Improved NO\textsubscript{x} Storage/Release Properties of Ceria-Based Lean NO\textsubscript{x} Trap Compositions with MnO\textsubscript{x} Modification

Marcos Schöneborn \textsuperscript{1,*}, Thomas Harmening \textsuperscript{1}, Javier Giménez-Mañogil \textsuperscript{2,©}, Juan Carlos Martínez-Munuera \textsuperscript{2} and Avelina García-García \textsuperscript{2,*}

\textsuperscript{1} SASOL Advanced Materials, Anckelmannsplatz 1, 20537 Hamburg, Germany
\textsuperscript{2} MCMA Group, Department of Inorganic Chemistry and Institute of Materials, University of Alicante, Carretera Sant Vicent del Raspeig s/n, 03690 Sant Vicent del Raspeig, Alacant, Spain

* Correspondence: marcos.schoeneborn@de.sasol.com (M.S.); a.garcia@ua.es (A.G.-G.); Tel.: +49-40636841241 (M.S.); Tel.: +34-965909419 (A.G.-G.)

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Abstract: Ceria/spinel-based lean NO\textsubscript{x} trap compositions with and without barium were modified with MnO\textsubscript{x} via incipient wetness impregnation. The effect of the MnO\textsubscript{x} layer on the aged materials (850 °C) as to the NO\textsubscript{x} storage and release properties was investigated via NO\textsubscript{x} adsorption (500 ppm NO/5% O\textsubscript{2}/balance N\textsubscript{2}) carried out at 300 °C in a dual-bed with a 1% Pt/Al\textsubscript{2}O\textsubscript{3} catalyst placed upstream of the samples to generate sufficient amounts of NO\textsubscript{2} required for efficient NO\textsubscript{x} storage. Subsequent temperature programmed desorption (TPD) experiments were carried out under N\textsubscript{2} from 300 °C to 700 °C. The addition of MnO\textsubscript{x} to the barium free composition led to a slightly reduced NO\textsubscript{x} storage capacity but all of the ad-NO\textsubscript{x} species were released from this material at significantly lower temperatures (\(\Delta T \approx 100 °C\)). The formation of a MnO\textsubscript{x} layer between ceria/spinel and barium had a remarkable effect on ageing stability as the formation of BaAl\textsubscript{2}O\textsubscript{4} was suppressed in favour of BaMnO\textsubscript{3}. The presence of this phase resulted in an increased NO\textsubscript{x} storage capacity and lower desorption temperatures. Furthermore, NO\textsubscript{x} adsorption experiments carried out in absence of the Pt-catalyst also revealed an unexpected high NO\textsubscript{x} storage ability at low NO\textsubscript{2}/NO ratios, which could make this composition suitable for various lean NO\textsubscript{x} trap catalysts (LNT) related applications.

Keywords: ceria; manganese; barium; spinel; lean NO\textsubscript{x} trap; passive NO\textsubscript{x} adsorber; NO\textsubscript{x} storage; NO oxidation

1. Introduction

The implementation of stricter environmental legislations for passenger cars globally, like Euro 6d, US Tier 3 and China 6B calls for improved catalytic systems for emission control [1]. A lot of attention is drawn to the development of improved NO\textsubscript{x} abatement systems (deNO\textsubscript{x}) for lean-burn engines. As these engines operate at \(\lambda > 1\), the abatement of NO\textsubscript{x} requires dedicated technologies, such as selective catalytic reduction (SCR) and lean NO\textsubscript{x} trap catalysts (LNT), also known as NO\textsubscript{x} storage/reduction catalysts (NSR) [2,3].

In SCR systems, an aqueous urea solution is injected into the exhaust gas via an onboard-tank leading to the formation of NH\textsubscript{3}, which then reacts with NO\textsubscript{x} over the catalyst via the standard (1) and fast (2) SCR reactions. Currently, the most common SCR catalysts are metal-substituted zeolites, like Fe-ZSM-5 or Cu-CHA [4].

\[
\begin{align*}
4\text{NO} + 4\text{NH}_3 + \text{O}_2 & \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O} \\
\text{NO} + \text{NO}_2 + 2\text{NH}_3 & \rightarrow 2\text{N}_2 + 3\text{H}_2\text{O}
\end{align*}
\]
The fast SCR reaction (2) is significantly more effective than reaction (1) at low temperatures in the range of 250–300 °C but it requires the presence of NO₂. Therefore, the SCR catalyst is typically positioned downstream of the diesel oxidation catalyst (DOC), which effectively increases the NO₂/NOₓ ratio [5,6]. Once the NO₂ concentration exceeds a certain threshold, the NO₂-SCR reaction (3) also takes place.

\[ 4\text{NH}_3 + 3\text{NO}_2 \rightarrow 7/2\text{N}_2 + 6\text{H}_2\text{O} \]  

(3)

The NOₓ abatement mechanism of lean NOₓ traps is based on alternating lean/rich cycles with long lean phases, in which NOₓ emissions from the exhaust gases are adsorbed on the catalyst. The stored ad-NOₓ species are desorbed and reduced to nitrogen on catalytically active noble metals in subsequent short rich periods at elevated temperatures [7]. Most common lean NOₓ trap catalysts contain a high surface-area material like γ-Al₂O₃, mixtures of BaO and CeO₂ and noble metals, typically Pt or Pd and Rh [8,9].

