

# Investigation on sulphation and regeneration of a commercial monolithic NO<sub>x</sub>-storage/reduction catalyst

E. Schreier, R. Eckelt, M. Richter, R. Fricke \*

*Institute for Applied Chemistry (ACA), P.O. Box 96 11 56, D-12474 Berlin, Germany*

Received 3 December 2004; accepted 24 March 2005

Available online 26 April 2005

## Abstract

Sulphur poisoning and regeneration of a commercial NSR catalyst by SO<sub>2</sub> were investigated in dependence on temperature and  $\lambda$  value. The amount of desorbed sulphur compounds during lean-rich regeneration cycles was found to increase with decreasing  $\lambda$  value (0.99–0.94) at constant temperature and with increasing temperature (660–720 °C) at constant  $\lambda$  value. At a regeneration temperature of 660 °C, removed sulphur components comprises mainly SO<sub>2</sub> at  $\lambda$  values near 1, whereas H<sub>2</sub>S and COS are released at lower  $\lambda$  values. At higher regeneration temperatures and low  $\lambda$  values more SO<sub>2</sub> is released, but COS and H<sub>2</sub>S formation also increases.

© 2005 Elsevier B.V. All rights reserved.

*Keywords:* NSR monolith; Sulphation; Regeneration; Lean-rich cycle

## 1. Introduction

Lean-burn gasoline engines reduce fuel consumption and thus avoid abundant CO<sub>2</sub> environmental impact and greenhouse effects. Because of the high concentration of oxygen in the exhaust gas the conventional three-way catalysts (TWCs) could not accomplish the necessary reduction of nitrogen oxides under permanent lean conditions. Besides other concepts the NO<sub>x</sub> storage/reduction (NSR) catalyst promises the highest potential to meet EURO IV emission limits [1,2]. Generally, NSR catalysts contain a storage component (alkaline earth metals) to capture NO<sub>x</sub> in form of surface nitrates from the exhaust during lean operation [2]. On board regeneration by short fuel-rich cycles is initiated when the implemented NO<sub>x</sub> sensor registers commencing breakthrough.

Poisoning of NO<sub>x</sub> storage/reduction (NSR) catalysts installed in lean-burn gasoline passenger cars by SO<sub>2</sub> is a serious problem for the required long term activity under road conditions [3,4]. The incorporated precious metals oxidise both NO and SO<sub>2</sub> during lean conditions leading to nitrate and sulphate surface species, respectively, on the alumina washcoat and catalyst components. The higher stability of earth alkaline sulphates in relation to the corresponding nitrates leads to a progressive blockage of the active sites of the catalyst for NO<sub>x</sub> storage and a decrease in the conversion efficiency of nitrogen oxides with time.

Poulston and Rajaram [5] investigated the regeneration of a nitrated or sulphated model Pt/Ba-based NO<sub>x</sub> trap catalyst using different reductants. When the model NSR catalyst is sulphated in SO<sub>2</sub> under lean conditions at 650 °C almost complete deactivation can be seen. Complete regeneration was not achieved, even under rich conditions at 800 °C in 10% H<sub>2</sub>/He. Barium sulphate formed after the high temperature ageing was partly converted to barium sulphide on reduction. However, if the H<sub>2</sub> reduced sample was exposed to a rich

\* Corresponding author. Tel.: +49 30 6392 4327; fax: +49 30 6392 4392.

*E-mail address:* [fricke@aca-berlin.de](mailto:fricke@aca-berlin.de) (R. Fricke).

condition in a gas mixture containing  $\text{CO}_2$  at 650 °C, the storage activity can be recovered. Under these rich conditions the  $\text{S}_2^-$  species become less stable than the  $\text{CO}_3^{2-}$ , which is active for storing  $\text{NO}_x$ . Samples which were lean aged below 600 °C in air containing 60 ppm  $\text{SO}_2$  after regeneration at  $\lambda = 0.95$  at 650 °C, have a similar activity window to a fresh catalyst. It is, therefore, important that  $\text{CO}_2$  is present during the rich regenerations of the sulphated model samples (as, of course, it would be under real conditions), as suppression of carbonate formation can lead to sulphide formation which is inactive for  $\text{NO}_x$  storage.

In an attempt to characterize the  $\text{SO}_2$  removal from a powdered  $\text{NO}_x$  trap catalyst containing Pt, Ba, Ce and Zr on a  $\gamma\text{-Al}_2\text{O}_3$  support by means of TPD and FTIR spectroscopy. Courson et al. [6] could show that longer regeneration periods promote sintering of the noble metal particles. In addition, they could show that it is essential for a successful regeneration to avoid formation of bulk sulphates.

Sedlmair et al. [7,8] identified two pathways of catalyst deactivation by  $\text{SO}_2$ . Under lean conditions (exposure to  $\text{SO}_2$  and  $\text{O}_2$ ) at 350 °C, the storage component forms barium sulphates, which are transformed from surface to hardly reducible bulk sulphate species. The irreversible blocking of the Ba sites led to a decrease in  $\text{NO}_x$  storage capacity. Under fuel rich conditions ( $\text{SO}_2/\text{C}_3\text{H}_6$ ) at 350–500 °C evidence for the formation of sulfides on the oxidation/reduction component (Pt) of the catalyst was found, which blocks the metal surface and thus hinders the further reduction of the sulphides.

