pt-1La failed to reach “steady state” operation, i.e., the NSE failed to reach a constant value. In contrast, no decrease in NSE was observed for Pt-Al after the third adsorption-desorption cycle, i.e., the catalyst reached a stable operating state in which the amount of NO_x adsorbed by the catalyst during each cycle reached a constant value.

Turning to the NO_x desorption behavior of the catalysts during cycling, as shown in Fig. 7, Pt-Al exhibited consistently higher low-temperature NDE than Pt-1La for each cycle. A slight increase in low-temperature NDE was initially observed over Pt-Al, although after 3 cycles the NDE appeared stable. However, Pt-1La displayed a continuous decrease in NDE during cycling; indeed, the difference in low-temperature NDE between these catalysts increased from 8% (1st cycle) to 19% (5th cycle). The total amount of NO_x desorbed below 250 °C during cycling is compared in Fig. 8b. For Pt-1La, a large amount of NO_x (20 μmol/g_{cat}) was desorbed below 250 °C during the first cycle, compared to 14 μmol NO_x/g_{cat} for Pt-Al. During subsequent cycles decreased NO_x desorption was observed from both catalysts; however, the extent of this decrease was much smaller for Pt-Al than Pt-1La. By the fourth cycle the amount of NO_x

desorbed from Pt-Al remained constant, whereas NO_x desorption from Pt-1La continued to fall throughout the five cycles, to a value below that of Pt-Al. Notably, neither Pt-Al nor Pt-1La reached a low temperature (below 250 °C) NDE value of 100% during the next cycle.

3.7. DRIFTS study

In an effort to gain insight into the mechanism of NO_x storage, NO_x storage and desorption over Pt-Al and Pt-1La were examined using DRIFTS. Fig. 8 depicts the evolution of DRIFT spectra acquired during NO_x storage at 100 °C. For Pt-Al, a band at 1660 cm⁻¹ appeared after 1 min, which in the literature has been ascribed to nitrate formed in the vicinity of surface OH groups [13]. TPD experiments described below suggest that this species is very weakly adsorbed (indeed the band almost disappears after NO is removed from the feed), which suggests that it is not a true nitrate species, these generally exhibiting significant thermal stability. For this reason, we tentatively assign this species to NO₂ interacting with OH groups. Simultaneously, two weak bands at 1540 and 1440 cm⁻¹ were observed which can be ascribed to nitrate and nitrite species, respectively [14-18]. With increased storage time, almost no growth was observed for the 1660 cm⁻¹ band. However, the band at 1540 cm⁻¹ continuously grew with time and became the dominant species at the end of the storage period. During this time, the nitrite band appeared to decrease in intensity. In addition, a small shoulder band located at 1610 cm⁻¹ became visible at around 10 min. Based on the simultaneous appearance of bands in the range ~1200-1315 cm⁻¹, the bands at 1610 and 1540 cm⁻¹ can be ascribed to bridging bidentate and monodentate nitrate, respectively [14-16]. In addition, the formation of bridging bidentate nitrite species cannot be excluded given that they would be expected to give rise to bands at 1320 and 1230 cm⁻¹ [15,16], i.e., in the region where bands are indeed observed. Different from the bridging bidentate nitrite, the band at ca. 1440 cm⁻¹ is assigned to monodentate (most likely linear) nitrite [17,18]. Finally,

a weak band at 1813 cm^{-1} was observed around 15 min, which is most likely related to NO adsorption on Pt ($\text{Pt}^0/\text{Pt}^+-\text{NO}$) [19,20].

