

Award DE-FC26-05NT42630 entitled, “Kinetic and Performance Studies of the Regeneration Phase of Model Pt/Ba/Rh NO_x Traps for Design and Optimization”

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Executive Summary

In this project a combined experimental and theoretical approach was taken to advance our understanding of lean NO_x trap (LNT) technology. Fundamental kinetics studies were carried out of model LNT catalysts containing variable loadings of precious metals (Pt, Rh), and storage components (BaO, CeO₂). The Temporal Analysis of Products (TAP) reactor provided transient data under well-characterized conditions for both powder and monolith catalysts, enabling the identification of key reaction pathways and estimation of the corresponding kinetic parameters. The performance of model NO_x storage and reduction (NSR) monolith catalysts were evaluated in a bench scale NO_x trap using synthetic exhaust, with attention placed on the effect of the pulse timing and composition on the instantaneous and cycle-averaged product distributions. From these experiments we formulated a global model that predicts the main spatio-temporal features of the LNT and a mechanistic-based microkinetic models that incorporates a detailed understanding of the chemistry and predicts more detailed selectivity features of the LNT. The NO_x trap models were used to determine its ability to simulate bench-scale

data and ultimately to evaluate alternative LNT designs and operating strategies.

The four-year project led to the training of several doctoral students and the dissemination of the findings as 47 presentations in conferences, catalysis societies, and academic departments as well 23 manuscripts in peer-reviewed journals. A condensed review of NO_x storage and reduction was published in an encyclopedia of technology.

Project Objectives and Scope

Objectives (Original)

- Carry out studies of regeneration kinetics on lean NO_x trap (LNT) catalysts;
- Evaluate and compare the effect of different reductants on LNT performance;
- Incorporate the kinetics findings and develop and analyze a first-principles based predictive LNT model for design and optimization;
- Test the new LNT designs in a heavy-duty diesel vehicle dynamometer facility.

Scope (Original)

The project combined fundamental kinetic studies of catalytic reactions and bench scale experimentation on monolithic reactors with first-principles based modeling, analysis and optimization of the transient/periodic operation of the NO_x trap and full scale testing of the trap in a heavy duty dynamometer facility.

Overall Accomplishments vs. Tasks

Task 1:

Carry out comprehensive mechanistic study of the regeneration of model Pt/Rh/Ba NSR catalysts with reductants H₂ and CO in the TAP reactor and TGA/DSC systems.

Success Criterion: The TAP reactor experiments will be considered successful if we can identify the mechanism of regeneration and extract the kinetic constants from the experimental data. Peer reviewed publication of at least two articles on the kinetics of regeneration will be considered as a success criterion.

Accomplishments:

The kinetic studies on NO_x storage and regeneration on Pt/Rh/Ba catalysts were carried out using a TAP (temporal analysis of products) reactor and fixed bed microreactors. Bench scale studies of light-off and NO_x conversion using different reductants were carried out on model LNT monoliths (with prescribed composition) supplied by an industrial collaborator (BASF).

TAP Study of NO Decomposition and Reduction on Pt/Al₂O₃:

A systematic study over Pt/Al₂O₃ powder and monolith catalysts was carried out using Temporal Analysis of Products (TAP) to elucidate the transient kinetics of NO decomposition and NO reduction with H₂. NO pulsing and NO-H₂ pump-probe experiments conveyed the sensitive effects of catalyst temperature, NO-H₂ pulse delay time and H₂/NO ratio on N₂, N₂O and NH₃ selectivity. At lower temperature (150 °C) decomposition of NO is negligible in the absence of H₂, indicating that N-O bond

scission is rate limiting. At higher temperature NO decomposition occurs readily on reduced Pt but the rate is inhibited by surface oxygen as reaction occurs. The reduction of NO by a limiting amount of H₂ at lower temperature indicates the reaction of surface NO with H adatoms to form N adatoms, which react with adsorbed NO to form N₂O or recombine to form N₂. In excess H₂, higher temperatures and longer delay times favor the production of N₂. The longer delay enables NO decomposition on reduced Pt with the role of H₂ being a scavenger of surface oxygen. Lower temperatures and shorter delay times are favorable for ammonia production. The sensitive dependence on delay time indicates that the fate of adsorbed NO depends on the concentration of vacant sites for NO bond scission, necessary for N₂ formation, and of surface hydrogen, necessary for hydrogenation to ammonia. A mechanistic-based microkinetic model is proposed that accounts for the experimental observations. The TAP experiments with the monolith catalyst show an improved signal due to the reduction of transport restrictions caused by the powder. The improved signal holds promise for quantitative TAP studies for kinetic parameters estimation and model discrimination.

[Further details in **Papers 1, 7 and 10** listed below.]

Isotopic TAP Study:

The above-mentioned TAP studies of the NO decomposition and NO_x + H₂ reduction chemistry were complemented by a systematic isotopic study over Pt/BaO/Al₂O₃ powder catalyst using Temporal Analysis of Products (TAP). This study elucidated the role of the Pt/BaO interface and spillover processes during NO_x storage and reduction. The sequential pre-nitration of Pt/BaO/Al₂O₃ using NO and ¹⁵NO followed by reduction with H₂ results in the preferential evolution of ¹⁵N containing species during initial H₂ pulses. The evolution shifts towards N containing species in later H₂ pulses. The data suggest that NO_x storage proceeds radially outward from the Pt crystallites and that some mobility of the stored NO_x species exists. The subsequent reduction is limited by transport of stored NO_x from BaO storage phase to the Pt/BaO interface. The evolution of N₂ and ¹⁵NN during ¹⁵NO–H₂ pump-probe on a pre-nitrated (using unlabeled NO) catalyst confirms the involvement of spillover processes at the Pt/BaO interface. The evolution of nitrogen takes place by NO decomposition as well as by the reaction of stored NO_x with H₂ to form adsorbed N and eventually N₂. A significant fraction of N₂ is also produced via NH₃ serving as an intermediate. The results suggest that the local gradients at the Pt/BaO interface in the stored NO_x are important and that these should be taken into account in NSR catalyst design and modeling.

