

Intra-channel evolution of carbon monoxide and its implication on the regeneration of a monolithic Pt/K/Al₂O₃ NO_x storage-reduction catalyst

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Abstract

Understanding how a reductant evolves and is utilized during regeneration of NO_x storage-reduction catalyst can lead to predictive kinetic models, improved catalysts and energy-efficient engine-catalyst systems. We performed practically relevant NO_x storage/regeneration cycling (56 s/4 s) experiments over a monolithic Pt/K/Al₂O₃ catalyst in a bench-flow reactor and resolved multiple transient reactions and exotherms. Carbon monoxide was the reductant and intra-channel speciation and temperature measurements were instrumental in resolving CO chemistry. Gas-phase O₂ reacted with CO very fast over the entire regeneration time, and was depleted at the catalyst front. The resulting exotherm was significant and dissipated slowly over time raising the subsequent storage temperature considerably. NO_x release/reduction by CO was also vigorous and primary NO_x removal occurred at early regeneration times. The NO_x-attributable exotherm was smaller than that of the O₂-CO reaction, but extended deeper into the front portion of catalyst due to axially distributed NO_x storage. Secondary NO_x release/reduction occurred after the primary and produced NH₃ as the main product. Hydrogen appeared when and where both the O₂ consumption and major NO_x release/reduction were near complete. We proposed that H₂ produced via water-gas shift (WGS) reaction had little impact on O₂ depletion and primary NO_x release/reduction under the conditions studied. Further study is necessary to assess the impact of WGS reaction on secondary NO_x release/reduction.

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1. Introduction

As planned regulations will mandate drastic reduction in NO_x emissions from diesel engines [1], considerable effort is being made to develop and implement cleaner diesel technology. Among multiple technical options being explored is NO_x storage-reduction (NSR) catalysts which have shown potential in meeting future NO_x emission standards [2]. Also known as lean NO_x traps (LNTs) or NO_x adsorber catalysts (NACs), NSR catalysts combine NO_x storage components (in general, alkali or alkaline-earth metal) with supported precious metals (similar to 3-way catalysts) [3–7]. Under typical lean

exhaust conditions, NSR catalysts reversibly store NO_x as nitrates or nitrites (storage step). As the extent of NO_x storage reaches a pre-determined level, the exhaust is made rich to release and reduce the stored NO_x (regeneration step). Lean/rich cycling circumvents the issue of poor NO_x removal efficiency of conventional 3-way catalyst under lean environment. Moreover, HC-SCR have been showing unsatisfactory performance despite much effort to improve their activity, selectivity, and stability [8]. However, periodic regeneration of NSR catalyst by creating rich environment results in extra fuel consumption and requires sophisticated engine-catalyst system control. Successful implementation of NSR technology, with minimum fuel penalty, will require improved catalyst design, optimized system configuration and control strategy, and predictive kinetic model. To this end, more complete understanding of NSR catalysis is necessary, particularly, about

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regeneration step, which is much less understood than storage step.

For example, how a reductant evolves and is utilized inside a catalyst channel during regeneration is important missing information in current open literature [3]. In this respect, carbon monoxide is an interesting species to study, as it is a dominant reductant produced from certain engine-managed regeneration strategies [9]. Under practical conditions, CO reductant is expected to interact with various exhaust species in addition to NO_x, such as residual gas-phase O₂ and H₂O. Therefore, reactions such as CO + NO_x, CO + O₂, CO + H₂O can occur simultaneously and compete. Inherently transient (i.e., fast cycling) and integral (i.e., propagation of the breakthrough front over catalyst) nature of NSR catalyst operation makes its evaluation challenging especially under practically relevant conditions (fast cycling, monolith, high reductant level, high reaction exotherms). Analytical tools with high temporal and spatial resolution are necessary to acquire more detailed kinetic and mechanistic details of NSR catalysis.

