DOE Award No. DE-EE0000205
PI: Michael P. Harold, University of Houston
Co-I: Mark Crocker, University of Kentucky
Project Title: Development of Optimal Catalyst Designs and Operating Strategies for Lean NOx Reduction in Coupled LNT-SCR Systems
Final Report Period: October 1, 2009 – September 30, 2013 (A no-cost extension was approved during the period of Oct.1, 2012 through Sept. 30, 2013)

Project Team Participants

University of Houston:
Vemuri Balakotaiah, Michael P. Harold (PI), Dan Luss

University of Kentucky:
Mark Crocker (Co-I)

Oak Ridge National Laboratory:
Jae-Soon Choi

Ford Motor Company:
Mark Dearth, Bob McCabe, Joe Theis

Executive Summary

Oxides of nitrogen in the form of nitric oxide (NO) and nitrogen dioxide (NO_2) commonly referred to as NOx, is one of the two chemical precursors that lead to ground-level ozone, a ubiquitous air pollutant in urban areas. A major source of NOx is generated by equipment and vehicles powered by diesel engines, which have a combustion exhaust that contains NOx in the presence of excess O_2. Catalytic abatement measures that are effective for gasoline-fueled engines such as the precious metal containing three-way catalytic converter (TWC) cannot be used to treat O_2-laden exhaust containing NOx. Two catalytic technologies that have emerged as effective for NOx abatement are NOx storage and reduction (NSR) and selective catalytic reduction (SCR). NSR is similar to TWC but requires much larger quantities of expensive precious metals and sophisticated periodic switching operation, while SCR requires an on-board source of ammonia which serves as the chemical reductant of the NOx. The fact that NSR produces ammonia as a byproduct while SCR requires ammonia to work has led to interest in combining the two together to avoid the need for the cumbersome ammonia generation system. In this project a comprehensive study was carried out of the fundamental aspects and application feasibility of combined NSR/SCR. The project team, which included university, industry, and national lab researchers, investigated the kinetics and mechanistic features of the underlying chemistry in the lean NOx trap (LNT) wherein NSR was carried out, with particular focus on identifying the operating conditions such as temperature and catalytic properties which lead to the production of ammonia in the LNT. The performance features of SCR on both model and commercial catalysts focused on the synergy between the LNT and SCR converters in terms of

utilizing the upstream-generated ammonia and alternative reductants such as propylene, representing the hydrocarbon component of diesel exhaust. First-principle models of the LNT and SCR converters, which utilized the mechanistic-based kinetics and realistic treatments of the flow and transport processes, in combination with bench-scale reactor experiments helped to identify the best designs for combining the NSR and SCR catalysts over a range of operating conditions encountered in practice. This included catalysts having multiple zones and layers and additives with the focus on determining the minimal precious metal component needed to meet emission abatement targets over a wide range of operating conditions. The findings from this study provide diesel vehicle and catalyst companies valuable information to develop more cost effective diesel emissions catalysts which helps to expand the use of more fuel efficient diesel power. The fundamental modeling and experimental tools and findings from this project can be applied to catalyst technologies used in the energy and chemical industries. Finally, the project also led to training of several doctoral students who were placed in research jobs in industry and academia.

Overall Project Goal

The overarching goal of this project was to identify the NOx reduction mechanisms operative in LNT (Lean NOx Traps) and *in situ* SCR (Selective Catalytic Reduction) catalysts, and to use this knowledge to design optimized LNT-SCR systems in terms of catalyst architecture and operating strategies. Central to the proposed research was the development of microkinetic descriptions of the catalytic chemistry incorporated into monolith reactor models. Mechanistic, kinetic and performance data from bench-scale, DRIFTS, and TAP reactors were utilized to build the microkinetic models. Using vehicle tests and bench-scale reactor tests, the optimal operating strategy for LNT-SCR systems was validated with respect to NOx conversion level and reductant consumption.

Comparison of Actual Accomplishments with Goals/Objectives of the Project

The project was divided into three phases which covered roughly 1-1.5 years of the four-year project. The verbatim objectives of the project are as follows:

<u>Phase 1 Objectives</u>:

- Elucidate the mechanism of the non-NH_3 pathway for NO_x reduction by means of bench-scale reactor, *in situ* DRIFTS reactor, and TAP reactor studies
- Map LNT selectivity to NH_3 as a function of catalyst composition (ceria content and type) and relevant process parameters (NO_x loading, purge duration, purge lambda and space velocity)
- Develop a microkinetic LNT model that takes into account the catalyst composition (storage component such as ceria and barium loading as well as precious metal such as Pt loading/dispersion) and H_2, CO, and C_3H_6 reductants
- Develop low-dimensional models for the LNT and the coupled LNT-SCR unit for different catalyst architectures incorporating microkinetics

<u>Phase 2 Objectives</u>:

- Establish the chemical basis for the dependence of LNT NH_3 selectivity on ceria content

- Determine optimum ceria type and content in model LNT catalysts to achieve best net NO_x conversion in serial LNT-SCR catalysts
- Establish the optimal operating strategy of serial and double layer catalyst systems with respect to NO_x conversion level and fuel penalty
- Determine the level of PGM reduction possible in the serial LNT-SCR catalyst system while providing equivalent performance to the corresponding LNT-only system
- Develop microkinetic SCR model that includes non-NH_3 mechanism
- Carry out experimental optimization study of segmented LNT-SCR catalyst configurations
- Establish sulfur evolution on serial and double layer LNT-SCR systems
- Perform simulations of the LNT and coupled LNT-SCR unit using the low-dimensional models to examine the performance features and to identify optimal periodic operation and how it depends on the axial and transverse distribution of the catalytic components

<u>Phase 3 Objectives</u>:

- Study the surface chemistry and dynamics associated with NH_3 storage and consumption during LNT-SCR lean-rich cycling
- Establish guidelines for limits on rich exposure and maximum temperature during LNT-SCR desulfation
- Quantify the NO_x storage-reduction behavior of aged LNT-SCR systems so as to pin-point the effects of aging on the different catalyst functions
- Complete microkinetic model for the LNT-SCR system
- Carry out modeling study of the LNT-SCR systems for real-time simulation and optimization
- Experimentally verify model predictions of different segmented LNT-SCR reactor configuration
- Use low-dimensional models to identify the optimal catalyst architectures and operating strategies of the overall LNT-SCR unit

The project was successful in conducting most of the tasks. The major activities of the four-year project are listed below with reference to the publications generated from the project. The summaries of all publications from the project are provided following the tasks.

PHASE 1

Task 1.1: Project management and planning

A kick-off meeting was held at the start of the project, involving all the participants, in order to review the technical scope and the project management plan. This meeting established the working logistics of the project to ensure the smooth coordination of activities throughout the duration of the project.

Task 1.2: Reactor study of non-NH_3 NO_x reduction mechanism

Reactor studies were performed to elucidate the mechanism of the non-NH_3 pathway for NO_x reduction previously identified. Studies focused on establishing the roles of the LNT and Cu-zeolite SCR catalysts in the observed catalysis, in addition to certain feed gas components (e.g., hydrocarbons, as well as the residual O_2 level in the rich phase).

<u>See Publications:</u> 11, 30, 34

Task 1.3: DRIFTS study of non-NH_3 NO_x reduction mechanism

The mechanism of the non-NH_3 pathway for NO_x reduction in LNT-SCR systems was studied by means of *in situ* DRIFTS measurements and other experiments.
See Publications: In preparation, 34

Task 1.4: TAP study of NO_x reduction with $H_2/CO/C_3H_6$ on LNT catalyst
TAP experiments were conducted on model monolith LNT formulations. The pulse timing and composition was varied to assess reactant mixing effects.
See Publications: 3, 22

Task 1.5: Kinetics study of NO_x storage and reduction with $H_2/CO/C_3H_6$ on LNT catalyst
Steady-state and transient NO_x storage and reduction experiments were carried out to quantify kinetics of the main reactions on the model LNT catalysts.
See Publications: 1, 3, 4, 9, 13, 16, 18, 22, 31

Sub-task 1.5.1. Steady-state kinetics of reactions on LNT catalysts
Steady-state kinetics experiments involved the following reaction systems: CO + H_2O; NO + CO with and without H_2O; among others. For each reaction system experiments probed a range of temperatures for both differential and integral operation.
See Publications: 13, 16

Sub-task 1.5.2. NO_x storage and NO oxidation on LNT catalysts
Experiments were carried out to quantify the storage of NO on LNT catalysts over a range of temperatures in the presence of O_2, CO_2, and H_2O.
See Publications: 4, 9

Task 1.6: Parametric study of LNT NO_x reduction selectivity
A matrix of experiments were performed using the existing model monolith LNT formulations
See Publications: 5, 6, 7, 9, 16, 18, 20, 21

Task 1.7: Development of microkinetic models
Developed microkinetic and when possible, global kinetic models of NO_x storage and reduction taking into account the catalyst composition and structure.
See Publications: 1, 3, 4, 9, 13, 16, 17, 18, 22, 29, 31, 35

Task 1.8: Development of low-dimensional models that take into account layered and axial distribution of the catalytic components
Monolith reactor models were developed that account for all the relevant transport processes and differing catalyst configurations, with incorporation of either global or microkinetic models.
See Publications: 13, 14, 17, 18

PHASE 2

Task 2.1: Spatiotemporal study of LNT NO_x reduction selectivity
To complement Task 1.6, SpaciMS was carried out to analyze NH_3 formation on the model LNT catalysts.
See Publications: 8, 21

Task 2.2: Isotopic TAP study of NO_x reduction on LNT and SCR catalysts
Selected isotopic TAP experiments were conducted to elucidate selected reaction pathways using ^{15}NO.
See Publications: 22

Task 2.3: Kinetics study of transient NO_x storage and reduction with H_2/CO/C_3H_6 on LNT catalyst
Transient NO_x storage and reduction experiments were carried out to quantify the transient kinetics and elucidate reaction pathways.
See Publications: 4, 16, 22, 29, 31

Task 2.4: Kinetics study of transient NO_x reduction with NH_3 on SCR catalyst
A similar set of experiments will be conducted to quantify the transient kinetics of NO_x reduction on the SCR catalyst.
See Publications: 2, 10, 12, 15, 23, 24

Task 2.5: Examine effect of PGM/ceria loading on LNT-SCR performance
NO_x storage and reduction characteristics of serial catalyst LNT-SCR systems were assessed.
See Publications: 4, 19, 25, 32, 34

Task 2.6: Prepare double layer LNT-SCR catalysts
Based on the insights gained in Tasks 2.1 and 2.2, prototype double layer LNT-SCR catalysts were formulated and prepared.
See Publications:

Task 2.7: Spatiotemporal study of LNT-SCR system performance
SpaciMS was employed to characterize the performance of the two system approaches (serial and double layer), particularly with respect to their transient behavior.
See Publications: 30, in preparation

Task 2.8: Sulfation-desulfation study of LNT-SCR system
The dynamics of LNT-SCR system desulfation was studied on a bench reactor. This task was affected by scope reduction resulting from Ford pulling from the project team.
See Publications: n/a

Task 2.9: Modeling and Simulation Studies
The low-dimensional and microkinetic models developed in Phase 1 were combined to examine the performance of the LNT and coupled LNT-SCR units under various operating conditions.
See Publications: 14, 17, 31, 32

PHASE 3

Task 3.1: Perform in situ DRIFTS study on LNT-SCR catalyst
Using ORNL's DRIFTS reactor, *in situ* DRIFTS measurements were performed on the monolithic LNT-SCR catalyst under simulated cycling conditions.
See Publications: 27

Task 3.2: Age LNT-SCR systems on bench reactor
Catalysts were aged on a synthetic gas bench according to a developed protocol and the aged catalyst tested versus fresh catalysts.
See Publications: 5, 7

Task 3.3: Comparison study of NO_x reduction selectivity for segmented LNT-SCR configurations
An experimental comparison was carried out of several segmented LNT-SCR configurations.
See Publications: 19, 25, 31, 32, 34

Task 3.4: Completion of microkinetic model development for LNT and SCR catalysts
Complete kinetic models were finalized for the LNT and SCR catalysts using a combination of bench-scale reactor, DRIFTS reactor, and TAP reactor data.
See Publications: 22, 27, 28, 29, 31, 35

Task 3.5: Optimization and real-time simulations of LNT-SCR catalyst with reactor model
Numerical simulations with various catalyst architectures (e.g. segmented, layered) were performed in order to identify the optimal catalyst distributions and operating strategies.
See Publications: 14, 32, in preparation

Task 3.6: Identification of optimal segmented LNT-SCR configuration
Bench-scale testing of the segmented and double-layer LNT-SCR system was carried out to identify the best configuration in terms of overall NO_x reduction.
See Publications: In preparation

Task 3.7: Reactor studies on aged LNT-SCR systems
Where possible, NO_x storage-reduction properties of the aged catalysts were evaluated to assess the effects of aging.
See Publications: In preparation

Task 3.8: Physico-chemical analysis of aged LNT-SCR systems
In order to examine the effects of aging on the physico-chemical properties of the catalysts, the aged LNT and SCR samples were characterized using various analytical methods.
See Publications: In preparation

Task 3.9: Vehicle tests on aged LNT-SCR system
Due to Ford pulling out of the project, this task was not completed.
See Publications: Not applicable

Accomplishments

The project accomplished many technical hurdles from the experimental and modeling activities. Below we provide the summaries of each of the peer-reviewed publications to illustrate these accomplishments. Above we link each of the tasks to these accomplishments.

