FAST CYCLING STORAGE AND REDUCTION OF NO: EXPERIMENTS AND MODELING

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Abstract

Experiments and modeling of NOx storage and reduction provides insight into the effect of cycling frequency on the control of emissions from diesel vehicles. Experiments reveal notable non-isothermal NOx conversion enhancement at high cycling frequency when using propene as the reductant while a negative trend is observed with propane. Modeling shows an interplay between generation of surface intermediates and N_2 selectivity as a function of the frequency and suggests a change in mechanism.

Keywords: CO, Propylene, Oxidation, NOx Reduction, Periodic, Ignition

Introduction

Current technologies to reduce NOx emission from diesel and lean burn vehicles are selective catalytic reduction (SCR) and NOx storage and reduction (NSR). NSR is more practical for light-duty passenger cars because SCR is cost prohibitive. NSR involves cyclic operation over a lean NOx trap (LNT) catalyst, which stores NOx under lean feed, followed by regeneration by a short rich feed purge containing a mix of CO, H_2 and hydrocarbons (HC). At low regeneration temperature NSR suffers from inefficient utilization of some reductants (CO, HCs) and undesired byproduct formation (N_2O, NH_3). At high temperature its performance is poor due to decreased NOx storage capacity. Toyota reported enhanced performance with the Di-Air ("Diesel NOx after-treatment by Adsorbed Intermediate Reductants) system. Di-Air is essentially NSR conducted at much higher lean-rich cycling frequency with significantly enhanced NOx conversion achieved at temperatures exceeding 400 ^oC (Bisaiji et al., 2012). Our recent findings support Toyota's claim of a new mechanism for selective NOx reduction involving selective conversion of adsorbed intermediates (Perng et al., 2014; Zheng et al., 2014, 2015). We have found that the system exhibits notable non-isothermal behavior that contributes to the conversion enhancement. We also observed conversion enhancement at low feed temperatures, conditions for which conventional NSR is ineffective. To date, there have been few reports of the effect of hydrocarbon reductant type or of modeling efforts to corroborate fast cycling experiments. The objective of this study is to develop a comprehensive model that captures the main trends observed during fast cycling NSR using model olefins and alkanes.

Experimental

Monolithic LNT catalysts provided by BASF (Iselin, NJ) contain $Pt/Rh/BaO/CeO_2/Al_2O_3$ with a washcoat loading of 4.6 g/in^3 and PGM loadings between of 90 and 120 g/ft^3 monolith. Small cylindrical catalyst samples (~55 channels, D = 0.42 in, L = 1 in) were drilled out of a large brick. A solenoid-actuated four-way valve generated the high-frequency HC pulsing via fast switching between lean and rich feed. Hydrogen, propylene, propane, and propene/propane mixtures were injected at different frequencies and concentrations into a feed containing NO in 5-10% O_2, 5% CO_2 and 3.5% H_2O. The space velocity was ~75k h^{-1}. Three different cycle timing, 60s lean/10 s rich, 30s lean/5s rich and 6s lean/1s rich, were used corresponding to conventional, medium-frequency, high-frequency NSR operation, respectively. Diffuse reflectance

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infrared Fourier transform spectroscopy (DRIFTS) was used on catalyst powders to identify surface species.

Results and Discussion

Experiments for a range of feeds and cycle timing reveal interesting dynamic features. Figure 1 shows the cycle-averaged NOx conversion for three cycle times (70, 35, 7 s) and fixed reductant duty fraction (14%). The data reveal that propene results in notable conversion enhancement for shorter cycle times, while propane leads to negative results. Thus the reactivity of the reductant plays an important role in fast cycling NSR. The enhancement using propene is more apparent if the cycle-averaged monolith temperature is the abscissa (Fig. 2). The addition of a top layer of a SCR catalyst (Cu-SAPO-34) has further beneficial impact at low temperatures.

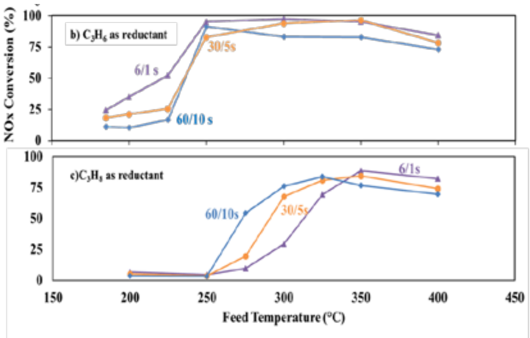

Figure 1. Comparison of cycle-averaged NOx reduction using H_2, C_3H_6, and C_3H_8 at three different cycle times (70, 35, and 7 s).

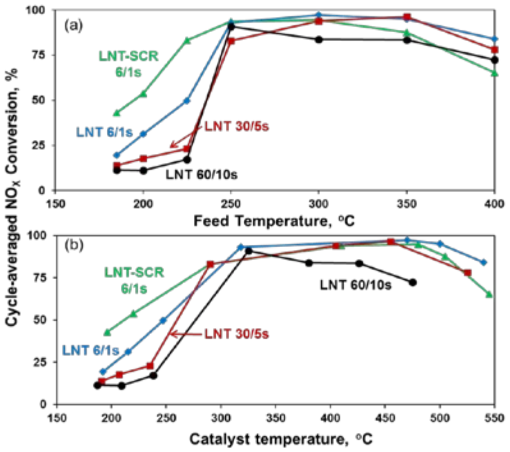

Figure 2. Cycle-averaged NOx reduction as a function of feed (a) and catalyst temperature (b)

DRIFTS measurements of model LNT catalysts provide evidence for an array of intermediates, including isocyanates, aldehydes, oximes, etc. The measurement of existence of isocyanic acid (HNCO) suggests an isocyanate route to N_2:

$$HNCO + 0.75\ O_2 \rightarrow 0.5N_2 + 0.5H_2O + CO_2$$

or related reactions. The oxidation may be enhanced by ceria, possibly through the spillover of oxygen to the precious metal crystallites. The complex set of surface catalyzed reactions generate organic oxygenates and nitrogenates which may react with NO, selectively producing N_2 and a lesser amount of byproduct N_2O.

Model Development

A 1+1 D monolith reactor model including the relevant transport processes was combined with a NSR kinetic model, which combined elements of models from Shakya et al. (2014) and Kota et al. (2013). A key feature of the kinetics is the generation of an olefinic surface isocyanate from propylene oxidation by O_2 and NO. Initial model results reveal an interesting interplay between the generation of the surface species and the N_2 selectivity as a function of the cycle frequency. A key feature of this mechanism is the cycle frequency: If the propylene is injected at a sufficiently high frequency, the desired HC-based NOx reduction may occur before the desorption of these intermediates, without the accumulation of surface nitrites and nitrates, and the production of deep reduction product NH_3. These and other simulation results provide insight into the complex fast cycling NOx storage and reduction.

Conclusions

This study advances the understanding of NOx storage and reduction by LNT conducted at high frequency. The results reveal an intriguing conversion enhancement that is a consequence of a non-isothermal and kinetic reaction pathway. At a sufficiently high frequency of injected propylene the desired HC-based NOx reduction occurs before the desorption of a reactive surface intermediate.

Acknowledgments

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