Dosimeter-Type NO\textsubscript{x} Sensing Properties of KMnO\textsubscript{4} and Its Electrical Conductivity during Temperature Programmed Desorption

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Abstract: An impedimetric NO\textsubscript{x} dosimeter based on the NO\textsubscript{x} sorption material KMnO\textsubscript{4} is proposed. In addition to its application as a low level NO\textsubscript{x} dosimeter, KMnO\textsubscript{4} shows potential as a precious metal free lean NO\textsubscript{x} trap material (LNT) for NO\textsubscript{x} storage catalysts (NSC) enabling electrical in-situ diagnostics. With this dosimeter, low levels of NO and NO\textsubscript{2} exposure can be detected electrically as instantaneous values at 380 °C by progressive NO\textsubscript{x} accumulation in the KMnO\textsubscript{4} based sensitive layer. The linear NO\textsubscript{x} sensing characteristics are recovered periodically by heating to 650 °C or switching to rich atmospheres. Further insight into the NO\textsubscript{x} sorption-dependent conductivity of the KMnO\textsubscript{4}-based material is obtained by the novel eTPD method that combines electrical characterization with classical temperature programmed desorption (TPD). The NO\textsubscript{x} loading amount increases proportionally to the NO\textsubscript{x} exposure time at sorption temperature. The cumulated NO\textsubscript{x} exposure, as well as the corresponding NO\textsubscript{x} loading state, can be detected linearly by electrical means in two modes: (1) time-continuously during the sorption interval including NO\textsubscript{x} concentration information from the signal derivative or (2) during the short-term thermal NO\textsubscript{x} release.
1. Introduction

Highly sensitive, selective, stable and fast responding NOx sensing devices are required for the reliable detection of low levels of NOx in a number of important application areas, including automotive and industrial emissions control, as well as environmental and air quality monitoring (immission) [1–3]. Often, the main requirement is the ability to monitor NOx mean concentration values over extended periods (e.g., 1-hour value for immission legislation [4], or the emitted concentration per driven distance [5]) instead of the instantaneous concentration. Dosimeter, integrating or accumulating-type sensors, largely operated as optical or mass sensitive devices, are designed to meet these requirements. Analyte accumulation affects the sensor signal and is achieved either by the generation of a reaction product with the sensor active layer [6–11], or irreversible sorption of NOx onto the surface layer [12–14], followed by periodic regeneration of the sorption capacity [12,14–17].

Recently, impedimetric or resistive NOx dosimeters, based on materials utilized in automotive lean NOx trap catalysts (LNT), were successfully introduced [6,11,18]. Around 400 °C, these carbonate-based materials enable long-term detection of low levels of NO and NO2 by monitoring the increase in conductivity with increased NOx loading. The zero-level is reset by regeneration, achieved either by a step change in temperature or by exposure to reducing atmospheres [6].

In this study, KMnO4 is investigated as a low-cost alternative to commercial LNT formulations in a dosimeter-type NOx sensing device. KMnO4 is known as a strong oxidant [19–21], forming nitrites and nitrates upon exposure to NOx, even above the KMnO4 decomposition temperature [22,23]. Following an investigation of its electrical properties, the NOx dosimeter-type sensing properties at elevated temperatures and the effect of periodic thermal regeneration are examined. The NOx dose is measured either during sorption or during regeneration by combining the conventional temperature programmed desorption method with the electrical sensor signal. This technique, denoted as eTPD, provides, for the first time, a quantitative correlation between the electrical properties and the NOx loading state of a material. This should be of interest for both sensing and catalyst diagnosis applications.

2. KMnO4/La-Al2O3 as Sensitive Layer

2.1. Sample Preparation and Characterization

The sensitive layer of the proposed NOx dosimeter was prepared from 17 mol% KMnO4 (Merck) deposited onto alumina, stabilized with 3% lanthanum (Puralox SCFa-140La3), serving as support oxide with surface area of 140 m2/g and mean particle diameter of 30 µm. The KMnO4/La-Al2O3 powder was prepared by multiple infiltration of an aqueous solution of KMnO4 into the La-Al2O3 powder, followed by drying at 100 °C and calcination at 600 °C for 5 h. Upon thermal decomposition KMnO4 is known to form various potassium- and manganese-containing compounds, like K2MnO4...
and K₃MnO₄, as well as manganese oxide MnO₂ existing in different oxidation states [22,24–30]. The decomposition of KMnO₄ is reported by Boldyrev [25,26] to become noticeable in the temperature range from 205 to 280 °C. KMnO₄-impregnation and firing decreased the surface area of the powder to 100 m²/g (obtained by BET method (named after the originators of the method: Brunauer, Emmett, and Teller) relying on the adsorption of gases to determine the specific surface area of powders). The SEM (scanning electron microscope) analysis of the fired KMnO₄/La-Al₂O₃ powder is given in Figure 1 as a backscatter electron (BSE) image. The powder consists of spherical La-Al₂O₃-rich particles in the range of some tens of µm, partly embedded in a potassium and manganese comprising matrix, which was confirmed by energy-dispersive X-ray spectroscopy (EDX) measurements.

**Figure 1.** SEM image (BSE) of KMnO₄/La-Al₂O₃ powder after firing. The Al-rich particles and the K-Mn-rich matrix are indicated.

The KMnO₄/La-Al₂O₃ powder was mixed with an organic binder (KD2721, Zschimmer & Schwarz) in order to obtain a processable paste. The paste was deposited by spatula onto a 96% pure alumina substrate equipped with gold interdigitated electrodes (area 5 × 6 mm, finger width/distance 100 µm) and fired at 600 °C. The sample was pre-conditioned for several hours at temperatures up to 650 °C in NOₓ containing oxygen-rich atmospheres.

**Figure 2.** Sensor setup and test apparatus including the gas dosing system, a quartz tube furnace containing the KMnO₄/La-Al₂O₃ sample and a chemiluminescence detector (CLD, 700 EL ht, Ecophysic).
The electrical properties of KMnO₄/La-Al₂O₃ were investigated in a test apparatus as sketched in Figure 2. Following installation in a quartz-tube furnace with inner diameter of 22 mm, the sample was heated to temperatures between 300 to 650 °C. The KMnO₄/La-Al₂O₃ layer was exposed to a 2 L/min lean gas flow (10% O₂, 50% N₂ humidified with a water bubbler at room temperature, and 5% CO₂ diluted in N₂ balance) with a gas exchange time of the system in the range of 8 s. The impedance \( Z \) of the KMnO₄/La-Al₂O₃ sample was recorded by an impedance analyzer (Alpha High Performance Frequency Analyzer, Novocontrol).

2.2. Electrical Properties in the Unloaded State

The electrical properties of KMnO₄/La-Al₂O₃ in the unloaded state (after regeneration of the NOₓ sorption sites) were evaluated from 300 to 650 °C by impedance spectroscopy in the frequency range of 1 Hz to 1 MHz. Plotting the impedances in the complex plane as Nyquist plots (real part \( Z' \) and imaginary part \( Z'' \)) yields near semicircular spectra at higher frequencies. This allows the bulk impedance to be modeled by a resistance \( R \) in parallel to a constant phase element \( CPE \) \( (R || CPE) \). The corresponding impedance \( Z_{CPE} \) expressed as a function of the model parameters \( n \) (ranging from 0 to 1) and \( Q \) as well as the angular frequency \( \omega \) is given in Equation (1):

\[
Z_{CPE}(\omega) = \frac{1}{Q} (i\omega)^{-n}
\]  

(1)

In Figure 3(a and b), examples for the corresponding Nyquist plots of the measured impedance data (dots) for 380 and 650 °C, together with the fitted \( R || CPE \) curves in the upper frequency range (solid curves) and the corresponding fitting parameters, are displayed. While the KMnO₄/La-Al₂O₃ sample has a resistance of 180 kΩ at 380 °C, it decreases to 3.4 kΩ upon heating to 650 °C.