Barium species, such as BaO or BaCO₃ act as the primary NOₓ storage component. They can adsorb large amounts of NOₓ in the form of surface nitrites and nitrates during lean operation which involves the progressive oxidation from NO to NO₂ and finally NO₃⁻. The mechanism of NOₓ adsorption on barium species has been investigated intensively [10–15]. According to these studies, the NOₓ adsorption takes place via two pathways in parallel. In the “nitrite” route, NO is catalytically oxidized and directly stored on barium sites in form of nitrite ad-species which can be further oxidized to nitrates.

The “nitrate” route is initiated by the catalytic oxidation of NO to NO₂ (4) which then react on barium sites in a disproportionation reaction, resulting in the formation of nitrate and NO (5).

\[ \text{NO} + 1/2\text{O}_2 \rightarrow \text{NO}_2 \]  

(4)

\[ 3\text{NO}_2 + \text{BaO} \rightarrow \text{Ba(NO}_3)_2 + \text{NO} \]  

(5)

The regeneration of NOₓ storage sites occurs during rich periods and forms harmless nitrogen via the reduction of NOₓ species with hydrogen. Cumaranatunge et al. proposed a mechanism that involves the intermediate generation of ammonia [16]. This mechanism has been confirmed in following studies in which various analytical techniques were applied [17,18]. The fundamental chemical reactions can be summarized as:

\[ \text{Ba(NO}_3)_2 + 8\text{H}_2 \rightarrow 2\text{NH}_3 + \text{BaO} + 5\text{H}_2\text{O} \]  

(6)

\[ 3\text{Ba(NO}_3)_2 + 10\text{NH}_3 \rightarrow 8\text{N}_2 + 3\text{BaO} + 15\text{H}_2\text{O} \]  

(7)

The addition of ceria, which has become a major component in catalyst compositions leads to superior NOₓ storage efficiencies, especially at temperatures below 300 °C [19,20]. Furthermore, ceria plays a substantial role in the water-gas-shift reaction as it provides hydrogen for the regeneration during rich periods and it has a positive impact on the NOₓ storage/release chemistry due to its interplay with platinum [21–24]. The mechanisms of NOₓ storage on ceria under lean conditions involve the formation of various ad-NOₓ species, such as linear, bidentate and chelating nitrites and nitrates. It was observed that the low-temperature (<100 °C) adsorption of NO on ceria primarily leads to the generation of surface nitrites whereas at higher temperatures nitrates are preferentially formed [19,25,26]. On the contrary, Ryou et al. did not observe the formation of nitrates on Pd/CeO₂ at 120 °C and they proposed that the presence of water suppresses the oxidation of nitrites [27]. The adsorption of NO₂ on ceria was studied in detail by Flitschew et al. who combined the well-established diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) with in-situ Raman spectroscopy [28,29]. The authors elaborated that NO₂ storage on ceria proceeds mainly in two pathways which both lead to the formation nitrate species. The first route involves the adsorption of NO₂ on cerium(III) sites which are thereby oxidized and transformed to active Ce(IV)-O species (8) which can then react with additional NO₂ to form nitrates (9). In the second pathway, NO₂ reacts directly with Ce(IV)-O sites without the contribution of cerium(III) (9).
Ce(III) + NO₂ → Ce(IV) ·· O²⁻ + NO \hspace{1cm} (8)

Ce(IV) ·· O²⁻ + NO₂ → Ce(III) ·· O-NO₂⁻ \hspace{1cm} (9)

Fine-tuning of the regeneration parameters, like temperature and modes of fuel-injection is a demanding task and crucial for the performance such as the long-time durability of the catalyst. Incomplete regeneration inevitably leads to catalyst degradation over time as relevant surface sites remain occupied with adsorbed NOₓ species. On the contrary, excess H₂ formed during long rich cycles and low temperatures leads to the generation of high levels of ammonia. This can be a serious concern in LNT-only systems \cite{18,30}. Another important aspect to be considered is the additional fuel-consumption required to enrich the exhaust gas, which eventually leads to increased CO₂ emissions. Therefore, NOₓ storage compounds that can effectively be regenerated are urgently needed.

The synergistic combination of passive SCR with LNT catalysts is an efficient solution to attain low NOₓ tailpipe emissions and to cope with high levels of NH₃, which may result from the total reduction of NOₓ. This approach has become a widespread and well-studied technology for several years \cite{31–38}. The low-temperature performance of LNT complements SCR and the ammonia generated during the rich regeneration phase can replace or supplement urea required for the SCR reactions.

One major deactivation mechanism of LNT catalysts is the solid acid-base reaction between Al₂O₃ and BaO at elevated temperatures resulting in the formation of BaAl₂O₄ and thus causing a loss of NOₓ adsorption sites \cite{39,40}. Improvements in this regard have been reported via the replacement of alumina with the less acidic spinel (MgAl₂O₄), leading to the formation of BaAl₂O₄ only at higher temperatures \cite{41,42}. In addition, the use of spinel in LNT catalysts has been described to improve the low temperature NOₓ storage efficiency and to contribute to enhanced SOₓ tolerance via the formation of sulphates with low thermal stability \cite{43}.

Another reported deactivation mechanism results from reaction of BaO and CeO₂ yielding BaCeO₃, which was detected in LNT formulations prepared by the impregnation of ceria with barium salts \cite{44}.

Despite the technological and chemical improvements achieved over the past 20 years, deactivation at elevated temperatures and optimized NOₓ storage/release properties are perpetual challenges in the design of new formulations for LNT catalysts.