1. Joshi, S., Y. Ren, M.P. Harold, and V. Balakotaiah, “Determination of Kinetics and Controlling Regimes for H_2 Oxidation on Pt/Al_2O_3 Monolithic Catalyst Using High Space Velocity Experiments,” *Applied Catalysis B: Environmental*, **102**, 484–495 (2011).
   Recently developed criteria [S.Y. Joshi, M.P.Harold , V. Balakotaiah, Chemical Engineering Science 65 (2010) 1729-1747] are used to characterize the various controlling regimes (kinetic, pore diffusion and mass transfer controlled) during H_2 oxidation on Pt/Al_2O_3 monolithic catalyst. The hydrogen conversion was measured over a wide range of temperatures and space velocities. Experiments at typical space velocities (10^4-10^5 hr^{-1}) revealed that complete conversion can be achieved at ambient temperature, a result of fast catalytic kinetics. The high activity complicates the analysis of relative importance of reaction, washcoat diffusion and mass transfer. High space velocity operation with accompanying theoretical analysis enabled an efficient determination of the intrinsic catalytic kinetics, quantification of the heat and mass transport coefficients and

determination of the relative importance of reaction, washcoat diffusion and external mass transport processes. Specifically, we investigated the effects of catalyst aging, space velocity and catalyst temperature on the regime transition. The analysis reveals that washcoat diffusion regime is dominant over a wide range of temperatures for the aged catalyst whereas the monolith transitions to a mass transfer controlled regime above 90 ^oC for the high dispersion fresh catalyst. The analysis also reveals that the ageing of the catalyst due to sintering of Pt crystallites not only reduces the pre-exponential factor but also the observed activation energy.

2. Metkar, P., N. Salazar, R. Muncrief, V. Balakotaiah, and M.P. Harold, "Selective Catalytic Reduction of NO with NH_3 on Iron Zeolite Monolithic Catalysts: Steady-State and Transient Kinetics ," *Applied Catalysis B: Environmental*, **104**, 110–126 (2011).
   An experimental study of steady-state and transient selective catalytic reduction (SCR) of NO with NH_3 on both commercial and in-house synthesized Fe-ZSM-5 (MFI type) monolith catalysts is presented. The reaction system was studied in a bench-flow reactor spanning a range of temperature, space velocity and washcoat thickness, affording an assessment of activity and selectivity, reaction pathways, temperature window, mass transport and pore diffusion effects. Experiments included NH_3 uptake and temperature-programmed desorption, steady-state and transient NO and NH_3 oxidation and standard SCR ($NO+NH_3+O_2$) reaction studies. Differential kinetics studies were performed for the standard SCR reaction and NO oxidation reaction systems to determine reaction orders and activation energies. In the temperature range of 200 – 300 ^oC the standard SCR reaction was found to be nearly first-order and half-order with respect to NO and O_2, respectively, but moderately negative-order (-0.3) with respect to NH_3. Agreement in the kinetics for both reaction systems suggests that the oxidation of NO is the rate determining step, in line with recent literature studies. Rate inhibition by ammonia appears to be the result of blockage of NO oxidation reaction sites; a necessary step for the standard SCR reaction. Water is shown to inhibit the oxidation of NO significantly and of NH_3 to a moderate extent, while having only a negligible effect on the standard SCR reaction. A mechanistic-based Langmuir-Hinshelwood kinetic model is proposed in which NH_3 reacts with surface bound NO_2 and nitrous acid via a NH_4NO_2 intermediate. A redox mechanism in which gaseous NO reacts with adsorbed oxygen (Eley Rideal like reaction) cannot be ruled out. In the absence of NH_3 these species serve to inhibit the adsorption of NO and/or O_2 during NO oxidation. Both external mass transfer limitations and washcoat diffusion limitations were ruled out for moderate temperature conditions ($\leq$300 ^oC). However, experiments on monoliths with different washcoat thicknesses conclusively show the appearance of washcoat diffusion limitations at higher temperatures ($\geq$ 350 ^oC).

3. Kumar, A., X. Zheng, M.P. Harold, and V. Balakotaiah, "Microkinetic Modeling of the NO + H_2 System on Pt/Al_2O_3 Catalyst Using Temporal Analysis of Products ," *J. Catalysis*, **279**, 12–26 (2011).
   A systematic experimental and modeling study of the NO + H_2 reaction system on Pt/Al_2O_3 catalyst was carried out using Temporal Analysis of Products (TAP). A microkinetic model was developed that explains the transient product distribution during various experimental TAP protocols. NO pulsing experiments show the inhibiting effect of oxygen poisoning and the kinetic limitations posed by N-O bond scission. The NO-H_2 pump-probe experiments

demonstrate the effect of temperature, H_2/NO ratio (≥ 1), and pulse delay time between consecutive NO and H_2 pulses on N_2, N_2O, and NH_3 selectivity. The simulations reveal the competition between surface N-N recombination and N and/or NO reaction with H to form N_2 and NH_3, respectively. The developed mechanistic – based microkinetic model accounts for all of the experimental data including the aforementioned selectivity versus pulse delay trends.

4. Xu, J., M. Harold, and V. Balakotaiah, "Microkinetic Modeling of NOx Storage on Pt/BaO/Al_2O_3 Catalysts: Pt Loading Effects," *Applied Catalysis B: Environmental,* **104**, 305-315 (2011).
   Platinum plays an important, multi-functional role during NOx storage and reduction (NSR). Understanding and predicting the effect of Pt loading is essential to optimize the lean NOx trap. In this study, a microkinetic model is developed for NOx storage on a series of Pt/BaO/Al_2O_3 catalysts with a range of Pt loadings (0 – 3.7 wt.%). A classification of the Ba sites into two storage site populations, proximal and non-proximal (bulk), is presented. A simple model for estimating the capacities of the two Ba site populations using the Pt loading is used to explain trends in the storage of NO/O_2 and NO_2/O_2. The model integrates existing literature models for NO_2 storage on BaO/Al_2O_3, Pt-catalyzed NO oxidation to NO_2, and spillover chemistry involving NO_2. Where possible, simplifications in the model are made based on sensitivity analyses. Literature estimates of kinetic parameters are adjusted if estimates of spillover rate constants are not sufficient to predict the storage data. The dual-site model comprises proximal storage sites that participate in the spillover chemistry and non-proximal sites that involve NO_2 that is generated by the Pt-catalyzed NO oxidation. The model shows reasonable agreement with the measured storage of NO and NO_2 in O_2 at 340 ^oC for a range of storage times and Pt loading. The model helps to elucidate the storage dynamics and the roles of Pt and should be useful for incorporation into a complete NOx storage and reduction model. Some further refinements to the model are discussed.

5. Wang, J., Y. Ji, U. Graham, C. Spindola Cesar de Oliveira, M. Crocker, "NOx Reduction on Fully Formulated Lean NOx Trap Catalysts Subjected to Simulated Road Aging: Insights from Steady-State Experiments", *Chin. J. Catal.*, **32** (2011) 736.
   Fully formulated lean NO_x trap (LNT) catalysts of the type Pt/Rh/BaO/Al_2O_3 were prepared with and without incorporation of CeO_2-ZrO_2 in the washcoat, and their NO_x reduction behavior was evaluated in steady-state, continuous flow experiments. In the fresh state, CeO_2-ZrO_2 addition was found to exert little effect on NO_x reduction activity using H_2, CO, and NH_3 as the reductants. However, after simulated road aging, NO_x reduction activity was significantly impaired for the CeO_2-ZrO_2-free catalyst, whereas the performance of the CeO_2-ZrO_2-containing analog was affected to only a minor degree. These differences are explained on the basis of high-resolution transmission electron microscopy measurements showing that Pt supported on CeO_2-ZrO_2 remained highly dispersed after aging, whereas Pt supported on BaO/Al_2O_3 underwent significant sintering. In addition, the Pt/CeO_2-ZrO_2 component did not accumulate sulfur during aging, unlike Pt/BaO/Al_2O_3 for which significant sulfation of the Ba phase occurred. For both catalysts, selectivity to NH_3 in NO and NO_2 reduction by H_2 increased after catalyst aging, indicative of a change in the relative surface coverages of N and H ad-atoms on the precious metal sites.

6. Wang, J., Y. Ji, V. Easterling, M. Crocker, M. Dearth, R.W. McCabe, "The effect of regeneration conditions on the selectivity of NO_x reduction in a fully formulated lean NOx trap catalyst", *Catal. Today*, 175 (2011) 83.
   The effect of regeneration conditions on NH_3 formation in a fully formulated Pt–Rh/BaO/Al_2O_3 lean NO_x trap catalyst was investigated. Experiments were performed on a bench flow reactor under simulated diesel exhaust conditions, employing NO_x storage/reduction cycles. Using CO/H_2 as the reductant, the selectivity of NO_x reduction to NH_3 increased with increasing regeneration time, reductant concentration and space velocity, and decreased with increasing amount of stored NO_x and increasing temperature. At a given temperature the effect of these parameters on NH_3 selectivity can be interpreted in terms of the local H_2:NO_x ratio at the precious metal sites and the extent to which NH_3 is consumed in the reductant front as it propagates through the catalyst. However, selectivity to NH_3 increased with increasing temperature (>300 °C) during rich purging using C_3H_6 as the reducing agent. It was shown that NH_3 selectivity was governed by the steam reforming activity of the catalyst, selectivity to NH_3 increasing with increasing H_2 generation. Experiments using a second catalyst to which ceria had been added as an OSC material confirmed these trends, although the presence of the ceria resulted in lower selectivity to NH_3 when using H_2 and/or CO as the reductant. After aging, the catalysts displayed increased selectivity to NH_3; this is attributed in part to lengthening of the NO_x storage-reduction zone, as demonstrated by SpaciMS data, and decreased OSC, resulting in decreased NH_3 consumption by NO_x and O_2 downstream of the reductant front.

7. Ji, Y., V. Easterling, U. Graham, C. Fisk, M. Crocker, J,-S. Choi, "Effect of aging on the NO_x storage and reduction characteristics of fully formulated lean NO_x trap catalysts", *Appl. Catal. B* 103 (2011) 413.
   In order to elucidate the effect of washcoat composition on lean NO_x trap (LNT) aging characteristics, fully formulated monolithic LNT catalysts containing varying amounts of Pt, Rh and BaO were subjected to accelerated aging on a bench reactor. Subsequent catalyst evaluation revealed that in all cases aging resulted in deterioration of the NO_x conversion as a consequence of impaired NO_x storage and NO_x reduction functions, while increased selectivity to NH_3 was observed in the temperature range 250–450 °C. Elemental analysis, H_2 chemisorption and TEM data revealed two main changes which account for the degradation in LNT performance. First, residual sulfur in the catalysts, associated with the Ba phase, decreased catalyst NO_x storage capacity. Second, sintering of the precious metals in the washcoat occurred, resulting in decreased contact between the Pt and Ba, and hence in less efficient NO_x spillover from Pt to Ba during NO_x adsorption, as well as decreased rates of reductant spillover from Pt to Ba and reverse NO_x spillover during catalyst regeneration. For the aged catalysts, halving the Pt loading from 100 to 50 g/ft^3 was found to result in a significant decrease in overall NO_x conversion, while for catalysts with the same 100 g/ft^3 Pt loading, increasing the relative amount of Pt on the NO_x storage components (BaO and La-stabilized CeO_2), as opposed to an Al_2O_3 support material (where it was co-located with Rh), was found to be beneficial. The effect of Rh loading on aged catalyst performance was found to be marginal within the range studied (10–20 g/ft^3), as was the effect of BaO loading in the range 30–45 g/L.