The electrical conductivity \( \sigma \) of the KMnO₄/La-Al₂O₃ specimen was estimated from the fitted \( R \)-values of the impedance in the \( R || C \) dominated frequency range taking into account the electrode geometry. The electrode geometry is estimated from the capacitance of the uncoated structure, assuming a parallel-plate capacitor, as described in [31]. The resulting Arrhenius-like representation of \( \sigma \) as a function of inverse temperature \( 1/T \) in Figure 3(c) gives a thermal activation energy of the conductivity \( E_A \) of 0.8 ± 0.1 eV. This thermally activated conductivity leads to an almost two decades increase from \( \sim 5 \cdot 10^{-7} \) S/cm at 380 °C to \( 3 \cdot 10^{-5} \) S/cm at 650 °C.

Information regarding the electrical conductivity of KMnO₄-based materials above the decomposition temperature in the literature is limited. In thermoelectric tests, KMnO₄ and its decomposition products were identified as \( n \)-type semiconductors by Boldyrev and Kabanov, and in the literature cited therein [26,28]. Upon thermal decomposition, the conductivity of KMnO₄ was found to increase, and depending on morphology, the conductivity was reported to range from \( 10^{-6} \) to \( 10^{-8} \) S/cm at 170 to 210 °C [26,28].

The lower conductivity of the KMnO₄/La-Al₂O₃ based material under investigation compared to the reported conductivity of pure KMnO₄ is attributed to the less conductive La-Al₂O₃ particles serving as support oxide in the applied sensitive coating. Recently published results on the K₂CO₃/La-Al₂O₃ system indicate a significant contribution of La-Al₂O₃ to the measured conductivity given its lower conductivity than that of pure K₂CO₃ [32].
3. NOx Sensing Properties

Similar to passive samplers, dosimeter-type gas sensors are operated in two alternating steps: Analyte molecules are progressively accumulated in the sensitive layer during a sorption period, followed by a regeneration procedure to release the formerly sorbed molecules. The focus of the next section is on the evaluation of the dosimeter-type NOx sensing characteristics of KMnO4/La-Al2O3 during NOx sorption as well as the efficiency of thermal regeneration.

3.1. Experimental Setup and Data Evaluation

To study the effect of NOx in the low ppm range, the KMnO4/La-Al2O3 sample was exposed to various NO and NO2 concentrations, cNO,in and cNO2,in for defined time intervals tNOx,in. NOx was admixed to the 2 L/min lean base gas flow (10% O2, 50% N2 humidified with a water bubbler at room temperature, and 5% CO2 diluted in N2 balance). The outlet concentrations were determined by a chemiluminescence detector, as illustrated in Figure 2. In accordance to the reported catalytic activity of Mn-containing LNTs [23,33–36], as well as to results on LNT-based NOx dosimeters [6,18], the NOx sorption studies were performed at a sorption temperature Tsorption of 380 °C, with periodic heating to 650 °C for regeneration.

The sample impedance was recorded continuously during NOx exposure. Since the fitted n-parameters of Z_{CPE} (Equation (1)) of KMnO4/La-Al2O3 in the high frequency range were found to be...
close to 1 (≈0.95), $Q$ can be approximated by the capacitance $C$ and the $R\|\text{CPE}$ equivalent circuit model can be simplified to an $R\|C$ circuit. Thus, $R$ is calculated from the absolute value of the impedance $|Z|$ and the phase angle $\phi$ at a fixed frequency according to Equation (2).

From the Nyquist plots in Figure 3, 10 kHz (marked in red) was selected as an appropriate measurement frequency to monitor the temperature dependent electrical properties in the $R\|C$ dominated range over time and was used, if not denoted otherwise. The absolute value of the relative resistance change due to NO$_x$ exposure $\Delta R_{rel}$ is denoted as the sensor signal, and is defined by Equation (3), with $R_0$ being the base resistance in the NO$_x$ unloaded state:

$$R = |Z| \cdot \frac{1 + \tan^2 \phi}{z}$$  \hspace{1cm} (2)

$$\Delta R_{rel} = \frac{|\Delta R|}{R_0} = \frac{R_0 - R}{R_0}$$  \hspace{1cm} (3)

The analysis in terms of dosimeter-type sensing properties during NO$_x$ sorption at constant flow rates is illustrated in Figure 4. During the NO$_x$ loading stage, $\Delta R_{rel}$ is expected to increase in the presence of NO$_x$ at $T_{\text{sorption}}$ due to progressive NO$_x$ accumulation, without recovery (Figure 4(a)). In the case of a constant flow rate, the cumulated NO$_x$ exposure (or dose) $A_{\text{NO}_x,\text{in}}$ is given by the time integral of $c_{\text{NO}_x,\text{in}}$ as sketched in Figure 4(b), resulting in the unit ppm·s [6,16,37].

**Figure 4.** Data analysis during progressive NO$_x$ accumulation at $T_{\text{sorption}}$: (a) increase in sensor response $\Delta R_{rel}$ during NO$_x$ sorption, (b) determination of cumulated NO$_x$ exposure $A_{\text{NO}_x,\text{in}}$, (c) characteristic $\Delta R_{rel}$ vs. $A_{\text{NO}_x,\text{in}}$ line.

At a constant NO$_x$ concentration, $A_{\text{NO}_x,\text{in}}$ scales linearly with $t_{\text{NO}_x,\text{in}}$. The resulting characteristic line in Figure 4(c) correlates $\Delta R_{rel}$ with $A_{\text{NO}_x,\text{in}}$. It has been shown in detail for a similar material in [6] that in the case of a linear correlation, the signal derivative of a NO$_x$ dosimeter at a constant flow rate increases with the actual NO$_x$ concentration.
3.2. Cumulative NO$_x$ Detection at 380 °C

The presence of NO$_x$ was found to decrease the resistivity of KMnO$_4$/La-Al$_2$O$_3$, with the electrical response continuing to satisfy the $R||C$ equivalent circuit (not shown). The temporal dependence of $R$ on NO$_x$ at 380 °C was studied by exposing the sample to pulses of NO and NO$_2$ for periods of $t_{NOx,in} = 100$ s with concentrations ranging up to 16 ppm. The pulse heights in terms of $c_{NO,in}$ and $c_{NO2,in}$, together with the resulting sensor response, are displayed in Figure 5(a). The sensor response $\Delta R_{rel}$ (Equation (3)) increases stepwise in the presence of NO and NO$_2$ without any recovery at 0 ppm NO$_x$. The slope of $\Delta R_{rel}$ vs. $t$ increases with $c_{NOx,in}$. The characteristic line in Figure 5(b) is extracted from the measured data points and the course of the NO$_x$ concentration according to Figure 4. $\Delta R_{rel}$ correlates almost linearly with the cumulated NO$_x$ exposure $A_{NOx,in}$, independent of the NO$_x$ species, up to at least 40% signal change with a NO$_x$ sensitivity of 4.8%/1,000 ppm·s. The specimen thus provides comparable sensitivity to both NO and NO$_2$. Small deviations of the NO$_2$ related data points from linearity at the initial stage of exposure may originate from NO$_2$ adsorption on the inner surface of the feed lines. The sensing characteristics and in particularly the sensitivity of NO$_x$ dosimeter with a comparable sensitive material were found to be dependent on the temperature as well as on the thickness of the sensitive layer [6,16].

