Catalysis Today 231 (2014) 125–134

Contents lists available at ScienceDirect

Catalysis Today

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

Fast lean-rich cycling for enhanced NO_x conversion on storage and reduction catalysts

Charles C.Y. Perng, Vencon G. Easterling, Michael P. Harold*

University of Houston, Houston, TX 77204, United States

ARTICLE INFO

Article history:
Received 16 October 2013
Received in revised form 14 January 2014
Accepted 20 January 2014
Available online 22 February 2014

Keywords:
NO_x
Platinum
Reduction
NO_x storage and reduction
Selective catalytic reduction
Propylene
Periodic operation

ABSTRACT

Lean NO_x ($NO + NO_2$) reduction was carried out using rapid periodic injection of C_3H_6 over a NO_x storage and reduction (NSR) monolith catalyst containing $Pt/Rh/BaO/CeO_2/Al_2O_3$. The effects of injection rate, feed temperature, rich phase composition, lean phase duration, and feed concentration of CO_2 were systematically varied to quantify their effects on the cycle-averaged NO_x and propylene conversions, and product selectivities. A factor of 10 increase in the injection frequency from conventional NSR cycling frequency of 0.014 to 0.14 Hz resulted in much higher NO_x conversion at high feed temperatures (above 300 °C). Both NO_x and propylene conversions were higher over the entire range of feed temperatures (150–400 °C). High frequency injection with propylene resulted in a nearly constant catalyst temperature, in contrast to large swings in the catalyst temperature during lower frequency injection. NO_x conversion exceeding 90% was achieved for a feed having a cycle-averaged stoichiometric number (lean to rich ratio) of 6; slower injection required a stoichiometric ratio of 4 to achieve the same NO_x conversion. The same high frequency operation using H_2 as the reductant not only did not show any enhancement, but resulted in decreased NO_x conversion. A prolonged approach to the cyclic steady state was observed during high frequency operation. Moreover, the detrimental effect of CO_2 on NO_x conversion was observed to decrease at higher frequencies. These observations collectively suggest that the generation of reactive intermediate species "$HC_xN_yO_z$", whose lifetime on the catalyst surface exceeds the cycle duration and which reacts with NO_x to produce N_2, are required to achieve conversion enhancement during high frequency operation. The degree of mixing of the rich and lean feeds upstream of the catalyst was found to be an important reactor design parameter that invites further study.

1. Introduction

Lean burn gasoline and diesel vehicles operate in oxygen excess conditions, which results in increased fuel efficiency. However, oxygen in the exhaust undermines the effectiveness of the conventional three-way catalytic converter in reducing NO_x to N_2. At the same time, NO_x emission limits have become more stringent; the current U.S. Tier 2, Bin 5 emission standards (fully implemented in 2009) for NO_x is 0.05 g/mi [1]; the EU emission standard for NO_x in diesel passenger vehicles is 0.18 g/km [2]. The mandate to reduce diesel engine NO_x emissions has posed a significant challenge in the treatment of NO_x emissions from lean burn vehicles. One of the earliest responses to this challenge was the development of the NO_x storage and reduction (NSR) process by Toyota researchers in the mid 1990s [3,4]. NSR involves deliberate lean-rich cycling over a multifunctional catalyst to achieve higher NO_x conversion. During the lean phase in which excess oxygen is present, NO is oxidized to NO_2 on the precious metal function (e.g. Pt, Rh) and subsequently stored on the storage function (e.g. BaO, CeO_2) in the form of nitrite and nitrate species. During the oxygen deficient rich phase, a reductant (e.g. H_2, CO, hydrocarbons) is introduced into the exhaust, which leads to the release of stored NO_x species and their subsequent reduction to N_2 on the precious metal sites [4,5].