8. Liu, Y., M.P. Harold, and D. Luss, "Spatiotemporal Features of Pt/CeO_2/Al_2O_3 Catalysts

During Lean/Rich Cycling," *Applied Catalysis A, General*, **397**, 35-45 (2011).
Infrared measurements reveal that cyclic shifts between lean and rich (H_2 and/or CO) feeds to a $Pt/CeO_2/Al_2O_3$ monolith catalyst generate complex, spatio-temporal temperature features. A sharp temperature rise occurs in the upstream of the monolith shortly after the cyclic introduction of either H_2/CO to a pre-oxidized catalyst or O_2 to a pre-reduced catalyst. This initial upstream temperature rise following the reduction of oxygen stored on a pre-oxidized catalyst is higher than following the oxidation of either H_2 or CO (or their mixture) stored on the monolith. The upstream hot zone temperature decreases with time without forming a downstream moving temperature front. The intricate transient temperature gradients are caused by a competition between the chemical and transport rate process. However, the effluent concentrations do not reflect these complex interactions. Only about 20% of the total oxygen trapped during the pre-oxidation with a 5% O_2/N_2 mixture at 350 ^oC is strongly bound or chemisorbed. Most of the oxygen that reacts at high temperature is loosely-bound. The introduction of a nitrogen sweep flow between the lean and rich feeds removes a significant amount of the loosely held oxygen, leading to a much more uniform reduction. Inadequate resolution of the spatio-temporal phenomena may lead to a misinterpretation of the apparent kinetics. The spatial features of the thermal fronts of the two reductants (CO or H_2) are similar. The amplitude of the hot spot of the two reactants differs due to differences in the temperature dependencies of their oxidation rates. The transient oxidation of CO/H_2 mixtures reveal H_2 enhanced CO oxidation likely due to a kinetic interaction seen in previous steady-state studies.

9. Ren, Y., and M.P. Harold, "NOx Storage and Reduction with H_2 on $Pt/Rh/BaO/CeO_2$: Effects of Rh and CeO_2 in the Absence and Presence of CO_2 and H_2O," *ACS Catalysis*, 1, 969-988 (2011).
The storage and reduction features of a family of $Pt/Rh/BaO/CeO_2/Al_2O_3$ washcoated monolith catalysts are compared in terms of NOx conversion and product selectivity using H_2 as the reductant. The catalyst composition, monolith temperature, regeneration time, and presence of H_2O and CO_2 in the feed were systematically varied to identify trends and to elucidate effects. In addition to cycling, experiments involving the reduction of a fixed amount of pre-stored NOx help to isolate differences in the regeneration features of the catalysts. The addition of both CeO_2 and Rh to Pt/BaO increases the cycle-averaged NOx conversion and selectivity to N_2. But oxygen storage on the ceria expectedly leads to the consumption of additional reductant during the regeneration. CeO_2 is shown to be an inferior NOx storage component, but as a supplement to BaO, CeO_2 provides the role of promoting the oxidation of NH_3 to N_2. The same stored oxygen is the likely cause for the enhanced NH_3 oxidation. On the other hand, Pt/BaO is shown to be the most effective catalyst for converting NOx to NH_3. Fixed NOx storage experiments show the existence of at least two rate controlling regimes, one that is reductant feed rate limited, another that is limited by NOx storage phase diffusion, and a third that has a chemical or textural origin. On Pt/BaO the first two regimes are clearly distinguishable whereas a more complex picture emerges for Pt/CeO_2, with which a fraction of the stored NOx is kinetically inaccessible to reduction. Water inhibits the oxidation of NO on each catalyst but the cycle-averaged NOx conversion is largely unaffected. In contrast, CO_2 has only a minor effect on the conversion during steady state NO oxidation but significantly inhibits the NOx conversion during cyclic storage and reduction. This effect is attributed to the known higher stability of $BaCO_3$

compared to BaO/Ba(OH)$_2$. The conversion of H_2 to the less effective reductant CO via reverse water gas shift chemistry is a contributing factor based on steady-state activity tests. This pathway is shown to be most important for the catalyst, containing Rh/CeO$_2$, a known effective water gas shift catalyst. Building on the existing literature, most of the observed trends are interpreted in terms of the likely reaction pathways and transport processes. The findings are assessed in terms of identifying the catalyst best suited to the specific NOx trap application.

10. Metkar, P., V. Balakotaiah, and M.P. Harold, "Experimental Study of Mass Transfer Limitations in Fe- and Cu-Zeolite Based NH_3 -SCR Monolithic Catalysts," *Chem. Eng. Sci.*, **66**, 5192–5203 (2011).
    An experimental study of steady-state selective catalytic reduction (SCR) of NO_x with NH_3 on both Fe-ZSM-5 and Cu-ZSM-5 monolithic catalysts was carried out to investigate the extent of mass transfer limitations in various SCR reactions. Catalysts with different washcoat loadings, washcoat thicknesses and lengths were synthesized for this purpose. SCR system reactions examined included NO oxidation, NH_3 oxidation, standard SCR, fast SCR, and NO_2 SCR. Comparisons of conversions obtained on catalysts with the same washcoat volumes but different washcoat thicknesses indicated the presence of washcoat diffusion limitations. NH_3 oxidation, an important side reaction in SCR system, showed the presence of washcoat diffusion limitations starting at 350 ^oC on Fe-zeolite and 300 ^oC on Cu-zeolite catalysts. Washcoat diffusion limitations were observed for the standard SCR reaction ($NH_3 + NO + O_2$) on both Fe-zeolite ($\geq$ 350 ^oC) and Cu-zeolite ($\geq$ 250 ^oC). For the fast ($NH_3 + NO + NO_2$) and NO_2 SCR ($NH_3 + NO_2$) reactions, diffusion limitations were observed throughout the temperature range explored (200-550 ^oC). The experimental findings are corroborated by theoretical analyses. Even though the experimentally observed differences in conversions clearly indicate the presence of washcoat diffusion limitations, the contribution of external mass transfer was also found to be important under certain conditions. The transition temperatures for shifts in controlling regimes from kinetic to washcoat diffusion to external mass transfer are determined using simplified kinetics. The findings indicate the necessity of inclusion of mass transfer limitations in SCR modeling, catalyst design and optimization.

11. J. Wang, Y. Ji, Z. He, M. Crocker, M. Dearth, R.W. McCabe, "A non-NH_3 pathway for NO_x conversion in coupled LNT-SCR systems", *Appl. Catal. B* **111-112** (2012) 562.
    NO_x storage-reduction experiments were performed using a coupled LNT-SCR system consisting of a low-precious metal loaded Pt/Rh LNT catalyst and a commercial Cu–zeolite SCR catalyst. Cycling experiments revealed that when a $CO + H_2 + C_3H_6$ mixture or C_3H_6 by itself was used as the reductant, the NO_x conversion over the SCR catalyst exceeded the conversion of NH_3 over the same catalyst. This is explained by the presence of propene, which slipped through the LNT catalyst and reacted with the LNT NO_x slip. Separate experiments, conducted under continuous flow and lean-rich cycling conditions, confirmed the ability of propene, as well as ethene, to function as a NO_x reductant over the SCR catalyst. Cycling experiments also revealed that the SCR catalyst was able to store propene, such that NO_x reduction by stored propene continued into the lean phase (after the switch from rich conditions). According to adsorption experiments, significant co-adsorption of NH_3 and propene occurred in the SCR catalyst, while under lean-rich cycling conditions the

contributions of NH_3 *and* C_3H_6 *to* NO_x *conversion were found to be essentially additive. These findings suggest that under actual driving conditions,* NO_x *reduction by non-*NH_3 *reductants (olefins and possibly other hydrocarbons) in the SCR catalyst can contribute to the mitigation of lean and rich phase* NO_x.

12. Metkar, P., V. Balakotaiah, and M.P. Harold, "Experimental Study of Selective Catalytic Reduction of NO_x on a Combined System of Fe and Cu-based Zeolite Monolithic Catalysts," *Applied Catalysis B: Environmental*, **111– 112**, 67– 80 (2012).

    Iron and copper-based zeolites are effective catalysts for the lean selective catalytic reduction (SCR) of NOx with NH_3*. Cu-zeolites are more active at lower temperatures (*$\leq$ *350* ^oC*) while Fe-zeolites are more active at higher temperatures (*$\geq$ *400* ^oC*). The effectiveness of a catalytic system comprising Fe- and Cu-based zeolites was examined for the standard (NO +* O_2 *+* NH_3*) and fast (NO +* NO_2 *+* NH_3*) SCR reactions. Experiments carried out with in-house and commercial Fe- and Cu-zeolite monoliths of varying lengths quantified their relative SCR activities. The commercial Cu-zeolite achieved complete NOx conversion for the standard SCR at 250* ^oC *while the commercial Fe-zeolite achieved high NOx conversion at higher temperatures (*$\geq$ *400* ^oC*) where it out-performed the Cu-zeolite. Subsequently, three configurations of combined Fe and Cu-zeolite catalysts were compared:*

    - *"Sequential brick" catalyst comprising Fe-zeolite and Cu-zeolite monolith*
    - *"Mixed washcoat" catalyst comprising a washcoat layer having equal mass*
    - *fractions of Fe- and Cu-zeolites*
    - *"Dual layer" catalyst comprising monolith coated with individual layers of Fe- and Cu-zeolites of different thicknesses and mass fractions*

    The sequential brick design with Fe-zeolite brick followed by a Cu-zeolite brick gave a higher conversion than the Cu/Fe sequence of equal loadings with the Fe(33%)/Cu(67%) achieving the highest NOx conversion over a wide range of temperatures. The mixed washcoat catalyst achieved NOx conversion that was nearly an average of the individual Fe-only and Cu-only catalysts. The dual layer catalyst with a thin Fe-zeolite (33% of the total washcoat loading) layer on top of a thicker Cu-zeolite layer (67%) resulted in very high NOx removal efficiencies over a wide temperature range for both the standard and fast SCR reactions. The performance of this dual-layer system was comparable to the series arrangement of Fe and Cu-bricks. The Cu-zeolite on Fe-zeolite dual layer catalyst was not nearly as effective for the same loadings. The Fe/Cu dual layer catalyst also exhibited superior performance for the fast SCR reaction. The results are interpreted in terms of the activities of each catalyst for SCR and ammonia oxidation. An assessment of the extent of washcoat diffusion limitations shows that the dual layer configuration is superior to the sequential brick configuration. The existence of an optimal loading distribution of the Fe- and Cu-zeolite catalysts as well as other intangible benefits of the dual layer SCR catalyst is discussed.

13. Joshi, S., Y. Ren, M.P. Harold, and V. Balakotaiah, "Determination of Kinetics and Controlling Regimes for Propylene and Methane Oxidation on Pt/Al_2O_3 Monolithic Catalyst Using High Space Velocity Experiments," *Ind. Eng. Chem. Res.*, ***51*** (22), 7482–7492 (2012).