Figure 5. NO$_x$ sensing properties at 380 °C (10% O$_2$, 50% N$_2$/H$_2$O, 5% CO$_2$ in N$_2$): (a) stepwise increase of sensor response $\Delta R_{rel}$ (Equation (3)) during cyclic exposure to NO or NO$_2$, (b) resulting linear $\Delta R_{rel}$ vs. $A_{NOx,in}$ characteristic line.
NO$_2$ on redox active sites provided by e.g., precious metals, followed by chemical NO$_2$ storage by reaction with the alkaline (earth-) carbonates, mainly BaCO$_3$ or K$_2$CO$_3$, to form nitrates [38–40]. The observed increase in the conductivity of fully formulated LNTs in NO$_x$ enables their application as total NO$_x$ sensors [6,11,41] or for in-situ diagnostics of automotive catalysts [41–43].

The requirement of an incorporated oxidant, for the purpose of NO sorption, was verified by electrical means. Pure BaCO$_3$ or K$_2$CO$_3$, on the other hand, accumulates only NO$_2$, enabling conductometric NO$_2$ dosimetry, without NO cross-sensitivity [15,32]. Given the ability of KMnO$_4$/La-Al$_2$O$_3$ to detect either NO or NO$_2$, the oxidizing properties of KMnO$_4$/La-Al$_2$O$_3$ are demonstrated to be sufficient to convert NO to NO$_2$ prior to nitrate formation. This is consistent with MnO$_x$, as a product of KMnO$_4$ decomposition [25,27], being known as an effective oxidizing agent in NO$_x$ reduction catalysts [22,24,33,34,36,44]. The contribution of MnO$_x$ to the NO$_x$ sorption capacity at 380 °C cannot be excluded [45–48].

The linear correlation between $\Delta R_{rel}$ and $A_{NOx,in}$ in the low loading state of the NO$_x$ dosimeter based on KMnO$_4$/La-Al$_2$O$_3$ in Figure 5 points on a sorption rate proportional to the NO$_x$ concentration. This linearity provides a dual-mode functionality: while the sensor response corresponds directly to the cumulated NO$_x$ exposure during the sorption period, the course of $c_{NOx,in}$ can be determined via the signal derivative as described in [6,14]. Furthermore, these results demonstrate that decomposed KMnO$_4$ can be utilized in NO$_x$ dosimeters and catalysts without any need for expensive precious metal additives due to its intrinsic oxidizing nature.

### 3.3. NO$_x$ Concentration Sensitivity at 650 °C

An important criterion for a useful sensor is the ability to refresh or regenerate the device following accumulation of the target gas analyte, which in this study is NO$_x$. The decreased thermodynamic stability of the formed nitrates upon heating limits the catalytic activity of LNTs [38–40,49] and alters the cumulative NO$_x$ sensing characteristics of carbonates and LNT-based sensors [6,17,18,32]. According to Becerra et al. [22], nitrate and nitrite-like compounds formed on KMnO$_4$-based materials decompose in the temperature range of ~550 to 670 °C. Hence, a thermal release of sorbed NO$_x$, leading to a recovery of the sorption sites of KMnO$_4$/La-Al$_2$O$_3$, seems feasible.

The effect of NO$_x$ on the resistivity of KMnO$_4$/La-Al$_2$O$_3$ was studied at 650 °C to investigate this temperature as being suitable for regeneration. The sample was exposed to the NO$_x$ concentration profile shown in Figure 6(a) with up to 8 ppm NO and 75 ppm NO$_2$. $\Delta R_{rel}$ is calculated from the impedance at 1 MHz due to the increased conductivity. Again, the conductivity of KMnO$_4$/La-Al$_2$O$_3$ increases in the presence of NO$_x$. But, as shown in Figure 6(b), at 650 °C, the value for $\Delta R_{rel}$ follows the course of $c_{NOx,in}$ (instead of $\int c_{NOx,in} \, dt$) being characteristic of a common concentration-detecting gas sensor response. Despite the corresponding concentration-related characteristic line in Figure 6(c), which gives a linear correlation, the low sensitivity of only 2.7%/100 ppm NO$_2$ limits the application of KMnO$_4$/La-Al$_2$O$_3$ as a NO$_x$ sensing material operated at 650 °C.

The reversibly sensor response at 650 °C in Figure 6 indicates that the equilibrium of the NO$_x$ sorption on the KMnO$_4$-based material is shifted to the side of the reactants and the resulting fast desorption goes along with the loss of NO$_x$ accumulation capability. Hence, 650 °C seems an appropriate temperature to release formerly sorbed NO$_x$ and to recover the sorption capacity, as well as
the electrical properties of KMnO₄/La-Al₂O₃. The reversibility of the sensor response of KMnO₄/La-Al₂O₃ at 650 °C is consistent with results on an LNT-based NOₓ dosimeter [17].

Figure 6. NOₓ concentration detection at 650 °C: (a) course of NOₓ concentration c_{NOₓ,in}, (b) sensor response ∆R_{rel}, (c) linear correlation between ∆R_{rel} and c_{NOₓ,in}.

3.4. Efficiency of Thermal Regeneration

In the following test series, the efficiency of thermal regeneration, the reproducibility of the dosimeter-type NOₓ sensing characteristics, and the influence of NOₓ exposure time were studied. The same KMnO₄/La-Al₂O₃ sample was exposed to 8 ppm NO₂ or NO at 380 °C in periods of 250, 500, 750, 1,000, and 2,000 s. Between each NOₓ exposure period, the sample was regenerated at 650 °C for about 5 min in the lean gas flow. The sensor responses as a function of t_{NO₂,in} and t_{NO,in} are compared in Figure 7. The five NO₂-borne curves of ∆R_{rel} depicted in Figure 7(a) are almost identical in the corresponding overlapping time scales; please note that the data points corresponding to the longest NO₂ exposure of 2,000 s are partly masked by the other data curves. The corresponding NO curves up to 1,000 s in Figure 7(b) are overlapping as well. The sensor behaves linearly (following an initial incubation period) up to a resistance change of about 40%, with the slope of ∆R_{rel} in Figure 7(a) being nearly constant up to about 1,000 s (8,000 ppm·s NO₂). The nonlinearity at the beginning of NOₓ exposure in Figures 5 and 7, i.e., the slight initial slope increase during the first 375 s in NO₂ (3,000 ppm·s NO₂), is assumed to be caused by NOₓ (in particular NO₂) being adsorbed on the feed gas lines resulting in a delayed sensor response. Further NO₂ exposure leads to a decrease in the slope and ∆R_{rel} reaches a value of 70% after half an hour in 8 ppm NO₂. By definition, ∆R_{rel} cannot reach 100%
as the conductivity increases, resulting in a flattening of the curve of $\Delta R_{rel}$ with continuing NO$_x$ loading. It is expected that a greater sensitive layer thickness would increase the linear range to higher NO$_x$ levels, but at reduced sensitivity (slope $d(\Delta R_{rel})/dA_{NOx,in}$), as reported for LNT-based dosimeters [16].

**Figure 7.** Repeated sensor response to 8 ppm NO$_x$ intervals with intermediate regeneration: (a) sensor response $\Delta R_{rel}$ during NO$_2$ for NO$_2$ exposure of $t_{NO2,in}$ as indicated, (b) $\Delta R_{rel}$ during NO for $t_{NO,in}$ as indicated.