[Further details in **Paper 18** listed below.]

TAP Study of Stored NO_x Diffusion

A systematic study over Pt/BaO/Al₂O₃ powder catalyst was carried out using Temporal Analysis of Products (TAP) to estimate the effective diffusivity of stored NO_x in the barium phase. The pre-nitration of Pt/BaO/Al₂O₃ using sequential pulses of NO followed by reduction with H₂ results in the evolution of N₂ and NH₃. The reduction was carried out in the NO_x transport limited regime in which diffusion of the stored NO_x from BaO storage phase to Pt/BaO interface was determined to be the rate controlling process. The effluent profiles of N containing species (2N₂+NH₃) were used to estimate stored NO_x diffusivity in barium phase and the apparent activation energy. The activation

energy (74 - 81 kJ/mol) is in good agreement with the estimated value of 75 kJ/mol from an independent NO_x trap experimental and modeling study. [Further details see **Paper 22** listed below.]

TAP Experimental & Kinetic Modeling Study

Our combined experimental and modeling approach led to the successful development of a microkinetic model that predicts many of the features from steady-state and transient atmospheric pressure data as well as transient ultrahigh vacuum (TAP) data. Figure 1 shows the overall breakdown of the reaction steps that comprise the microkinetic model. These were developed over systematic analyses of steady-state data, NO_x storage data, and LNT experiments. The catalytic chemistry of NSR is complex as evidenced by the large number of elementary and lumped steps. The microkinetic model was incorporated into a model of the NO + H₂ on Pt/Al₂O₃ reaction system in the TAP reactor. This was a stringent test of the kinetic model that was developed for atmospheric pressure flow reactor, but applied to an ultrahigh vacuum transient system. The NO pulsing experiments showed the inhibiting effect of oxygen poisoning and the kinetic limitations posed by N-O bond scission. The NO-H₂ pump-probe experiments demonstrated the effect of temperature, H₂/NO ratio, and pulse delay time between consecutive NO and H₂ pulses on N₂, N₂O, and NH₃ selectivity. The simulations revealed the competition between surface N-N recombination and N and/or NO reaction with H to form N₂ and NH₃, respectively. The developed mechanistic – based microkinetic model accounts for all of the experimental data including the aforementioned selectivity versus pulse delay trends. An example result is shown in Figure 2 in which the measured and predicted NH₃ selectivity is shown as a function of temperature for several different delay times. The model successfully predicts a decrease selectivity shift as either the delay time or temperature is increased.

[Further details in **Paper 23** listed below.]

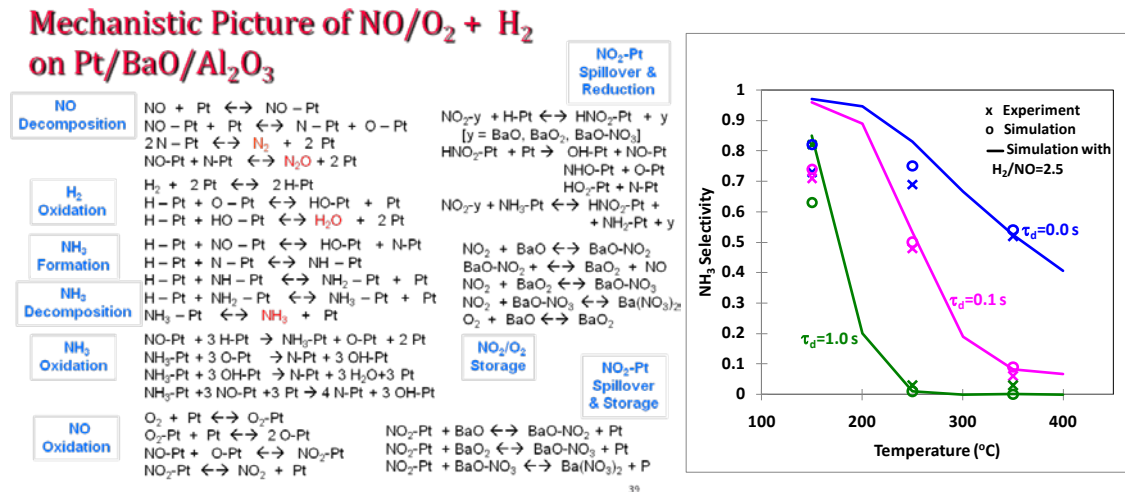


Figure 1. Overall microkinetic model for NO_x storage and reduction on Pt/BaO/Al₂O₃.

Figure 2. Dependence of NH₃ selectivity on temperature for three different delay times during the pump-probe experiment of NO + H₂ on Pt/BaO/Al₂O₃.

Task 2:

Evaluate performance of the model NO_x storage and reduction (NSR) catalysts in a bench scale NO_x trap using synthetic lean burn and diesel exhaust, with particular attention placed on differences in reductant type and injection protocols.

Success Criterion: The bench scale experiments will be considered successful if we can generate lightoff and NO_x conversion data using different reductants and injection policies. Publication of at least two peer reviewed articles containing this type of data will be considered as a success criterion.

Accomplishments:

Earlier in the project we carried out systematic studies of small cores of Pt/BaO monolith catalysts to better understand the main performance features of the storage and reduction processes. These studies led to more detailed studies of spatio-temporal behavior, Pt dispersion effects, and NO oxidation. These are highlighted below.

Steady-State Multiplicity in a Lean NO_x Trap Using Propylene as the Reductant:

Multiplicity was experimentally observed during steady-state and periodic lean NO_x reduction with C₃H₆ on a model Pt/BaO/Al₂O₃ monolithic catalyst. The dependencies of the monolith temperature, hydrocarbon and NO_x conversion were determined as a function of feed temperature in both steady-state and periodic operation. The nonisothermal multiplicity is attributed to the exothermic propylene oxidation and thermal feedback in the solid phase. The steady-state NO_x conversion achieves a maximum within the region of multiplicity and very near the extinction point. Periodic experiments, which involve switching between lean and rich operation, reveal an expanding region of multiple states as the amount of propylene is increased by increasing the rich pulse duration. A NO_x trap reactor model confirms the existence of multiple branches of states during both steady-state and periodic operation, and captures the main trends that are experimentally observed.

