



## The electrical properties of NO<sub>x</sub>-storing carbonates during NO<sub>x</sub> exposure

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### ARTICLE INFO

#### Article history:

Received 9 September 2011

Received in revised form 27 March 2012

Accepted 7 May 2012

Available online 2 June 2012

#### Keywords:

In-situ characterization

Electrical properties

Lean NO<sub>x</sub> traps

NO<sub>x</sub> storage

Barium carbonate

Potassium carbonate

### ABSTRACT

In order to gain a deeper understanding of the different components in multi-component automotive catalyst systems and integrating type NO<sub>x</sub>-sensors, in-situ electrical methods are examined. The conductivity of BaCO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub>, key components in automotive NO<sub>x</sub> storage catalysts, was examined as a function of gas composition and temperature. Impedance measurements performed on BaCO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, and equimolar mixtures of both, demonstrated that, in all cases, the resistance decreases in the presence of NO<sub>2</sub> gas with progressive NO<sub>x</sub> sorption on the carbonate surface. Mixing the hygroscopic but low resistivity K<sub>2</sub>CO<sub>3</sub> with the very highly resistive but stable BaCO<sub>3</sub> resulted in greater stability than K<sub>2</sub>CO<sub>3</sub> alone, as well as improved ability to measure resistivity changes. The resistance of the mixture recovered about 50% of its value after removing NO<sub>2</sub> from the gas stream, believed to result from migration of sorbed NO<sub>x</sub> from K to Ba, instead of desorption alone. These results on NO<sub>x</sub> trap materials show that in-situ impedance spectroscopy measurements offer real-time characterization of NO<sub>x</sub> loading levels in lean NO<sub>x</sub> trap catalyst components.

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### Introduction

Multi-component catalyst systems are used for the reduction of harmful gases in industrial and automotive exhausts. In the case of lean operated internal combustion engines, NO<sub>x</sub> storage catalysts, also called lean NO<sub>x</sub> traps or LNTs, reduce NO<sub>x</sub> emissions by storing NO<sub>x</sub> during lean operation. This is followed by periodically switching to rich engine operation to regenerate the storage media by reducing the stored NO<sub>x</sub> to N<sub>2</sub> [1,2]. The processes occurring in these multi-component systems are complex, since components with different and/or overlapping functionalities are required to interact with each other. For the effective operation of those catalysts, knowledge about the amount of NO<sub>x</sub> loading at any given time in the cycle is essential. Currently, these catalyst systems are controlled ex-situ by monitoring the emitted gas concentrations downstream of the LNT. However, by applying direct in-situ methods to monitor the NO<sub>x</sub> loading state of the LNT, it would be possible to operate the system with a higher catalytic efficiency. Furthermore, such direct measurements, in a controlled setting, would also provide a deeper understanding of the involved chemical processes and interactions between the different components.

Since carbonates commonly serve to store NO<sub>x</sub> in multi-component catalyst systems, their electrical characterization is the subject of this initial study. These investigations on micrometer-sized carbonate materials, however, should be viewed as a preliminary step in understanding the processes active in the LNT, since both the composition (lack of high-surface area alumina as stabilizing support oxide and precious metals [1–3]) and morphology (lack of fine highly dispersed carbonate, influenced by the nature of the oxide support [4,5]) of the model systems examined here differ in some important ways from real world LNT catalysts. In fact, very similar materials, as examined here, are the basis of novel impedimetric integrating (or accumulating) NO<sub>x</sub> sensors [6–9].

The electrical properties of the pure NO<sub>x</sub> storage components BaCO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, and their equimolar mixture are examined and analyzed under controlled NO<sub>x</sub> exposure and temperature using impedance spectroscopy, performed on powder compacts and thick films applied to alumina substrates. In each system, large resistance changes are observed during NO<sub>2</sub> exposure. This is in agreement with earlier publications on barium-based commercial LNT formulations [10–13], showing that the electrical properties of the catalyst, under application oriented gas conditions, are a function of NO<sub>x</sub> loading. Like BaCO<sub>3</sub>, the considerably lower resistive K<sub>2</sub>CO<sub>3</sub> also exhibits large changes in resistance in the presence of NO<sub>2</sub>, but in conjunction with morphological changes under hydrothermal conditions. However, the morphology can be partially stabilized by mixing with BaCO<sub>3</sub>. The results presented here represent the initial part of an investigation aimed at achieving an improved understanding of LNT catalyst performance and component functionalities by application of direct, in-situ electrical probes.

