



Spatiotemporal distribution of NO_x storage and impact on NH₃ and N₂O selectivities during lean/rich cycling of a Ba-based lean NO_x trap catalyst[☆]

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ABSTRACT

We summarize results from an investigation of the spatiotemporal distribution of NO_x storage and intermediate gas species in determining the performance of a fully formulated, Ba-based, lean NO_x trap catalyst under lean/rich cycling conditions. By experimentally resolving spatiotemporal profiles of gas composition, we found that stored NO_x was significantly redistributed along the monolith axis during the rich phase of the cycle by release and subsequent downstream re-adsorption. Sulfur poisoning of upstream NO_x storage sites caused the active NO_x-storage zone to be displaced downstream. This axial displacement in turn influenced rich-phase NO_x release and re-adsorption. As sulfur poisoning increased, NH₃ slip at the catalyst exit also increased due to its formation closer to the catalyst outlet and decreased exposure to downstream oxidation by surface oxygen. N₂O formation was found to be associated with nitrate reduction rather than oxidation of NH₃ by stored oxygen. We propose that the observed evolution of N₂O selectivity with sulfation can be explained by changes in the spatiotemporal distribution of NO_x storage resulting in either increased or decreased number of precious-metal sites surrounded by nitrates.

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1. Introduction

Lean NO_x trap (LNT) or NO_x storage/reduction (NSR) catalysts are composed of typical 3-way-catalyst components – precious metals (Pt, Pd, Rh), supports (Al₂O₃, CeO₂, TiO₂), and oxygen storage capacity (OSC: CeO₂–ZrO₂) – and alkali or alkaline-earth metals (Ba, K) [1–4]. In the fuel-lean (or excess oxygen) exhausts of lean-burn engines, LNTs store NO_x as nitrates or nitrites such as Ba(NO₃)₂, Ba(NO₂)₂, KNO₃, and KNO₂. LNTs must be periodically regenerated, releasing and reducing the stored NO_x by briefly switching the exhaust conditions to fuel rich. During the cyclic lean/rich operation, precious metals also play important roles in, for example, NO oxidation to NO₂, nitrates formation, and NO reduction.

Since the 1990s, LNT chemistry has been extensively studied, providing fundamental insights into the relevant reactions, mechanisms, kinetics, and roles of different catalytic components [2,3]. The majority of this previous research has focused on differential

measurements, thus considering the reactions in a non-integral (i.e., zero-dimensional) context. More recently, models that include the integral effects of sequential reactions under relevant cycling conditions have been proposed [5–11]. These models and recent experimental studies [12–22] have demonstrated that it is important to consider the effects of spatiotemporal coupling among the different “local” reactions in understanding overall LNT performance. One prime example of the importance of spatiotemporal coupling is the role of NH₃ as described below.

It is now well accepted that NH₃ can be a major local product when nitrates are reduced by H₂ (and/or CO in the presence of H₂O), and ammonia can effectively reduce nitrates into N₂ [12–14,19–22]. Direct measurements of NH₃ inside a monolith coated with Pt/Ba/Al₂O₃ recently confirmed that NH₃ formed near the monolith inlet reduces downstream nitrates while traveling along the length of the catalyst [19]. These results explain the reason why NH₃ is observed at late regeneration times at the catalyst outlet and global NH₃ selectivity is usually low under typical cycling conditions [12]. It is interesting to note that the NH₃ front generally moves slightly ahead of that of H₂ [19]. This spatial and temporal separation of NH₃ and H₂ fronts is likely due to the higher reactivity of H₂ especially at low temperatures [21,22], allowing it to reduce more stable nitrates behind the NH₃ front. This is an important consideration when interpreting the sequence of reduction reactions and regeneration selectivity since it implies that NH₃ would typically reach unregenerated downstream surfaces first.

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Another example of the complex spatiotemporal coupling involved in LNT chemistry is the sulfation-induced increase in NH_3 selectivity. In our previous study [4,17,18], detailed intra-catalyst gas analyses revealed that sulfur poisons NO_x storage/reduction function in a plug-like manner along the catalyst axis. The plug-like poisoning of NO_x storage sites (mainly Ba) displaces the NH_3 -forming “active” NO_x storage/reduction zone downstream and shortens the downstream OSC-only zone. As a consequence, downstream NH_3 oxidation by OSC was reduced, thereby allowing more NH_3 slip at the reactor exit.

This paper complements the previous studies mentioned above with additional spatiotemporal information. In particular, we describe how the distribution of NO_x storage evolves within the catalyst over space and time affecting the global performance of a fully formulated LNT under lean/rich cycling conditions. By resolving gas transients directly along the catalyst, we will characterize three processes influencing the distribution of NO_x storage: (i) lean-phase adsorption; (ii) rich-phase re-adsorption of NO_x slipped from the upstream NSR zone; and (iii) sulfation-induced downstream displacement of the active NO_x storage zone. We then explain how changes in the distribution of NO_x storage coupled with local chemistry impact global lean-phase NO_x storage, rich-phase NO_x slip, and overall NH_3 and N_2O selectivities.