[Further details in **Paper 2** listed below.]

Steady-State Reduction of NO with H₂ in O₂ on Pt/BaO Monolith Catalysts:

Comprehensive steady-state experiments of the selective catalytic reduction of NO on a series of Pt, Pt/BaO, and BaO monolithic catalysts were carried out to evaluate the light-off, NO_x conversion and product distribution features as a function of the feed composition, temperature and catalyst composition. The reaction between NO and H₂ produces a mixture containing N₂O, NH₃, and N₂, the composition of which is a function of the catalyst temperature and NO/H₂ ratio in the feed. NO inhibits the reaction at low temperatures as revealed by light-off temperature and supporting kinetic data. NO_x conversions were found to be complete at space velocities below 90,000 hr⁻¹ and above 100 °C for Pt loadings exceeding 1.27 wt. %. At low temperature and O₂ concentration the NO-H₂ reaction mainly produces N₂O and is positive(negative) order in H₂ (NO). The light-off temperature of the NO-H₂ system is dictated by these kinetics as well as the Pt loading. Complementary theoretical analyses elucidate selected kinetic trends and the

effect of Pt loading on the conversion versus temperature trends. The NO-H₂-O₂ data are interpreted with a phenomenological reaction network model. Particular attention focused on the production and consumption of ammonia, a problematic byproduct during conventional NO_x storage and reduction (NSR). NH₃ is a major product under O₂ deficient conditions typical of the rich pulse in NSR, while N₂ and N₂O are the main products at higher O₂ concentrations (lean conditions). NH₃ oxidation ignites on Pt catalysts at 170-180 °C; in the ignited state a mixture of N₂, NO, NO₂ and N₂O is produced, the composition of which is sensitive to the NH₃/O₂ feed ratio and temperature. Experiments involving a feed containing H₂, NH₃, and NO reveal that H₂ is a much more effective reductant than NH₃. For temperatures exceeding 150 °C an equimolar mixture of the three components results in complete NO reduction by H₂ with negligible conversion of NH₃. The decomposition of NH₃ is observed above 330 °C but is kinetically inhibited by H₂. A comparison of the Pt and Pt/BaO catalysts reveals similar steady-state behavior. The BaO catalyst exhibited a non-negligible but lower activity and a different product distribution than the Pt and Pt/BaO catalysts.

[Further details in **Paper 4** listed below.]

Performance Studies of the Lean NO_x Trap Using H₂ as the Reductant

The performance of a model Pt/BaO/Al₂O₃ monolith catalyst was studied using H₂ as the reductant. The dependence of product selectivities on operating parameters is reported; including the durations of regeneration and storage times, feed composition and temperature, and monolith temperature. The data are explained in terms of a phenomenological model factoring in the transport, kinetic, and spatio-temporal effects. The Pt/BaO catalyst exhibits high cycle-averaged NO_x conversion above 100 °C, generating a mixture of N₂ and byproducts NH₃ and N₂O. The cycle-averaged NO_x conversion exhibits a maximum at about 300 °C corresponding to the NO_x storage maximum. The N₂ selectivity exhibits a maximum at a somewhat higher temperature, at which point the NH₃ selectivity exhibits a minimum. This trend conveys the intermediate role of NH₃ in reacting with stored NO_x. Both N₂ and N₂O are also formed during the storage steps from the oxidation of NH_x species produced during the regeneration.

[Further details in **Paper 6** listed below.]

Spatio-Temporal Features of the Lean NO_x Trap Using H₂ as the Reductant

The regeneration of a model Pt/BaO/Al₂O₃ monolith catalyst was studied with hydrogen as the reductant to elucidate the reaction pathways to molecular nitrogen and ammonia. NO_x storage and reduction experiments (NSR) were conducted with a 2 cm length monolith for a wide range of feed conditions. The NSR experiments were replicated for a series of monoliths of progressively decreasing length, enabling the construction of spatio-temporal profiles of reactant and product concentrations. The results show that there are two primary competing routes to the desired N₂ product; specifically a direct route from the reduction of stored NO_x by H₂ ($\text{H}_2 + \text{NO}_x \rightarrow \text{N}_2$) or by a sequential route through NH₃ ($\text{H}_2 + \text{NO}_x \rightarrow \text{NH}_3$; $\text{NH}_3 + \text{NO}_x \rightarrow \text{N}_2$). A comparison between H₂ and NH₃ as reductant feeds during NSR revealed H₂ is a more effective reductant in terms of NO_x conversion for temperatures below approximately 230 °C. At higher temperatures (230 to 380 °C), the regeneration of stored NO_x is feed-limited and the difference between the reductants H₂ and NH₃ is found to be small with

H₂ being a slightly superior reductant. Experimental measurements of the traveling front velocity are compared with a simple feed-limited model that assumes complete consumption of H₂ as stored NO_x is depleted. At lower temperatures the regeneration is limited by chemical processes at the Pt/Ba interface. The findings are pieced together to establish a phenomenological description of the spatio-temporal features of the lean NO_x trap with hydrogen as the reductant.

[Further details in **Paper 5** listed below.]