The reproducibility of the sensor response in Figure 7 indicates that the sorption sites of the KMnO$_4$/La-Al$_2$O$_3$-based dosimeter material can be recovered by releasing sorbed NO$_x$ thermally. Heating up to 650 °C restores the NO$_x$ sensing characteristics at 380 °C, independent of the former NO$_x$ exposure duration. The base resistance in the unloaded state $R_0$ was found to decrease slightly with time without impacting the NO$_x$ sensitivity. This might be attributed to small morphological changes during thermal aging, which, however, are too small to be seen by SEM. It is noteworthy to mention that the dosimeter principle avoids such long term signal drifts by definition, since the zero level of $\Delta R_{rel}$ is reset after each regeneration step. This is one of the key advantages of conductometric dosimeters compared to classical semiconductor gas sensors.

4. Electrical Conductivity during Temperature Programmed Desorption (eTPD)

As in temperature programmed desorption (TPD) studies, the course of the NO$_x$ concentration due to NO$_x$ desorption during thermal regeneration gives quantitative information about the amount of stored NO$_x$ in KMnO$_4$/La-Al$_2$O$_3$. Combining TPD with simultaneous electrical characterization (eTPD), an electrical readout of the cumulative sorbed NO$_x$ during the short thermal regeneration periods
results. To obtain further insight into the relation between the NOX loading state and the electrical behavior during NOX sorption and release, eTPD is applied to the KMnO4/La-Al2O3 formulation.

4.1. eTPD Setup and Data Evaluation

eTPD on KMnO4/La-Al2O3 is performed with the experimental arrangement shown in Figure 2. The eTPD related data and their evaluation are summarized in Figure 8.

**Figure 8.** Data analysis for eTPD: (a) time dependence of conductance log $G$ and outlet NOX concentration $c_{\text{released}}$, (b) determination of released amount $A_{\text{released}}$ and electrical response $F_G$, (c) $F_G$ as a function of $A_{\text{released}}$.

To recover the NOx sensing characteristics of KMnO4/La-Al2O3 in between the NOx sorption intervals in the lean gas flow in Figure 7, the sample was heated from 380 °C ($T_{\text{sorption}}$) to 650 °C ($T_{\text{desorption}}$) with a heating rate of 74 °C/min from 425 to 635 °C, while monitoring the impedance at 10 kHz. The temperature increase started at $t_{\text{heat}}$, 50 s after the end of the preceding NOx dosing interval. The resulting NOx desorption curve (Figure 8(a)) is displayed as a NOx concentration $c_{\text{released}}$. At $t_{\text{start}} = t_{\text{heat}} + 50$ s an increase of NOx is observed in the outlet until $t_{\text{end}}$. As illustrated in Figure 8(b), at a constant flow rate, the time integral of $c_{\text{released}}$, evaluated in the time interval of $t_{\text{end}} - t_{\text{start}} = 300$ s, reflects the released NOx amount $A_{\text{released}}$. $A_{\text{released}}$ is expected to be proportional to the quantity of sorbed NOx, if the sorption sites are fully recovered by heating.
The conductance \( G \) of KMnO₄/La-Al₂O₃, with \( G = 1/R \), was found to be affected by the temperature and the NOₓ loading level, both changing during thermal regeneration. As sketched in Figure 8(a), NOₓ release results in a convergence of \( G \) to \( G₀ = 1/R₀ \), \( G₀ \) being the temperature dependent conductance in the unloaded state. The time integral of the conductance upon heating, relative to those of \( G₀ \), is evaluated as the cumulative electrical response \( F_G \). \( F_G \) is calculated according to Equation (4) and is shown in Figure 8(b) as the area between the curves corresponding to the two loading states. In the ideal case, \( F_G \) would be a measurand for \( A_{\text{released}} \) (Figure 8(c)) and would depend linearly on the cumulative sorbed NOₓ amount.

\[
F_G = \int_{t_{\text{start}}}^{t_{\text{end}}} (\log G(t) - \log G₀(t)) \, dt \tag{4}
\]

4.2. Evaluation of the Released Amount

In Figure 7, the resistance responses of KMnO₄/La-Al₂O₃ during an NO₂ sorption series at 380 °C with various exposure periods \( t_{\text{NO₂,in}} \) are reported. The subsequent regeneration by heating to 650 °C to release the formerly sorbed NOₓ can be analyzed in terms of TPD. The corresponding outlet NOₓ concentrations \( c_{\text{released}} \) in the lean 2 L/min gas flow, with a resolution of 0.1 ppm given by the CLD, for \( t_{\text{NO₂,in}} \) up to 1,000 s are compared in Figure 9. After 1,000 s in 8 ppm NO₂ (red curve, as indicated in Figure 9), KMnO₄/La-Al₂O₃ starts to release NOₓ at about 400 °C. \( c_{\text{released}} \) increases with temperature, and at about 550 °C, a maximum is reached at about 1.3 ppm. Shorter NO₂ exposure periods, representing a lower amount of NOₓ loading, yield lower peak heights of \( c_{\text{released}} \). At 650 °C, \( c_{\text{released}} \) reaches zero for all curves, indicating the end of NOₓ release. Additionally, both peak maximum and desorption onset are shifted to lower temperatures with increasing \( t_{\text{NO₂,in}} \). The latter points to a lower stability of the sorbed NOₓ with increased NOₓ loading. Concerning the low values of \( c_{\text{released}} \), it should be considered that the evolved NOₓ is diluted in the 2 L/min lean gas flow and that the sensitive KMnO₄ coating amounts only to an area of about 30 mm² (5 × 6 mm).

The reproducibility of the dosimeter-type NOₓ sensing characteristics at 380 °C (Figure 7) and the missing NOₓ accumulation at 650 °C (Figure 6) reveal that the NOₓ sorption capacity of KMnO₄/La-Al₂O₃ can be recovered by heating to 650 °C. Therefore, the quantity of sorbed NO₂ on KMnO₄/La-Al₂O₃ can be estimated from the subsequently thermally released NOₓ amount \( A_{\text{released}} \), being the area under the desorption peak as shown in Figure 8(b). Figure 9(b) reveals that \( A_{\text{released}} \) and hence the amount of NOₓ sorbed in KMnO₄/La-Al₂O₃ increases almost linearly (with only a small offset) with NO₂ exposure, reflected by \( t_{\text{NO₂,in}} \). Consequently, NO₂ is sorbed on KMnO₄/La-Al₂O₃ with a time constant sorption rate during the 8 ppm NO₂ exposure periods. After 1,000 s in 8 ppm NO₂, resulting in a cumulated NO₂ exposure of 8,000 ppm-s, about 150 ppm-s NOₓ are released. This indicates that only about 1.9% of the NO₂ in the passing gas flow is sorbed in the KMnO₄ based sensitive layer. The gas velocity of 5.3 m/min together the sensitive area length of 6 mm amounts to a residence time of about 70 ms, being comparable to those in catalysts [37]. However, the huge gas volume above the sensitive layer in the 22 mm diameter quartz tube inhibits full NOₓ storage in this NOₓ dosimeter setup. The small offset of \( A_{\text{released}} \) in Figure 9(b) amounts to about \( A_{\text{offset}} \approx 15 \) ppm·s⁻¹. If one divides this value by the integration time of 300 s, one obtains an average concentration of 0.05 ppm NOₓ. A closer look at Figure 9(a) reveals that this is (roughly) the offset of the NOₓ...
concentration measurement by the CLD with a resolution of 0.1 ppm. As a conclusion, the offset of $A_{\text{released}}$ can be attributed to an integration error. The analysis of the corresponding data after NO exposure yield the same qualitative results (data not shown here) but with a smaller offset. Hence, a further explanation might be the partial overlap of $c_{\text{released}}$ with the preceding decay of $c_{\text{NO}_2,\text{in}}$ due to NO$_2$ adsorption in the feed lines.