Turning to Pt-1La, similar to Pt-Al, three bands at 1656 , 1543 and 1440 cm^{-1} appeared simultaneously at the beginning of NOx storage. Three additional bands located at 1610 , 1580 and 1550 cm^{-1} appeared around 5 min and became progressively more intense as the experiment progressed, while related bands grew at 1313 and 1236 cm^{-1} . Based on the literature [14,15], the 1610 , 1580 and 1550 cm^{-1} bands can be assigned to bridging bidentate nitrate, chelating bidentate nitrate and monodentate nitrate species, respectively. Of these species, the monodentate nitrates were formed preferentially, being the dominant species towards the end of the NOx storage experiment. Compared to Pt-Al, the absorption bands observed for Pt-1La were significantly more intense, particularly for bridging/chelating nitrate species. These results imply that new NOx storage sites are created when Al_2O_3 is modified by La_2O_3 , which explains why Pt-1La shows superior NSE compared to Pt-Al. Another notable observation is the fact that the intensity of the nitrite band remained fairly constant for Pt-1La during the course of the experiment, in contrast to Pt-Al for which the band progressively decreased in intensity after the first 5 – 10 min.

The evolution of surface species on Pt-Al and Pt-1La during TPD is shown in Fig. 9. After switching to O_2/Ar feed gas at $100\text{ }^\circ\text{C}$, the species at 1660 cm^{-1} (“ AlOH-NO_2 ”) on Pt-Al almost immediately disappeared, indicating that NO_2 is weakly adsorbed on the surface OH groups. In contrast, the two nitrate bands (1610 and 1553 cm^{-1}) initially become stronger with increase of the temperature, the monodentate nitrate (1538 cm^{-1}) remaining the dominant species. This growth of the nitrate species suggests that instead of desorption, one or more NOx species present - such as nitrite - were converted to nitrate species. However, it is noteworthy that as the

temperature was raised, subtle changes were observed in the band intensity ratios of the three main nitrate species present (bridging, chelating and monodentate); indeed, as shown in Fig. 9, the nitrate bands at higher wavenumber became more intense relative to the low wavenumber band as the temperature was raised. Therefore, it is not inconceivable that the interconversion of species with very different molar absorption coefficients may be responsible, in part at least, for the initial increase in total nitrate band intensity. Under the oxidizing conditions used, the nitrate species appeared very stable, only undergoing decomposition above 400 °C; this is consistent with results reported by Venkov et al. [13]. A small fraction of the nitrate species still remained on the surface at 500 °C.

In the case of Pt-1La, similar to Pt-Al, OH-bound NO₂ species disappeared at 100 °C when NO was removed from the feed, while nitrite species also appeared to be largely removed. Consequently, bridging bidentate nitrate (1610 cm⁻¹), chelating nitrate (1584 cm⁻¹) and monodentate nitrate (1549 cm⁻¹) became the main surface species present. These nitrate bands grew in intensity with increasing temperature, while their distribution also changed with temperature, the band assigned to chelating nitrate species becoming the most intense signal above 250 °C. A significant drop in the intensity of these three nitrate bands was observed at 450 °C, indicating that most of the nitrate species underwent thermal decomposition at this temperature. At 500 °C, only a small amount of monodentate nitrate species remained on the surface.

3.8. Comparison of NO_x adsorption on Al₂O₃, Pt/Al₂O₃ and pre-reduced Pt/Al₂O₃

To provide insights into the mechanism of NO_x storage on Al₂O₃-based PNAs, additional DRIFTS and microreactor measurements were performed using Pt-Al and the bare Al₂O₃ support.

Fig. 10 depicts DRIFTS spectra collected during NO_x storage on Pt-Al in the absence of O₂. Unlike NO_x storage in the presence of O₂, a strong band at ca. 1660 cm⁻¹ was not observed. This suggests that the 1660 cm⁻¹ band is not the product of NO adsorption, i.e., that it is associated with NO₂ adsorption. Instead, intense nitrate (1618, 1582, 1549 cm⁻¹) and nitrite (1472 cm⁻¹) bands appeared. The observation of nitrate bands indicates that even in the absence of O₂ in the feed, surface oxidation of NO can occur. Given that sample pre-treatment occurred in the presence of O₂, it is likely that Pt was present as the oxide, which underwent reduction by NO [21] with subsequent spillover of NO₂ to the alumina and nitrate formation.