Pt Dispersion Effects on Activity and Selectivity of the Lean NO_x Trap

This study provides insight into the effect of Pt dispersion on the overall rate and product distribution during NO_x storage and reduction. The storage and reduction performance of Pt/BaO/Al₂O₃ monoliths with varied Pt dispersion (3, 8, and 50%) and fixed Pt (2.36 wt.%) and BaO (12.7 wt.%) loadings is reported. At low temperature (<200 °C), the differences in storage and reduction activity were the largest between the three catalysts. The amount of NO_x stored increased with increased dispersion, as did the amount of stored NO_x that was reduced. These trends are attributed to larger Pt surface area and Pt-BaO interfacial perimeter, the latter of which enhances the spillover of surface species between the precious metal and storage components. At high temperature (370 °C), the stored NO_x was almost completely regenerated for the three catalysts. However, the regeneration of the 3% dispersion catalyst was much slower, suggesting a rate limitation involving the reverse spillover of stored NO_x to Pt and/or of adsorbed hydrogen from Pt to BaO. The results indicate that the catalyst dispersion and operating conditions may be tuned to achieve the desired ammonia selectivity. For the aerobic regeneration feed, the most (net) NH₃ was generated by the 50% dispersion catalyst at the lowest temperature (125 °C), by the 3% dispersion catalyst at the highest temperature (340 °C), and by the 10% dispersion catalyst at the intermediate temperatures (170 - 290 °C). Similar trends were observed for the net production of NH₃ with an anaerobic regeneration feed. A phenomenological picture is proposed that describes the effects of Pt dispersion consistent with the established spatio-temporal behavior of the lean NO_x trap.

[Further details in **Paper 11** listed below.]

NO Oxidation Study:

Modeling and experimental studies on model Pt/Al₂O₃ and Pt/BaO/Al₂O₃ catalysts are performed to elucidate the kinetics of NO oxidation, which is a key step during the lean phase of NO_x trap operation. Experiments show that a steady state is never truly achieved during NO oxidation; a continuous decrease in the reaction rate with time is observed on both the catalysts. This decrease is distinct from and beyond the prompt inhibition of the NO oxidation reaction observed with NO₂ in the feed or product. NO oxidation carried out after catalyst pretreatments with H₂, O₂ and NO₂ indicates that NO₂ is responsible for the deactivation while NO₂ storage plays a negligible role. Experiments with NO₂ as the feed elucidate its role in the production of NO, either by storage or decomposition, for a wide range of temperatures. The highly oxidizing nature of NO₂ suggests that the Pt surface could be covered with oxygen, either as chemisorbed O or as Pt oxides, which results in slow poisoning of the catalyst. Microkinetic analysis of the NO oxidation reaction shows O₂ adsorption as the rate determining step and

predominant surface species to be adsorbed NO and O. Based on the microkinetic studies, a global kinetic model is proposed which includes the inhibiting effect of NO₂ on the NO oxidation reaction. The importance of including coverage of NO in the global model at low temperatures is shown, which is neglected in the current literature global models. The model predicts the experimental observations for a wide range of temperatures within acceptable error limits. However, prediction of the transient data requires modeling of NO₂ storage, decomposition and the complex NO₂ inhibition chemistry in addition to other surface reactions.

[Further details in **Paper 13** listed below.]

H₂ Oxidation Study:

Recently developed criteria are used to characterize the various controlling regimes (kinetic, pore diffusion and mass transfer controlled) during H₂ oxidation on Pt/Al₂O₃ monolithic catalyst. The hydrogen conversion was measured over a wide range of temperatures and space velocities. Experiments at typical space velocities (10⁴-10⁵ 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 °C 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.

[Further details in **Paper 20** listed below.]

Task 3:

(a) Develop and analyze a first-principles based predictive lean NO_x trap model that incorporates a detailed understanding of the chemistry and transport processes.

Success Criterion: Development of a NO_x trap model (in the form of a computer code) that can predict the bench scale experiments quantitatively. This code will be part of the deliverables (see below). Publication of two peer-reviewed articles that compare the model predictions to bench-scale experimental studies and/or explore other reactor configurations that optimize LNT performance will be considered a success criterion.

Accomplishments:

A large number of bench scale experiments were carried out to provide basic data for development of models of NO_x storage and reduction. A LNT model based on global kinetics was developed to predict the main spatio-temporal features using H₂ as the

reductant. We found that incorporation of gradients at the scale of the Pt crystallites was necessary to predict certain trends for lower dispersion catalysts. Detailed modeling of the NO_x trap was carried out using kinetic parameters determined in the bench reactor and tested in TAP reactor experiments. The success in predicting the TAP data provided incentive to pursue the development of the microkinetic model of the complete NO_x storage and regeneration cycle. In simulations of the overall cycle carried out during the final months of the project, several of the features observed experimentally are captured by the model, including the so-called “NO_x puff” during the initial part of the regeneration as well as the breakthrough of H₂ and the plug-like evolution of NH₃. (See example results in Figure 102.) This work was completed with former UH doctoral graduate, Dr. Jin Xu, who is now a faculty member in China. Our plan to complete the development of this model so it can be used in subsequent studies focused on ammonia generation during the regeneration step for LNT/SCR applications.

Microkinetic Models for Steady-State NO Reduction on Pt/BaO/Al₂O₃ Catalysts:

Experimental results describing the product distribution during the reduction of NO by H₂ on Pt/Al₂O₃ and Pt/BaO/Al₂O₃ catalysts are presented in the temperature range 30-500°C and H₂/NO feed ratio range of 0.9 to 2.5. A microkinetic model that describes the kinetics of NO reduction by H₂ on Pt/Al₂O₃ is proposed and most of the kinetic parameters are estimated from either literature data or from thermodynamic constraints. The microkinetic model is combined with the short monolith flow model to simulate the conversions and selectivities corresponding to the experimental conditions. The predicted trends are in excellent qualitative and reasonable quantitative agreement with the experimental results. Both the model and the experiments show that N₂O formation is favored at low temperatures and low H₂/NO feed ratios, N₂ selectivity increases monotonically with temperature for H₂/NO feed ratios of 1.2 or less but goes through a maximum at intermediate temperatures (around 100°C) for H₂/NO feed ratios 1.5 or higher. Ammonia formation is favored for H₂/NO feed ratios of 1.5 or higher and intermediate temperatures (100 to 350°C) but starts to decompose at a temperature of 400°C or higher. The microkinetic model is used to determine the surface coverages and explain the trends in the experimentally observed selectivities.