Numerous studies have been conducted with the goal of identifying the catalytic properties and operating conditions that achieve high NO_x conversion. Reviews of NSR catalysts were provided earlier by Epling et al. [6], and more recently by Roy and Baiker [7] and Harold [8]. Exhaust temperatures below 200 °C pose a particular challenge because of a combination of inadequate NO oxidation and stored NO_x regeneration activity of the NSR catalyst. On the other hand, at high temperatures (>400 °C) the thermodynamic stability of stored nitrates decreases so that the high NO_x reduction rate cannot be fully exploited. As a result of these limiting behaviors, a maximum in the cycle-averaged NO_x conversion is achieved at intermediate temperatures (300–350 °C) [6,9–11]. Another challenge is the unwanted release of NO/NO_2 at the initial stages of the regeneration, the so-called "NO_x puff". This release is due to the shift in the gas phase composition which in turn

---

* Corresponding author.
E-mail address: mharold@uh.edu (M.P. Harold).

0920-5861/$ – see front matter © 2014 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.cattod.2014.01.026

effects the decomposition of nitrites/nitrates, further exasperated by exotherms associated with rich mixtures containing O_2. When the amount of reductant is insufficient to react with the released NO_x, a spike in the effluent NO_x is observed [6,12]. The puff can be mitigated by careful manipulation of the cycle timing and regeneration conditions [13]. Complicating the situation is the production of undesired NO_x reduction byproducts such as N_2O and NH_3, which are typically more problematic at lower temperatures [10,14]. The selectivity of these unwanted byproducts has been explained by a moving front concept by multiple groups [11,15–22].

Process parameters can have a significant effect on LNT performance. These include the cycle timing and feed composition. Intermediate values for total cycle length and rich duty cycle were shown by Kabin et al. [10] to achieve a maximum NO_x conversion, with the optimum values depending on flow conditions. Muncrief et al. [23] determined that short pulses of high concentration achieve a higher NO_x conversion than longer pulses of reduced concentration. The dynamic storage capacity, which represents the amount of NO_x stored prior to NO_x breakthrough, was also reported to achieve a maximum around 350 °C. Since H_2O and CO_2 are in large excess in vehicle exhaust, understanding their effects on LNT performance can provide additional insight into the application of storage and reduction processes. Epling et al. [24] reported that the presence of CO_2 was found to have a detrimental effect on both the trapping efficiency of the catalyst and the induction time before NO_x slip occurs during storage. This is attributed to the formation of more stable Ba carbonate species, on which NO_x storage is more difficult. The presence of H_2O also reduces the trapping efficiency of the catalyst by eliminating NO_x adsorption on γ-Al_2O_3 sites. The effect of both CO_2 and H_2O in the feed stream is similar to CO_2 alone, and it has been proposed that carbonate species are able to displace hydroxide species.

More recent studies have led to an even more detailed understanding of NSR. Spatially-resolved measurements confirmed earlier work that NH_3 is an important intermediate which is formed upstream and consumed downstream [15,17,19,25,26]. Through the use of a fast switching apparatus and isotopically labeled nitric oxide (^{15}NO), Breen et al. [27] observed the presence of two N_2 peaks during NSR cycling experiments. The first N_2 peak was due to the reduction of stored NO_x, as the feed was switched from the lean phase to the rich phase. The second N_2 peak occurred as the feed was switched back from rich to lean conditions. One explanation proposed by the authors for the second N_2 peak is the reaction between gas phase NO_x and NH_3 formed from the hydrolysis of isocyanates on the catalyst surface. Dasari and Harold [28] recently shed new insight on the roles of the competing water gas shift and isocyanate pathways during NSR.

