Micro-kinetic modeling of Lean NOx Trap regeneration chemistry

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Introduction

Control of NOx emissions from diesel or lean burn gasoline engines is a considerable technical barrier that must be overcome if the fuel efficiency advantages of these engines are to be fully realized. Lean NOx traps (LNTs) are one technology under consideration for lean NOx control. LNTs trap NOx in the form of nitrites and nitrates on the catalyst surface during normal lean operation. Periodic brief rich excursions are used to release the stored NOx and catalytically reduce it. The desired reduction product is N_2, but it is also possible to form N_2O and NH_3. Since these byproducts are pollutants, it is usually necessary to minimize their formation. However, in some instances (such as hybrid LNT/SCR systems), formation of NH_3 is desired. Because generating rich conditions in a lean burn engine involves consuming excess fuel, it is important to utilize the reductants as efficiently as possible. The goal of this work is to develop a detailed mechanism of the reactions taking place during LNT regeneration to enable optimization of the catalyst effluent concentrations and minimization of the associated fuel penalty.
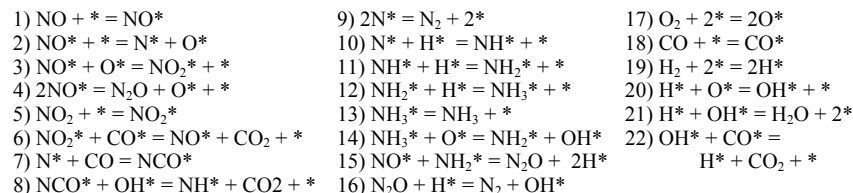
Materials and Methods

The experimental apparatus, procedure, and results are described in detail elsewhere [1]. Briefly, the measurements were made with a monolith core sample (22mm OD, 12mm length) from a commercial NOx trap supplied by Umicore Autocat USA Inc. The washcoat contained γ-Al_2O_3, BaO and ZrO_2-Ce_2O_3, along with Pt, Pd, and Rh (82:26:6) at a total PM loading of 3990 g/m^3. Reaction rate measurements were performed on a flow reactor during 5°C/min. temperature ramps between 100°C and 500°C. The inlet gas typically included 5% CO_2, 5% H_2O, 500ppm NO or NO_2, and varying concentrations (500 to 5000ppm) of H_2 or CO. Experiments were also performed with NH_3 or N_2O in the feedgas to identify possible secondary reactions. The total flow rate was adjusted to give a GHSV of 100,000 h^{-1}. Catalyst outlet concentrations were tracked with chemiluminescent NOx analyzers and a Fourier Transform Infrared (FTIR) spectrometer. An in-situ Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) setup was also used to identify surface intermediates.

Based on these experiments, a set of elementary reactions likely to occur during LNT regeneration was compiled. Using these reactions, the steady-state plug flow reactor code PLUG (part of the Chemkin package) was used to compute steady state exit concentrations at intervals of 50°C between 100°C and 500°C for each set of experimental inlet conditions. The rates of the reactions were adjusted to match the predictions with corresponding experimental data through an iterative optimization process. By performing sensitivity analyses and eliminating reactions that did not have a major impact on the overall agreement between the predictions and experimental data, a likely minimal set of reactions required to model the lean NOx trap under rich conditions was obtained. Thermodynamic consistency of the overall mechanism was ensured by imposing algebraic constraints on the kinetic parameters during the calibration process. A more detailed description of the modeling approach and results from a previous version of the mechanism can be found in [2].

Results and Discussion

The mechanism resulting from this process is shown below. It is based on two key simplifying assumptions: NOx storage sites do not affect the reduction kinetics, and there is only one type of surface reduction site (the Umicore LNT contained three noble metals).

1) $NO + * = NO*$
2) $NO* + * = N* + O*$
3) $NO* + O* = NO_2* + *$
4) $2NO* = N_2O + O* + *$
5) $NO_2 + * = NO_2*$
6) $NO_2* + CO* = NO* + CO_2 + *$
7) $N* + CO = NCO*$
8) $NCO* + OH* = NH* + CO2 + *$
9) $2N* = N_2 + 2*$
10) $N* + H* = NH* + *$
11) $NH* + H* = NH_2* + *$
12) $NH_2* + H* = NH_3* + *$
13) $NH_3* = NH_3 + *$
14) $NH_3* + O* = NH_2* + OH*$
15) $NO* + NH_2* = N_2O + 2H*$
16) $N_2O + H* = N_2 + OH*$
17) $O_2 + 2* = 2O*$
18) $CO + * = CO*$
19) $H_2 + 2* = 2H*$
20) $H* + O* = OH* + *$
21) $H* + OH* = H_2O + 2*$
22) $OH* + CO* = H* + CO_2 + *$

In spite of these simplifications, the mechanism generates reasonably good fits to the experimental data for all cases (see figure 1 for a sample case). More importantly, the mechanism captures key trends for reduction product speciation: formation of N_2O at low temperatures, high selectivity to N_2 for stoichiometric feeds, high selectivity to NH_3 with excess reductant, and secondary oxidation of NH_3 by both O_2 and NOx to form N_2O.
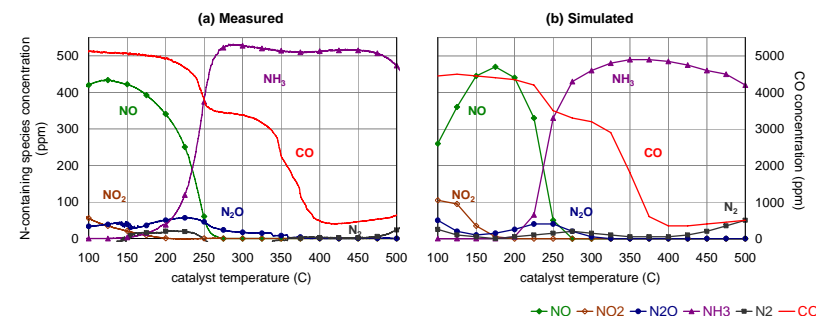
Figure 1. Product speciation as a function of temperature over the Umicore LNT catalyst for 500ppm NO_2/5000ppm CO/5% H_2O/5% CO_2/balance N_2.

Figure 1 highlights the high degree of selectivity to NH_3 in the presence of excess reductant. It also exhibits a low temperature drop in CO concentration which coincides with the onset of NH_3 formation. This feature required the inclusion of a second pathway for NH_3 formation from CO besides water gas shift. DRIFTS experiments showed NCO peaks that diminished in the presence of H_2O, motivating the addition of the isocyanate hydrolysis reaction (eqn. 8).

Significance

This mechanism will enable more accurate modeling of LNT operation and optimization of both product speciation and reductant utilization during regeneration.

References

1. Pihl, J.A., Parks, J.E., and Daw, C.S., *SAE paper* 2006-01-3441.
2. Larson, R., Chakravarthy, V.K., Pihl, J.A., and Daw, C.S., *SAE paper* 2006-01-3446.