In this study, our goal was to resolve multiple reactions and associated exotherms occurring during fast lean/rich cycling experiments over Pt/K/Al₂O₃ catalyst with CO reductant and get improved understanding of regeneration step. Well-controlled bench experiments were performed and special emphasis was put on intra-channel speciation and temperature measurements by deploying spatially-resolved capillary-inlet mass spectrometer (SpaciMS) and phosphor thermography (PhosT), respectively. Concerted use of SpaciMS and PhosT made it possible to study dynamic chemistry along the monolith channels as it developed over space and time. Our focus was not on evaluating the effect of different reaction parameters (e.g., temperature, concentration, gas composition), but on capturing important reaction features (e.g., nature and sequence of reactions) based on our transient observations under a chosen set of conditions.

2. Experimental

A Pt/K/Al₂O₃/cordierite catalyst was prepared and provided by a catalyst manufacturer (EmeraChem). The substrate was 31 cells per cm² Rauschert cordierite monolith. The monolith was dipped into an aqueous slurry containing a high surface area (160 m² g⁻¹) alumina. Excess solution was drained, the sample was allowed to dry, and then was calcined for 1 h in ambient air. The platinum and potassium components were then added by incipient wetness methods. First, a proprietary platinum salt dissolved in water was impregnated onto a coated monolith and calcined in ambient air. Potassium was subsequently deposited by using aqueous carbonate solution and the sample was dried in ambient air. For the bench reactor study, a sample was removed from the monolith block by boring out a 2.54 cm-diameter and 7.62 cm-long core.

The core was wrapped in fiber glass insulation tape and inserted into a quartz reactor tube which was enclosed in an electric furnace. The tape eliminates gas bypass around the sample during the experiments. The reactor tube was positioned horizontally in a furnace such that the catalyst core was located

Table 1

Details of the standard NO_x storage/regeneration cycling experiment

	Storage (lean)	Regeneration (rich)
Duration	56 s	4 s
Space velocity	30000 h ⁻¹	30000 h ⁻¹
NO	250 ppm	0 ppm
CO	0%	4%
O ₂	8%	1%
H ₂ O	5%	5%
N ₂	Balance	Balance

towards the outlet end of the reactor tube. All reactant gas lines were preheated to enhance the catalyst temperature uniformity. Gas mixtures were metered using mass-flow controllers, with H₂O introduced into a heated zone using a high-precision liquid metering pump. A rapid switching valve system was used to alternate between the lean and rich gas mixtures (with mixed flows already fully established) so that the lean/rich/lean transitions in these experiments were almost instantaneous. Tables 1–3 list the typical conditions of cycling experiments. The reactor was equipped with a bypass line so that both the entering and exiting gases could be analyzed by MKS FT-IR analyzer.

Intra-channel gas phase speciation was performed by using SpaciMS developed in the Fuels, Engines, and Emissions Research Center at Oak Ridge National Laboratory [9–11]. The mass spectrometer, employed in this study had a magnetic-sector mass filter, which allows quantitative measurement of H₂ [12] as well as H₂O, total NO_x, O₂, and CO₂. A minimally invasive capillary inlet system (sampling rate = ca. 10 μL/min, probe size = ca. 185 μm) was employed to transport time-varying species pools to the mass spectrometer for analysis. Capillary probes were introduced from the reactor inlet and positioned at different catalyst locations.

Table 2

Details of the cycling experiment without NO

	Storage (lean)	Regeneration (rich)
Duration	56 s	4 s
Space velocity	30000 h ⁻¹	30000 h ⁻¹
NO	0 ppm	0 ppm
CO	0%	4%
O ₂	1%	1%
H ₂ O	5%	5%
N ₂	Balance	Balance

Table 3

Details of the cycling experiment without NO and O₂

	Storage (lean)	Regeneration (rich)
Duration	56 s	4 s
Space velocity	30000 h ⁻¹	30000 h ⁻¹
NO	0 ppm	0 ppm
CO	0%	4%
O ₂	0%	0%
H ₂ O	5%	5%
N ₂	Balance	Balance

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