Expanding upon the discovery of this second N_2 peak, researchers at the Toyota Motor Corporation have developed a high performance deNO_x system, given the name "Diesel NO_x aftertreatment by Adsorbed Intermediate Reductants" ("Di-Air") [29]. The Di-Air method utilizes rapid periodic injection of hydrocarbons (HCs) to achieve enhanced performance over traditional NSR. Toyota researchers reported higher NO_x conversions over a wider range of space velocities, temperatures and sulfur exposures than conventional NSR cycling. The performance enhancement was attributed to intermediates generated from the reaction between adsorbed NO_x and partially oxidized hydrocarbons produced in the front portion of the catalyst during rapid periodic injection. Through in situ DRIFTS (diffuse reflectance infrared Fourier transform spectroscopy) measurements, the authors assigned a peak to the intermediate surface species containing both N and C. Inoue et al. [30] further investigated the thermal stability of the intermediate species using temperature programmed desorption. The intermediates produced from C_3H_6 (represented by R–NCO and R–CN) were found to remain on the catalyst up to 600 °C. It was concluded that the intermediates have a strong affinity for the NSR catalyst which enables them to remain on the catalyst surface at higher temperatures, thereby providing an alternative pathway for stored NO_x reduction to N_2.

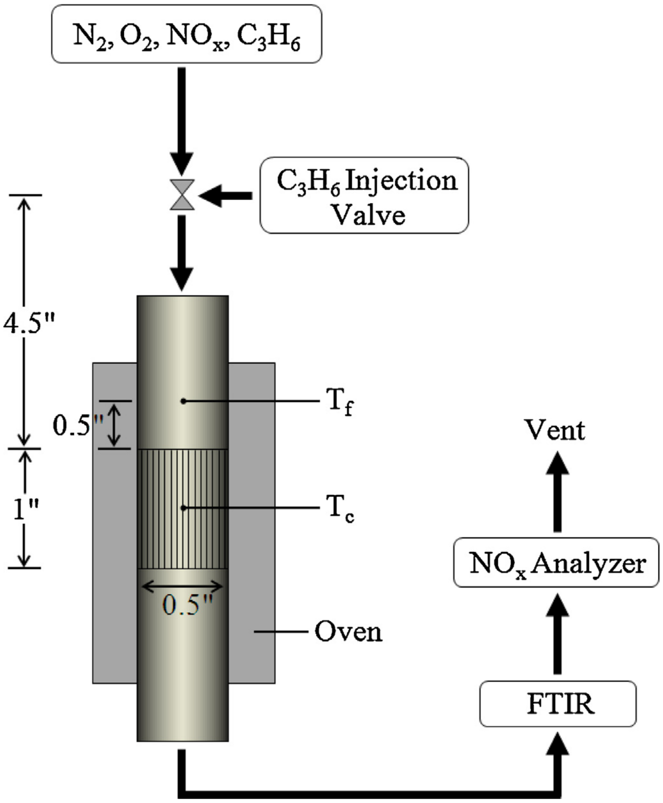

Fig. 1. Schematic of the reactor and analyzer system.

The current study examines the effect of rapid periodic injection of C_3H_6 on the performance of a model NSR catalyst through the systematic variation of several operating parameters. The objective is to gain a better understanding of the effects of injection frequency, to determine the generality of these effects, and to build a phenomenological mechanism with propylene as the reductant over a Pt/Rh/BaO/CeO_2/Al_2O_3 catalyst. Both transient concentrations and cycle-averaged performance metrics (conversion, selectivity, and catalyst temperature) are measured as a function of the reductant injection frequency. The temperature range over which high conversion of NO_x and propylene are obtained is determined, as are the effects of C_3H_6 feed composition during the rich phase, as well as the lean phase duration (length). A proposed mechanistic picture is interpreted by examining the inhibitory effect of CO_2 and comparing propylene and hydrogen injection over a range of frequencies.

2. Experimental description

A schematic of the experimental apparatus is shown in Fig. 1. The monolith catalysts used in this study were provided by BASF (Iselin, NJ). The catalysts contain Pt/Rh/BaO/CeO_2/Al_2O_3, with specifications of 80 g Pt/ft^3 monolith, 10 g Rh/ft^3 monolith, 15 wt.% Ba (in wash coat), and 17 wt.% Ce on a γ-alumina support. Small cylindrical catalyst samples (D = 0.5 in, L = 1 in) were cut from the larger cylindrical core using a drill press equipped with a dry diamond drill bit. The catalyst was wrapped with ceramic paper to prevent gas bypass and placed in a quartz tube reactor heated by a tube furnace.