    The performance of a catalytic reactor is bounded by the kinetic regime at low temperature (or before light-off) and mass transfer controlled regime at high temperature. Pore diffusion *may also be significant at intermediate temperature. We utilize the recently developed criteria[1] to characterize the controlling regimes during lean oxidation of CH_4 and C_3H_6 in Pt/Al_2O_3 monolithic reactors. First, we determine the global kinetics of lean oxidation of CH_4 and C_3H_6 in a Pt/Al_2O_3 monolithic catalyst. We also present a method for accurate estimation of effective diffusivity and external mass transfer coefficient under reacting conditions. Further, we characterize the relative contributions of chemical kinetics, washcoat diffusion and external mass transfer as a function of various catalyst design and operating parameters. The analysis reveals that methane oxidation is kinetically controlled over a wide range of temperatures (350 to 600 ^oC) whereas the propylene oxidation has a more classical transition between kinetic and mass transfer controlled regimes. We demonstrate the application of the bench scale results for efficient reactor design. The analysis reveals that monolithic catalyst with lower cell density and thicker washcoat gives optimum steady state performance for the case of CH_4 oxidation. We also determine optimum Pt loading for C_3H_6 oxidation that gives best steady state performance for a given operating temperature.*

14. Kota, A., D. Luss and V. Balakotaiah, "Modeling and Optimization Studies of Combined LNT-SCR Catalyst Systems", *Ind. Eng. Chem. Res*., **51**, 6686-6696 (2012).
Several experimental studies have been conducted to determine the NO_x reduction by a series of LNT (lean NO_x trap) and SCR (selective catalytic reduction) catalytic bricks. An important goal is to minimize the required precious metal loading in the LNT while keeping the NO_x emission below a specified level. We present a mathematical model of this system using hydrogen as the reductant. Simulations are used to determine the influence of the architecture of the LNT–SCR bricks, nonuniform precious metal loading in the LNT bricks, and the cycle time at temperatures in the range of 200–350 °C. The simulations lead to the following observations: (a) Low temperature reduction is the limiting step in the optimization of precious group metal (PGM) loading in LNT. (b) The NO_x conversion increases as the number of the sequential bricks (with total length fixed) increase and reach an asymptotic limit. From a practical point of view, there is little incentive in using more than two sequential pairs. (c) Nonuniform precious metal loading of the LNT bricks results in only a minor improvement in the deNO_x performance. (d) The cycle time has a significant impact on the NO_x conversion. In the simulated example, the NO_x conversion at low temperatures is increased by about 15–20% by reducing the cycle time by a factor of 2. (e) Even at low temperature operation, diffusional limitations in the washcoat are most likely to be important in the LNT but not in the SCR operation. The NO_x conversion and ammonia selectivity are reduced when washcoat diffusion is dominant in the LNT.

15. Metkar, P., M.P. Harold, and V. Balakotaiah, "Experimental and Kinetic Modeling Study of NO Oxidation: Comparison between Fe and Cu-zeolite Catalysts," *Catalysis Today,* **184** 115– 128 (2012).
NO oxidation is considered as the rate determining step of the standard selective catalytic reduction (SCR) reaction (NO + NH_3 + O_2) on metal-exchanged zeolite catalysts. A comprehensive experimental and kinetic modeling study of NO oxidation reaction was carried out and a comparison made between Fe-ZSM-5, Cu-ZSM-5 and recently developed small pore Cu-chabazite catalysts. Steady state integral measurements of NO oxidation show Fe-zeolite to be a more active NO oxidation catalyst than Cu-zeolite. Both NO_2 temperature programmed desorption and decomposition experiments show that the NO_2 is more strongly

bound on the Cu-chabazite compared to Fe-ZSM-5. Increasing amounts of NO_2 in the NOx feed decrease the NO oxidation activity on both the catalysts. Differential kinetic studies show a positive order rate dependence of NO oxidation reaction with respect to both NO (~1) and O_2 (~0.5) while showing a negative order dependence with respect to NO_2 (-0.5 to -1), which confirms that the NO_2 inhibits the NO oxidation reaction. NO_2 inhibition on NO oxidation was found to be more severe on Cu-chabazite (~ -1 order) compared to Fe-ZSM-5 (~ -0.5 order). The overall activation energy of NO oxidation was found to be 39 kJ/mol on Fe-ZSM-5 compared to 56 kJ/mol on Cu-chabazite. The presence of feed water strongly inhibits the NO oxidation reaction. Transient NO_2 uptake experiments reveal nitrate formation on both catalysts. Catalysts pretreatments by different oxidizing/reducing agents (O_2, NO_2, H_2 and NH_3) did not affect steady state NO oxidation results. Experiments with monolith catalysts having the same washcoat volume but different washcoat thicknesses rule out the presence of washcoat diffusion limitations for NO oxidation. A global kinetic model is developed which accurately predicts the experimentally observed reaction orders, NO conversions and NO_2 and water inhibition effects for a wide temperature range and different feed conditions. The kinetic model accounts for the experimentally observed instability of nitrates in the presence of feed NO and shows that the steady state NO oxidation data can be predicted with a global kinetic model assuming a surface reaction between adsorbed O atoms and gaseous NO as the rate determining step.

16. Dasari, P., R. Muncrief, and M.P. Harold, "Elucidating NH_3 Formation During NO_χ Reduction by CO on Pt-BaO/Al_2O_3 in Excess Water," *Catalysis Today*, **184**, 43–53 (2012).
The reduction of NO was investigated with CO, H_2, CO+H_2O and CO+H_2 as the reducing species on a Pt-BaO/Al_2O_3 monolith catalyst over an intermediate temperature range (200 - 300 ^oC). NH_3 is a major product of the NO + CO + H_2O system under conditions of CO inhibition. The data are interpreted by the known NH_3 formation route in which the NO is reduced by H_2 formed by the water gas shift (WGS) reaction. In the absence of water, the strong adsorption of CO leads to sharp transitions between a high rate mass transport controlled regime and a lower rate kinetically controlled regime between 200 and 300 ^oC. Differential kinetics and integral experiments are reported at 270 ^oC. The intrinsic order with respect to CO in the latter regime is -1. When water is added with the CO feed, the regime transitions are more gradual and mitigated by the enhancement afforded by the hydrogen formed by the WGS reaction. Kinetic evidence for the effect of hydrogen is the much lower inhibition by CO during the WGS reaction (-0.23 order). When H_2 is added to the NO + CO mixture (without H_2O) in the CO inhibited feed regime NH_3 and CO_2 are the major products even for low H_2/NO feed ratios (~1). Collectively, the steady-state findings are consistent with the major NH_3 formation pathway involving reaction of surface H (from WGS) and OH (from water) with adsorbed NO and N. The NH3 formation route involving the hydrolysis of a surface isocyanate species formed from the reaction of NO and Co , is only of secondary importance.

17. Shakya, B., M.P. Harold, and V. Balakotaiah, "Crystallite-Scale Model for NOx Storage and Reduction on Pt/BaO/Al_2O_3: Pt Dispersion Effects on NOx Conversion and Ammonia Selectivity," *Catalysis Today*, **184**, 27-42 (2012).
A recently developed crystallite-scale regeneration model [D. Bhatia, M.P. Harold and V. Balakotaiah, Catalysis Today 151 (2010) 314] is extended and new data are reported that

provide insight about cyclic NO_x storage and reduction (NSR). The model is based on the concept of NO_x spillover from Pt to BaO and diffusion in the barium phase during storage and the reverse process during regeneration. The model is shown to predict the main features of NO_x storage, such as the increase in NO_x breakthrough time with increased Pt dispersion for fixed Pt loading. The increase in NO_x storage with Pt dispersion is a result of (i) an increase in exposed Pt area which leads to a higher intrinsic NO oxidation activity, and (ii) an increase in the interfacial perimeter between Pt and BaO which promotes the rate of NO_x spillover. These effects outweigh the known increase in activity with crystallite size. The model is used to simulate the complete lean-rich cycles in order to elucidate the effects of Pt dispersion on various cycle-averaged variables such as NO_x/H_2 conversion and N_2/NH_3 selectivity. The simulations show that a higher stored NO_x diffusivity is needed to satisfactorily predict experimental conversion and selectivity trends. This finding suggests the possible involvement of enhanced diffusion, likely of the reductant, during the regeneration. With this modification the model effectively predicts the dependence of cycle-averaged conversion and selectivity on Pt dispersion and rich phase duration. The model is used to study various storage and regeneration timing protocols, such as the use of shorter cycle times to achieve a high cycle-averaged NO_x conversion and NH_3 selectivity for low dispersion catalysts. The model also predicts incomplete storage phase utilization both at the crystallite and reactor scales. For example, a reactor containing high Pt dispersion catalyst tends to utilize the storage phase effectively at the crystallite scale but can have significant axial storage non-uniformities, whereas a reactor containing low dispersion Pt catalyst tends to have a more axially uniform storage but poorer local utilization.

18. Harold, M.P., “NOx Storage and Reduction in Lean Burn Vehicle Emission Control: A Catalytic Engineer’s Playground,” *Current Opinion in Chemical Engineering*, **1**, 1-9 (2012).
    This invited review describes the reduction of NO_x ($NO + NO_2$) in lean burn vehicle exhaust is the latest challenge to catalytic engineers to meet increasingly stringent emissions standards. The lean NO_x trap (LNT) is an adsorptive catalytic reactor in which NO_x is stored as nitrates in excess O_2 and then reduced during a brief regeneration. The multi-functional Pt-based LNT catalyst must carry out NO oxidation, NO_x storage, and NO_x reduction, all within a 1-2 minute cycle and achieve >95% NO_x conversion. This review describes studies of the transient coupling between reaction and transport, and links between catalyst composition, structure and NO_x conversion and selectivity to N_2 and NH_3. A glimpse is offered of emerging lean NO_x reduction technologies and the new challenges they pose.

19. Liu, Y., M.P. Harold, and D. Luss, “Coupled NO_x Storage and Reduction and Selective Catalytic Reduction Using Dual-layer Monolithic Catalysts,” *Appl. Catal. B. Environmental*, **121-122**, 239-251 (2012).
    Lean reduction of NO_x (NO & NO_2) by H_2 and CO was conducted over monolithic catalysts consisting of a selective catalytic reduction (SCR) catalyst layer deposited on top of a lean NO_x trap (LNT) catalyst. An increase in the CO/H_2 ratio decreased the cycle-averaged NO_x conversion. CO poisoning was especially significant below 250 ^oC for the ceria-free LNT catalyst. The low-temperature NO_x reduction was increased either by use of an LNT-SCR dual-layer catalyst or deposition of CeO_2 on the LNT catalyst. However, the ceria decreased the high-temperature reductive conversion of NO_x due to promotion of the undesired NH_3

oxidation. Ceria zoning o enhanced the monolith NO_x conversion. Downstream loading of ceria led to the highest NO_x reduction at both low- and high- temperatures due to the beneficial interaction of the ceria and H_2. The low-temperature NO_x conversion of an aged dual-layer catalyst could be increased by a higher SCR catalyst loading. However, at high temperatures NO_x reduction was independent of the SCR loading. The ratio of the lean to rich feed duration and the total cycle time were optimized to improve the NO_x conversion in a temperature range from 150 to 400 ºC. The highest cycle-averaged NO_x conversion was obtained with a 30s:5s lean-rich cycle containing 1.25% total reductant for all CO/H_2 ratios for a lean feed containing 500 ppm NO and 5% O_2.

20. C. Shi, Y. Ji, U.M. Graham, G. Jacobs, M. Crocker, Z. Zhang, Y. Wang, T.J. Toops, NOx Storage and Reduction Properties of Model Ceria-based Lean NOx Trap Catalysts", *Appl. Catal. B*, **119-120** (2012) 183-196.
    Three kinds of model ceria-containing LNT catalysts, corresponding to $Pt/Ba/CeO_2$, $Pt/CeO_2/Al_2O_3$ and $Pt/BaO/CeO_2/Al_2O_3$, were prepared for comparison with a standard LNT catalyst of the $Pt/BaO/Al_2O_3$ type. In these catalysts ceria functioned as a NO_x storage component and/or a support material. The influence of ceria on the microstructure of the catalysts was investigated, in addition to the effect on NO_x storage capacity, regeneration behavior and catalyst performance during lean/rich cycling. The $Pt/Ba/CeO_2$ and $Pt/BaO/CeO_2/Al_2O_3$ catalysts exhibited higher NO_x storage capacity at 200 and 300 °C relative to the $Pt/BaO/Al_2O_3$ catalyst, although the latter displayed better storage capacity at 400 °C. Catalyst regeneration behavior at low temperature was also improved by the presence of ceria, as reflected by TPR measurements. These factors contributed to the superior NO_x storage-reduction performance exhibited by the $Pt/Ba/CeO_2$ and $Pt/BaO/CeO_2/Al_2O_3$ catalysts under cycling conditions in the temperature range 200–300 °C. Overall, $Pt/BaO/CeO_2/Al_2O_3$ (which displayed well balanced NO_x storage and regeneration behavior), showed the best performance, affording consistently high NO_x conversion levels in the temperature range 200–400 °C under lean-rich cycling conditions.