A comparison was also made of NO_x adsorption on Pt-Al and Al₂O₃ (no Pt added). As shown in Fig. 11, DRIFTS spectra collected over Al₂O₃ during NO_x storage at 100 °C in the presence of O₂ showed similar bands to Pt-Al (Fig. 8, top), although the distribution of these bands is not exactly the same as for Pt-Al. However, this implies that NO_x is stored mainly on Al₂O₃ rather than Pt. This is consistent with the observation of only a very weak band corresponding to Pt-based NO species (ca. 1813 cm⁻¹), the relative lack of stable, adsorbed NO_x species on Pt being ascribed to the oxidized state of the Pt. To explore this point, DRIFTS measurements were performed during NO_x storage at 100 °C on Pt-Al which was first reduced under flowing H₂ at 450 °C for 1 h. As shown in Fig. 12, in addition to intense nitrate (1610, 1585, 1560 cm⁻¹) and nitrite (1468, 1350 cm⁻¹) bands, new bands appeared at 1779 cm⁻¹, 1929 cm⁻¹, 2241 cm⁻¹ and 2533 cm⁻¹. The broad band at 1779 cm⁻¹ is assigned to linear Pt⁰-NO species [22,23], this band being the first band to appear at short storage times. Moreover, the intensity of this band implies that NO_x storage on Pt can make a significant contribution to the overall NO_x storage capacity. The bands at 1929, 2241 and 2533 cm⁻¹ are related to three different types of NO adsorption, corresponding to mononitrosyl (NO-Al³⁺), NO⁺-Al³⁺ and NO⁻-Al³⁺ species, respectively [11,24].

Apparently, the reductive treatment of Pt-Al prior to NO_x storage results in increased NO_x storage on both Al₂O₃ and Pt sites.

To further confirm the role of Pt in NO_x storage and desorption, additional microreactor experiments were performed, comprising NO_x adsorption (at 120 °C) and desorption, for bare Al₂O₃ and pre-reduced Pt-Al. As shown in Fig. 13, bare Al₂O₃ showed lower NSE compared to Pt-Al. The NSE value for the first 2 min doubled after the addition of Pt, demonstrating the promotional role of Pt in NO_x storage. Notably, a pre-reduction treatment (prior to NO_x storage) caused tremendous improvement in the NSE, as evidenced by a NSE value of 100% for the first 2 min of NO_x storage for pre-reduced Pt-Al. Unfortunately, the reverse effect was observed on NO_x desorption behavior, as demonstrated by NDE below 250 °C decreasing in the order: Al₂O₃ > Pt-Al > pre-reduced Pt-Al (see insert in Fig. 13).

4. Discussion

NO_x storage efficiency measurements indicate that the addition of 1 wt% La to Al₂O₃ results in the creation of new NO_x storage sites, a fact which can be attributed to the higher basicity of La₂O₃ compared to Al₂O₃. This is reflected in increased NSE at storage times of <30 min. However, further increase in the La loading failed to increase the NSE. Both XRD and XPS analysis confirmed that there was a poor La dispersion on the Al₂O₃ surface at the 10 wt% loading, albeit this is below the supposed monolayer value. The small surface La/Al atomic ratio at the loading of 1 wt% is likely due to the fact that at low loadings La occupies defect sites in the Al₂O₃ structure [25]. Presumably, some of those defect sites were buried in the Al₂O₃ and hence not all of the La was detected by XPS. Indeed, in a recent study Kwak et al. utilized solid-

