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\textsubscript{x} trap catalysts reduce harmful NO\textsubscript{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\textsubscript{x} sensor signal. Alternatively, the NO\textsubscript{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\textsubscript{x} storing carbonates (Prof. Moos) as well as their interaction to oxidize and store NO\textsubscript{x} under close to reality conditions.

The electrical conductivity of the pure NO\textsubscript{x} storage components BaCO\textsubscript{3} and K\textsubscript{2}CO\textsubscript{3} increases with increasing NO\textsubscript{2} loading, whereas NO has no influence because of missing oxidizing properties. The cyclic dosage of NO\textsubscript{x} 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\textsubscript{2}CO\textsubscript{3} exhibits a five orders higher electrical conductivity than BaCO\textsubscript{3} and hence is more suitable for the electrical in-situ catalyst diagnosis. In the case of low NO\textsubscript{x} loadings, the conductivity of K\textsubscript{2}CO\textsubscript{3} increases linearly with the applied NO\textsubscript{x} dose, being the product of duration and concentration. For a better handling of hygroscopic K\textsubscript{2}CO\textsubscript{3}, it was deposited on pure and lanthanum stabilized alumina (La-)Al\textsubscript{2}O\textsubscript{3} known as high surface support oxide in catalysts. In the interesting temperature range, the increase in the conductivity in NO\textsubscript{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\textsubscript{x} dose on the conductivity decreases with increasing carbonate content. This can be explained by the lower nitrate fraction.

The deposition of K\textsubscript{2}CO\textsubscript{3} on the multivalent oxides CeO\textsubscript{2} and MnO\textsubscript{2}, serving as precious metal free oxidants, enables to store NO as well as NO\textsubscript{x} and hence to detect in situ and electrically the total NO\textsubscript{x} loading level. Since the sensitivities towards NO and NO\textsubscript{x} are almost equal, MnO\textsubscript{2} seems to have sufficient oxidizing properties. Additionally, the irreversibility of the increase in the conductivity in NO\textsubscript{x} reveals high nitrate stability under sorption conditions. Hence, as a precious metal free model catalyst, the oxidant and NO\textsubscript{x} storage component KMnO\textsubscript{4} was deposited on the support oxide La-Al\textsubscript{2}O\textsubscript{3} and decomposed thermally. In the low loading state, there is a linear correlation between the decrease in the resistance and the applied NO\textsubscript{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\textsubscript{4} based catalyst provides a constant sorption rate for NO and NO\textsubscript{x} and the resistance decreases linearly with the NO\textsubscript{x} loading level. Besides of detecting the loading level of the catalyst...
time-continuously during NO\textsubscript{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\textsubscript{2}CO\textsubscript{3} based materials are very promising for the electrical in-situ diagnosis of the NO\textsubscript{x} loading state of the catalysts. An electrical characterization of different model catalysts reveals that the conductivity increase in NO\textsubscript{x}, bases on NO oxidation followed by the formation of stable nitrates. While pure carbonates can be applied to detect NO\textsubscript{2}, the sensitivity to NO is achieved by additional oxidizing catalyst components. The NO\textsubscript{x} loading level of KMnO\textsubscript{4} on La-Al\textsubscript{2}O\textsubscript{3}, as a precious metal free NO\textsubscript{x} storage catalyst, can be detected electrically and in-situ either during NO\textsubscript{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\textsubscript{4}/La-Al\textsubscript{2}O\textsubscript{3} can also be applied as sensitive layer in a resistive NO\textsubscript{x} dosimeter for the long-term sensing of the cumulated amount of NO and NO\textsubscript{2} in the sub ppm range.

Project related publications (selection)


- A. Groß, T. Weller, H.L. Tuller, R. Moos, Electrical Conductivity Study of NO\textsubscript{x} Trap Materials BaCO\textsubscript{3} and K\textsubscript{2}CO\textsubscript{3}/La-Al\textsubscript{2}O\textsubscript{3} during NO\textsubscript{x} Exposure, Sensors and Actuators B: Chemical 187 (2013) 461-470, doi: 10.1016/j.snb.2013.01.083.


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