Catalysis Today 176 (2011) 56–62

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Impact of thermal and vehicle aging on the structure and functionalities of a lean NOx-trap

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ARTICLE INFO

Article history:
Received 28 September 2010
Received in revised form 21 March 2011
Accepted 22 March 2011
Available online 6 July 2011

Keywords:
Lean NOx Trap (LNT)
NOx storage catalyst
Thermal aging
Vehicle aging
Sulfation
SO_2
Operando FTIR

ABSTRACT

Investigations of the aging behaviour of a commercial lean NOx trap (LNT) are reported in this paper. Two aging processes were tested and compared: a hydrothermal aging at 800 °C and a vehicle aging corresponding to a 80,000 km use. Samples were characterized with Operando FTIR, XRF, XRD, SEM-EDX, TEM, and BET analyses. LNT functionalities were evaluated using a flow reactor capable of performing NOx storage and conversion measurements, and correlated with the LNT structure evolution due to aging. The results highlighted that Pt sintering had an impact on the NO oxidation functionality and also deteriorated the Pt/Ba interface. It was hence partly responsible for the NSC decrease. Both aging processes had a similar impact on the LNT NOx storage capacity (NSC) although their structural evolutions were different: $BaAl_2O_4$ formation on the hydrothermal aged catalyst versus barium poisoned by sulphur on the vehicle aged catalyst.

1. Introduction

Emissions of nitrogen oxides (NOx) and particulate matter (PM) produced by Diesel-powered vehicles represent a major environmental and health issue in highly populated areas. A number of exhaust gas after treatment systems have been developed in recent years for Diesel engines such as the Diesel particulate filter (DPF) regarding PM abatement and the Lean NOx-Trap (LNT) or urea Selective Catalytic Reduction system (SCR) regarding NOx emission reduction from lean burn engine. LNTs achieve NOx conversion through successive cycles of lean and rich operating conditions [1]. The concept is based on the adsorption of NOx on a trapping material during long periods of excess oxygen followed by shorter periods with a lack of oxygen during which the stored NOx are released and reduced to mainly N_2, but also partly N_2O or NH_3. Reductants are mainly hydrocarbons issued from a specific fuel injection strategy into the cylinder or the exhaust pipe. Lean/rich transitions are managed by the engine control unit. Main components of the catalytic washcoat are usually alumina for the support, Pt, Pd and Rh as noble metals to provide oxidative and reductive functionalities, and a basic additive (often a barium salt) known for its high affinity for NOx as a storage component [2].

NOx traps also show some undesired reactivity in regards to sulphur compounds which are present in exhaust gases from both Diesel and gasoline engines [3–6]. SO_3 reacts with barium and alumina to form barium and aluminium sulphates which are more stable than the corresponding nitrates. This causes gradual saturation of the storage material with sulphur and loss of activity towards NOx storage [5]. Periodic desulfation (DeSOx) hence require higher temperatures which are detrimental to the life of the catalyst. For this reason, deactivation by sulphur and the corresponding thermal aging are key obstacles to a widespread implementation of the LNT [7–12].

The work described in this paper focuses on the impact of aging on the functionalities of a commercial lean NOx-trap. Two aging processes were tested and compared: a hydrothermal aging at 800 °C and a vehicle aging corresponding to a 80,000 km use and considered as a reference. Functionalities were evaluated on a Synthetic Gas Bench (SGB) and reactivity results were correlated with the analysis of the structural and chemical evolution of the catalyst. A FTIR *Operando* study allowed to further analyse the mechanisms occurring on the catalyst surface and to highlight the most critical points.

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doi:10.1016/j.cattod.2011.03.049

2. Experimental

2.1. Catalyst

The commercial NOx trap that was investigated in this study was supplied by RENAULT. It has a square monolithic honeycomb structure of 400 cells per square inch (cpsi). The thin ceramic walls are coated with a NOx storage/reduction catalyst. The catalytic coating was characterized by X-ray fluorescence analysis (XRF), X-ray diffraction (XRD), scanning electron microscopy with elemental analysis by energy-dispersive X-ray spectroscopy (SEM-EDX). TEM observations were performed on a JEOL 2100F 200 kV microscope equipped with a X-ray dispersive Spectrometer. X-ray diffraction (XRD) patterns were obtained with a PANalytical X'Pert Pro MPD Diffractometer with Bragg-Brentano X-ray tube Cu anticathode (wavenumber kA1 = 1.5406 Å). Samples were loosely packed in a shallow cavity (0.2 cm deep and 1 cm in diameter). The washcoat was separated from the cordierite support before being analysed.

2.2. Aged catalysts

NOx trap samples were hydrothermally aged in a furnace at 800 °C for 5 h under a flow of 10% O_2, 10% H_2O and N_2.

The vehicle aged trap underwent an accelerated aging of 35,000 km with a 10 ppmS fuel, which was equivalent to a mileage of 80,000 km. The catalyst underwent a total of 4 h of desulfation, with a maximum temperature of 780 °C.