Figure 9. NO$_x$ release during heating to 650 °C after 8 ppm NO$_2$ exposure for 250 s, 500 s, 750 s, and 1,000 s: (a) outlet NO$_x$ concentration $c_{\text{released}}$, (b) area $A_{\text{released}}$ below the curve as depicted in Figure 8(b) as a function of NO$_2$ loading time $t_{\text{NO}_2,\text{in}}$.

The observed sensor response $\Delta R_{\text{rel}}$ of KMnO$_4$/La-Al$_2$O$_3$ during NO$_x$ sorption at 380 °C (Figure 7) obviously corresponds to the amount of loaded NO$_x$. In Figure 10, $\Delta R_{\text{rel}}$ caused by 8 ppm NO or NO$_2$ for up to 1,000 s, is related to $A_{\text{released}}$, which is obtained from the subsequent regeneration shown in Figure 9. For NO exposure, as well as for NO$_2$ exposure, $\Delta R_{\text{rel}}$ increases linearly with $A_{\text{released}}$. Hence, in the investigated range, $\Delta R_{\text{rel}}$ serves as a linear measure for the NO and NO$_2$ loading levels of KMnO$_4$/La-Al$_2$O$_3$, and due to the constant NO$_x$ sorption rate (Figure 9(b)), also for the cumulated NO$_x$ exposure (NO$_x$ dose). Thereby, the conductivity of KMnO$_4$/La-Al$_2$O$_3$ is slightly more sensitive to NO compared to NO$_2$. From a catalytic point of view, it would be expected that NO$_2$ in the gas flow influences the material’s properties more than NO, since NO$_2$ can be sorbed directly as nitrate, whereas NO needs to be oxidized first [23,36]. However, the manganese oxide components of the decomposed KMnO$_4$ might become reduced upon oxidizing NO, thereby affecting the conductivity of KMnO$_4$/La-Al$_2$O$_3$ and hence the NO sensitivity. The delay in the sensor response resulting in an x-axis intercept in Figure 10 is expected to be caused by the already discussed inaccuracy of the determination of $A_{\text{released}}$ by integration of small values of evolved NO$_x$ ($A_{\text{offset}} \approx 15$ ppm·s in Figure 9(b)). In addition, NO$_x$
(in particular NO₂) adsorption to the feed lines lowers the sensor response but increases the analyzed value for the desorbed amount.

**Figure 10.** Correlation between the sensor response \( \Delta R_{\text{rel}} \) during NO and NO₂ sorption and the NOₓ amount \( A_{\text{released}} \) obtained from subsequent TPD.

Combining the classical TPD method, with the dosimeter-type electrical response of KMnO₄/La-Al₂O₃, demonstrates the possibility of sensing NOₓ exposure and of electrically monitoring the NOₓ loading level of the NOₓ sorbent *in-situ*, both with linear correlation at low loading.

### 4.3. Electrical Information upon Thermal Regeneration

The conductance upon releasing NOₓ provides information about the amount of previously sorbed NOₓ. This may also be useful for NOₓ dosimetry. Figure 11a depicts the courses of the conductance \( G \) during thermal regeneration after exposure to 8 ppm NO₂, for the different loading states indicated by its specific NOₓ exposure period \( t_{\text{NO}_2,\text{in}} \). The course of the temperature is shown for comparison (black dots). \( G_0 \) reflects the conductance in the NOₓ unloaded state corresponding to \( t_{\text{NO}_2,\text{in}} = 0 \).

Being thermally activated, \( G_0 \) increases by nearly two orders of magnitude, which agrees with Figure 3. At 380 °C, the conductance in the partly NOₓ loaded state \( G \) is higher than \( G_0 \). The difference between \( G \) and \( G_0 \) corresponds to the cumulative NOₓ response, \( \Delta R_{\text{rel}} \) (Figure 7). With progressive temperature, log \( G \) increases like log \( G_0 \). The difference between log \( G \) and log \( G_0 \) increases with \( t_{\text{NO}_2,\text{in}} \), indicating a correlation with the NOₓ loading level. Between about 480 and 530 °C, the curves of \( G \) start to converge to those of \( G_0 \). Finally, above about 620 °C (230 s) all curves of \( G \) coincide with \( G_0 \) indicating that the unloaded state is recovered. A more detailed analysis reveals that the inflection point in the course of log \( G \) corresponds to the onset of NOₓ release shown in Figure 9(a) as \( c_{\text{released}} \).

The temperature of the minimum in the slope of log \( G \) coincides with the temperature of the maximum of \( c_{\text{released}} \). Both are being shifted to lower temperatures, the higher the former loading level was. Hence, the convergence of the curves of log \( G \) to the reference in the unloaded state can be attributed to thermal NOₓ release from KMnO₄/La-Al₂O₃, which decreases the temperature-dependent conductivity to the unloaded value.
Figure 11. cTPD results after 8 ppm NOx for up to 1,000 s: (a) conductance log $G$ and temperature $T$ during TPD, (b) cumulated electrical response $F_G$ (calculated acc. to Equation (4)) vs. the NOx loading time $t_{NO_2,in}$, (c) $F_G$ as a function of the amount of released NOx $A_{released}$ for NO and NO2 loading, as determined in Figure 9.

The comparison of the curves of the conductance $G$ during regeneration (Figure 11(a)) suggests that the deviation of the course of log $G$ from log $G_0$ might reflect the amount of previously sorbed NOx. In fact, Figure 11(b) reveals a linear correlation between $F_G$ calculated according to Equation (4) and the preceding sorption interval $t_{NO_2,in}$. Accounting for the time constant NO and NO2 sorption rate in the low loading state (exemplarily shown for NO2 in Figure 9(b)), $F_G$ is also a linear function of $A_{released}$ as shown in Figure 11(c) for NO and NO2 exposure, respectively. Therefore, besides of $\Delta R_{rel}$, the cumulated electrical response $F_G$ of KMnO4/La-Al2O3 during regeneration may also be a suitable sensor signal for the cumulated NOx exposure and the in-situ loading level. Again, the resulting sensitivity to NO is slightly higher than those to NO2. Furthermore, the sensor response exhibits an offset, in particular, for NO2. Besides of the small integration error $A_{offset}$ when determining the area under the low level concentration curve during desorption in Figure 9a, these offsets likely originate from NO2 adsorption in the feed lines.
Considering the electrode geometry, the conductivity $\sigma$ can be calculated from the conductance and the data from Figure 11(a) can be plotted in an Arrhenius-like representation in the area of a constant heating rate as depicted in Figure 12. The data points of the electrical characterization of the KMnO$_4$/La-Al$_2$O$_3$ sample after equilibration at various temperatures shown in Figure 3(c) are added to Figure 12 as black dots. Concerning the thermally activated conductivity in the unloaded state, the direct comparison reveals that the eTPD data agree well with those obtained in the equilibrated state. This confirms the recovery of the sorption sites by heating to 650 °C. The NO$_x$ saturated state of the carbonates was found to give a more pronounced transition in the curve of the equilibrated temperature-dependent conductivity upon thermal decomposition [32].