2. Experimental

2.1. Catalyst

A fully formulated LNT monolith (Umicore; washcoated honeycomb cordierite monolith of 97 cells per cm^2) manufactured for lean gasoline applications was utilized in the present study. This particular catalyst has been adopted as a representative commercial LNT for study in the Crosscut Lean Exhaust Emissions Reduction Simulations (CLEERS) research community [23] and more details about this catalyst can be found in previous publications [4,7,8,17,18,24–26]. Briefly, the catalyst contains magnesium, aluminum, cerium, zirconium, and barium as major washcoat components. Other elements of significance were platinum, palladium, rhodium, lanthanum, iron, and titanium. Four compositionally distinct grains were found to constitute the washcoat [4]: (i) Mg/Al mixed oxide with Pt, Ce; (ii) Al oxide with Rh, Pd; (iii) Ce/Zr mixed oxide with Pt, Pd, Ba (high Ba content); (iv) Ce/Zr mixed oxide with Pt, Pd, Ba (low Ba content). The bulk density of the catalyst (mass of monolith substrate + washcoat per volume) was ca. 570 g L^{-1} and the total surface area (substrate + washcoat) was determined to be $27.1 \text{ m}^2 \text{ g}^{-1}$ by N_2 adsorption using the BET method.

Prior to the reactor measurements, the as-received catalyst was pre-conditioned to establish reproducible performance. The pre-conditioning included:

- (1) Hydrothermal treatment at 700°C for 16 h in flowing 10% H_2O in air;
- (2) Followed by at least four consecutive cycles of sulfation (3.4 g sulfur loading per liter catalyst volume at 325 or 400°C) and desulfation (temperature programmed reduction up to 700°C).

2.2. Lean/rich cycling experiments with spatiotemporally resolved gas analysis

The NO_x storage/reduction performance of the catalyst was evaluated in a laboratory bench flow reactor. A 2.1-cm-diameter and 7.4-cm-long core was wrapped in Zetex insulation tape and inserted into a horizontal quartz reactor tube (2.2-cm inside diameter). The reactor tube was heated by an electric furnace, and

synthetic exhaust gas mixtures were prepared using pressurized gas bottles (ultra high purity grade, Air Liquide). The gases were metered with mass flow controllers (Unit Instruments Series 7300, Kinetics Electronics) and pre-heated before entering the quartz reactor. Water was introduced by a peristaltic cartridge pump (Cole-Parmer) to a heated zone, vaporized and added to the simulated exhaust mixture. A rapid switching 4-way valve system was used to alternate between the lean and rich gas mixtures (60/5-s lean/rich cycling). The lean-phase mixture contained 300 ppm NO , 10% O_2 , 5% H_2O , 5% CO_2 and inert balance (N_2 or Ar), and the rich-phase mixture contained 3.4% H_2 , 5% H_2O , 5% CO_2 and inert balance (N_2 or Ar). The gas hourly space velocity (GHSV) was $30,000 \text{ h}^{-1}$.

For spatiotemporally resolved *in situ* gas analysis, in-house-developed spatially resolved capillary inlet mass spectrometers (SpaciMS) [27] were used. Gas was sampled continuously from axially different locations inside a catalyst channel using a small capillary probe (185- μm OD, 50- μm ID) and fed into a mass spectrometer for speciation. In addition, a high-speed FTIR gas analyzer (MKS) provided temporally resolved species profiles by measuring the reactor effluents.

To induce catalyst sulfation, 40 ppm SO_2 was continuously introduced to the reactant gas stream during lean/rich cycling at 400°C for a specified time. Following the sulfur exposure, the system was allowed to equilibrate for at least 0.5 h under lean/rich cycling without SO_2 . This sulfation process resulted in virtually complete sulfur uptake with negligible sulfur breakthrough as confirmed by two sulfur analyzers (API-Model 100 A: UV fluorescence SO_2 , and AMETEK-Western Research Series 900: non-dispersive UV SO_2 , H_2S).

From the above-mentioned lean/rich cycling experiments, three types of measurements were obtained:

- (1) Spatiotemporal profiles of NO_x and H_2 concentrations at 400°C at three different sulfur loadings (0, 1.7, and 3.4 g sulfur per liter, S/L; SpaciMS measurements);
- (2) Spatial profiles of time-integrated NO_x , NH_3 , and N_2 concentrations at 300°C at two different sulfur loadings (0 and 3.4 g S/L; SpaciMS measurements);
- (3) Global performance – lean NO_x storage, rich NO_x slip, NO_x conversion, NH_3 and N_2O selectivities – at 400°C with increasing sulfur loading (measured during sulfation from 0 to 3.4 g S/L with the FTIR gas analyzer at the outlet of the catalyst).

2.3. Transient NH_3 response experiments

Using the same bench-reactor setup described in Section 2.2, the transient response of the unsulfated catalyst (0 g S/L) to an NH_3 pulse was studied in either pre-oxidized or pre-nitrated surface state. First, the catalyst was exposed to either 10% O_2 (to pre-oxidize the surface) or 300 ppm $\text{NO} + 10\% \text{O}_2$ (to pre-nitrate the surface) for 5 min at 200, 300, or 400°C . During these pre-exposures, the other gas constituents were 5% H_2O , 5% CO_2 , and N_2 balance with a GHSV of $30,000 \text{ h}^{-1}$. After a subsequent 5-min neutral purging in 5% H_2O , 5% CO_2 , and N_2 balance, 300-ppm NH_3 was introduced to the reactor for 4 min. The gas composition was monitored at the reactor outlet using the high-speed FTIR gas analyzer.

3. Results and discussion

3.1. The effects of lean-phase adsorption, rich-phase release and re-adsorption, and sulfation-induced poisoning on the distribution of NO_x storage

To maintain high NO_x conversion under fast lean/rich cycling conditions, both storage and regeneration must be rapid and

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