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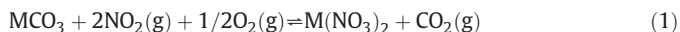
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## Lean NO<sub>x</sub> trap (LNT) catalysts

### Background on the catalytic properties of LNTs

LNT catalysts reduce NO<sub>x</sub> emissions in the automotive exhaust by first storing NO<sub>x</sub> chemically by forming metal nitrates under excess oxygen conditions and then releasing it, with subsequent reduction to N<sub>2</sub>, under rich-burn conditions [1,2,14]. They operate with the assistance of NO<sub>x</sub> and oxygen storage materials (providing a buffer of oxygen [15,16]) and precious metal redox catalysts [1,2,17].

NO<sub>x</sub> is stored chemically by oxidizing NO to NO<sub>2</sub> [18] and subsequently incorporating acidic NO<sub>2</sub> into alkaline (earth-) metal carbonates “MCO<sub>3</sub>”, e.g. BaCO<sub>3</sub> or K<sub>2</sub>CO<sub>3</sub>, by forming the corresponding nitrates “M(NO<sub>3</sub>)<sub>2</sub>” (Eq. (1)) [16].



Depending on the gas composition (content of H<sub>2</sub>O, CO<sub>2</sub> and O<sub>2</sub>) and the temperature, the NO<sub>x</sub> sorbent material may coexist as hydroxides, oxides, and carbonates, thus influencing the NO<sub>x</sub> storage reactions [1]. However, thermodynamic calculations reveal that upon lean-rich cycles in CO<sub>2</sub> containing gases, carbonates are mainly providing the NO<sub>2</sub> storage capacity [14].

The LNT regeneration and NO<sub>x</sub> conversion process occurs upon introduction of reducing gas following Eq. (2) (with, e.g. here H<sub>2</sub> as the reductant).



The examination of the influence of NO<sub>x</sub> on the electrical properties of two carbonates, BaCO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub>, will be the initial focus of this study. In addition to the lower resistivity of K<sub>2</sub>CO<sub>3</sub>, it provides a higher NO<sub>x</sub> storage capacity, compared to BaCO<sub>3</sub>, due to its larger basicity [1,14,19] and, along with higher nitrate stability at elevated temperatures, it is an attractive material for LNTs [16,19]. However, morphological changes readily occur in K<sub>2</sub>CO<sub>3</sub> under hydrothermal conditions due to K-migration [16,20]. Therefore, mixing BaCO<sub>3</sub> with the less resistive but less stable K<sub>2</sub>CO<sub>3</sub> may result in improved overall stability with electrically measurable NO<sub>x</sub> loading states. The NO<sub>2</sub> storage mechanism is the same for both materials: In the presence of Pt, NO can either be incorporated as nitrite which is then further oxidized to nitrate or NO<sub>2</sub> can be directly incorporated as a nitrate, without the help of precious metals (Eq. (1)) [21–23]. Toops et al. [24] verified with DRIFT spectroscopy that on Pt/K/γ-Al<sub>2</sub>O<sub>3</sub> at 250 °C, NO<sub>x</sub> is primarily stored as free nitrate ions. Piacentini et al. [5] observed the stepwise NO<sub>x</sub> uptake upon pulsed NO dosing at 300 °C on various Ba-based LNT formulations using thermogravimetry and verified Ba(NO<sub>3</sub>)<sub>2</sub> formation by comparing XRD spectra prior to and following NO exposure.

The NO<sub>x</sub> conversion of commercial formulations is typically maximal in the range of 300–400 °C due to slow kinetics of the NO oxidation reaction at lower temperatures and the thermodynamic equilibrium between NO and NO<sub>2</sub> as well as the decreased thermodynamic stability of the formed nitrates at elevated temperatures [3,16]. In automotive applications, the lean storage period lasts for about 1 to 2 min while the regeneration occurs in only a few seconds (3–5 s) [3]. The larger molar volume of the formed nitrate (e.g. Ba(NO<sub>3</sub>)<sub>2</sub> has almost twice the molar volume of BaCO<sub>3</sub>) is believed to reduce the particle pore size, which decreases the diffusion coefficient of the gaseous species into the solid [25]. Therefore, nitrate formation occurs mainly on the particles' surface (modeled as a nitrate shell [25]) with the fraction of the alkali-sites in the washcoat being involved in the NO<sub>x</sub> storage process determined to be in the range of 10 to 40% depending on the catalyst formulation and the applied gas conditions [23,26,27]. It is reported that for a Pt/BaO/Al<sub>2</sub>O<sub>3</sub> catalyst, over 85% NO<sub>x</sub> conversion is achieved utilizing only 10% of the available Ba-sites and that even after long term exposure, 28% utilization is not exceeded [26]. Scholz et al. [27]

conclude that the presence of H<sub>2</sub>O and CO<sub>2</sub> influences the participation of the Ba-sites in the storage process and that, with both gases, the Ba-utilization value is lowest. A comparison between potassium and barium based catalysts is given in [23]: about the same amount of NO<sub>x</sub> was stored on both catalysts (with the same molar loading of storage components), but accounting for the stoichiometry of KNO<sub>3</sub> and Ba(NO<sub>3</sub>)<sub>2</sub>, it turns out that the Ba utilization is in the range of 24% and that for K is almost double (40%).