state ^{27}Al NMR to demonstrate the presence of defect sites in the Al_2O_3 surface [26], which were assigned to coordinatively unsaturated pentacoordinate Al^{3+} . At low loadings, Pt preferentially resides on these defect sites, resulting in high dispersions. In this study, the observed decrease in the Pt dispersion (from 87% to 53%) after doping with 1 wt% La may be due to the occupancy of these defect sites by La, forcing Pt to adsorb on sites where it is less strongly bound. The formation of nanocrystalline La_2O_3 at the 3 wt% La loading also demonstrated that the La was no longer highly dispersed on the Al_2O_3 surface after the defect sites were fully occupied. The fact no further improvement in NSE was achieved at the La loadings above 1 wt% suggests that the poor dispersion of the La phase limited its ability to adsorb NO_x effectively. Alternatively, it can be speculated that, as it seems likely, the Pt particles are located primarily on the Al_2O_3 surface rather than on the crystalline La_2O_3 phase, inefficient NO_x spillover from the Pt particles to the La_2O_3 phase limited NO_x adsorption on this phase.

According to TPD measurements, Pt-1La generally exhibits slightly lower NDE below 250 °C than Pt-Al. However, due to the fact that Pt-1La was able to store more NO_x than Pt-Al, the amount of NO_x desorbed below 250 °C by Pt-1La was in some cases greater, in absolute terms, than for Pt-Al. This was mainly the case for NO_x stored at low temperatures (80-120 °C) for relatively short periods. However, the results of adsorption-desorption cycling experiments revealed almost no benefit of La addition with respect to NO_x storage or desorption after the third cycle. Although the formation of strong NO_x adsorption sites by doping with La significantly improves the initial NO_x storage efficiency, these strong sites cannot usefully participate during cyclic operation, i.e., they cannot be regenerated at 250 °C. On the contrary, their creation appears to result in the loss of weak NO_x storage sites which are located on Al_2O_3 , as demonstrated by the lower amount of NO_x desorbed from Pt-1La, compared to Pt-Al, after

three or more adsorption-desorption cycles. To develop more efficient Al_2O_3 -based PNA materials, it is evident that new sites must be introduced which can function as relatively weak NO_x adsorption sites.

Notably, during adsorption-desorption cycling neither Pt-Al nor Pt-1La reached 100% NDE (below 250 °C) during the next cycle. This is significant, given that after several adsorption-desorption cycles, NO_x should be mainly adsorbed on weak adsorption sites (the strong adsorption sites having been mostly filled); despite this, it is evident that a portion of the adsorbed NO_x cannot be desorbed below 250 °C. A possible reason for this is provided by the DRIFTS measurements discussed below, from which it is evident that a portion of the weakly adsorbed NO_x species such as nitrite and OH-bound NO_2 can be converted to (more thermally stable) nitrate species during heating to 250 °C, instead of undergoing thermal release during desorption. Another possible reason why the NDE does not reach 100% is that NO_x initially adsorbed on weak sites may migrate to strong adsorption sites. The latter may correspond to subsurface sites or sites that reside far from Pt (assuming that NO_x adsorption initially occurs mainly at Pt with subsequent spillover to the alumina), i.e., sites that are kinetically inaccessible during the 10 min adsorption phase, but which are accessible during the subsequent temperature ramp. Either way, these results imply that upon prolonged adsorption-desorption cycling, a new equilibrium would eventually be established, corresponding to saturation of all but the weakest/most kinetically accessible storage sites.

As indicated above (section 3.7) DRIFTS data imply that NO_x thermally released below 250 °C, corresponding to the first desorption event observed during microreactor NO_x -TPD studies, arises mainly from desorption of one or more NO_x species such as OH-bound NO_2 and/or nitrite species. At higher temperatures (~400-500 °C), thermal decomposition of nitrate species

represents the main source of released NO_x. However, the fact that nitrate bands initially grow in intensity during TPD implies that some of the nitrite and/or OH-bound NO₂ species can be converted to nitrate species instead of undergoing thermal release. Nitrate species are very stable under oxidizing condition, some of them remaining on the surface at temperatures up to and including 500 °C.

