



Contents lists available at ScienceDirect

Catalysis Today

journal homepage: [www.elsevier.com/locate/cattod](http://www.elsevier.com/locate/cattod)

## Catalyzed soot filters (CSF) with H<sub>2</sub>S control function for lean NO<sub>x</sub> trap (LNT) systems

Yuejin Li<sup>a,\*</sup>, Michael Weinstein<sup>a</sup>, Matthew Caudle<sup>a</sup>, Steven Steeley<sup>a</sup>, Gerd Grubert<sup>b</sup>, Alfred Punke<sup>b</sup><sup>a</sup> BASF Corporation, 25 Middlesex-Essex Turnpike, Iselin, NJ, 08830, USA<sup>b</sup> BASF Catalysts Germany GmbH, Seligmannellee 1, 30173, Hannover, Germany

### ARTICLE INFO

#### Article history:

Received 1 October 2016

Received in revised form

19 December 2016

Accepted 27 December 2016

Available online xxx

#### Keywords:

Catalyzed soot filter

Lean NO<sub>x</sub> trapH<sub>2</sub>S suppression

### ABSTRACT

A lean NO<sub>x</sub> trap (LNT) based emission control system typically consists of a LNT catalyst for NO<sub>x</sub> reduction and CO/HC oxidation and a catalyzed soot filter (CSF) for particulate filtration and CO/HC oxidation. During LNT's operation, it is required that sulfur compounds bound to the catalyst surface must be periodically removed in a reducing environment to recover the NO<sub>x</sub> storage sites. However, this desulfation process produces high levels of H<sub>2</sub>S emission, which must be suppressed. A series of catalyzed soot filters has been investigated for H<sub>2</sub>S suppression, and CuO based filters were found to be very efficient in converting H<sub>2</sub>S to SO<sub>2</sub>. Only 0.05 g/in<sup>3</sup> bulk CuO can convert 500 ppm H<sub>2</sub>S to SO<sub>2</sub> with 100% efficiency at GHSV = 34,000 h<sup>-1</sup> after a high temperature aging treatment (800 °C/16 h with 10% H<sub>2</sub>O). However, CuO was found to severely poison the precious metal (PGM) functions in the filter, dramatically reducing its CO/HC oxidation activity. The degree of poisoning is proportional to the CuO loading and also related to the proximity between CuO and the PGM within the filter microstructure. A zoned coating approach, where CuO and PGM occupy two non-overlapping zones in the axial direction, has been systematically investigated with both laboratory reactor and engine tests. The zoned H<sub>2</sub>S-CSFs, with CuO in the front of the filter and the PGM in the rear, were demonstrated to be effective catalysts that can fulfil both H<sub>2</sub>S suppression and CO/HC oxidation requirements.

© 2016 Elsevier B.V. All rights reserved.

### 1. Introduction

LNT and Selective Catalytic Reduction (SCR) are two commercially available NO<sub>x</sub> control technologies for light-duty diesel vehicles to meet Euro 6 emission regulations [1]. Each system has certain advantages and disadvantages in cost and performance, and both are being explored to meet the Euro 6c regulations. When compared to a SCR system, a LNT system has limited efficiency at high speed/high load driving conditions (high NO<sub>x</sub> flux) because of the limitation in NO<sub>x</sub> storage capacity, and therefore it is mainly used for smaller cars. On the other hand, the LNT system has a lower total cost of ownership, which continues making it an attractive approach for further technology development [2]. In addition to NO<sub>x</sub> reduction, a LNT catalyst is also a very effective Diesel Oxidation Catalyst (DOC) because it usually contains a high level of precious metals. A LNT-based system must also include a catalyzed

soot filter (CSF) for particulate filtration and other gas conversion functionalities (see Fig. 1).

