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Materials World Network - In-situ Investigation of Model Multi Component Catalyst Systems

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Prof. Harry L. Tuller, Ceramics and Electronic Materials group

Summary

Lean NO_x trap catalysts reduce harmful NO_x emissions of leanly operated engines by chemically storing nitrogen oxides as nitrates in the range of 350 °C to 400 °C and reducing them in short periods with rich atmospheres. By now, the control of the required lean/rich switch as the storage capacity is exhausted is done by catalyst system models based on a NO_x sensor signal. Alternatively, the NO_x loading level of a catalyst could also be diagnosed directly and *in situ* by electrical means. Various model catalysts with defined contents of the different functional components were prepared for a detailed analysis of the loading level dependent electrical conductivity of the catalysts. The focus of the cooperation with Prof. Harry L. Tuller (Massachusetts Institute of Technology) was on oxygen storing oxides (Prof. Tuller) and on NO_2 storing carbonates (Prof. Moos) as well as their interaction to oxidize and store NO_x under close to reality conditions.

The electrical conductivity of the pure NO_x storage components $BaCO_3$ and K_2CO_3 increases with increasing NO_2 loading, whereas NO has no influence because of missing oxidizing properties. The cyclic dosage of NO_2 results in a stepwise increase of the conductivity due to the formation of stable nitrates. However, the conductivity recovers during regeneration in reducing atmospheres. K_2CO_3 exhibits a five orders higher electrical conductivity than $BaCO_3$ and hence is more suitable for the electrical *in-situ* catalyst diagnosis. In the case of low NO_2 loadings, the conductivity of K_2CO_3 increases linearly with the applied NO_2 dose, being the product of duration and concentration. For a better handling of hygroscopic K_2CO_3, it was deposited on pure and lanthanum stabilized alumina (La-)Al_2O_3 known as high surface support oxide in catalysts. In the interesting temperature range, the increase in the conductivity in NO_2 without a cross sensitivity to NO was found to be not affected by the electrically insulating support oxide particles. However, the effect of the same NO_2 dose on the conductivity decreases with increasing carbonate content. This can be explained by the lower nitrate fraction.

The deposition of K_2CO_3 on the multivalent oxides CeO_2 and MnO_2, serving as precious metal free oxidants, enables to store NO as well as NO_2 and hence to detect *in situ* and electrically the total NO_x loading level. Since the sensitivities towards NO and NO_2 are almost equal, MnO_2 seems to have sufficient oxidizing properties. Additionally, the irreversibility of the increase in the conductivity in NO_2 reveals high nitrate stability under sorption conditions. Hence, as a precious metal free model catalyst, the oxidant and NO_x storage component $KMnO_4$ was deposited on the support oxide La-Al_2O_3 and decomposed thermally. In the low loading state, there is a linear correlation between the decrease in the resistance and the applied NO_x dose. Regeneration of the storage capacity via nitrate decomposition occurs in reducing atmospheres as well as by increasing the temperature. The evaluation of the thermal regeneration, denoted “eTPD analysis” (electrical characterization during temperature programmed desorption), allows the correlation between electrical properties and real loading level of the catalyst. In the low loading state, the $KMnO_4$ based catalyst provides a constant sorption rate for NO and NO_2 and the resistance decreases linearly with the NO_x loading level. Besides of detecting the loading level of the catalyst

time-continuously during NO_x sorption, it can also be also analyzed time-discretely by the course of the conductivity during thermal regeneration.

Owing to their good conductivity, K_2CO_3 based materials are very promising for the electrical *in-situ* diagnosis of the NO_x loading state of the catalysts. An electrical characterization of different model catalysts reveals that the conductivity increase in NO_x bases on NO oxidation followed by the formation of stable nitrates. While pure carbonates can be applied to detect NO_2, the sensitivity to NO is achieved by additional oxidizing catalyst components. The NO_x loading level of $KMnO_4$ on La-Al_2O_3, as a precious metal free NO_x storage catalyst, can be detected electrically and *in-situ* either during NO_x sorption at 380 °C or during thermal regeneration by heating to 650 °C. Due to the constant sorption rate in the low loading state, $KMnO_4$/La-Al_2O_3 can also be applied as sensitive layer in a resistive NO_x dosimeter for the long-term sensing of the cumulated amount of NO and NO_2 in the sub ppm range.

Project related publications (selection)

- A. Groß, M. Kremling, I. Marr, D.J. Kubinski, J.H. Visser, H.L. Tuller, R. Moos, Dosimeter-type NO_x sensing properties of $KMnO_4$ and its electrical conductivity during temperature programmed desorption, Sensors 13 (2013) 4428-4449, doi: 10.3390/s130404428.
- A. Groß, T. Weller, H.L. Tuller, R. Moos, Electrical Conductivity Study of NO_x Trap Materials $BaCO_3$ and K_2CO_3/La-Al_2O_3 during NO_x Exposure, Sensors and Actuators B: Chemical 187 (2013) 461-470, doi: 10.1016/j.snb.2013.01.083.
- A. Groß, D. Hanft, G. Beulertz, I. Marr, D. Kubinski, J. Visser, R. Moos, The Effect of SO_2 on the Sensitive Layer of a NO_x Dosimeter, Sensors and Actuators B: Chemical 187 (2013) 153-161, doi: 10.1016/j.snb.2012.10.039.
- A. Groß, S.R. Bishop, D.J. Yang, H.L. Tuller, R. Moos, The Electrical Properties of NO_x-storing Carbonates during NO_x exposure, Solid State Ionics 225 (2012) 317-323, doi: 10.1016/j.ssi.2012.05.009.
- D. Chen, S.R. Bishop, H.L. Tuller, Praseodymium-cerium oxide thin film cathodes: Study of Oxygen Reduction Reaction Kinetics, Journal of Electroceramics 28 (2012) 62–69, doi: 10.1007/s10832-011-9678-z.

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