In this regard, the addition of manganese to LNT compositions aiming at improved performance has been proposed and studied by several authors. MnOₓ–CeO₂ mixed oxides present high oxygen storage abilities and improved redox properties. They are typically obtained by coprecipitation, sol-gel synthesis or similar routes leading to high level of homogeneity. The interesting properties predestine these mixed oxides for a substitution of pure ceria in various applications and their superior ability to oxidize soot and NO has already been reported \cite{45–47}. Le Phuc et al. observed significantly improved performance of MnOₓ–CeO₂ containing Pt/Mn-Ce/Ba/Al LNT catalysts in NOₓ reduction during rich phases, which they attributed to the improved oxygen mobility of the mixed oxide as compared to pure CeO₂ \cite{48}.

In another work, Le Phuc studied the contribution of crystalline Mn₂O₃ as to the NOₓ storage performance in Mn/Ba/Al compositions which were investigated in the fresh state, that is, without applying thermal ageing prior to testing \cite{49}. It was found that the manganese sesquioxide only led to improved NOₓ storage performance in a narrow compositional range whereas higher or lower concentrations had a detrimental effect on the storage efficiency.

Zhang et al. detected the formation of BaMnO₃ in the system Pd/Mn/Ba/Al. The presence of this phase led to superior NO oxidation abilities and NOₓ storage performances of the fresh catalysts \cite{50}. Similar but not identical observations were made by Xiao et al, who noticed the occurrence of BaMnO₃ only after calcination at 800 °C \cite{51}. This is in accordance with our own investigations, in which we detected this phase in the system Al/Mg/Ce/Mn/Ba after calcination at 850 °C \cite{52}.

However, the impact of ageing at elevated temperature as to the NOₓ storage/release properties of the manganese modified formulations has not been reported yet.
In this work, we present a novel route for the preparation of manganese modified LNT compositions leading to a MnO$_x$ layer on ceria/spinel mixtures rather than homogeneous MnO$_x$-CeO$_2$ mixed oxides. Firstly, the impact on this route in altering the NO$_x$ storage/release properties of the resulting spinel/ceria/manganese compositions is investigated. Secondly, the stabilizing function of the MnO$_x$ layer as a protective barrier between spinel/ceria and barium is rationalized. The materials described herein were thermally aged at 850 °C prior to testing in order to study their thermal stability, which is a common procedure to simulate catalyst ageing under real conditions [53]. NO$_x$ storage experiments were carried in a dual-bed with a 1% Pt/Al$_2$O$_3$ catalyst placed upstream from the samples. This arrangement mimics a diesel oxidation catalyst, which is typically present in state-of-the-art lean-burn catalyst systems and generates high concentrations of NO$_2$. It was shown in previous studies that NO$_2$ can be stored much more efficiently than NO on barium and cerium species [19,54].

In order to study the NO oxidation ability provided by the manganese species, additional NO$_x$ adsorption experiments were carried out in absence of the Pt/alumina catalyst. The thermal stability of the ad-NO$_x$ species is important to estimate how efficiently the corresponding NO$_x$ storage sites can be regenerated. Therefore, the NO$_x$ release properties of our new formulations were investigated in temperature programmed desorption (TPD) experiments.

2. Materials and Methods

2.1. Sample Preparation

MnO$_x$ modified carriers with loadings of 9 wt% (calculated as MnO$_2$) were prepared by incipient wetness impregnation of homogeneous compositions MgAl$_2$O$_4$/CeO$_2$ (PURALOX MG20 Ce20, commercially available from SASOL) using an aqueous solution of manganese acetate tetrahydrate. The dried samples were then calcined in air at 600 °C.

Both, the Mn-free and the Mn-modified materials were used as starting materials for further wet-impregnation with a barium acetate solution to obtain a loading of approximately 15 wt% BaO. All samples were aged in air at 850 °C for 4 h prior to analyses. Henceforth, the samples are referred to as MgCe (PURALOX MG20 Ce20), MgCe-Mn (MgCe modified with MnO$_x$), MgCe-Ba (MgCe modified with BaO) and MgCe-Mn-Ba (MgCe subsequently modified with MnO$_x$ and BaO). The chemical compositions of the samples are summarized in Table 1.

| Sample      | Al$_2$O$_3$ | MgO | CeO$_2$ | MnO$_2$ | BaO |
|-------------|-------------|-----|---------|---------|-----|
| MgCe        | 63.0        | 17.0| 20.0    | 0       | 0   |
| MgCe-Mn     | 58.3        | 14.9| 17.7    | 9.1     | 0   |
| MgCe-Ba     | 52.8        | 14.7| 17.0    | 0       | 15.5|
| MgCe-Mn-Ba  | 48.4        | 13.3| 15.5    | 7.3     | 15.5|

2.2. Sample Characterization

Surface area (Brunauer-Emmett-Teller method, BET) and porosity measurements were performed by nitrogen adsorption at −196 °C using a Micromeritics Tri-Star 3000 system. The samples were outgassed overnight at 300 °C under vacuum prior to the measurements. X-ray powder diffraction was conducted on a Phillips X’Pert diffractometer using Cu-Kα radiation (λ = 1.540598 Å). Powder diffractograms were recorded between 5° and 90° (2θ), with a step-width of 0.02°. The sample compositions were determined after digestion in an MLS 1200 microwave apparatus by Inductively Coupled Plasma Atomic Emissions Spectrometer (ICP-OES) using a Spectroflame instrument (SPECTRO). X-ray photoelectron spectra (XPS) were obtained using a K-alpha spectrophotometer (Thermo-Scientific), with a high-resolution monochromator. It comprises a source of electrons and ions for automated load compensation. The X-ray radiation source is equipped with an Al anode (1486.6 eV). The pressure of the analysis chamber was constantly set at 5 x 10⁻⁹ mbar. The detector
was kept in constant energy mode with a pass energy of 200 eV for the survey spectrum and 50 eV for the sweep in each individual region. The binding energy was adjusted using the C-1s transition, appearing at 284.6 eV. Binding energy values measured are accurate to ±0.2 eV. The values of binding energy and kinetic energy were adjusted with the Peak-Fit software of the spectrophotometer. The Mg-1s, Al-2p, Ce-3d, Mn-2p, Ba-3d regions (along with C-1s and O-1s regions) were employed to analyse the surface composition of the carriers in the present study.