A steady-state microkinetic model for NO reduction by H₂ and NH₃ in O₂ on alumina supported Pt/BaO monolith catalysts is developed based on the measurements from a parallel experimental study (Clayton et al., Appl. Catal. B. Environ., 2008). The microkinetic model describes pertinent Pt-catalyzed regeneration chemistry during NO_x storage and reduction with H₂. Kinetic parameters not available from the literatures are estimated to capture the experimental trends and to meet thermodynamic constraints. The kinetic model is incorporated into a short monolith reactor model to simulate the steady state NH₃/O₂, NH₃/NO and NO/NH₃/H₂ reaction systems. The predicted conversion and product distribution are in excellent qualitative and good quantitative agreement with the experimental data. Among other features, the model predicts for the three reaction systems the nonlinear light-off, and the product selectivity dependencies on temperature and feed composition. The model predicted trends in the species surface coverages with operating conditions help to elucidate the selectivity trends. A sensitivity analysis of the rate constants identified the critical steps in the reaction network. The effect of external mass transfer on the conversions and product distributions are assessed and discussed.

[Further details in **Papers 3 and 8** listed below.]

Global Model of a Pt/BaO/Al₂O₃ Lean NO_x Trap Using H₂ as the Reductant:

A global kinetic model for NO_x storage and reduction for the case of anaerobic regeneration with hydrogen is developed, based on parallel experimental studies from our group. The existence of two different types of BaO storage sites on the catalyst is proposed, which differ in their storage as well as regeneration activity. The two-site model explains the close to complete NO_x storage at the start of the storage phase and the gradual emergence of NO and NO₂ during later storage times. The effluent concentrations and concentration fronts of the reactants and products within the monolith are predicted by the model, providing insight into the mechanisms of regeneration and storage. The H₂ front velocities are predicted to increase as the H₂ front propagates down the length of the monolith, thus showing the presence of more stored NO_x in the front of the reactor. Figure 3 shows an example comparison of experimental measurements and model predictions. The simulations show that even though regeneration is fast, H₂ concentration fronts are not very steep, which is attributed to the lower regeneration activity of the “slow” sites. The model captures the formation of NH₃ and the NH₃ concentration fronts, which reveal the reaction of NH₃ formed upstream with the stored NO_x downstream of the H₂ front. The lower diffusivity of NH₃ as compared to H₂ is shown to be responsible for the wider width of the NH₃ front and earlier appearance of NH₃ in the effluent than H₂.

[Further details in **Papers 5 and 14** listed below.]

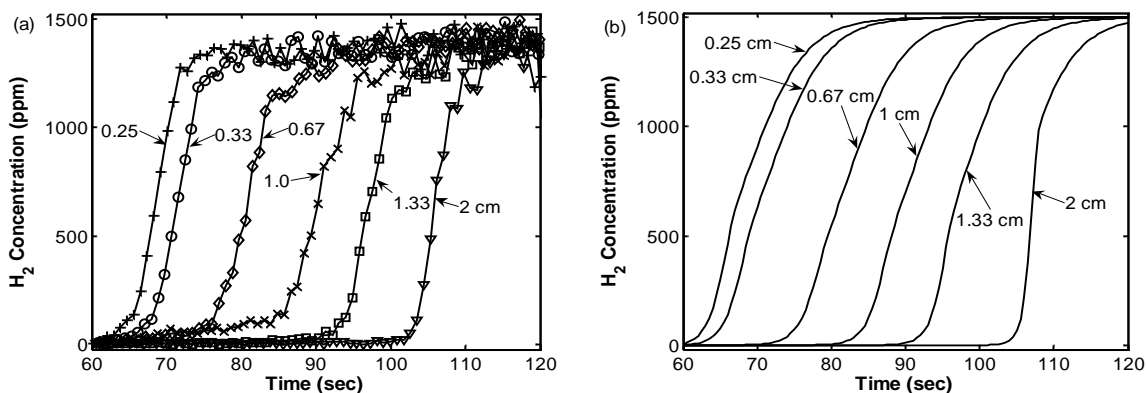


Figure 3. Example simulation using a LNT model comprising global kinetic description. The conditions are 340 °C with a 60 second storage and 30 second regeneration using an anaerobic feed of H₂.

Modeling of Pt Crystallite Size Effect on NO_x Storage and Reduction:

A crystallite-scale model is incorporated into a reactor-scale model to study the effect of Pt dispersion and temperature during the regeneration of a lean NO_x trap (LNT), based on a parallel experimental study [R.D. Clayton, M.P. Harold, V. Balakotaiah, C.Z. Wan, Appl. Catal., B 90 (2009) 662.]. It is shown that for a fixed Pt loading, an increase in the Pt dispersion results in an increase in the interfacial perimeter between Pt and Ba, where the reduction of NO_x takes place. The rate determining process during the regeneration is found to be the diffusion of stored NO_x within the Ba phase towards the

Pt/Ba interface. The transient product distribution for three catalysts having varied Pt dispersions (3.2%, 8% and 50%) is explained by the localized stored NO_x gradients in the Ba phase. Temperature-dependent NO_x diffusivities in the Ba phase are used to predict the breakthrough profiles of H₂, N₂ and NH₃ over a range of catalyst temperatures. Figure 4 compares experimental data with model predictions. Finite gradients in the stored NO_x concentration are predicted in the Ba phase, thus showing that the nitrate ions are not sufficiently mobile at lower temperatures for the low dispersion catalysts. The model predicts that the highest amount of NH₃ is produced by the low dispersion catalyst (3.2% dispersion) at high temperatures, by the high dispersion catalyst (50% dispersion) at low temperatures, and by the medium dispersion catalyst (8% dispersion) at intermediate temperatures, which is consistent with the experimental data. The model considers the consumption of chemisorbed oxygen on Pt by H₂, which is used to predict the low effluent N₂ concentration for the 50% dispersion catalyst as compared to the 8% dispersion catalyst. Finally, a novel design is proposed to maximize the amount of NH₃ in the effluent of a LNT, which can be used as a feed to a selective catalytic reduction (SCR) unit placed downstream of the LNT. [Further details in **Papers 5, 11, and 19** listed below.]