The investigation of NO$_x$ sorption on KMnO$_4$/La-Al$_2$O$_3$ demonstrates that eTPD enables one to correlate the analyte-induced electrical response quantitatively with the actual analyte loading state. This is achieved by observing the electrical properties and the gas desorption characteristics simultaneously. The eTPD method might enhance the understanding of the analyte sorption related electrical properties of functional materials applied for gas sensing or catalysis. Approaches on interpreting the conductivity during thermally releasing gas species are reported in the literature as well, but—to our knowledge—only without a simultaneous quantitative analysis of the desorption peak and hence with a missing correlation with the actual loading state under identical conditions. Colin et al. [50] and Fortin et al. [51] modeled the electrical influence of chemisorbed gases on semiconductors upon heating and verified it for the system oxygen-CdSe. The slope of the conductivity is reported to give information on desorption or binding energies of the species [51–53]. Rossé et al. [53] explains in detail the course of the resistivity in the Arrhenius-like representation during TPD being dependent on the heating rate and the amount of chemisorbed species. Additionally, the recovery of the initial loading state is described as a convergence to the unloaded reference. This description agrees fully with the interpretation of the results on NO$_x$ loaded KMnO$_4$/La-Al$_2$O$_3$ in Figure 11. However, applying eTPD, these electrical results were additionally verified by the analysis of the simultaneous desorption peak (Figure 9(a)). Yamazoe et al. [54] and Rodríguez-Gonzáles et al. [55] compared the conductivity with the evolution of desorbed gases as well, but these tests were performed on multiple samples in different setups. The Simon group [55–57] investigated the temperature dependent...
NH₃ loading level of zeolites being active for the selective catalytic reduction (SCR) of NOₓ. The conductivity upon heating reveals information on the conduction mechanism, the NH₃ desorption temperature as well as the SCR active temperature region allowing for in-situ reaction monitoring. Kubinski et al. [58] demonstrated that the average resistance during the thermally-induced NH₃ release from an SCR zeolite catalyst correlates with the former NH₃ exposure. This enables in-situ monitoring of the amount of sorbed NH₃ with a higher sensitivity compared to those in the NH₃ sorption mode [58].

The equivalency of the two conductivity-related sensor responses ΔR_{rel} and F_{G} of KMnO₄/La-Al₂O₃ as a measure for the cumulated NOₓ exposure is demonstrated in Figure 13 as a monotone and almost linear correlation, independent of the type of exposed NOₓ species. Both values can be applied as NOₓ dosimeter-type sensor responses and correlate linearly with the quantity of sorbed NOₓ, enabling in-situ monitoring of the loading state, although they are analyzed upon NOₓ sorption at 380 °C (ΔR_{rel}) and upon NOₓ release by heating up to 650 °C (F_{G}), respectively. Hence, dependent on the application and the information of interest, two different sensing modes are feasible with the proposed impedimetric NOₓ dosimeter based on KMnO₄. In both cases, NOₓ is accumulated in the sensitive layer at sorption temperature and thermally released during periodic regeneration intervals. However, in the first method, the change in the conductance during NOₓ accumulation in the low loading state is monitored as a continuous and linear measure for the cumulated NOₓ exposure as well as for the amount of sorbed NOₓ. Concentration information can be obtained time-continuously from the signal derivative. On the contrary, in the second method, the integrated difference between the conductivity during NOₓ release upon heating and the conductivity in the unloaded state serves as the measurand. Unfortunately, no time-continuous information on the NOₓ concentration can be obtained.

Figure 13. Correlation between electrical responses ΔR_{rel} (during sorption) and F_{G} (upon regeneration) affected by NOₓ exposure.

Simultaneous NOₓ detection in the sorption and release mode may be realized on one single sensor platform, with multiple independently heated sensitive layers, as described in [17]. A combination of both sensing modes to extract further information will be the focus of further research. The redundant
sensing information is expected to enable a plausibility consideration of the time resolved sensor signal during NO\textsubscript{x} sorption and of the regeneration success. Additionally, the linear measurement range for the NO\textsubscript{x} exposure is expected to be enhanced in the regeneration mode. Another important issue of gas sensors is the sensitivity to other gases as well as poisoning of sensitive layers, e.g., by SO\textsubscript{2} \cite{59,60}. Since interfering gases might affect NO\textsubscript{x} sorption and release as well as the temperature-dependent conductivity differently, a combination of the electrical responses upon NO\textsubscript{x} sorption and release might be particularly useful.

5. Conclusions

This initial study demonstrates the suitability of decomposed KMnO\textsubscript{4} deposited on La-stabilized alumina as dosimeter-type sensitive material with two different operation methods and as a NO\textsubscript{x} sorbent in catalysts with electrical in-situ characterization potential. The impedimetric sensor response to low levels of NO and NO\textsubscript{2} was found to be irreversible under isothermal conditions at 380 °C. These dosimeter-type sensing characteristics are reproducible if sorbed NO\textsubscript{x} is released by heating up to 650 °C to recover the sorption capacity. The resistance change of KMnO\textsubscript{4}/La-Al\textsubscript{2}O\textsubscript{3} in the low loaded state correlates linearly with the cumulated NO\textsubscript{x} exposure, enabling low level NO\textsubscript{x} detection due to the NO\textsubscript{x} oxidizing and sorbing capability of the KMnO\textsubscript{4}-based material. The sensor responds slightly more sensitively to NO than to NO\textsubscript{2}.

By combining the electrical response with thermal programmed desorption (eTPD), the change in the electrical properties of KMnO\textsubscript{4}/La-Al\textsubscript{2}O\textsubscript{3} can be related to the thermally released quantity of NO\textsubscript{x}. This novel method enables the quantitative correlation between the electrical response and the NO\textsubscript{x} loading in the sensor (or catalyst) material. The amount of NO\textsubscript{x} sorbed on KMnO\textsubscript{4}/La-Al\textsubscript{2}O\textsubscript{3}, estimated from the released amount, increases linearly with the cumulated NO\textsubscript{x} exposure (or dose), resulting in a time constant NO\textsubscript{x} sorption rate. The resistance change during NO\textsubscript{x} sorption correlates linearly with the amount of sorbed NO\textsubscript{x} and hence with the NO\textsubscript{x} exposure. Therefore, information on the NO\textsubscript{x} concentration can be obtained time-continuously from the signal derivative. Additionally, the thermally activated conductivity of KMnO\textsubscript{4} is affected by the NO\textsubscript{x} release upon heating. The deviation from the course of the temperature-dependent conductivity in the unloaded state is another linear measure for the previously stored amount of NO\textsubscript{x}. As a result, NO\textsubscript{x} exposure and NO\textsubscript{x} loading dependent electrical response can be analyzed either during NO\textsubscript{x} sorption or release enabling dosimeter-like NO\textsubscript{x} sensing or electrical in-situ monitoring.