2.3. NO\textsubscript{x} Storage/Release Tests

NO\textsubscript{x} adsorption experiments were conducted in a quartz tubular reactor connected to specific NDIR-UV gas analysers for NO, NO\textsubscript{2}, CO, CO\textsubscript{2} and O\textsubscript{2}, with the measurement data recorded every 10 seconds. The NO\textsubscript{x} adsorption (500ppm NO/5%O\textsubscript{2}/balance N\textsubscript{2}) was performed at 300 °C in a dual-bed configuration with a 1% Pt/Al\textsubscript{2}O\textsubscript{3} commercial catalyst (supplied by Sigma-Aldrich) placed upstream of the sample using a global flow gas of 500 mL/min. The catalyst effectively oxidizes NO to NO\textsubscript{2}, which is required for effective NO\textsubscript{x} storage. Subsequent temperature programmed desorption (TPD) experiments were carried out under N\textsubscript{2} from 300 °C to 700 °C (5 °C/min) in order to study the thermal stability of the various stored NO\textsubscript{x} species. Besides NO\textsubscript{x} storage ability, this is another important aspect in order to assess the suitability of the different materials for the development of new LNT catalysts.

In addition, NO\textsubscript{x} adsorption experiments in single-bed configuration were performed without the Pt/alumina catalyst in order to study the NO oxidation ability of the individual samples and to gain further insight into the role of the individual manganese species in the NO\textsubscript{x} storage processes.

3. Results

3.1. Structural Properties

The phase composition of the samples was analysed by powder X-ray diffraction. It can be seen in Figure 1 that all samples contain MgAl\textsubscript{2}O\textsubscript{4} and CeO\textsubscript{2} in crystalline form.

![Figure 1. Powder X-ray diffraction (XRD) patterns of (a) MgCe and MgCe-Mn (b) MgCe-Ba and MgCe-Mn-Ba with simulated reflection positions of MgAl\textsubscript{2}O\textsubscript{4}, CeO\textsubscript{2}, BaAl\textsubscript{2}O\textsubscript{4} and BaMnO\textsubscript{3}. For better clarity, the reflections of MgAl\textsubscript{2}O\textsubscript{4} and CeO\textsubscript{2} are not marked in (b).](image)

The addition of MnO\textsubscript{x} to the MgAl\textsubscript{2}O\textsubscript{4}/CeO\textsubscript{2} composition does not lead to the occurrence of additional reflections in the powder pattern, thus pointing to a homogeneous dispersion of the MnO\textsubscript{x} species among the surface without the formation of additional crystalline domains detectable by X-ray diffraction (XRD).

The Ba-containing samples with and without manganese exhibit remarkable differences. In MgCe-Ba, a substantial formation of crystalline BaAl\textsubscript{2}O\textsubscript{4} is observed. This phase is also present in MgCe-Mn-Ba but the intensity of the relevant reflections is decreased in the X-ray pattern of this material. Most importantly, the formation of BaMnO\textsubscript{3} is detected in MgCe-Mn-Ba. This phase
adopting the perovskite structure is more accurately described as BaMnO$_{3-\delta}$, reflecting the possible formation of vacancies in the oxygen sublattice in conjunction with a partial reduction of manganese (IV). The presence of this phase indicates a close proximity of barium and manganese achieved via the preparation procedure and is in accordance with previous studies, in which the occurrence of BaMnO$_3$ in the systems Ba/MnO$_x$-CeO$_2$ and Mn/Ba/Al$_2$O$_3$ was also reported [48,50,51,55,56]. No indication of crystalline binary manganese oxides is found in the XRD pattern of MgCe-Mn-Ba. Other authors, however, reported on the occurrence of isolated and crystalline species Mn$_2$O$_3$ or MnO$_2$ in similar systems [49,50]. Remarkable structural and compositional differences of manganese modified supports as a function of the use of either Mn-acetate or Mn-nitrate for preparation were observed and studied by Kapteijn et al., underlining the crucial role of the preparation route as to the resulting phase composition and arrangement [57]. No indication of the presence of BaCeO$_3$ is found in either sample, proving that the formation of this phase is thermodynamically unfavoured under the conditions of preparation and ageing.

Data on the physical properties of all samples is summarized in Table 2.

| Sample      | $S_{\text{BET}}$ (m$^2$/g) | $r_p$ (nm) | $V_p$ (cm$^3$/g) |
|-------------|-----------------------------|------------|------------------|
| MgCe        | 96                          | 13         | 0.64             |
| MgCe-Mn     | 104                         | 10         | 0.53             |
| MgCe-Ba     | 68                          | 11         | 0.37             |
| MgCe-Mn-Ba  | 59                          | 11         | 0.31             |

Incorporation of about 15% of BaO on the solid precursors by means of wet impregnation followed by aging at 850 °C leads to a significant decrease in BET surface areas and pore volumes of the resulting samples. Nevertheless, the large average pore radius present in all samples is a good indication of their suitability as functional supports for LNT catalysts.