Notably, the reductive treatment of Pt-Al prior to NO_x storage results in significantly increased NSE, DRIFTS data being consistent with increased NO_x storage on both Al₂O₃ and Pt sites. This improved NO_x storage on Al₂O₃ can be explained by several factors. First, metallic Pt is more active for NO oxidation as opposed to oxidized Pt as reported in the literature [21, 27]. This is because the binding ability of Pt oxide towards O, O₂ and NO is weaker than metallic Pt. Indeed, the activation energies for NO oxidation are different over oxidized Pt compared to metallic Pt [28]. Therefore, increased NO₂ formation can be expected over reduced Pt during NO storage, leading to increased nitrate formation on the alumina. Second, NO spillover from Pt to Al₂O₃ should be improved due to increased NO adsorption on metallic Pt sites. Indeed, Al₂O₃-based NO bands (NO-Al³⁺, NO⁺-Al³⁺ and NO⁻-Al³⁺) were observed during NO_x storage on the pre-reduced sample.

Finally, it is noteworthy that the addition of Pt significantly weakened low-temperature NO_x desorption efficiency, while a more significant drop in NDE took place after the pre-reduction treatment, such that less than 10% of stored NO_x was thermally released below 250 °C. The amounts of NO_x desorbed below 250 °C are compared in Table 2. The Pt-Al sample displayed the highest overall amount of NO_x desorbed, the pre-reduced Pt-Al sample displaying the worst overall NO_x desorption efficiency (and lowest amount of NO_x desorbed). From this it follows that both pretreatment and storage conditions significantly impact NO_x storage and desorption

behavior over Pt-promoted Al_2O_3 -based PNA materials. Specifically, it is apparent that a strongly oxidizing Pt function, while beneficial for NO_x storage, inhibits low temperature NO_x release during TPD under oxidizing conditions. This can be attributed to the ability of metallic Pt to oxidize released NO to NO_2 , which can then be readsorbed to form thermally stable nitrates. In the case of oxidized Pt, a better balance is achieved between NO_x storage and desorption, due to the weaker oxidizing function of the Pt. When Pt is absent, as for the bare alumina, the other extreme is reached: NSE is poor, whereas NO_x desorption efficiency is high, resulting in the release of moderate amounts of NO_x at low temperatures.

5. Conclusions

The NO_x storage and desorption properties of Al_2O_3 -based PNA materials were investigated using microreactor and DRIFTS measurements. Addition of La enhanced NO_x storage efficiency during short NO_x storage periods but resulted in a deterioration in NO_x desorption efficiency below 250 °C (irrespective of whether CO_2 and H_2O were present or not). DRIFTS results confirmed that higher concentrations of nitrate species formed on the La-promoted sample relative to $\text{Pt}/\text{Al}_2\text{O}_3$. During NO_x adsorption-desorption cycling, repeated cycles resulted in a significant decrease in the NO_x storage capacity, accompanied by a continuous decrease in low-temperature NO_x desorption efficiency (<250 °C). These effects were more significant for the La-promoted $\text{Pt}/\text{Al}_2\text{O}_3$ sample, with the consequence that it desorbed smaller amounts of NO_x below 250 °C after five cycles than the $\text{Pt}/\text{Al}_2\text{O}_3$ analogue.

DRIFTS measurements indicated that during NO_x -TPD, nitrites and other weakly bound species were initially removed from the surface. Additionally, some of the weakly bound NO_x species

present were converted to strongly adsorbed nitrate species, the nitrates being thermally stable under oxidizing conditions up to 400 °C. The DRIFTS data also implied that NO_x was mainly stored on Al₂O₃ when Pt was oxidized, i.e., when the sample was pre-treated under lean conditions. However, application of a reduction treatment prior to NO_x storage significantly improved the NO_x storage efficiency of Pt/Al₂O₃. In this case NO_x species adsorbed on the Pt sites were observed, in addition to NO_x stored on Al₂O₃. Hence, when metallic Pt is present, the contribution of NO_x stored on the Pt sites cannot be ignored with respect to the overall NO_x storage capability. The powder reactor study further confirmed the promotional role of Pt in NO_x storage and even more significant improvement in NO_x storage efficiency after Pt was reduced. However, NO_x desorption efficiency was negatively impacted by Pt addition especially after Pt was reduced. Overall, the unreduced Pt-Al showed the best low temperature NO_x desorption capability.