2.3. IR operando measurements

The purpose of FTIR Operando study was to analyse NOx and carbonates storage sites of the LNT samples under representative running conditions so as to determine the impact of thermal aging on the storage sites. The description of the Operando setup, with gas line and analysis tools (IR, MS and chemiluminescence) and the IR reactor cell is described in [13]. The material was pressed into self-supporting wafers of 10 mg cm^{-2} and placed into the quartz reactor equipped with KBr windows. For the analysis of the surface, operando measurements were carried out with a Nicolet FT-IR Nexus spectrometer equipped with a MCT detector, using a setup described in [13]. FT-IR spectra were collected with a resolution of 4 cm^{-1}. The analysis of the outlet gases was performed by means of a Pfeiffer Omnistar mass spectrometer. Likewise FT-IR spectra of the gas phase were collected using a gas microcell. The sample was activated in the same way as SGB (described in Section 2.4).

The lean reacting gas composition was 900 ppmC HC, 800 ppm CO, 270 ppm H_2, 300 ppm NOx, 5% CO_2, 15% O_2 and 2% H_2O in Ar as carrier gas. The total flow was fixed to 25 cm^3 min^{-1}. This composition is equivalent to that used in the synthetic gas bench and is very similar to a real composition of a typical Diesel exhaust. Binary mixtures were also used to improve the understanding of NOx storage mechanisms.

2.4. Synthetic gas bench

The purpose of the synthetic gas bench study was to quantify NOx storage and reduction capacities of the LNT samples under representative running conditions so as to evaluate the impact of thermal aging. The following experiments were performed:

- sample pre-treatment
- isothermal NOx storage experiments with different gas compositions
- rich pulses to mimic storage/reduction cycles occurring in real driving conditions

Table 1
Gas compositions used for the tests. Gas composition also included H_2 = CO/3, H_2O = 4% and N_2 = balance.

Eq. ratio	HC (ppmC)	CO	NO (ppm)	CO_2 (%)	O_2 (%)
0.3	900	800	300	5	15
1.1	4500	4%	0	11	1.5

LNT samples prepared for the SGB study were cylinders 25 mm in diameter and 50 mm in length cut from the monolith. Experiments were carried out in a flow reactor under atmospheric pressure and realistic flow conditions with a simulated Diesel exhaust gas stream. The catalyst sample was placed in a quartz tube. A thermocouple in front of the catalyst was used to control the temperature and another one was inserted downstream from the catalyst. The quartz tube was placed in an electrically heated oven. Valves allowed to rapidly switch from one gas composition to another, and to generate alternating rich and lean phases. Gas compositions were chosen close to a lean Diesel environment [equivalence (Eq.) ratio = 0.3] and to a rich pulse environment (Eq. ratio = 1.1) as detailed in Table 1. Other compositions were also tested when considered useful to better understand the catalyst behaviour. Propylene was used to represent unburned hydrocarbons emitted by engine combustion.

The gas hourly space velocity was 30,000 h^{-1}. All gases were fed to the reactor via mass flow controllers, while water vapor was injected through a vaporizer in a N_2 flow. Analysed gases were CO_2, O_2, CO, HC, NOx, NO and NO_2, N_2O and NH_3 for some of the tests.

2.4.1. Sample pre-treatment

All samples were pre-treated to stabilize their active surface and thus their catalytic activity so as to ensure a good test reproducibility. The gas flow was switched between 290 s lean feed periods (Eq. ratio = 0.3) and 15 s rich pulses (Eq. ratio = 1.1, see Table 1). Temperature was increased at 5 °C/min rate from 50 °C up to 620 °C and then stabilized at 620 °C for 2 h. The catalyst was cooled back to room temperature in a synthetic air flow.

2.4.2. Isothermal NOx storage

The gas temperature was increased up to the desired value under a N_2 flow. The experiment then switched to a lean feed and both NO and NO_2 were monitored downstream from the catalyst. The gas mixture switched back to N_2 after the NOx trap became saturated and the temperature was increased so as to thermally release the complete amount of stored NOx (N_2-TPD: temperature programmed desorption). The NOx storage capacity (NSC), the NO oxidation efficiency and the deNOx of the LNT were determined at different temperatures and storage times.

2.4.3. Lean–rich cycling conditions

The method to evaluate NOx storage, reduction and global conversion efficiency of the NOx trap is by cycling between lean and rich conditions to mimic engine operation. In this test, the gas temperature was increased up to the desired value (300 °C) under a N_2 flow. The gas flow was then switched between 290 s lean feed periods (Eq. ratio = 0.3) and 15 s rich pulses (Eq. ratio = 1.1). It was switched back to N_2 after the lean/rich cycling exhibited a repeatable behaviour, and a temperature programmed desorption was performed. The NOx storage efficiency in the lean phase, the NOx reduction efficiency in the rich phase and the overall NOx conversion efficiency were determined as described below.