The analysis of the XPS results (Table 3) becomes complex because the samples suffer from significant levels of carbon contamination due to the presence of carbonates. Carbonation also inevitably occurs under real exhaust conditions. Therefore, purging of the samples via heat treatment in inert gas prior to the NO$_x$ storage tests was not applied. Considering the sequential preparation of the samples, both the atomic surface analysis and the metal ratios broadly reflect the decrease in Al, Mg and Ce content after addition of manganese and barium. In addition, the decrease in manganese content after subsequent impregnation with barium is reflected by the XPS results.

| Element | Sample                  |
|---------|-------------------------|
| C       | MgCe 33.46 | MgCe-Mn 43.7 | MgCe-Ba 50.4 | MgCe-Mn-Ba 58.1 |
| O       | 40.0 | 37.7 | 35.5 | 30.1 |
| N       | 0.4 | 0.3 | 0.7 | 0.5 |
| Al      | 17.3 | 11.1 | 10.5 | 8.5 |
| Ce      | 2.9 | 2.5 | 0.7 | 0.5 |
| Mg      | 2.3 | 2.3 | 1.1 | 1.0 |
| Mn      | 0.0 | 2.5 | 0.0 | 0.7 |
| Ba      | 0.0 | 0.0 | 1.2 | 0.8 |

The ratios were calculated based on the content of the elements.
3.2. NO\textsubscript{x} Storage

3.2.1. Dual-bed Experiments

The results of the NO\textsubscript{x} adsorption tests measured in dual-bed configuration are displayed in Table 4.

Table 4. Amounts of NO\textsubscript{x} stored on the samples in dual-bed experiments.

| Samples without Ba     | NO\textsubscript{x} Stored (10\textsuperscript{-3} mmol/m\textsuperscript{2} carrier) | Samples with Ba          | NO\textsubscript{x} Stored (10\textsuperscript{-3} mmol/m\textsuperscript{2} carrier) |
|------------------------|-----------------------------------------|--------------------------|-----------------------------------------|
| MgCe                   | 3.23                                    | MgCe-Ba                  | 4.41                                    |
| MgCe-Mn                | 2.60                                    | MgCe-Mn-Ba               | 6.27                                    |

The total NO\textsubscript{x} retention capacity expressed as mmol of NO\textsubscript{x} stored/m\textsuperscript{2} of carrier follows the order—MgCe-Mn < MgCe < MgCe-Ba << MgCe-Mn-Ba. It is worth mentioning that the surface areas of the samples with barium are significantly lower, resulting in a different order of NO\textsubscript{x} retention capacity if expressed as mmol of NO\textsubscript{x} stored/g of carrier—MgCe-Mn < MgCe-Ba < MgCe << MgCe-Mn-Ba. This is of importance as the reduction in surface area upon Ba-addition and ageing clearly contribute to the deactivation of the support in terms of NO\textsubscript{x} storage ability. In order to study the role of the different species present in the samples, the surface area related expression is applied in this work.

In the case of the Ba-free samples, the presence of MnO\textsubscript{x} slightly reduces the NO\textsubscript{x} storage capacity, thus illustrating that the MnO\textsubscript{x} as such does not contribute to the NO\textsubscript{x} storage process at all or only to a negligible extend. Apparently, relevant NO\textsubscript{x} storage sites of ceria and spinel are partially occupied and thus inactivated by Mn-species. This can also be deduced from the XPS analyses revealing a lower surface concentration of cerium and also a higher surface concentration of carbon species in the MnO\textsubscript{x} modified samples. MgCe-Ba (less cerium and magnesium but barium on the surface) shows a marked but unexpected small increase in NO\textsubscript{x} retention capacity compared to MgCe, which indicates that only a small amount of unreacted (and X-ray invisible) BaO or BaCO\textsubscript{3} is still present after ageing. MgCe-Mn-Ba on the contrary, exhibits superior NO\textsubscript{x} storage ability, pointing to a significant stabilizing and hence beneficial effect of MnO\textsubscript{x} on the Ba-assisted NO\textsubscript{x} storage process. The introduction of MnO\textsubscript{x} as protective layer between BaO and spinel/ceeria leads to the formation of BaMnO\textsubscript{3} and reduces the amount of undesired BaAl\textsubscript{2}O\textsubscript{4} generated after ageing, as observed in the XRD pattern. Thus, the occurrence of the perovskite phase most likely accounts for the high retained NO\textsubscript{x} storage ability after ageing.

3.2.2. Single-bed Experiments

Single-bed experiments without the Pt/alumina catalyst were conducted to study the effect of Mn-addition on NO oxidation ability. The absence of the noble metal catalyst is required as its outstanding oxidation capacity does not allow for a proper investigation of the NO oxidation contribution of the carriers. Table 5 compiles the NO and NO\textsubscript{2} levels quantified for the samples MgCe and MgCe-Mn during NO\textsubscript{x} adsorption in single-bed experiments.