21. V. Easterling, Y. Ji, M. Crocker, M. Dearth, R.W. McCabe, "Application of spaciMS to the study of ammonia formation in lean NOx trap catalysts", *Appl. Catal. B*, **123-124** (2012) 339.
    SpaciMS was employed to understand the factors influencing the selectivity of NO_x reduction in two fully formulated LNT catalysts, both degreened and thermally aged. Both catalysts contained Pt, Rh, BaO and Al_2O_3, while one of them also contained La-stabilized CeO_2. The amount of reductant required to fully regenerate each catalyst was first determined experimentally based on the OSC of the catalyst and the NO_x storage capacity (NSC). In this way a correction was made for the change in catalyst OSC and NSC after aging, thereby eliminating these as factors which could affect catalyst selectivity to NH_3. For both catalysts, aging resulted in an elongation of the NO_x storage–reduction (NSR) zone due to a decrease in the concentration of NO_x storage sites per unit catalyst length. In addition to decreased lean phase NO_x storage efficiency, stretching of the NSR zone affected catalyst regeneration. Three main effects were identified, the first being an increase of the NO_x "puff" that appeared during the onset of the rich front as it traversed the catalyst. Spatially, NO_x release tracked the NSR zone, with the result that the NO_x concentration peaked closer to the rear of the aged catalysts. Hence the probability that NO_x could re-adsorb downstream of the reduction front and subsequently undergo reduction by NH_3 (formed in the reduction front)

was diminished, resulting in higher rich phase NO_x *slip. Second, the stretching of the NSR zone resulted in increased selectivity to* NH_3 *due to the fact that less catalyst (corresponding to the OSC-only zone downstream of the NSR zone) was available to consume* NH_3 *by either the* NH_3*-*NO_x *SCR reaction or the* NH_3*-*O_2 *reaction. Third, the loss of OSC and* NO_x *storage sites, along with the decreased rate of* NO_x *diffusion to Pt/Rh sites (as a result of Pt/Rh–Ba phase segregation), led to an increase in the rate of propagation of the reductant front after aging. This in turn resulted in increased* H_2*:*NO_x *ratios at the Pt/Rh sites and consequently increased selectivity to* NH_3*.*

22. Zheng, X., A. Kumar, and M.P. Harold, "Isotopic Study of Pt-Catalyzed NO Reduction by NH_3 on Pt Catalysts Using Temporal Analysis of Products," *Catalysis Today*, 197, 66– 75 (2012).
    A Temporal Analysis of Products (TAP) study was carried out of the anaerobic NO + NH_3 *reaction system on Pt sponge and Pt/*Al_2O_3 *catalysts. Temperature, pulse timing, and feed composition were varied to quantify the conversion and product selectivities. Isotopically labeled nitric oxide (*1^5NO*) was used to follow reaction pathways to molecular nitrogen and nitrous oxide. A variation in the delay time between sequential pulses of* ^{15}NO *and* NH_3 *had a significant effect on the reaction path to molecular nitrogen. A mixed feed (no delay time) above the light-off temperature resulted in a product mixture nearly balanced between the mixed product* ^{15}NN*, and the two single-source products* $^{15}N_2$*, and* N_2*. With increased delay time the selectivity of* ^{15}NN *decreased significantly in favor of* $^{15}N_2$ *and* N_2*. The data suggest at least two major routes to nitrogen formation, one involving direct NO decomposition on reduced Pt sites and the other involving reaction between NHx species and NO. There is also kinetic evidence for a slower, third minor route involving an unidentified surface complex, possibly* HNO_{ad}*. The alumina support is shown to suppress this effect of delay time through ammonia adsorption, serving as a source-sink. The trends are interpreted with a mechanistic model constructed from a sequence of elementary steps.*

23. Metkar, P.S., M.P. Harold, and V. Balakotaiah, "Kinetic Model of NH_3-Based Selective Catalytic Reduction of NOx on Fe-ZSM-5 and Cu-Chabazite, and Dual Layer Fe/Cu Zeolitic Monolithic Catalysts," *Chem. Engin. Sci.*, **87**, 51–66 (2013).
    A comprehensive experimental and modeling study of selective catalytic reduction of NOx with NH_3 *was carried out on Fe-ZSM-5 and Cu-chabazite (CHA) catalysts. The experiments reveal that Cu-CHA catalyst has a higher* NH_3 *storage capacity and activity for* NH_3 *oxidation and standard SCR compared to Fe-ZSM-5. The NOx reduction activity on the Fe-ZSM-5 catalyst was found to be strongly dependent on the* NO_2 *feed fraction in contrast to Cu-CHA catalyst for which NOx conversion was much less sensitive to* NO_2*. In the presence of excess* NO_2*, both* N_2O *and ammonium nitrate were produced on both catalysts although Fe-ZSM-5 catalyst had a higher selectivity towards these byproducts compared to Cu-CHA. For different feed conditions (*$NO_2/NOx = 0$ *to 1), Cu-CHA was a more active NOx reduction catalyst at lower temperatures (*$\leq 350\ ^oC$*) while Fe-ZSM-5 was more active at higher temperatures (*$\geq 400\ ^oC$*). Global kinetic models were developed to predict the main features of several SCR system reactions investigated experimentally. The models account for* NH_3 *adsorption,* NH_3 *oxidation, NO oxidation, standard SCR, fast SCR,* NO_2 *SCR, ammonium nitrate formation and its decomposition to* N_2O*,* N_2O *decomposition and* N_2O *reduction by* NH_3*. The 1 + 1 dimensional reactor model accounts for potential washcoat diffusion*

limitations. The model accurately predicts the steady state NOx and NH_3 conversions and the selectivity of the different products formed during these reactions. The model was used to predict the performance of standard and fast SCR reactions on combined systems of Fe- and Cu-zeolite monolithic catalysts which were found to have higher NOx conversion activity over a wider temperature range than with individual Fe- and Cu-zeolite catalysts as reported in our earlier study (Metkar et al., 2012b). Among various configurations of the combined catalysts, either a single brick made up of a dual-layer catalyst with a thin Fe-zeolite layer on top of a thick Cu-zeolite layer or a sequential arrangement of short Fe-ZSM-5 brick followed by longer Cu-CHA brick resulted in high NOx removal efficiency over a wide temperature range of practical interest.

24. Harold, M.P., and P. Metkar, "Lean NOx Reduction by NH_3 on Fe-Exchanged Zeolite and Layered Fe/Cu Zeolite Catalysts: Mechanisms, Kinetics and Transport Effects ," invited chapter to appear in Selective Catalytic Reduction for Vehicle Applications, I. Nova and E. Tronconi, Editors, in press (2013).
    This invited chapter reviews the selective catalytic reduction of NOx on Fe-based zeolite catalysts in terms of kinetics, mechanism, and transport effects.

25. Liu, Y., Y. Zheng, M.P. Harold, and D. Luss, "Lean NO_x Reduction on LNT-SCR Dual-layer Catalysts by H_2 and CO," *Appl. Catalysis B. Environmental*, **132-133**, 293-303 (2013).
    Lean reduction of NO_x (NO & NO_2) by H_2 and CO was conducted over monolithic catalysts consisting of a selective catalytic reduction (SCR) catalyst layer deposited on top of a lean NO_x trap (LNT) catalyst. An increase in the CO/H_2 ratio decreased the cycle-averaged NO_x conversion. CO poisoning is especially significant below 250 ^oC for the ceria-free LNT catalyst. The low-temperature NO_x reduction was increased either by use of an LNT-SCR dual-layer catalyst or addition of CeO_2 in the LNT catalyst. However, the ceria decreased the high-temperature reductive conversion of NO_x due to promotion of the undesired NH_3 oxidation. Ceria zoning can enhance the monolith NO_x conversion. Downstream loading of ceria led to the highest NO_x reduction for both low- and high- temperatures due to the beneficial interaction of the ceria and H_2. The low-temperature NO_x conversion of an aged dual-layer catalyst could be increased by using a higher SCR catalyst loading. However, the high-temperature NO_x reduction was independent of the SCR loading. The ratio of the lean to rich feed duration and the total cycle time were optimized to improve the NO_x conversion in a temperature range from 150 to 400 ºC. The highest NO_x conversion was obtained with a 30s:5s lean-rich cycle for all CO/H_2 ratios.

26. Liu, Y., M.P. Harold, and D. Luss, "Lean NO_x Reduction with H_2 and CO in Dual-layer LNT-SCR Monolithic Catalysts: Impact of Ceria Loading," *Topics in Catal.*, **56**, 104–108 (2013).
    A series of monolithic catalysts consisting of a layer of selective catalytic reduction (SCR) catalyst deposited on top of lean NO_x trap (LNT) catalyst were synthesized for lean reduction of NO_x (NO&NO_2) with H_2 and CO. The LNT catalyst exhibited a rather low NO_x conversion below 250 ºC due to CO inhibition. The top SCR layer comprising Cu/ZSM5 significantly increased the NO_x conversion at low temperature by its reaction with NH_3 \formed during the regeneration phase. The addition of CeO_2 to the LNT layer \ promoted the water gas shift reaction ($CO + H_2O \leftrightarrow H_2 + CO_2$). The WGS reaction mitigated the

CO inhibition and the generated H_2 enhanced the low-temperature catalyst regeneration. The ceria addition decreased the performance at high temperatures due to increased oxidation of NH_3. The ceria loading was optimized by applying a non-uniform axial profile. A dual-layer catalyst with an increasing ceria loading axial profile improved the performance over a wide (low and high) temperature range.

27. Y. Ji, T.J Toops, M. Crocker, “Isocyanate formation and reactivity on a Ba-based LNT catalyst studied by DRIFTS”, *Appl. Catal. B*, **140-141** (2013) 265.
    Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and mass spectrometry (MS), coupled with the use of isotopically-labeled reactants ($^{15}N^{18}O$ and ^{13}CO), were employed to study the formation of isocyanate species during NOx reduction with CO, as well as isocyanate reactivity toward typical exhaust gas components. DRIFTS demonstrated that both Ba–NCO and Al–NCO were simultaneously formed during NOx reduction by CO under dry lean-rich cycling conditions. The Ba–NCO band was more intense than that of Al–NCO, and became comparatively stronger at high temperatures. During rich purging at 300 and 400 °C, a near linear relationship was found between the increase in Ba–NCO band intensity and the decrease in Ba–NO_3 band intensity, suggesting that Ba–NCO is directly derived from the reaction of Ba nitrate with CO. Both temperature-programmed surface reaction (TPSR) and isothermal reaction modes (ISR) were utilized to study the reactivity of isocyanate species under lean conditions. Simultaneous DRIFTS and mass spectrometric measurements during TPSR indicated that isocyanate reaction with H_2O, O_2, NO and NO/O_2 took place almost immediately the temperature was raised above 100 °C, and that all NCO species were removed below 300 °C. The evolution of the NCO IR bands during ISR at 350 °C demonstrated that the kinetics of NCO hydrolysis are fast, although a delay in N_2 formation indicated that N_2 is not the initial product of the reaction. In contrast, immediate N_2 evolution was observed during NCO reaction with O_2 and with NO + O_2. Overall, it can be inferred that under dry cycling conditions with CO as the sole reductant, N_2 is mainly generated via NCO reaction with NO/O_2 after the switch to lean conditions, rather than being evolved during the rich phase. However, in the presence of water, isocyanate undergoes rapid hydrolysis in the rich phase, N_2 generation proceeding via NH_3.