The deactivation of the storage component, i.e., the loss of the  $\text{NO}_x$  storage capacity, resulted mainly from the formation of Ba-sulphates accumulating in the bulk phase, which have a high thermal stability (above 800 °C) and, therefore, cannot be removed under the typical operation conditions of a NSR catalyst. Besides the formation of  $\text{SO}_4^{2-}$  species on the storage component at the beginning of the  $\text{SO}_2$  exposure under rich conditions, an adsorption of  $\text{SO}_2$  on the noble metal component was observed resulting in the formation of sulphur deposits. The oxidation of these sulphur species with a subsequent spillover of  $\text{SO}_4^{2-}$  species to the storage component during lean conditions could accelerate the deactivation of the storage capacity.

Regeneration has to avoid severe reduction of sulphur compounds because of  $\text{H}_2\text{S}$  and COS formation. It is of primary interest to know at which  $\lambda$  value during on-board regeneration the formation of unwanted sulphur compounds ( $\text{H}_2\text{S}$ , COS) occurs. The aim of this paper is to investigate the adsorption of  $\text{SO}_2$  from a wet gas mixture under lean conditions and the following removal of the deposited sulphate in dependence on  $\lambda$  values and to analyse the nature of S compounds released into the gas phase. The regeneration of the catalysts

was performed by switching between rich and lean conditions within intervals of 5 s at different  $\lambda$  values, temperatures, and space velocities.

## 2. Experimental

The experiments were performed in a quartz tube flow reactor system with on line coupled mass spectrometric analysis (Omnistar, Pfeiffer Vacuum). The main components of the commercial monolithic NSR catalyst are Pt–Pd–Ce–Zr–La–Al and Ba and were supported from the appropriate chemical compounds on a cordierite support. A core (size 1 in.  $\times$  1.25 in.) of this catalytic system was placed into the quartz wool tape. Two thermocouples were directly placed in front of the monolith and behind, so that temperature gradients could be monitored. Directly behind the monolith sample, the inlet capillary of the mass spectrometer was positioned to avoid analytical artefacts by secondary gas phase reactions in the free reactor volume. A commercial Lambda sensor in the feed line served for continuous measurements of the  $\lambda$  value which represents the concentration ratio of air offered into the system to air necessary for a complete combustion of fuel (i.e.,  $\lambda = 1$  means that exactly the necessary concentration of air is offered,  $\lambda < 1$  means excess fuel ('rich' conditions) and  $\lambda > 1$  excess of air ('lean' conditions)).

Gas mixtures were prepared by appropriate mixing of premixed gas components and controlled by mass flow controllers (MKS Instruments). The change of lean-to-rich feed composition was accomplished by removal of oxygen from the feed. To enable rapid cycling without significant disturbance of flow dynamics, two side streams of identical flow rates, one consisting of  $\text{CO}/\text{H}_2/\text{O}_2/\text{N}_2$  and the other of  $\text{CO}/\text{H}_2/\text{N}_2$ , could be directed into the main stream by a 4-way valve (VICI AG, Valco International). The valve was switched by a microelectric actuator with remote control. Before  $\text{SO}_2$  uptake the catalyst was pretreated at 550 °C in a  $\text{N}_2$  stream which has contained 10%  $\text{O}_2$  and 10%  $\text{H}_2\text{O}$ . The adsorption of  $\text{SO}_2$  was performed in a gas mixture of 50 or 250 ppm  $\text{SO}_2$ , 11%  $\text{O}_2$  and 10%  $\text{H}_2\text{O}$  balanced to 100% with  $\text{N}_2$  at 350 °C. The total gas flow was 480  $\text{Lh}^{-1}$  corresponding to a space velocity of 30.000  $\text{h}^{-1}$ . The adsorption time was different.

The quantitative estimation of the sulphur content was determined by optical emission spectroscopy with excitation by inductively coupled plasma (OES-ICP) with the spectrometer Optima 3000 XL (Perking Elmer).

The regeneration of the sulphated monoliths was investigated by cycling between lean and rich feed composition in intervals of 5 s ("wobbling"). The lean mixture consisted of 11%  $\text{O}_2$ , 15%  $\text{CO}_2$ , 10%  $\text{H}_2\text{O}$  and  $\text{CO}/\text{H}_2$  (3/1) balanced by  $\text{N}_2$  and the rich mixture contained 0%  $\text{O}_2$ , 15%  $\text{CO}_2$ , 10%  $\text{H}_2\text{O}$  and  $\text{CO}/\text{H}_2$  (3/

Download English Version:

<https://daneshyari.com/en/article/10242958>

Download Persian Version:

<https://daneshyari.com/article/10242958>

[Daneshyari.com](https://daneshyari.com)