Table 5. NO\textsubscript{2}/NO ratios and amounts of NO\textsubscript{x} stored on the different samples obtained under single-bed configuration.

| Sample     | NO\textsubscript{2}/NO Ratio | NO\textsubscript{x} Stored (10\textsuperscript{-3} mmol/m\textsuperscript{2} carrier) |
|------------|------------------------------|-----------------------------------------|
| MgCe       | 0.07                         | 1.27                                    |
| MgCe-Mn    | 0.43                         | 1.03                                    |
| MgCe-Ba    | 0.08                         | 1.40                                    |
| MgCe-Mn-Ba | 0.48                         | 6.39                                    |
MgCe-Mn presents a significantly higher NO$_2$ production than MgCe evident from the NO$_2$/NO ratios obtained in single-bed experiments, revealing its superior NO oxidation activity promoted by MnO$_x$ addition. The ability of binary manganese oxides, especially Mn$_2$O$_3$, to oxidize NO has also been observed and described in detail by Guo et al. [58]. Although the analysis of the oxidation state of manganese is not part of this study, the presence of highly dispersed Mn$_2$O$_3$ species in MgCe-Mn therefore appears to be a valid assumption.

Although the difference in NO$_2$/NO ratios between MgCe-Ba and MgCe-Mn-Ba is in the same range as in the Ba-free samples, a remarkable higher NO$_x$ storage ability is found in MgCe-Ba-Mn in the single-bed experiments. The amount of stored NO$_x$ is in the same range as observed in dual-bed experiments and is around 4.5 times higher than that observed for MgCe-Ba. The amounts of stored NO$_x$ observed in single-bed and dual-bed experiments are summarized in Figure 3. The NO and NO$_2$ adsorption progressions shown in Figure 2c,d prove that the high NO$_x$ storage efficiency of MgCe-Mn-Ba results from the effective NO$_2$ production in conjunction with the availability of storage sites. NO as such is only adsorbed to a negligible extend. The value of Ba-Mn interactions for fast NO$_x$ storage has previously been reported by Zhang et al. [50]. They have found that the NO oxidation ability of Mn-sites in close proximity to NO$_x$ storage sites of barium leads to very high NO$_x$ storage efficiencies. It can be speculated that the perovskite BaMnO$_3$, which accommodates manganese in the rather high oxidation state +IV, combines both, high redox potential and efficient NO$_x$ storage sites in one solid. The high activity of BaMnO$_3$ for NO and soot oxidation has also been pointed out by Gao et al. [55].

**Figure 2.** Profiles of NO and NO$_2$ of during NO$_x$ adsorption at 300 °C under single-bed (SB) and dual-bed (DB) conditions. (a) NO and (b) NO$_2$ profiles of MgCe and MgCe-Mn. (c) NO and (d) NO$_2$ profiles of MgCe-Ba and MgCe-Mn-Ba. Profiles of Pt/alumina are included for comparison.
in one solid. The high activity of BaMnO$_3$ for NO and soot oxidation has also been pointed out by Gao et al. [55].

Figure 3. Stored amounts of NOx observed in single-bed and dual-bed experiments.

3.3. NOx Release

3.3.1. TPD after NOx Adsorption under Dual-Bed Configuration

The temperature programmed desorption (TPD) of NO$_x$, NO and NO$_2$ after NO/O$_2$ retention under dual-bed configuration was analysed in the temperature range of 300–700 °C. Figure 4 shows the TPD profiles of the different samples. The shape of the TPD profile of MgCe with two maxima—the first one centred at about 360 °C and the second centred at about 450 °C—indicates that there are two main ad-NO$_x$ species present on this sample. The individual contribution of NO and NO$_2$ with the quantification given in Table 6 reveals that a significant fraction of the stored NO$_x$ is released from this sample in the form of NO$_2$. The NO$_2$ desorption takes place in a wide temperature window between 300 and 510 °C. The release of NO takes place in two steps, the first centred at about 350 °C and the second centred at about 490 °C.

The presence of barium leads to distinct changes in the TPD profiles in MgCe-Ba and MgCe-Mn-Ba. Significantly more NO is released from MgCe-Ba than from MgCe with the concentration of NO$_2$ being almost identical. Similar to MgCe, the NO profile of MgCe-Ba shows two peaks. The first one is centred at about 350 °C and shows a comparative shape and peak area than the corresponding peak in MgCe. The second peak is centred at about 530 °C, with a much larger peak area. The NO release is taking place between 440 °C and 610 °C, so that the maximum desorption temperature of NO is increased by about 120 °C compared to MgCe. The concentrations and release temperatures of NO$_2$ are very similar for MgCe and MgCe-Ba although the main contribution of NO$_2$ in MgCe-Ba originates from the desorption processes taking place between 400 °C and 520 °C.

Table 6. Released amounts of NO$_x$, NO and NO$_2$ after adsorption under dual-bed configuration.

| Sample       | NO$_x$ Released ($10^{-3}$ mmol/m$^2$ carrier) | NO Released ($10^{-3}$ mmol/m$^2$ carrier) | NO$_2$ Released ($10^{-3}$ mmol/m$^2$ carrier) |
|--------------|-----------------------------------------------|--------------------------------------------|-----------------------------------------------|
| MgCe         | 2.47                                          | 0.79                                       | 1.68                                          |
| MgCe-Mn      | 0.97                                          | 0.78                                       | 0.19                                          |
| MgCe-Ba      | 4.69                                          | 3.15                                       | 1.54                                          |
| MgCe-Mn-Ba   | 4.76                                          | 4.39                                       | 0.37                                          |
The observations made in the TPD profiles of MgCe and MgCe-Ba lead to the conclusion that the active barium species form comparatively strongly bound ad-NO\textsubscript{x} species, which mainly form NO upon decomposition. This is in line with studies from Lietti et al. [11,12], who reported that NO is the main decomposition product of NO\textsubscript{x} species stored on barium, with TPD profiles very similar to the high temperature peak shown in Figure 4e. This furthermore supports the assumption (see Section 3.2.1) that there are still active barium species left on MgCe-Ba although only BaAl\textsubscript{2}O\textsubscript{4} can be detected in the X-ray pattern.