### Overview on the electrical properties of carbonates, nitrites and LNT materials

The electrical properties of pure BaCO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub>, as well as a mixture of both, isolated from the other catalyst components (such as Pt), in NO<sub>x</sub> containing lean atmospheres are investigated in this initial study for potential application in the field of gas sensing and as an in-situ tool for catalyst characterization. In the past, it has been shown that the state of a commercial barium-based LNT catalyst (freshly regenerated, NO<sub>x</sub> loaded, in the reduced state, and sulfated) can be detected in-situ by electrical means [10,12,16]. The observation that the NO<sub>x</sub> loading level of LNTs is reflected in the magnitude of conductivity led to the development of integrating (accumulating-type) NO<sub>x</sub> sensors, which measure the amount of NO<sub>x</sub> by chemical accumulation in the carbonate layer [6–8]. But to our knowledge, the effect of successive surface NO<sub>x</sub> sorption on pure carbonates upon exposure to NO<sub>2</sub> (like in LNT catalysts) on the electrical properties has not been reported. Only Park et al. [20] measured the conductivity of various K<sub>2</sub>O/BaO/Al<sub>2</sub>O<sub>3</sub>-catalyst mixtures at 200 °C as packed oxidized powder in NO<sub>2</sub> and found that electrical conductivity increased with increasing K<sub>2</sub>O content. The enhanced strength of interaction between the barium storage sites and NO<sub>2</sub> in the Ba/K catalyst is explained by electrons spreading out from the potassium phase into the high resistive barium fraction.

The electrical properties of BaCO<sub>3</sub> are only sparsely reported [28,29] while those of K<sub>2</sub>CO<sub>3</sub> and Ba(NO<sub>3</sub>)<sub>2</sub> or KNO<sub>3</sub> are well described [30–41]. Additionally, K<sub>2</sub>CO<sub>3</sub> and Ba(NO<sub>3</sub>)<sub>2</sub> were investigated as solid electrolytes for electrochemical gas sensors for CO<sub>2</sub> and NO<sub>2</sub> (Type II) [38,41–44]. In the following, a brief overview on the literature is given. Guth et al. [30] doped K<sub>2</sub>CO<sub>3</sub> with alkaline earth carbonates (amongst others: Ba) and showed that the extrinsic conductivity increased independent of the type of dopant supporting a cation vacancy conductivity mechanism. The conductivity data on pure K<sub>2</sub>CO<sub>3</sub> are in good agreement with those shown in [31–33]. The enhancement of conductivity due to increasing vacancy concentrations was also observed by Cleaver et al. [34] for Ca<sup>2+</sup> incorporated into KNO<sub>3</sub>. Even though the ionic radii of K<sup>+</sup> and Ba<sup>2+</sup> are very similar, a low solubility of Ba(NO<sub>3</sub>)<sub>2</sub> in KNO<sub>3</sub> was found [34]. Fermor et al. [35] pointed out that the crystallinity and therefore the preparation highly influence the conductivity of KNO<sub>3</sub>. The Arrhenius plot of pure KNO<sub>3</sub> complies with those reported in [34,36,37]. Due to its high resistivity, BaCO<sub>3</sub> has not attracted much interest as a solid electrolyte. Tamaki et al. [28] applied BaCO<sub>3</sub> as sensitive layer in a conductive-type NO<sub>x</sub> sensor at 650 °C, with decreasing resistance upon exposure to NO<sub>x</sub>, due to negatively charged adsorbates and reports p-type semiconducting properties. In Ba(NO<sub>3</sub>)<sub>2</sub>, charge transfer appears to occur via anion Frenkel defects [40,39,45] since doping with K<sup>+</sup>, which should create anion vacancies, enhances the conductivity [45]. Composites of carbonates and nitrates, e.g. with fine dispersed Al<sub>2</sub>O<sub>3</sub>, not only result in a higher thermal and mechanical stability, but also in an increased conductivity possibly due to interface interactions and defect formation at the grain boundaries (composite effect) [32,37–39]. The conductivity of alkali metal nitrates was found to be highest in composites with 40 to 60 mol% Al<sub>2</sub>O<sub>3</sub> due to the formation of an amorphous phase with a disordered sublattice resulting in an increased cationic conductivity [37]. According to Reddy et al. [39], the dispersion of Al<sub>2</sub>O<sub>3</sub> in Ba(NO<sub>3</sub>)<sub>2</sub> enhances the

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