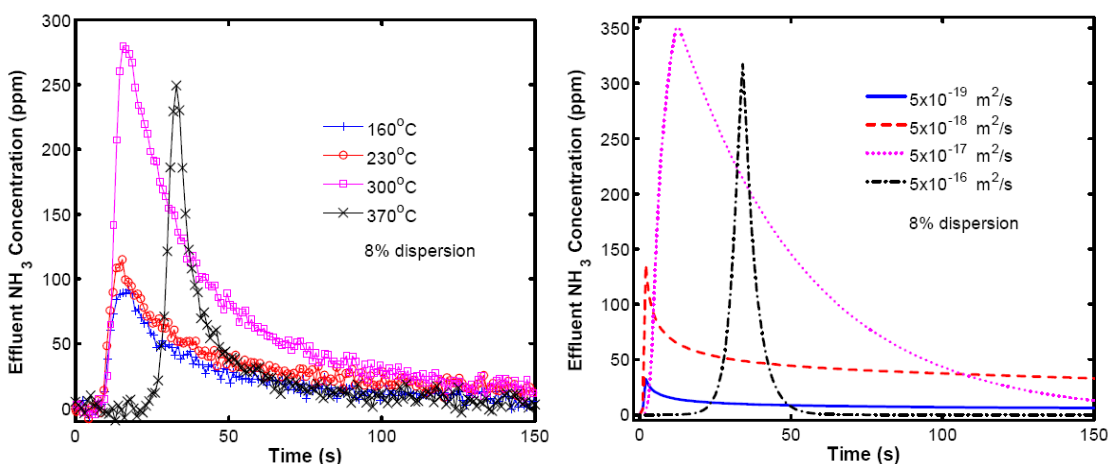


Figure 4. Example simulation using a LNT model comprising global kinetic description of the regeneration chemistry as well as crystallite level gradients. The conditions are 340 °C with a 60 second storage and 30 second regeneration using an anaerobic feed of H₂.

Microkinetic Models for NO_x Storage and Reduction on Pt/BaO/Al₂O₃ Catalysts:

A NO_x storage model with two types of barium sites was systematically developed. A kinetic model for NO₂ storage on BaO via gas-surface reactions was evaluated by comparing with the experimental measurements. The model parameters were modified by a fit of the data. Then a parametric sensitivity study was carried out to identify the relative importance of different gas-surface reactions. It was shown that several of the reactions are slow and can be neglected. The formation of Ba(NO₃)₂ on BaO (without Pt) is a slow process and can be neglected for the practical storage time during an NSR operation.

The sensitivity study also provided clues for the development of the spillover chemistry at the Pt-BaO interface. Two spillover reaction steps were proposed without increasing the number of surface species, and an estimation of the rate constants were carried out based on a series of assumptions. A storage model was constructed to include NO oxidation on Pt, NO_x storage reactions between gas and barium surface species, and spillover reactions between platinum and barium surface species. Barium sites in the proximity of Pt and far from Pt particles were also differentiated during the model development. The model captured the major trends of experimental measurements. Specifically, the Pt promoted NO_x storage and nonmonotonic NO (NO₂) effluent concentration as a function of Pt loading in the short time range of NO₂ (NO) storage were predicted. The dependence of surface reaction rates on catalyst loading was discussed based on physical analysis. Two qualitative contradictions between the model predictions and experimental observations were investigated. One experimental observation missed by the model predictions is the high NO formation peak in the short time range, which indicates that the dependence of proximal barium sites on Pt concentration is not linear but of a lower order. An upper bound of proximal barium concentration was estimated to be in the range of 140 – 180 mol/m³. The other contradiction is a secondary NO storage feature probably due to support effects.

The present model is able to predict an accurate NO_x breakthrough point and significant nitrate formation of NO storage on B3 catalyst in the presence of O₂, and meets the requirements of the current study. This storage model, without further modifications, was used to simulate the cyclic NSR experiments conducted on B3 catalyst. Good agreements with experimental data were obtained and the result will be documented in a forthcoming publication that is in preparation. Figure 5 shows representative simulation results from this model. The model captures key trends in the data including the NO_x puff and delayed appearance of NH₃ in the effluent. The model also predicts the

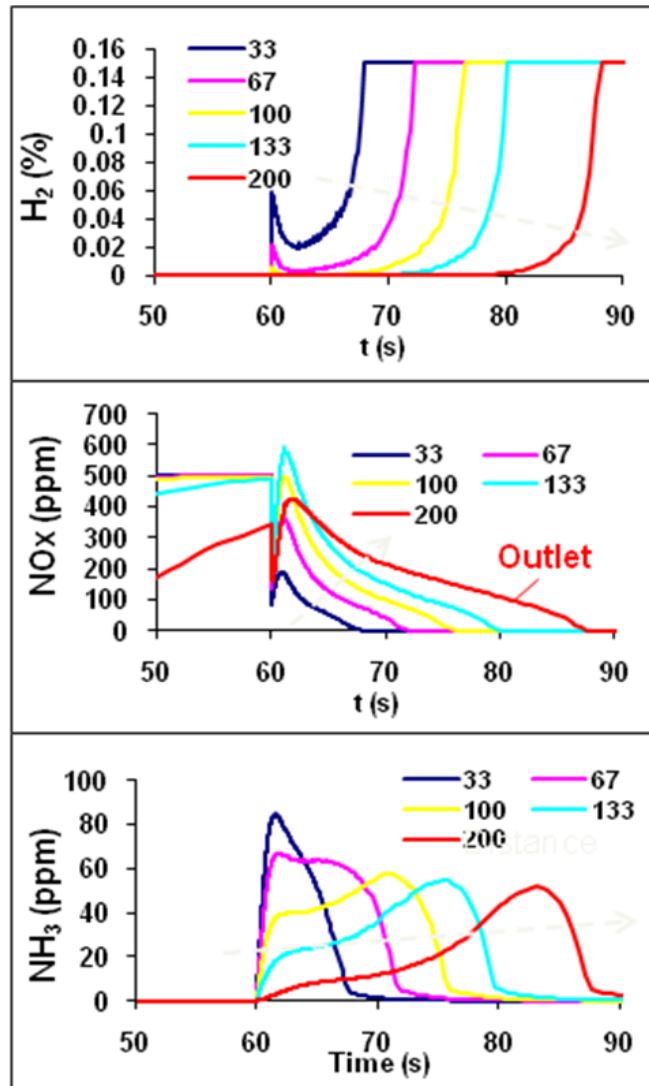


Figure 5. Example simulation using the full microkinetic model comprising the reaction steps shown in Figure 5. The conditions are 340 °C with a 60 second storage and 30 second regeneration using an anaerobic feed of H₂.

formation of N₂O at the beginning of the regeneration, in agreement with the experiments. Further tuning of the model is needed.
[Details in **Paper 21** listed below.]