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Table 1. Physical properties of the catalysts

Catalyst	BET SA (m ² /g)	Pore Volume (cm ³ /g)	Mean pore Radius (nm)	Pt dispersion (%)	La/Al atomic ratio (XPS)
Pt-Al	195.5	0.491	5.022	87.0	--
Pt-1La	191.5	0.483	5.049	53.0	0.004
Pt-3La	186.6	0.467	5.033	49.1	0.025
Pt-10La	167.4	0.421	5.031	42.0	0.036

Table 2. Comparison of NDE and amount of NO_x desorbed up to 250 °C

	NDE, <250 °C (%)	Amount of NO _x desorbed, <250 °C (μmol/g _{cat})
Al ₂ O ₃	88.3	25.9
Pt-Al	55.5	29.1
Pt-Al (pre-reduced)	9.2	11.0

Figure Captions:

Fig. 1. Comparison of NO_x storage efficiency during NO_x adsorption at 120 °C. Feed: 300 ppm NO, 5% O₂, 5% CO₂, 3.5% H₂O, He as balance.

Fig. 2. (a) NO_x thermal release profiles during temperature-programmed desorption. Feed: 5% CO₂, 3.5% H₂O, 5% O₂, He bal. NO_x pre-adsorbed at 120 °C for 30 min. (b) Comparison of NO_x desorption efficiency for two different temperature ranges (100-250 °C and 250-500 °C).

Fig. 3. Effect of temperature on NO_x storage efficiency. Feed: 300 ppm NO, 5% O₂, 5% CO₂, 3.5% H₂O, He bal.

Fig. 4. Effect of NO_x storage temperature on NO_x desorption efficiency and amount of NO_x desorbed below 250 °C (storage time = 30 min).

Fig. 5. Effect of NO_x storage time on NO_x desorption efficiency and amount of NO_x desorbed below 250 °C (NO_x stored at 120 °C).

Fig. 6. Comparison of NO_x adsorption efficiency during NO_x storage at 120 °C (10 min) for consecutive NO_x adsorption-desorption cycles.

Fig. 7. Comparison of amount of NO_x desorbed below 250 °C during TPD for consecutive NO_x adsorption-desorption cycles.

Fig. 8. Evolution of surface species during NO_x storage at 100 °C. Feed: 300 ppm NO, 5% O₂, Ar balance. Top: Pt-Al; bottom: Pt-1La.

Fig. 9. DRIFT spectra collected during NO_x-TPD. Feed: 5% O₂, Ar balance. NO_x stored at 100 °C for 30 min. Top: Pt-Al; bottom: Pt-1La.

Fig. 10. DRIFT spectra collected for Pt-Al during NO_x storage at 100 °C in the absence of O₂.

Fig. 11. DRIFT spectra collected for bare Al₂O₃ during NO_x storage at 100 °C. Feed: 300 ppm NO, 5% O₂, Ar as balance.

Fig. 12. DRIFT spectra collected for Pt-Al during NO_x storage at 100 °C. Feed: 300 ppm NO, 5% O₂, Ar as balance. Note: the catalyst was pretreated with H₂ at 450 °C for 30 min.

Fig. 13. NO_x storage efficiency at 120 °C as a function of storage time for three samples: bare Al₂O₃, Pt-Al, and pre-reduced Pt-Al.

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Graphical abstract

Graphical abstract .