The presence of MnO\textsubscript{x} forming a layer on spinel/ceria displays unexpected substantial effects on the NO\textsubscript{x} release chemistry of the samples with and without BaO. The NO\textsubscript{x} desorption is dominated by NO in the Mn-containing samples with only minor contribution of NO\textsubscript{2} in marked contrast to the Mn-free samples. In the case of the Mn-Ba combination, an additional contribution of NO species released in the range of 420–520 °C is observed, thus pointing to the generation of additional storage sites. This contribution can be linked to the presence of BaMnO\textsubscript{3} since this desorption peak is absent in MgCe-Mn. Secondly, the NO\textsubscript{x} release process is much more efficient in the MnO\textsubscript{x} modified samples, in particular in MgCe-Mn. As it can be seen in Figure 4a–c, the NO\textsubscript{x} desorption is taking place in the narrow range 300–450 °C. The high temperature desorption of NO and NO\textsubscript{2} is completely absent in the MnO\textsubscript{x} modified sample. A similar observation is made in the TPD profile of MgCe-Mn-Ba, in which the decreased fraction of NO\textsubscript{x} desorbed at higher temperatures upon manganese modification is also apparent.

3.3.2. TPD after NO\textsubscript{x} Adsorption under Single-bed Configuration

Effects induced by MnO\textsubscript{x} addition are even more pronounced in the TPD profiles of MgCe and MgCe-Mn after NO\textsubscript{x} storage under single-bed configuration (Figure 5 and Table 7).

Figure 4. Temperature programmed desorption (TPD) profiles (dual-bed configuration) of MgCe and MgCe-Mn (a) NO\textsubscript{x}, (b) NO (c) NO\textsubscript{2} and MgCe-Ba and MgCe-Mn-Ba (d) NO\textsubscript{x}, (e) NO (f) NO\textsubscript{2}.
Table 6. Released amounts of NO\textsubscript{x}, NO and NO\textsubscript{2} after adsorption under dual-bed configuration.

| Sample       | NO\textsubscript{x} Released (10\textsuperscript{-3} mmol/m\textsuperscript{2}carrier) | NO Released (10\textsuperscript{-3} mmol/m\textsuperscript{2}carrier) | NO\textsubscript{2} Released (10\textsuperscript{-3} mmol/m\textsuperscript{2}carrier) |
|--------------|---------------------------------------------|----------------------------------------------------------------|-----------------------------------------------|
| MgCe         | 2.47                                        | 0.79                                                          | 1.68                                          |
| MgCe-Mn      | 0.97                                        | 0.78                                                          | 0.19                                          |
| MgCe-Ba      | 4.69                                        | 3.15                                                          | 1.54                                          |
| MgCe-Mn-Ba   | 4.76                                        | 4.39                                                          | 0.37                                          |

3.3.2. TPD after NO\textsubscript{x} Adsorption under Single-Bed Configuration

Effects induced by MnO\textsubscript{x} addition are even more pronounced in the TPD profiles of MgCe and MgCe-Mn after NO\textsubscript{x} storage under single-bed configuration (Figure 5 and Table 7).

Table 7. Released amounts of NO\textsubscript{x}, NO and NO\textsubscript{2} after adsorption under single-bed configuration.

| Sample             | NO\textsubscript{x} Released (10\textsuperscript{-3} mmol/m\textsuperscript{2}carrier) | NO Released (10\textsuperscript{-3} mmol/m\textsuperscript{2}carrier) | NO\textsubscript{2} Released (10\textsuperscript{-3} mmol/m\textsuperscript{2}carrier) |
|--------------------|---------------------------------------------|----------------------------------------------------------------|-----------------------------------------------|
| MgCe               | 0.59                                        | 0.18                                                          | 0.41                                          |
| MgCe-Mn            | 0.36                                        | 0.32                                                          | 0.04                                          |
| MgCe-Ba            | 1.34                                        | 1.34                                                          | 0                                             |
| MgCe-Mn-Ba         | 5.05                                        | 4.61                                                          | 0.44                                          |

The majority of stored NO\textsubscript{x} species is released from MgCe in the range of about 320–490 °C in the form of NO\textsubscript{2}. The asymmetry of the NO\textsubscript{2} peak indicates the presence of differently bound ad-NO\textsubscript{x} species with the main population being desorbed at the peak maximum of about 440 °C.

TPD profiles of MgCe-Mn show a significant increase in NO desorption whereas the concentration of released NO\textsubscript{2} is close to zero. The high-temperature desorption peak of NO detected in MgCe is not present in MgCe-Mn but a new one is observed ranging from 300–460 °C. This can be understood in conjunction with the dual-bed experiments, see Section 3.3.1, Figure 4b. Upon the addition of manganese, the low-temperature NO peak gains intensity whereas the high-temperature peak disappears. The absence of the high-temperature NO peak and the low concentration of detectable NO\textsubscript{2} in MgCe-Mn are in accordance with the dual-bed experiments and support the theory of inhibited ceria/spinel sites by manganese species.