A LNT catalyst accomplishes NO<sub>x</sub> abatement by decoupling of two separate processes, NO<sub>x</sub> storage in a lean period (normal diesel engine operation) and reduction of the stored NO<sub>x</sub> with a short (a few seconds) rich transient [3–5]. During the lean period, NO emitted from the combustion process is oxidized to NO<sub>2</sub> on a Pt catalyst, which is further converted to nitrate and stored on the basic components. During the rich period, the stored nitrate is liberated and reduced to N<sub>2</sub> in a way similar to NO<sub>x</sub> reduction on a Three-Way Catalyst (TWC). A conventional diesel engine exhaust is overwhelmingly lean with very high levels of O<sub>2</sub> (e.g., 10%). Typically, rich pulses are generated by in-cylinder post-injection of diesel fuel during the expansion stroke. Alkaline earth or alkali metals, such as barium, are typically used in commercial LNT formulations. Barium is a strong base which reacts with the acidic NO<sub>x</sub> species very effectively to form Ba(NO<sub>3</sub>)<sub>2</sub>. However, the sulfur species in the exhaust, derived from diesel fuel and lubricating oil, also react with the barium component, forming BaSO<sub>4</sub>. Barium sulfate is more thermally stable than Ba(NO<sub>3</sub>)<sub>2</sub> by 45–60 kcal/mol between 200 and 700 °C [6], and, as a result, the LNT catalyst grad-

\* Corresponding author.

E-mail address: [yuejin.li@basf.com](mailto:yuejin.li@basf.com) (Y. Li).

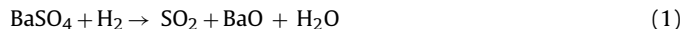


**Fig. 1.** Schematic representation of catalyst configuration for the H<sub>2</sub>S suppression experiment.

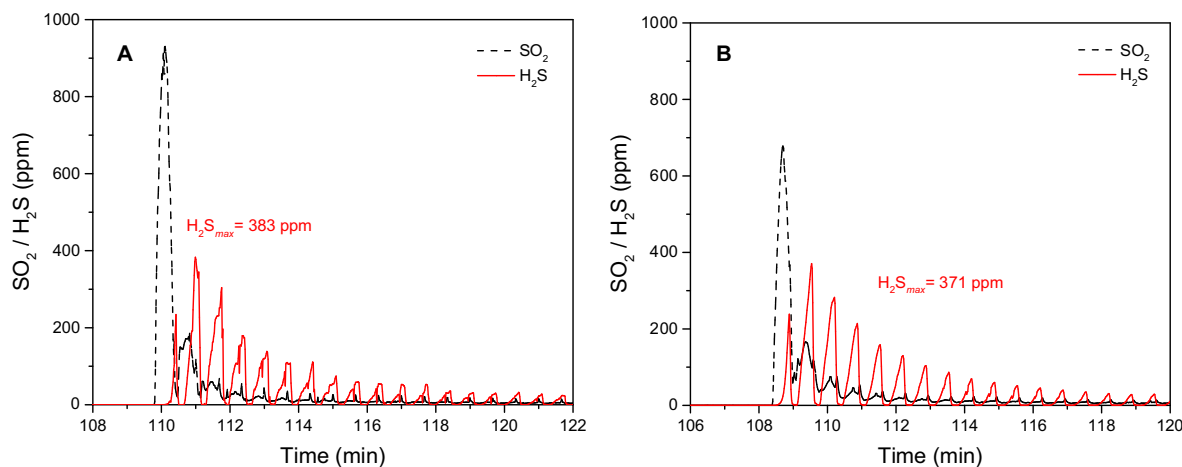
usually loses its NO<sub>x</sub> storage capacity. To continue performing its deNO<sub>x</sub> function, sulfur must be removed from the poisoned LNT catalyst with a rich feed ( $\lambda < 1$ ) (or rich/lean alternating feed) at high temperatures ( $T > 600^\circ\text{C}$ ).

Extensive work on LNT desulfation and the resulting sulfur species have been reported [7–14]. High levels of H<sub>2</sub>S emission were often reported during the LNT desulfation either in lab or engine tests. The intensity of H<sub>2</sub>S formation depends on the lambda value of the desulfation feed and the mode of the desulfation operation, i.e. continuous rich vs. rich/lean modulation. The lower the lambda value (more reducing) of the desulfation feed, the higher the H<sub>2</sub>S formation (and higher desulfation efficiency). Continuous rich desulfation generates mostly H<sub>2</sub>S. The formation of H<sub>2</sub>S can be reduced by rich/lean modulation. For example, in an engine desulfation test, Erkkfeldt et al. reported that the peak H<sub>2</sub>S formation was about 1150 ppm with  $\lambda = 0.95$  at  $700^\circ\text{C}$ , whereas the peak H<sub>2</sub>S was about 700 ppm with  $\lambda = 0.98$  at the same temperature [7]. In an engine bench experiment, Asik et al. was able to reduce the peak H<sub>2</sub>S formation from 300 ppm obtained from a continuous desulfation to 160 ppm by using rich/lean modulation [8].