Task 4:

Test prototype NSR device in the exhaust of an actual or simulated diesel vehicle.

Success Criterion: Testing and successful demonstration of at least one NO_x trap on the exhaust stream of a commercial vehicle.

Accomplishments:

In the current project we were not able to evaluate NSR catalysts with actual vehicle exhaust. The expansion of the UH “Texas Diesel Testing and Research Center” required a longer period of construction than was anticipated. (The expansion was funded by the Texas Commission on Environmental Quality.) This delayed the completion of the bench-scale reactor until well into the fourth year of the current project. The system was eventually completed but the exhaust from the heavy-duty chassis and engine dynamometers is still underway. Alternatively, a single cylinder engine experiment was completed and is now generating diesel exhaust for use in the bench-scale reactor system. We anticipate using these facilities in the new DOE Vehicle Technologies grant.

Additional Activities and Accomplishments

In work that primarily utilized funding from Ford with additional funds from DOE, we carried out more fundamental/generic studies of transport and reaction in catalytic monolith reactors.

Co-oxidation of CO and H on Pt/Al₂O₃: Interaction Effects on the Light-Off Behavior:

Both microkinetic and global kinetic models were developed to predict the co-oxidation of H₂ and CO on Pt-based catalysts. A bifurcation analysis was also carried out to predict the effect of each species on the light-off. A comparison of the light off curves generated using the global model and microkinetic model is done and the effect of rate parameters on the region of multiplicity is investigated.

[Further details in **Paper 9** listed below.]

Low Dimensional Models for Real Time Simulations of Catalytic Monoliths:

In this study we present accurate low-dimensional models for real time simulation, control and optimization of monolithic catalytic converters used in automobile exhaust treatment. These are derived rigorously using the Liapunov-Schmidt (LS) technique of bifurcation theory and are expressed in terms of three concentration and two temperature modes. They include washcoat diffusional effects without using the concept of effectiveness factor and reduce to the classical two-phase models in the limit of vanishingly thin washcoat. The models are validated by comparing the solutions with the exact solution for some special cases and their usefulness is illustrated by simulating the transient behavior of the three-way converter and comparing the predictions with

detailed solution. It is shown that these new models are robust and accurate with practically acceptable error, speed up the computations by orders of magnitude, and can be used with confidence for the real time simulation and control of monolithic and other catalytic reactors.

[Further details in **Paper 12** listed below.]

Internal Mass Transfer Coefficients in Catalytic Monoliths:

We utilize the recently developed concept of internal or intraphase mass transfer coefficient to simplify the problem of diffusion and reaction in more than one spatial dimension for a washcoated monolith of arbitrary shape. We determine the dependence of the dimensionless internal mass transfer coefficient (Sh_i) on washcoat and channel geometric shapes, reaction kinetics, catalyst loading and activity profile. It is also reasoned that the concept of intraphase transfer coefficient is more useful and fundamental than the classical effectiveness factor concept. The intraphase transfer coefficient can be combined with the traditional external mass transfer coefficient (Sh_e) to obtain an overall mass transfer coefficient (Sh_{app}) which is an experimentally measurable quantity depending on various geometric and transport properties as well as kinetics. We present examples demonstrating the use of Sh_{app} in obtaining accurate macro-scale low-dimensional models of catalytic reactors by solving the full 3-D convection-diffusion-reaction problem for a washcoated monolith and comparing the solution with that of the simplified model using the internal mass transfer coefficient concept.

[Further details in **Paper 15** listed below.]

Controlling Regimes in Catalytic Monoliths:

It is well known that the performance of a catalytic monolith is bounded by two limits: the kinetic regime at low temperatures (or before the ignition for the case of exothermic reactions) and the external mass transfer controlled regime at sufficiently high temperatures (or after the ignition). The washcoat diffusional resistance can also be significant over an intermediate range of temperatures. The transition temperatures at which the controlling regime changes from kinetic to washcoat diffusion to external mass transfer depend on the various geometric properties of the monolith, flow properties, the catalyst loading and washcoat properties. We present analytical criteria for determining these transition temperatures. These are derived using the recently developed low-dimensional model and the concepts of internal and external mass transfer coefficients. The criteria are more general than those in the literature and are useful in analyzing the experimental data. Further, we present an explicit expression for the experimentally measurable dimensionless apparent mass transfer coefficient (Sh_{app}) in terms of individual transfer coefficients in each phase. It is shown that Sh_{app} can be lowered by orders of magnitude compared to the theoretical upper bound obtained in the limit of external mass transfer control. Low values of Sh_{app} are obtained due to a small value of effective diffusivity in the washcoat, low catalyst loading or a reaction with low activation energy. The analytical criteria may be used for the design of monolith properties and experimental conditions so that the performance of the monolith approaches the upper limit defined by the external mass transfer controlled limit.

[Further details in **Papers 17 and 20** listed below.]