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References

1. Fergus, J.W. Materials for high temperature electrochemical NO\textsubscript{x} gas sensors. Sens. Actuators B Chem. 2007, 121, 652–663.
2. Yamazoe, N.; Miura, N. Environmental gas sensing. Sens. Actuators B Chem. 1994, 20, 95–102.
3. Afzal, A.; Gioff, N.; Sabbatini, L.; Torsi, L. NO\textsubscript{x} sensors based on semiconducting metal oxide nanostructures: Progress and perspectives. Sens. Actuators B Chem. 2012, doi:10.1016/j.snb.2012.05.026.
4. Directive 2008/50/EC of the European parliament and of the council of 21 May 2008 on ambient air quality and cleaner air for Europe. Off. J. EU 2008, L152/1, 1–44.
5. Twigg, M.V. Progress and future challenges in controlling automotive exhaust gas emissions. Appl. Catal. B 2007, 70, 2–15.
6. Groß, A.; Beulertz, G.; Marr, I.; Kubinski, D.J.; Visser, J.H.; Moos, R. Dual mode NO\textsubscript{x} sensor: Measuring both the accumulated amount and instantaneous level at low concentrations. Sensors 2012, 12, 2831–2850.
7. Matsuguchi, M.; Kadowaki, Y.; Tanaka, M. A QCM-based NO\textsubscript{2} gas detector using morpholine-functional cross-linked copolymer coatings. Sens. Actuators B Chem. 2005, 108, 572–575.
8. Sasaki, D.Y.; Singh, S.; Cox, J.D.; Pohl, P.I. Fluorescence detection of nitrogen dioxide with perylene/PMMA thin films. Sens. Actuators B Chem. 2001, 72, 51–55.
9. Tanaka, T.; Guilleux, A.; Ohyama, T.; Maruo, Y.Y.; Hayashi, T. A ppb-level NO\textsubscript{2} gas sensor using coloration reactions in porous glass. Sens. Actuators B Chem. 1999, 56, 247–253.
10. Jung, W.; Sahner, K.; Leung, A.; Tuller, H.L. Acoustic wave-based NO\textsubscript{2} sensor: Ink-jet printed active layer. Sens. Actuators B Chem. 2009, 141, 485–490.
11. Geupel, A.; Schönauer, D.; Röder-Roith, U.; Kubinski, D.J.; Mulla, S.; Ballinger, T.H.; Chen, H.-Y.; Visser, J.H.; Moos, R. Integrating nitrogen oxide sensor: A novel concept for measuring low concentrations in the exhaust gas. Sens. Actuators B Chem. 2010, 145, 756–761.
12. Brunet, J.; Parra Garcia, V.; Pauly, A.; Varenne, C.; Lauron, B. An optimised gas sensor microsystem for accurate and real-time measurement of nitrogen dioxide at ppb level. Sens. Actuators B Chem. 2008, 134, 632–639.
13. Yamazoe, N.; Shimanoe, K. Overview of Gas Sensor Technology. In Science and Technology of Chemiresistor Gas Sensors; Aswal, D.K., Gupta, S.K., Eds.; Nova Science Publishers, Inc.: New York, NY, USA, 2007; pp. 1–31.
14. Shu, J.H.; Wikle, H.C.; Chin, B.A. Passive chemiresistor sensor based on iron (II) phthalocyanine thin films for monitoring of nitrogen dioxide. Sens. Actuators B Chem. 2010, 148, 498–503.
15. Groß, A.; Bishop, S.R.; Yang, D.J.; Tuller, H.L.; Moos, R. The electrical properties of NO\textsubscript{x}-storing carbonates during NO\textsubscript{x} exposure. Solid State Ionics 2012, 225, 317–323.
16. Groß, A.; Richter, M.; Kubinski, D.J.; Visser, J.H.; Moos, R. The effect of the thickness of the sensitive layer on the performance of the accumulating NO\textsubscript{x} sensor. Sensors 2012, 12, 12329–12346.
17. Brandenburg, A.; Kita, J.; Groß, A.; Moos, R. Novel tube-type LTCC transducers with buried heaters and inner interdigitated electrodes as a platform for gas sensing at various high temperatures. *Sens. Actuators B Chem.* 2013, doi:10.1016/j.snb.2012.12.119.

18. Geupel, A.; Kubinski, D.J.; Mulla, S.; Ballinger, T.H.; Chen, H.Y.; Visser, J.H.; Moos, R. Integrating NOx sensor for automotive exhausts—a novel concept. *Sens. Lett.* 2011, 9, 311–315.

19. Fruhberger, B.; Stirling, N.; Grillo, F.G.; Ma, S.; Ruthven, D.; Lad, R.J.; Frederick, B.G. Detection and quantification of nitric oxide in human breath using a semiconducting oxide based chemiresistive microsensor. *Sens. Actuators B Chem.* 2001, 76, 226–234.

20. Brogren, C.; Karlsson, H.T.; Bjerle, I. Absorption of NO in an alkaline solution of KMnO4. *Chem. Eng. Technol.* 1997, 20, 396–402.

21. Wei, Z.-S.; Niu, H.-J.; Ji, Y.-F. Simultaneous removal of SO2 and NOx by microwave with potassium permanganate over zeolite. *Fuel Process. Technol.* 2009, 90, 324–329.

22. Becerra, M.E.; Arias, N.P.; Giraldo, O.H.; López-Suárez, F.E.; Illán-Gómez, M.J.; Bueno-López, A. Soot combustion manganese catalysts prepared by thermal decomposition of KMnO4. *Appl. Catal. B* 2011, 102, 260–266.

23. Lesage, T.; Saussey, J.; Malo, S.; Hervieu, M.; Hedouin, C.; Blanchard, G.; Daturi, M. Operando FTIR study of NOx storage over a Pt/K/Mn/Al2O3-CeO2 catalyst. *Appl. Catal. B* 2007, 72, 166–177.

24. Becerra, M.-E.; Arias, N.-P.; Giraldo, O.-H.; López-Suárez, F.-E.; Illán-Gómez, M.-J.; Bueno-López, A. Alumina-supported manganese catalysts for soot combustion prepared by thermal decomposition of KMnO4. *Catalysts* 2012, 2, 352–367.

25. Boldyrev, V.V. Mechanism of thermal decomposition of potassium permanganate in the solid phase. *J. Phys. Chem. Solids* 1969, 30, 1215–1223.

26. Boldyrev, V.V. Topochemistry of thermal decompositions of solids. *Thermochimica Acta* 1986, 100, 315–338.

27. Galwey, A.K.; Brown, M.E. An appreciation of the chemical approach of V. V. Boldyrev to the study of the decomposition of solids. *J. Therm. Anal. Calorim.* 2007, 90, 9–22.

28. Kabanov, A.A. The application of electrophysical effects to the study of the thermal decomposition of solids. *Russ. Chem. Rev.* 1971, 40, 953–963.

29. Rosseinsky, D.R.; Tonge, J.S. Electron transfer in solids. Temperature dependence of dielectric relaxation and conductivity in mixed-valence potassium manganate–permanganate. *J. Chem. Soc. Faraday Trans.* 1982, 78, 3595–3595.

30. Kappenstein, C.; Pirault-Roy, L.; Guérin, M.; Wahdan, T.; Ali, A.A.; Al-Sagheer, F.A.; Zaki, M.I. Monopropellant decomposition catalysts: V. Thermal decomposition and reduction of permanganates as models for the preparation of supported MnOx catalysts. *Appl. Catal. A* 2002, 234, 145–153.

31. Schönauer, D.; Moos, R. Detection of water droplets on exhaust gas sensors. *Sens. Actuators B Chem.* 2010, 148, 624–629.

32. Groß, A.; Weller, T.; Tuller, H.L.; Moos, R. Electrical conductivity study of NOx trap materials BaCO3 and K2CO3/La-Al2O3 during NOx exposure. *Sens. Actuators B Chem.* 2013, doi:10.1016/j.snb.2013.01.083.