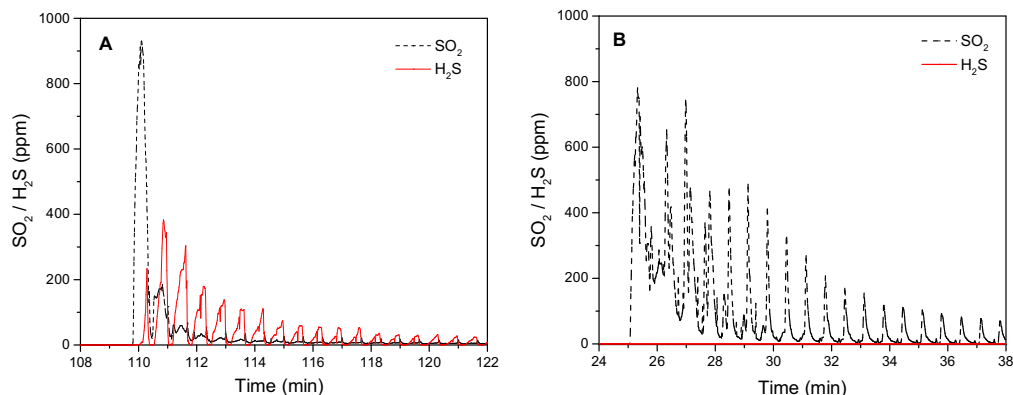
It is generally recognized that during LNT desulfation H<sub>2</sub>S is formed via a two-step process: sulfate reduction to SO<sub>2</sub> and further reduction of SO<sub>2</sub> to H<sub>2</sub>S [8,13,14]. The following chemical equations [Eqs. (1) and (2)] can be used to describe the desulfation process. H<sub>2</sub>S is more likely to form than SO<sub>2</sub>, as long as H<sub>2</sub> is available, because the free energy of formation ( $\Delta G$ ) for Eq. (2) is  $-35.5$  to  $-33.5$  kcal/mol between  $600$  and  $700^\circ\text{C}$  [6]. Thus, it is extremely difficult to avoid H<sub>2</sub>S formation during LNT desulfation.



H<sub>2</sub>S is a highly toxic gas, which exerts its toxic effects primarily as a central nervous system toxin (neurotoxin) and as a local irritant [15]. H<sub>2</sub>S has a rotten-egg smell with a smell threshold of 0.02 ppm. Although not one of the regulated emission gases, H<sub>2</sub>S as a by-product of the LNT catalysis must be controlled. In the early days of TWC development, Ni was used as a H<sub>2</sub>S-getter to control H<sub>2</sub>S emission [16–18]. This concept was also reported for H<sub>2</sub>S control during LNT desulfation. By incorporating Ni as a component of the LNT catalyst, Asik et al. reported that the H<sub>2</sub>S emission over the FTP test cycle was reduced to 1/3 of that of a Ni-free LNT catalyst [8]. Using a stand-alone Ni-based H<sub>2</sub>S-trap placed behind a LNT catalyst, Elwart et al. conducted LNT desulfation experiments under rich/lean modulation conditions and were able to cut the maximum H<sub>2</sub>S emission by half [10]. They studied the desulfation with a LNT + (passive) SCR system, where the SCR catalyst is a Cu-zeolite [12]. The H<sub>2</sub>S emission was found to be significantly suppressed with the downstream Cu-zeolite based SCR catalyst.



**Fig. 2.** Filter-out SO<sub>2</sub> and H<sub>2</sub>S concentration profiles during LNT desulfation tests with a blank filter (A) and a CSF reference (B); GHSV (filter) =  $34,000\text{ h}^{-1}$ .



**Fig. 3.** Filter-out SO<sub>2</sub> and H<sub>2</sub>S concentration profiles during LNT desulfation tests with a blank filter (A) and a CuO-containing CSF (B); GHSV (filter) =  $68,000\text{ h}^{-1}$ .

Download English Version:

<https://daneshyari.com/en/article/6504995>

Download Persian Version:

<https://daneshyari.com/article/6504995>

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