28. C. Shi, Z. Zhang, M. Crocker, L. Xu, C. Wang, C. Au, A. Zhu, “Non-thermal plasma-assisted NO_x storage and Reduction on a $LaMn_{0.9}Fe_{0.1}O_3$ perovskite catalyst”, *Catal. Today*, **211** (2013) 96.
    Based on its high NO_x storage capacity (NSC), a study of the properties of $LaMn_{0.9}Fe_{0.1}O_3$ in NO_x storage-reduction catalysis was undertaken. The microstructure of the $LaMn_{0.9}Fe_{0.1}O_3$ catalyst was characterized by XRD, XPS and H_2-TPR techniques and compared with that of $LaMnO_3$. The role of Fe doping in $LaMnO_3$ on the perovskite structure and on NO_x storage capacity was clarified. Though the $LaMn_{0.9}Fe_{0.1}O_3$ perovskite has high NSC values even at relatively low temperature (<300 °C), it shows much lower activity during lean-rich cycling compared with a traditional Pt/BaO/Al_2O_3 catalyst, indicating that regeneration of stored NO_x is the rate limiting step for the perovskite catalyst. By employing an H_2-plasma in the rich phase to assist reduction of the stored NO_x, the NO_x conversion is greatly improved, especially at low temperature. The results of the present study show that by combining the high NO_x storage capacity of the perovskite in the lean

phase with non-thermal plasma-assisted activation of the reductant in the rich phase, high NO_x conversion can be obtained at low temperature.

29. Dasari, P., R. Muncrief, and M.P. Harold, "Cyclic Lean Reduction of NO by CO in Excess H_2O on Pt-Rh/Ba/Al_2O_3: Elucidating Mechanistic Features and Catalyst Performance," *Topics in Catalysis*, in press (2013).
    This study provides insight into the mechanistic and performance features of the cyclic reduction of NOx by CO in the presence and absence of excess water on a Pt-Rh/Ba/Al_2O_3 NOx storage and reduction (NSR) catalyst. At low temperatures (150-200 ˚C), CO is ineffective in reducing NOx due to self-inhibition while at temperatures exceeding 200 ˚C, CO effectively reduces NOx to main product N_2 (selectivity > 70%) and byproduct N_2O. The addition of H_2O at these temperatures has a significant promoting effect on NOx conversion while leading to a slight drop in the CO conversion, indicating a more efficient and selective lean reduction process. The appearance of NH_3 as a product is attributed either to isocyanate (NCO) hydrolysis and/or reduction of NOx by H_2 formed by the water gas shift chemistry. After the switch from the rich to lean phase, second maxima are observed in the N_2O and CO_2 concentration versus time, in addition to the maxima observed during the rich phase. These and other product evolution trends provide evidence for the involvement of isocyanates as important intermediates, formed during the CO reduction of NO on the precious metal components, followed by their spillover to the storage component. The reversible storage of the isocyanates on the Al_2O_3 and BaO and their reactivity appears to be an important pathway during cyclic operation on Pt-Rh/Ba/Al_2O_3 catalyst. In the absence of water the isocyanates are not completely reacted away during the rich phase, which leads to their reaction with NO and O_2 upon switching to the subsequent lean phase, as evidenced by the evolution of N_2, N_2O and CO_2. In contrast, negligible product evolution is observed during the lean phase in the presence of water. This is consistent with a rapid hydrolysis of isocyanates to NH_3, which results in a deeper regeneration of the catalyst due in part to the reaction of the NH_3 with stored NOx. The data reveal more efficient utilization of CO for reducing NOx in the presence of water which further underscores the isocyanate mechanism. Phenomenological pathways based on the data are proposed that describes the cyclic reduction of NOx by CO under dry and wet conditions.

30. Raj, R. M.P. Harold and V. Balakotaiah, "Experimental studies on NO inhibition on C_3H_6 oxidation on Cu-chabazite monolithic catalyst, elucidating the mechanistic pathway of NO_x selective reduction by C_3H_6," *Ind. Eng. Chem. Res.,* dx.doi.org/10.1021/ie4009343 (2013).
    Bench- flow reactor and in-situ DRIFTS experiments were carried out to elucidate the features of propylene + NO + O_2 reaction system on Cu–SSZ13 (chabazite) monolithic catalyst. Experiments were conducted under both steady state and transient conditions for application-relevant feed conditions. Steady-state conversion data of the C_3H_6 light-off in the presence of excess O_2 (5%) shows inhibition by a much smaller amount of NO (500 ppm). Corresponding data in the presence of NO_2 reveals a transition in the C_3H_6 light-off curve; for temperatures below 350^{o}C the C_3H_6 conversion is higher in the presence of NO_2 as compared to O_2 whereas above 350^{o}C the C_3H_6 conversion in the absence of NO_2 is higher. The reduction of NO_2 to NO and N_2 is enhanced by the addition of C_3H_6, which facilitates the reduction of Cu sites favorable for the NO_2 reduction. Spatially-resolved concentration profiles using a series of monolith pieces of different lengths provide insight

into the reaction pathways. The spatial profiles show that NO_2 is completely reduced in the front part of monolith at temperatures above 350^oC. On the other hand, NO that is formed from the NO_2 reduction increases along the length in the temperature range of 200^oC-350^oC and exhibits a maximum value above 350 ^oC. Similarly, C_3H_6 oxidation is inhibited by NO at the light-off temperature of the C_3H_6 oxidation reaction (~350^oC) while there is no effect of NO on C_3H_6 oxidation reaction below the light-off temperature. The results clearly suggest that inhibition is not due to a competitive adsorption process but due to the generation of partially oxidized hydrocarbon species that react with NO to form O- and N- containing surface intermediates which serve to block the active catalytic sites. In-situ DRIFTS measurements confirm the formation and existence of –NCO like species over catalyst surface on exposure to NO after a 45 min of exposure to C_3H_6 and O_2. A phenomenological reaction mechanism is proposed that involves the formation of inhibiting intermediates through the reaction of NO with oxygenates, which then react further to form N_2.

31. Shakya, B., M.P. Harold, and V. Balakotaiah, "Effect of cycle time on NH_3 generation on Low Pt Dispersion Pt/BaO/Al_2O_3: Experiments and Crystallite-Scale Modeling," *Chem. Eng. Journal,* accepted for publication (June, 2013).

A crystallite scale monolithic reactor model for NOx storage and reduction (NSR) is used to explain the effects of lean-rich cycle time on the performance of low dispersion (3% and 8%) Pt/BaO/Al_2O_3 catalysts. Two sets of experiments were carried out to identify the conditions that result in adequate NOx conversion and NH_3 yield. In the first set (Set 1), the rich phase duration was varied while fixing the amount of reductant and lean storage time. In the second set (Set 2), the total cycle time was varied while maintaining a fixed lean to rich duration. The experiments were simulated using the crystallite-scale model that accounts for the diffusion of stored NOx in the storage phase. The Set 1 results show that for the 8% dispersion catalyst the NOx conversion increased while NH_3 selectivity decreased with increasing rich time (Set 1), indicating that a more prolonged regeneration is favorable in terms of NOx conversion. The Set 2 results show that for the same catalyst the NOx conversion decreases and ammonia selectivity increases slightly with increasing total cycle time. The NH_3 yield remained essentially constant for different rich times (set 1) while it achieved a slight maximum with total cycle time. Similar NOx conversion trends were observed for the 3% dispersion catalyst but the conversion were lower as a result of a lower overall activity. The model simulations are in reasonably good agreement with the experimental trends indicating that the underlying coupling between reaction, storage and diffusion limitations is likely to be correct. The model suggests that the decrease in NH_3 selectivity for longer and more dilute regeneration is due to the consumption of NH_3 downstream in the reactor whereas a smaller fraction of the generated NH_3 is consumed during short concentrated rich phase because of the high H_2 concentration (i.e. locally high H_2:NO ratio). For the 3% catalyst, the H_2 concentration is present in excess throughout the monolith for all cases giving high selectivity to NH_3 but low NOx conversion. The model is used to identify conditions for improved LNT performance in terms of NH_3 generation for its application in combined NSR/SCR systems. Finally, it is shown that for the low dispersion catalyst, solid state NOx diffusion in the barium phase is the dominant transport process occurring within the monolith channel and that other transport processes such as external mass transport and diffusion in the washcoat have minor effect on the predicted conversion and selectivity values.

32. Shakya, B., M.P. Harold, and V. Balakotaiah, "Modeling and Analysis of Dual-layer NOx Storage and Reduction and Selective Catalytic Reduction Monolithic Catalyst," *Chem. Eng. Journal,* to appear (2013).

A simulation study of dual-layer NOx storage/reduction (NSR) and selective catalytic reduction (SCR) monolithic catalyst is carried out using 1D+1D model of catalytic monolith with individually calibrated global kinetic models. The model is used to elucidate the complex spatiotemporal processes occurring within the washcoat and along the length of the reactor. Specifically, the simulations are used to address the following: (i) general features of dual-layer NSR+SCR configuration, (ii) effects of temperature, (iii) effects of washcoat loading of individual component, and (iv) impact of catalyst architecture. In the dual-layer configuration, NH_3 *generated in the underlying NSR layer is stored in the outer SCR layer (exposed to the fluid phase) during the rich phase which then reacts with the NOx during the subsequent lean phase. The simulation results show that multiple combinations of catalyst (washcoat) loading can attain a given NOx conversion and* N_2 *selectivity, and that there exists a loading of SCR washcoat for a given NSR catalyst for which the NOx conversion is maximum. At higher loading of SCR washcoat, the amount of* NH_3 *generated in the NSR is not sufficient to fully utilize the SCR catalyst. As a result, only a fraction of the SCR layer closer to the NSR layer is utilized while the rest acts as an inert layer, creating an undesired diffusional barrier which ultimately lowers the NOx conversion. Simulations of the dual-brick monolith are also performed to analyze the architectural effects on performance of the combined system. Under identical conditions (same residence time, monolith volume, fraction of individual catalyst and operating conditions), the simulations show that dual-layer configuration outperforms the dual-brick in terms of NOx conversion and* NH_3 *slip, largely because the* NH_3 *generated in the LNT layer is better utilized in the SCR layer. Finally, at higher temperatures the functionality of the SCR component is greatly reduced because of the higher rate of* NH_3 *consumption in the NSR layer lowering the* NH_3 *yield. As a consequence, comparable performances are obtained for both the configurations.*

33. Y. Zheng, Y. Liu, M.P. Harold, and D. Luss, "LNT-SCR Dual-layer Catalysts Optimized for Lean NOx Reduction by H_2 and CO," *Appl. Catalysis B. Environmental,* to appear (2013).

Monolithic catalysts consisting of a layer of selective catalytic reduction (SCR) catalyst deposited on top of a lean NO_x *trap (LNT) catalyst were optimized to provide high* NO_x *conversion at both low and high temperatures with minimal precious group metal (PGM) loading using* H_2*/CO reductant mixtures. The optimized dual-layer catalyst circumvents the need for urea feed and has the potential to reduce the expensive PGM loading by up to 38% from that of LNT only catalyst under laboratory test. We investigated the impact of catalyst design variables, such as SCR and LNT zoning, the ceria level in LNT, as well as SCR zeolite type (ZSM-5, SSZ-13) layer thickness. Zoning of either or both the SCR and LNT in the dual-layer catalysts enables an increase of the low-temperature* NO_x *conversion, and minimizes the high temperature (300-400* ^oC*) conversion loss caused by the SCR diffusion resistance and undesired* NH_3 *oxidation by the LNT. High ceria loading of the LNT enhanced* NH_3 *generation,* NO_x *adsorption and mitigated CO poisoning at low temperatures (150-250* ^oC*). Commercial Cu-SSZ-13 exhibited a higher* NH_3 *storage capacity and better low-temperature SCR activity than the in-house synthesized Cu-ZSM-5, and improved the low-temperature* NO_x *conversion of the dual-layer catalysts. The diffusion resistance in the top active Cu-zeolite layer inhibited the overall* NO_x *reduction as shown by replacing it with an inert Na-*

ZSM-5 layer with a high Si/Al ratio. Washcoat diffusion limitations adversely affect the high temperature performance more than the NH_3 oxidation to NO_x. The experiments revealed that diffusion limitations in the top SCR layer loading of 1.0 g/in^3 started at 150 ^oC using a pure H_2 feed and at 250 ^oC using a CO/H_2 feed.