The NO\textsubscript{x}-TPD profile of MgCe-Mn-Ba is very similar to the profile obtained after adsorption in dual-bed experiments whereas the low-temperature peak associated with NO release is absent in the profile of MgCe-Ba, thus illustrating the similarity of ad-NO\textsubscript{x} species formed on BaMnO\textsubscript{3} with and without the platinum oxidation catalyst. The presence and intensity of the low-temperature NO peaks of MgCe-Mn and especially MgCe-Mn-Ba demonstrate that the corresponding ad-NO\textsubscript{x} species are only...
formed if considerable amounts of NO\textsubscript{2} are available in the feed gas or in other words: if an effective NO → NO\textsubscript{2} oxidant is present.

4. Discussion

The effect of MnO\textsubscript{x} addition to LNT compositions based on Mg\textsubscript{2}Al\textsubscript{2}O\textsubscript{4}/CeO\textsubscript{2} on the NO\textsubscript{x} storage/release properties was investigated at an adsorption temperature of 300 °C. The results clearly show that both, compositions with and without barium, can be improved significantly by the formation of a MnO\textsubscript{x} layer on the spinel/ceria mixture. The advantages of adding manganese are different in both type of materials indicating that at least two directions in the development of novel LNT catalysts may be pursued.

1. Barium-free compositions. The formation of a manganese oxide layer on Mg\textsubscript{2}Al\textsubscript{2}O\textsubscript{4}/CeO\textsubscript{2} primarily alters the chemical nature of the generated ad-NO\textsubscript{x} species, as they exhibit lower thermostabilities than those generated without Mn-addition. This approach is clearly different from the formation of MnO\textsubscript{x}-CeO\textsubscript{2} mixed oxides, which is described in several studies [45–47].

The presence of the MnO\textsubscript{x} layer significantly narrows the temperature range, in which the full amount of stored NO\textsubscript{x} is desorbed and lowers the maximum desorption temperature by about 100 °C. This finding makes the manganese modified composition an appealing candidate for the development of passive NO\textsubscript{x} adsorbers (PNA). In contrast to conventional LNT catalysts, passive NO\textsubscript{x} adsorbers are regenerated at elevated temperatures without additional rich pulses. This approach has already been described in the early 2000s [59,60] but has gained particular attention just recently due to the stricter legal requirements for NO\textsubscript{x} emissions and the implementation of the more realistic and challenging test procedure WLTP (Worldwide Harmonized Light-Duty Vehicles Test Procedure) for type approval. PNA in combination with passive SCR catalysts can effectively improve the cold start NO\textsubscript{x} conversion at temperatures lower than 200 °C without causing additional fuel penalties [61]. The performance of PNA is determined by (a) the ability to store NO\textsubscript{x} at low temperatures of about 150 °C and (b) effective NO\textsubscript{x} release in a narrow and low temperature range, so that the conversion over the SCR catalyst such as the recovery of NO\textsubscript{x} storages sites can take place efficiently. Ceria- and manganese-based PNA have already been described in literature but our newly developed composition Mg\textsubscript{2}Al\textsubscript{2}O\textsubscript{4}/CeO\textsubscript{2} with MnO\textsubscript{x} appears to be an interesting and sophisticated alternative due to its narrow NO\textsubscript{x} release window from 300–450 °C [62,63]. Although the observed NO\textsubscript{x} release behaviour is very promising, the assessment of the low-temperature NO\textsubscript{x} storage efficiency has not been investigated yet and is part of ongoing studies.

2. Compositions with barium. In the case of Mn-free sample, BaAl\textsubscript{2}O\textsubscript{4} is formed upon ageing at 850 °C, evidently leading to a decrease in NO\textsubscript{x} storage sites. The introduction of a protective layer of MnO\textsubscript{x} between spinel/ceria and barium beneficially suppresses the formation of BaAl\textsubscript{2}O\textsubscript{4} in favour of BaMnO\textsubscript{3}. This perovskite phase accommodating manganese (IV) was proven to be very active for NO\textsubscript{x} storage even at low NO\textsubscript{2}/NO ratios. This beneficial effect was not observed in former investigations of Ba/Mn/alumina compositions prepared by a sequential impregnation of γ-Al\textsubscript{2}O\textsubscript{3} with barium and manganese salts followed by calcination at only 500 °C, not leading to the formation of BaMnO\textsubscript{3} [49]. This illustrates that the temperature treatment along with the resulting phase composition has a crucial impact on the resulting NO\textsubscript{x} storage properties. The NO\textsubscript{x} retention ability and the NO\textsubscript{x} release mechanisms of the manganese modified material do not change if the sample is positioned downstream of an external Pt-catalyst. This is of enormous relevance as state of the art barium-based LNT catalysts require high levels of NO\textsubscript{2} for effective NO\textsubscript{x} conversion [54]. The observation suggests that LNT catalysts based on this formulation can tolerate a reduced noble metal (Pt/Pd) content without losing performance. Furthermore, these materials offer the opportunity for the development of new deNO\textsubscript{x} concepts, in which the LNT function is not mandatorily placed downstream of the DOC function or in which the DOC requires a certain level of NO\textsubscript{x} retention ability itself.

A detailed understanding of the chemistry involved in the generation of the various ad-NO\textsubscript{x} species presenting different thermostabilities could be gained by operando DRIFTS measurements.
in combination with Raman spectroscopy and other sophisticated techniques. These investigations might provide a complementary overview on the diverse processes taking place on the surface of the materials during NO\textsubscript{x} storage and release. The individual contributions of the different compounds present in the compositions could be elucidated and rationalized this manner. These studies are in progress and will be presented in following publications.

5. Patents

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