33. Wu, X.; Lin, F.; Wang, L.; Weng, D.; Zhou, Z. Preparation methods and thermal stability of Ba-Mn-Ce oxide catalyst for NOx-assisted soot oxidation. *J. Environ. Sci.* 2011, 23, 1205–1210.
34. Wu, X.; Liu, S. Lin, F.; Weng, D. Nitrate storage behavior of Ba/MnO\textsubscript{x}-CeO\textsubscript{2} catalyst and its activity for soot oxidation with heat transfer limitations. *J. Hazard. Mater.* **2010**, *181*, 722–728.

35. Xiao, J.-H.; Li, X.-H.; Deng, S.; Xu, J.-C.; Wang, L.-F. The NO\textsubscript{x} oxidation-storage and tolerance of SO\textsubscript{2} poison of Mn/Ba/Al\textsubscript{2}O\textsubscript{3} catalyst. *Acta Phys. Chim. Sin.* **2006**, *22*, 815–819.

36. Xiao, J.; Li, X.; Deng, S.; Wang, F.; Wang, L. NO\textsubscript{x} storage-reduction over combined catalyst Mn/Ba/Al\textsubscript{2}O\textsubscript{3}–Pt/Ba/Al\textsubscript{2}O\textsubscript{3}. *Catal. Commun.* **2008**, *9*, 563–567.

37. Beulertz, G.; Groß, A.; Moos, R.; Kubinski, D.J.; Visser, J.H. Determining the total amount of NO\textsubscript{x} in a gas stream – Advances in the accumulating gas sensor principle. *Sens. Actuators B Chem.* **2012**, *175*, 157–162.

38. Gill, L.J.; Blakeman, P.G.; Twigg, M.V.; Walker, A.P. The use of NO\textsubscript{x} adsorber catalysts on diesel engines. *Top. Catal.* **2004**, *28*, 157–164.

39. Roy, S.; Baiker, A. NO\textsubscript{x} storage-reduction catalysis: From mechanism and properties to storage-reduction performance. *Chem. Rev.* **2009**, *109*, 4054–4091.

40. Epling, W.S.; Campbell, L.E.; Yezerets, A.; Currier, N.W.; Parks, J.E., II. Overview of the fundamental reactions and degradation mechanism of NO\textsubscript{x} storage/reduction catalysts. *Catal. Rev. Sci. Eng.* **2004**, *46*, 163–245.

41. Fremerey, P.; Reiß, S.; Geupel, A.; Fischerauer, G.; Moos, R. Determination of the NO\textsubscript{x} loading of an automotive lean NO\textsubscript{x} trap by directly monitoring the electrical properties of the catalyst material itself. *Sensors* **2011**, *11*, 8261–8280.

42. Moos, R.; Zimmermann, C.; Birkhofer, T.; Knezevic, A.; Plog, C.; Busch, M.R.; Ried, T. Sensor for Directly Determining the State of a NO\textsubscript{x} Storage Catalyst. In Proceedings of the SAE World Congress and Exhibition, Detroit, MI, USA, 14–17 April 2008; doi:10.4271/2008-01-0447.

43. Moos, R.; Wedemann, M.; Spörl, M.; Reiß, S.; Fischerauer, G. Direct catalyst monitoring by electrical means: An overview on promising novel principles. *Top. Catal.* **2009**, *52*, 2035–2040.

44. Le Phuc, N.; Courtois, X.; Can, F.; Royer, S.; Marecot, P.; Duprez, D. NO\textsubscript{x} removal efficiency and ammonia selectivity during the NO\textsubscript{x} storage-reduction process over Pt/BaO(Fe, Mn, Ce)/Al\textsubscript{2}O\textsubscript{3} model catalysts. Part I: Influence of Fe and Mn addition. *App. Catal. B* **2011**, *102*, 353–361.

45. Bentrup, U.; Brückner, A.; Richter, M.; Fricke, R. NO\textsubscript{x} adsorption on MnO\textsubscript{2}/NaY composite: An *in situ* FTIR and EPR study. *Appl. Catal. B* **2001**, *32*, 229–241.

46. Fricke, R.; Schreier, E.; Eckelt, R.; Richter, M.; Trunschke, A. Non-isothermal NO\textsubscript{x} storage/release over manganese based traps: Mechanistic considerations. *Top. Catal.* **2004**, *30/31*, 193–198.

47. Kijlstra, W.S.; Brands, D.S.; Poels, E.K.; Bliek, A. Mechanism of the selective catalytic reduction of NO by NH\textsubscript{3} over MnO\textsubscript{x}/Al\textsubscript{2}O\textsubscript{3}. *J. Catal.* **1997**, *171*, 208–218.

48. Li, W.B.; Yang, X.F.; Chen, L.F.; Wang, J.A. Adsorption/desorption of NO\textsubscript{x} on MnO\textsubscript{2}/ZrO\textsubscript{2} oxides prepared in reverse microemulsions. *Catal. Today* **2009**, *148*, 75–80.

49. Takeuchi, M.; Matsumoto, S. NO\textsubscript{x} storage-reduction catalysts for gasoline engines. *Top. Catal.* **2004**, *28*, 151–156.

50. Colin, Y.; Fortin, B.; Raoult, F. Resistance variation of a semiconduction thin film during a thermal desorption. *Phys. Status Solidi A* **1981**, *67*, 485–495.

51. Fortin, B.; Larzul, H.; Lebigot, J.; Raoult, F.; Rosse, G. Model for the resistance variation of a thin semiconducting film during temperature- programmed desorption: Application to the O\textsubscript{2}-CdSe system. *Thin Solid Films* **1985**, *131*, 51–68.
52. Sanjines, R.; Lévy, F.; Demarne, V.; Grisel, A. Some aspects of the interaction of oxygen with polycrystalline SnOx thin films. Sens. Actuators B Chem. 1990, 1, 176–182.
53. Rossé, G.; Raoul, F.; Fortin, B. Regeneration of CdSe thin films after oxygen chemisorption. Thin Solid Films 1984, 111, 175–181.
54. Yamazoe, N.; Fuchigami, J.; Kishikawa, M.; Seiyama, T. Interactions of tin oxide surface with O2, H2O and H2. Surf. Sci. 1979, 86, 335–344.
55. Rodríguez-González, L.; Rodríguez-Castellón, E.; Jiménez-López, A.; Simon, U. Correlation of TPD and impedance measurements on the desorption of NH3 from zeolite H-ZSM-5. Solid State Ionics 2008, 179, 1968–1973.
56. Simons, T.; Simon, U. Zeolites as nanoporous, gas-sensitive materials for in situ monitoring of DeNOx-SCR. Beilstein J. Nanotechnol. 2012, 3, 667–673.
57. Simons, T.; Simon, U. Zeolite H-ZSM-5: A Microporous Proton Conductor for the in situ Monitoring of DeNOx-SCR. Mater. Res. Soc. Symp. Proc. 2011, doi:10.1557/opl.2011.1337.
58. Kubinski, D.J.; Visser, J.H. Sensor and method for determining the ammonia loading of a zeolite SCR catalyst. Sens. Actuators B Chem. 2008, 130, 425–429.
59. Groß, A.; Hanft, D.; Beulertz, G.; Marr, I.; Kubinski, D.J.; Visser, J.H.; Moos, R. The effect of SO2 on the sensitive layer of a NOx dosimeter. Sens. Actuators B Chem. 2012, doi:10.1016/j.snb.2012.10.039.
60. Rettig, F.; Moos, R.; Plog, C. Sulfur adsorber for thick-film exhaust gas sensors. Sens. Actuators B Chem. 2003, 93, 36–42.

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