34. Zheng, Y., M.P. Harold, and D. Luss, "Optimization of LNT-SCR Dual-layer Catalysts for Lean NOx Reduction by H_2 and CO," *SAE Journal*, accepted pending revision (2013).
Monolithic catalysts consisting of a layer of SCR catalyst deposited on top of a LNT catalyst were optimized to provide high NO_x conversion at both low and high temperatures with minimal precious group metal (PGM) loading for effective diesel NO_x emission control. In this study we demonstrate the application of LNT & SCR zoning in dual-layer catalyst to improve NO_x reduction efficiency and show the potential to reduce the expensive PGM loading by up to 40% from that of LNT only catalyst without degrading its deNO_x performance under simulated diesel exhaust conditions. We investigated the NO_x reduction pathway in the SCR layer of the dual-layer catalyst using simulated rich exhaust of C_3H_6/CO/H_2 as reductants. The non-NH_3 reduction pathway by N-containing organic intermediates via the synergy of LNT and SCR catalysts can play a major role in the incremental NO_x conversion over SCR layer at low temperatures (<= 225 ^oC). The roles of NH_3 and C_3H_6 as reductants for NO_x conversion over the SCR catalyst increase with temperature (> 225 ^oC). The impact of SCR and LNT zoning as well as SCR layer thickness, were studied. Zoning of either or both the SCR and LNT in the dual-layer catalysts improved the low-temperature NO_x conversion, and minimized the high-temperature (300-400 ^oC) conversion loss caused by the SCR layer diffusion resistance and undesired NH_3 oxidation. The performance decline due to the Cu-zeolite layer diffusion resistance was shown by replacing it with an inert Na-zeolite layer with a high Si/Al ratio.

35. Dasari, P., R., V. Easterling, and M.P. Harold, "Effect of CO_2 During NOx Storage and Reduction by H_2 at Low Temperature ,"*Applied Catalysis B. Environmental,* in preparation (December, 2013).
The low to moderate temperature (<300 ^oC) behavior of a Pt/Ba lean NOx trap (LNT) catalyst is of interest especially during vehicle startup. Recent studies by our group have reported a nonmonotonic dependence of cycle average NOx conversion versus temperature during the cyclic reduction of NOx on Pt/Rh/Ba/Al_2O_3 in the presence of excess CO_2 [Ren and Harold, ACS Catalysis, 2011; Liu et al., Appl. Catal. B, 2013; Liu et al., Top. Catal., 2013]. At catalyst temperature of about 200 ^oC the NOx conversion exhibits a noted minimum whereas this feature is not observed in the absence of CO_2. To determine the origin of this behavior, the formation and stability of barium carbonate and nitrite/nitrate species on a model Pt-Rh/Ba/Al_2O_3 LNT catalyst was studied using gas phase Fourier transform infrared (FTIR) spectroscopy. The catalyst was exposed to various mixtures including CO_2+O_2, NO+O_2, and NO+O_2+CO_2 in the temperature range of 150 to 350 ˚C. The temporal effluent gas composition revealed that surface carbonates exist over the entire temperature range, but are relatively less stable at temperatures exceeding 230 ˚C. During exposure to NO+O_2+CO_2 nitrite/nitrate formation competes with carbonate formation. The competition is manifested as a nonmonotonic uptake of nitrites/nitrates as the temperature is increased over the stated range. A phenomenological picture of the uptake is proposed to account for the measurements. At low temperatures (< 200 ^oC) NOx stores on Ba sites in the proximity of the Pt. apparently relying on the spillover of adsorbed O and NO species. At higher temperatures the increased rate of NO oxidation reaction forms NO_2, which stores on

the Ba sites further from the PGM sites through a disproportionation mechanism. The local minimum in NOx conversion at ~ 200 ˚C is a result of the drop in NOx storage capacity of the catalyst due to the competition offered by CO_2 *for storage sites, while at higher temperatures (> 230 ˚C) the storage capacity is partly restored due to the decrease in the carbonate stability.*

Products Developed Under the Award

Publications Since Project Inception

1. Joshi, S., Y. Ren, M.P. Harold, and V. Balakotaiah, "Determination of Kinetics and Controlling Regimes for H_2 Oxidation on Pt/Al_2O_3 Monolithic Catalyst Using High Space Velocity Experiments," *Applied Catalysis B: Environmental*, **102**, 484–495 (2011).
2. Metkar, P., N. Salazar, R. Muncrief, V. Balakotaiah, and M.P. Harold, "Selective Catalytic Reduction of NO with NH_3 on Iron Zeolite Monolithic Catalysts: Steady-State and Transient Kinetics ," *Applied Catalysis B: Environmental*, **104**, 110–126 (2011).
3. Kumar, A., X. Zheng, M.P. Harold, and V. Balakotaiah, "Microkinetic Modeling of the NO + H_2 System on Pt/Al_2O_3 Catalyst Using Temporal Analysis of Products ," *J. Catalysis*, **279**, 12–26 (2011).
4. Xu, J., M. Harold, and V. Balakotaiah, "Microkinetic Modeling of NOx Storage on $Pt/BaO/Al_2O_3$ Catalysts: Pt Loading Effects," *Applied Catalysis B: Environmental*, **104**, 305-315 (2011).
5. Wang, J., Y. Ji, U. Graham, C. Spindola Cesar de Oliveira, M. Crocker, "Fully Formulated Lean NOx Trap Catalysts Subjected to Simulated Road Aging: Insights from Steady-State Experiments", *Chin. J. Catal.*, **32** (2011) 736.
6. Wang, J., Y. Ji, V. Easterling, M. Crocker, M. Dearth, R.W. McCabe, "The effect of regeneration conditions on the selectivity of NO_x reduction in a fully formulated lean NOx trap catalyst", *Catal. Today*, 175 (2011) 83.
7. Ji, Y., V. Easterling, U. Graham, C. Fisk, M. Crocker, J,-S. Choi, "Effect of aging on the NO_x storage and reduction characteristics of fully formulated lean NO_x trap catalysts", *Appl. Catal. B* 103 (2011) 413.
8. Liu, Y., M.P. Harold, and D. Luss, "Spatiotemporal Features of $Pt/CeO_2/Al_2O_3$ Catalysts During Lean/Rich Cycling," *Applied Catalysis A, General*, **397**, 35-45 (2011).
9. Ren, Y., and M.P. Harold, "NOx Storage and Reduction with H_2 on $Pt/Rh/BaO/CeO_2$: Effects of Rh and CeO_2 in the Absence and Presence of CO_2 and H_2O," *ACS Catalysis*, 1, 969-988 (2011).
10. Metkar, P., V. Balakotaiah, and M.P. Harold, "Experimental Study of Mass Transfer Limitations in Fe- and Cu-Zeolite Based NH_3 -SCR Monolithic Catalysts," *Chem. Eng. Sci.*, **66**, 5192–5203 (2011).
11. J. Wang, Y. Ji, Z. He, M. Crocker, M. Dearth, R.W. McCabe, "A non-NH_3 pathway for NO_x conversion in coupled LNT-SCR systems", Appl. Catal. B **111-112** (2012) 562.
12. Metkar, P., V. Balakotaiah, and M.P. Harold, "Experimental Study of Selective Catalytic Reduction of NO_x on a Combined System of Fe and Cu-based Zeolite Monolithic Catalysts," Applied Catalysis B: Environmental, **111– 112**, 67– 80 (2012).
13. Joshi, S., Y. Ren, M.P. Harold, and V. Balakotaiah, "Determination of Kinetics and Controlling Regimes for Propylene and Methane Oxidation on Pt/Al_2O_3 Monolithic Catalyst Using High Space Velocity Experiments," Ind. Eng. Chem. Res., in press (2012).

14. Kota, A., D. Luss and V. Balakotaiah, "Modeling and Optimization Studies of Combined LNT-SCR Catalyst Systems", *Ind. Eng. Chem. Res.*, **51**, 6686-6696 (2012).
15. Metkar, P., M.P. Harold, and V. Balakotaiah, “Experimental and Kinetic Modeling Study of NO Oxidation: Comparison between Fe and Cu-zeolite Catalysts,” Catalysis Today **184** 115–128 (2012).
16. Dasari, P., R. Muncrief, and M.P. Harold, “Elucidating NH_3 Formation During NO_χ Reduction by CO on $Pt\text{-}BaO/Al_2O_3$ in Excess Water,” Catalysis Today, **184**, 43–53 (2012).
17. Shakya, B., M.P. Harold, and V. Balakotaiah, “Crystallite-Scale Model for NOx Storage and Reduction on $Pt/BaO/Al_2O_3$: Pt Dispersion Effects on NOx Conversion and Ammonia Selectivity,” Catalysis Today, **184**, 27-42 (2012).
18. Harold, M.P., “NOx Storage and Reduction in Lean Burn Vehicle Emission Control: A Catalytic Engineer’s Playground,” Current Opinion in Chemical Engineering, **1**, 1-9 (2012).
19. Liu, Y., M.P. Harold, and D. Luss, “Coupled NO_x Storage and Reduction and Selective Catalytic Reduction Using Dual-layer Monolithic Catalysts,” Appl. Catal. B. Environmental, **121-122**, 239-251 (2012).
20. C. Shi, Y. Ji, U.M. Graham, G. Jacobs, M. Crocker, Z. Zhang, Y. Wang, T.J. Toops, NOx Storage and Reduction Properties of Model Ceria-based Lean NOx Trap Catalysts”, *Appl. Catal. B*, **119-120** (2012) 183-196.
21. V. Easterling, Y. Ji, M. Crocker, M. Dearth, R.W. McCabe, “Application of spaciMS to the study of ammonia formation in lean NOx trap catalysts”, *Appl. Catal. B*, **123-124** (2012) 339.
22. Zheng, X., A. Kumar, and M.P. Harold, “Isotopic Study of Pt-Catalyzed NO Reduction by NH_3 on Pt Catalysts Using Temporal Analysis of Products,” Catalysis Today, 10.1016/j.cattod.2012.06.025 (2012).
23. Metkar, P.S., M.P. Harold, and V. Balakotaiah, “Kinetic Model of NH_3-Based Selective Catalytic Reduction of NOx on Fe-ZSM-5 and Cu-Chabazite, and Dual Layer Fe/Cu Zeolitic Monolithic Catalysts,” Chem. Engin. Sci., **87**, 51–66 (2013).
24. Harold, M.P., and P. Metkar, “Lean NOx Reduction by NH_3 on Fe-Exchanged Zeolite and Layered Fe/Cu Zeolite Catalysts: Mechanisms, Kinetics and Transport Effects ,” invited chapter to appear in Selective Catalytic Reduction for Vehicle Applications, I. Nova and E. Tronconi, Editors, in press (2013).
25. Liu, Y., M.P. Harold, and D. Luss, “Lean NO_x reduction on LNT-SCR dual-layer catalysts by H_2 and CO,” *Appl. Catalysis B. Environmental,* dx.doi.org/10.1016/j.apcatb.2012.10.034 (October, 2012).
26. Liu, Y., M.P. Harold, and D. Luss, “Lean NO_x Reduction with H_2 and CO in Dual-layer LNT-SCR Monolithic Catalysts: Impact of Ceria Loading, “Top. Catal., **56**, 104–108 (2013).
27. Y. Ji, T.J Toops, M. Crocker, “Isocyanate formation and reactivity on a Ba-based LNT catalyst studied by DRIFTS”, *Appl. Catal. B*, **140-141** (2013) 265.
28. C. Shi, Z. Zhang, M. Crocker, L. Xu, C. Wang, C. Au, A. Zhu, “Non-thermal plasma-assisted NO_x storage and Reduction on a $LaMn_{0.9}Fe_{0.1}O_3$ perovskite catalyst”, *Catal. Today*, **211** (2013) 96.
29. Dasari, P., R. Muncrief, and M.P. Harold, “Cyclic Lean Reduction of NO by CO in Excess H_2O on $Pt\text{-}Rh/Ba/Al_2O_3$: Elucidating Mechanistic Features and Catalyst Performance,” *Topics in Catalysis*, in press (2013).
30. Raj, R. M.P. Harold and V. Balakotaiah, “Experimental studies on NO inhibition on C_3H_6 oxidation on Cu-chabazite monolithic catalyst, elucidating the mechanistic pathway of NO_x selective reduction by C_3H_6,” *Ind. Eng. Chem. Res.*, accepted for publication (April, 2013).

