Bayreuther Beiträge zur Sensorik und Messtechnik

Band 2

Cedric Zimmermann

Neuartiger Sensor zur Bestimmung des Zustandes eines NOx-Speicherkatalysators

Shaker Verlag
Aachen 2007

Bibliografische Information der Deutschen Nationalbibliothek
Die Deutsche Nationalbibliothek verzeichnet diese Publikation in der Deutschen Nationalbibliografie; detaillierte bibliografische Daten sind im Internet über http://dnb.d-nb.de abrufbar.

Zugl.: Bayreuth, Univ., Diss., 2007

Copyright Shaker Verlag 2007
Alle Rechte, auch das des auszugsweisen Nachdruckes, der auszugsweisen oder vollständigen Wiedergabe, der Speicherung in Datenverarbeitungs-anlagen und der Übersetzung, vorbehalten.

Printed in Germany.

ISBN 978-3-8322-6084-2
ISSN 1862-9466

Shaker Verlag GmbH • Postfach 101818 • 52018 Aachen
Telefon: 02407 / 95 96 - 0 • Telefax: 02407 / 95 96 - 9
Internet: www.shaker.de • E-Mail: info@shaker.de

Summary

One possible technical solution for removing nitrogen oxides (NO_x) from exhausts of lean burn internal combustion engines is the NO_x-storage catalyst (NSC) system. During a lean phase of a few minutes, the catalyst adsorbs NO_x. Right before the storage capacity is exhausted and the catalyst begins to allow NO_x to pass, the engine is operated richly for a few seconds. During this ‘‘regeneration phase’’, stored NO_x is released and reacts with the reducing components that are present in the rich exhaust. After regeneration, the engine is operated leanly again. This complex process works best with an exhaust gas sensor downstream NSC, providing at least twofold functionality: An NO_x output determines increasing NO_x emissions, indicating that NO_x-storage capacity is exhausted and to prevent HC or CO breakthroughs, a λ probe determines the precise end of the regeneration phase, which is indicated by a λ decrease from stoichiometric to rich. The sensor signals serve as a basis for an extensive model that describes the NSC storage status.
It is a crucial disadvantage that no means are available to gauge directly the catalyst NO_x loading level and the catalyst quality.

This thesis investigates whether an in-situ measurement of the complex electrical impedance of the catalyst coating (NSC status gauge) is an appropriate means to determine directly the catalyst status.

Four key questions are addressed:
1.) Can such a “NSC status gauge” directly measure the degree of NO_x loading?
2.) Are ageing processes, either due to thermal stress or due to sulfur poisoning, detectable by the “NSC status gauge”?
3.) Can the time dependent NO_x storage and regeneration process be directly gauged?
4.) Can the time dependent sulfur poisoning and desulfurization process be directly gauged?

The key issues to answer these four questions are the basic chemical mechanisms that occur during NO_x adsorption and regeneration. In chapter 2, they are compiled from literature.
All the phenomena that affect the storage catalyst capacity should be detected by “NSC status gauge”. As shown in chapter 5, the sensor consists of interdigital electrodes that are deposited on a thin planar substrate. On the reverse side of the substrate, a heater is applied. Both sides are covered with the original catalyst coating, allowing detecting directly electrical impedance and temperature of the film.

Both a synthetic sensor test bench, in which the initial and fundamental tests were performed (cf. chap. 6 to 8), and an appropriate lean burn engine test bench, in which sensors and catalysts were investigated close to reality (chap. 9), are introduced briefly in chap. 4.

At first, dependency of the complex impedance of the catalyst coating on frequency, gas composition, and temperature was investigated. The three stationary conditions, namely freshly regenerated (reduced) in rich exhaust, oxidized without NO (lean), and oxidized and fully loaded (lean with NO) could have been distinguished easily. The main result to be emphasized is the correlation between sensor impedance and the amount of NO_x stored in the catalyst (chap. 6.2). All phenomena affecting the catalyst status can be detected by the sensor and distinguished from each other.

It was shown that -after calibration- the sensor is able to detect fully the absolute amount of stored NO_x. In addition, thermal aging as well as sulfurization of the catalyst film can be detected (chap. 6.4).

In order to explain the physical processes that lead to both sensor behavior and catalyst behavior, different model powders were prepared and investigated. It was shown that the strong impedance change during regeneration is due to a reduction of ceria that acts as an oxygen storage material. The NO_x loading degree is reflected by the transition from barium carbonate to barium nitrate (the NO_x storage component). It can be detected by impedance spectroscopy as well. The overall sensor behavior can be modeled using the General Effective Media Theory.

Chapter 9 describes initial experiments performed in an engine test bench. Four sensors were integrated in an NSC. All results obtained from the synthetic gas test bench were confirmed. It could be shown that such a set of sensors can detect the location of the loading front, the loading status, as well as the regeneration status. Sulfurization and desulfurization could be studied as well.