31. Shakya, B., M.P. Harold, and V. Balakotaiah, "Effect of cycle time on NH_3 generation on Low Pt Dispersion $Pt/BaO/Al_2O_3$: Experiments and Crystallite-Scale Modeling," *Chem. Eng. Journal,* accepted for publication (June, 2013).
32. Shakya, B., M.P. Harold, and V. Balakotaiah, "Modeling and Analysis of Dual-layer NOx Storage and Reduction and Selective Catalytic Reduction Monolithic Catalyst," *Chem. Eng. Journal,* to appear (2013).
33. Y. Zheng, Y. Liu, M.P. Harold, and D. Luss, "LNT-SCR Dual-layer Catalysts Optimized for Lean NOx Reduction by H_2 and CO," *Appl. Catalysis B. Environmental*, to appear (2013).
34. Zheng, Y., M.P. Harold, and D. Luss, "Optimization of LNT-SCR Dual-layer Catalysts for Lean NOx Reduction by H_2 and CO," *SAE Journal*, accepted pending revision (2013).
35. Dasari, P., R., V. Easterling, and M.P. Harold, "Effect of CO_2 During NOx Storage and Reduction by H_2 at Low Temperature ,"*Applied Catalysis B. Environmental,* in preparation (December, 2013).

Presentations Since 2010

1. "Kinetic and Mechanistic Studies of Selective Catalytic Reduction of NO_x on Fe-Zeolite Monolithic Catalysts," presented at the AIChE National Meeting, Salt Lake City, 11/10 (with P. Metkar, presenter, R. Muncrief, V. Balakotaiah).
2. "Steady-state Reactions of NO, CO and H_2O on $Pt\text{-}Ba/Al_2O_3$ Monolith," presented at the AIChE National Meeting, Salt Lake City, 11/10 (with P. Dasari, presenter, R. Muncrief).
3. "TAP Studies of NOx Reduction Using H_2 and NH_3," presented at the AIChE National Meeting, Salt Lake City, 11/10 (with A. Kumar, V. Balakotaiah).
4. "Effect of Pt Dispersion On Observed Kinetics During Oxidation of H_2 On Pt/Al_2O_3 Monolithic Catalyst," presented at the AIChE National Meeting, Salt Lake City, 11/10 (with S. Joshi, V. Balakotaiah).
5. "Effect of Pt Dispersion On Observed Kinetics: Oxidations of Methane and Propylene On Pt/Al_2O_3 Monolithic Catalyst," presented at the AIChE National Meeting, Salt Lake City, 11/10 (with V. Balakotaiah, presenter, S. Joshi).
6. "Determination of Controlling Regimes in Catalytic Monoliths," presented at the AIChE National Meeting, Salt Lake City, 11/10 (poster; with V. Balakotaiah, presenter, S. Joshi).
7. "TAP Studies of NOx Reduction," presented at the Spring National Meeting of ACS, Anaheim, 3/10 (with X. Zheng, A. Kumar, V. Balakotaiah).
8. "Spatio-temporal Features of Periodic Oxidation of H_2 and CO on $Pt/CeO_2/Al_2O_3$," CLEERS, Dearborn, MI, 4/11 (with Y. Liu and D. Luss).
9. V. Easterling, M. Crocker, M. Dearth, R.W. McCabe, M.P. Harold, "A Spatio-temporal Study of Lean NOx Trap Regeneration", oral presentation (OB09) at the 22nd North American Catalysis Society Meeting, June 5-10, 2011, Detroit, MI.
10. M. Dearth, G. Cavataio, L. Xu, H. Jen, R.W. McCabe, J. Wang, Y. Ji, L. He, M. Crocker, "A Non-NH_3 Pathway for NOx Conversion in Coupled LNT-SCR Systems", oral presentation (OC19) at the 22nd North American Catalysis Society Meeting, June 5-10, 2011, Detroit, MI.
11. C. Shi, Y. Ji, T.J. Toops, M. Crocker, "NO_x Storage and Reduction Properties of Ceria-based Lean NO_x Trap Catalysts", poster presentation (P-Mo-119) at the 22nd North American Catalysis Society Meeting, June 5-10, 2011, Detroit, MI.
12. M. Harold, Catalysis Club of Philadelphia, *Multi-Functional Catalysts and Reactors for Lean NOx Reduction,* Newark, DE, 5/11.
13. M. Harold, North American Catalysis Society, North American Meeting, Keynote Lecture:

Probing and Exploiting Interactions between Storage, Reaction and Transport Processes During Lean NOx Reduction, Detroit, MI, 6/11.

14. "Kinetic and Mechanistic Studies of Selective Catalytic Reduction of NO_x on Cu- and Fe-Zeolite Monolithic Catalysts," presented at the North American Catalysis Society Meeting, Detroit, 6/11 (with P. Metkar, presenter, V. Balakotaiah).
15. "Steady-state Reactions of NO, CO and H_2O on Pt-Ba/Al_2O_3 Monolith," presented at the North American Catalysis Society Meeting, Detroit, 6/11 (with P. Dasari, presenter, R. Muncrief).
16. C. Shi, Y. Ji, U. Graham, G. Jacobs, T.J. Toops, M. Crocker, "NOx storage and reduction properties of ceria-promoted lean NOx trap catalysts", oral presentation at the 242nd ACS National Meeting, Denver, CO, August 28-September 1, 2011, FUEL-2; Preprints of Symposia - American Chemical Society, Division of Fuel Chemistry, 2011, 56(2), 3-4.
17. M.P. Harold, M. Crocker, M. Dearth, R. McCabe, V. Balakotaiah, D. Luss, J.S. Choi, "Development of Optimal Catalyst Designs and Operating Strategies for Lean NOx Reduction in Coupled LNT-SCR Systems", poster presented at the 2010 Directions in Engine-Efficiency and Emissions Research (DEER) Conference, Detroit, MI, September 27-30, 2010.
18. "Experimental and Kinetic Modeling Study of Selective Catalytic Reduction of NOx on Fe- and C-Based Zeolitic Monolithic Catalysts, presented at AIChE Annual Meeting, Minneapolis, 10/11 (with P. Metkar, presenter, and V. Balakotaiah).
19. "Modeling the Effect of Pt Dispersion During Steady-State NO Oxidation and Transient NOx Storage and Regeneration on Pt/BaO/Al_2O_3 Lean NOx Trap Catalysts," presented at AIChE Annual Meeting, Minneapolis, 10/11 (with B. Shakya, presenter, and V. Balakotaiah).
20. "NOx Storage and Reduction by Multilayer Monolithic Catalysts," presented at AIChE Annual Meeting, Minneapolis, 10/11 (with Y. Liu presenter, and D. Luss).
21. "Studies of NH_3 Formation over Pt/BaO/Al_2O_3 LNT Monoliths in the Presence of Excess Water," presented at AIChE Annual Meeting, Minneapolis, 10/11 (with P. Dasari and R. Muncrief).
22. "Determination of Controlling Regimes for Various SCR Reactions on Zeolitic-Based Monolithic Catalysts," poster presented at AIChE Annual Meeting, Minneapolis, 10/11 (with P. Metkar, presenter, and V. Balakotaiah).
23. "NOx Reduction in Dual-Layer LNT/SCR Catalysts," CLEERS, Dearborn, MI, 4/12 (with Y. Liu and D. Luss).
24. "Kinetic and Reactor Modeling of the NH_3-SCR Converter: Fe- and Cu-Exchanged Zeolites as Single or Dual Layers," AIChE Annual Meeting, Pittsburgh, 10/12 (with P. Metkar, B. Shakya, and V. Balakotaiah).
25. "Modeling and Simulation of Dual-Layer NO_x Storage and Reduction (NSR) and Selective Catalytic Reduction (SCR) Monolithic Catalyst," AIChE Annual Meeting, Pittsburgh, 10/12 (with B. Shakya, presenter, and V. Balakotaiah).
26. "Spatiotemporal Studies of NH_3 Formation Over Pt-Rh/BaO/Al_2O_3 LNT Monolith in the Presence of Excess CO_2 and H_2O," AIChE Annual Meeting, Pittsburgh, 10/12 (with P. Dasari, presenter, and R. Muncrief).
27. "Mechanistic Studies of Selective Catalytic Reduction of NO_x with C_3H_6 on Cu based Zeolite Monolith Catalyst," AIChE Annual Meeting, Pittsburgh, 10/12 (with R. Raj, presenter, and V. Balakotaiah).

28. "Lean NOx Reduction with H_2 and CO Over Dual-Layer LNT-SCR Monolithic Catalysts," NASCRE 3, Houston, 3/13 (with Y. Zheng, presenter, and D. Luss).
29. "Cyclic Lean Reduction of NO by CO in Excess H_2O on Pt-Rh/Ba/Al_2O_3: Elucidating Mechanistic Features and Catalyst Performance," NASCRE 3, Houston, 3/13 (with P. Dasari, poster presenter).
30. **"**Modeling and Simulation of Layered Lean NO_x Trap and Selective Catalytic Reduction Monolithic Catalysts," NASCRE 3, Houston, 3/13 (with B. Shakya, presenter).
31. "Mechanistic Studies of Selective Catalytic Reduction of NO_x with C_3H_6 on Cu based Zeolite Monolith Catalyst," NASCRE 3, Houston, 3/13 (with R. Raj, presenter, and V. Balakotaiah).
32. Y. Ji, T.J Toops, M. Crocker, "Isocyanate Formation and Reactivity on a Ba-based LNT Catalyst Studied by DRIFTs and Mass Spectrometry", oral presentation O-W-Com-13, 23rd North American Catalysis Society meeting, Louisville, KY, June 2-7, 2013.
33. J. Wang, Y. Ji, M. Crocker, "Effect of Aging on NOx Reduction in Coupled LNT-SCR Systems", poster presentation P-W-BRC-34, 23rd North American Catalysis Society meeting, Louisville, KY, June 2-7, 2013.
34. M.-Y. Kim, J.-S. Choi, M. Crocker, "Roles of C_3H_6 in NH_3 Generation and NOx Reduction over a Cu-chabazite SCR Catalyst under Lean/Rich Cycling Conditions", poster presentation P-Tu-BRC-112, 23rd North American Catalysis Society meeting, Louisville, KY, June 2-7, 2013.
35. D. Kim and M. Crocker, "Adsorption and Desorption of Propene on a Cu-Chabazite Catalyst", poster presentation P-M-BRC-70, 23rd North American Catalysis Society meeting, Louisville, KY, June 2-7, 2013.
36. **"**Modeling and Simulation of Layered Lean NO_x Trap and Selective Catalytic Reduction Monolithic Catalysts," NAM, Louisville, KY 6/13 (with B. Shakya, presenter, and V. Balakotaiah).
37. "Spatiotemporal Studies of NH_3 Formation Over Pt-Rh/BaO/Al_2O_3 LNT Monolith in the Presence of Excess CO_2 and H_2O," Louisville, KY 6/13 (poster; with P. Dasari, presenter).

Collaborations Fostered

The project involved close cooperation between researchers from several organizations (UH, UK, Ford, ORNL, BASF). Several publications identified above involved researchers from two or more organizations. BASF provided catalysts used in most of the studies. This enabled data to be compared from the various experiments.

Technologies/Techniques Developed

This project helped to advance combined NOx storage & reduction and selective catalytic reduction (NSR + SCR), as well as certain aspects of the individual technologies.

Inventions/Patent Applications

The following patent application is currently under review:

Harold, M.P., and P. Metkar, US Provisional Patent Application, "Multi-Component and Layered Formulations for Enhanced Selective Catalytic Reduction Activity," June 6, 2011**.**

Computer Modeling Products

Models developed in this project were solved numerically. The models used were custom, with the details provided in the publications. The information is not proprietary and the results can be easily checked. Details are provided in the PhD theses of the graduate students supported by DOE funds.