Reports/Publications/Presentations

Reports: Quarterly Report (10/1/07 – 12/31/07);
Quarterly Report (1/1/08 – 3/31/08)
Quarterly Report (4/1/08 – 6/30/08);
Annual Report (7/1/08 – 8/15/08)
Quarterly Report (10/1/08 – 12/31/08);
Quarterly Report (1/1/09 – 3/31/09)
Quarterly Report (4/1/09 – 6/30/09);
Quarterly Report (7/1/09 – 9/30/09)

Refereed Journal Publications (from project start):

Paper 1: Medhekar, V., V. Balakotaiah, and M.P. Harold, “TAP Study of NO_x Storage and Reduction on Pt/Al₂O₃ and Pt/Ba/Al₂O₃,” *Catalysis Today*, **121**, 226-236 (2007).

Paper 2: Sharma, M., R.D. Clayton, M.P. Harold, and V. Balakotaiah, “Multiplicity in Lean NO_x Traps,” *Chem. Engng. Science*, **62**, 5176-5181 (2007).

Paper 3: Xu, J., R.D. Clayton, V. Balakotaiah and M.P. Harold, “Experimental and Microkinetic Modeling of Steady-State NO Reduction by H₂ on Pt/BaO/Al₂O₃ Monolith Catalysts,” *Appl. Catal. B. Environmental*, **77**, 395-408 (2008).

Paper 4: Clayton, R.D., M.P. Harold, and V. Balakotaiah, “Selective Catalytic Reduction of NO by H₂ in O₂ on Pt/BaO/Al₂O₃ Monolith NO_x Storage Catalysts,” *Appl. Catal. B. Environmental*, **81**, 161-181 (2008).

Paper 5: Clayton, R.D., M.P. Harold, and V. Balakotaiah, “NO_x Storage and Reduction with H₂ on Pt/BaO/Al₂O₃ Monolith: Spatio-Temporal Resolution of Product Distribution,” *Appl. Catal. B. Environmental*, **84**, 616-630 (2008).

Paper 6: Clayton, R.D., M.P. Harold, and V. Balakotaiah, “Performance Features of Pt/BaO Lean NO_x Trap with Hydrogen as Reductant,” *AIChE J.*, **55**, 687-700 (2009).

Paper 7: Kumar, A., V. Medhekar, M.P. Harold, and V. Balakotaiah, “NO Decomposition and Reduction on Pt/Al₂O₃ Powder and Monolith Catalysts Using the TAP Reactor,” *Appl. Catal. B. Environmental*, **90**, 642-651 (2009).

Paper 8: Xu, J., M.P. Harold, and V. Balakotaiah, “Microkinetic Modeling of Steady-State NO/H₂/O₂ on Pt/BaO/Al₂O₃ Monolith Catalysts,” *Appl. Catal. B. Environmental*, **89**, 73-86 (2009).

Paper 9: Bhatia, D., V. Balakotaiah and M.P. Harold, “Kinetic and Bifurcation Analysis of the Co-Oxidation of CO and H₂ in Catalytic Monolith Reactors.” *Chem. Eng. Sci.*, **64**, 1544-1558 (2009).

Paper 10: Kumar, A., V. Medhekar, M.P. Harold, and V. Balakotaiah, “NO Decomposition and Reduction on Pt/Al₂O₃ Powder and Monolith Catalysts Using the TAP Reactor,” *Appl. Catal. B. Environmental*, **90**, 642-651 (2009).

Paper 11: Clayton, R.D., M.P. Harold, V. Balakotaiah, and C.Z. Wan “Effect of Pt Dispersion on NO_x Storage and Reduction in Pt/BaO/Al₂O₃ Catalyst,” *Appl. Catal. B. Environmental*, **90**, 662-676 (2009).

Paper 12: Joshi, S.Y., M.P. Harold, and V. Balakotaiah, “Low-dimensional Models for Real Time Simulations of Catalytic Monoliths”, *AIChE Journal*, **55**, 1771-1783 (2009).

Paper 13: Bhatia, D., V. Balakotaiah, M.P. Harold, and R. McCabe, “Experimental and

Kinetic Study of NO Oxidation on Model Pt Catalysts,” *J. Catalysis*, **266**, 106-119 (2009).

Paper 14. Bhatia, D., R.D. Clayton, M.P. Harold, and V. Balakotaiah, “A Global Kinetic Model for NO_x Storage and Reduction on Pt/BaO/Al₂O₃ Monolithic Catalysts,” *Catalysis Today*, **147S**, S250-S256 (2009).

Paper 15. Joshi, S., M.P. Harold, and V. Balakotaiah, “On the use of Internal Mass Transfer Coefficients in Modeling of Diffusion and Reaction in Catalytic Monoliths”, *Chem. Eng. Sci.*, **64**,4976-4991 (2009).

Paper 16. Harold, M.P., and V. Balakotaiah, “Catalytic After-treatment of NO_x from Diesel Exhaust,” *McGraw-Hill Yearbook of Science and Technology 2010*, McGraw-Hill, New York, 59-62 (2010).

Paper 17. Joshi, S., M.P. Harold, and V. Balakotaiah, “Overall Mass Transfer Coefficients and Controlling Regimes in Catalytic Monoliths, *Chem. Eng. Sci.*, **65**, 1729-1747 (2010).

Paper 18. Kumar, A., M.P. Harold, and V. Balakotaiah, “Isotopic TAP Studies of NO Decomposition and Reduction on Pt/BaO/Al₂O₃ Catalysts,” *J. Catalysis*, doi:10.1016/j.jcat.2009.12.018 (2010).

Paper 19. Bhatia, D., R.D. Clayton, V. Balakotaiah, and M.P. Harold, “Modeling the Effect of Pt Dispersion and Temperature During Anaerobic Regeneration of a Lean NO_x Trap Catalyst,” *Catalysis Today* **151**, 314–329 (2010).

Paper 20. Joshi, S., Y. Ren, M.P. Harold, and V. Balakotaiah, “Determination of Kinetics and Controlling Regimes for H₂ Oxidation on Pt/Al₂O₃ Monolithic Catalyst Using High Space Velocity Experiments,” *Appl. Catal. B. Environ.*, under review (May, 2010).

Paper 21. Xu, J., M. Harold, and V. Balakotaiah, “Microkinetic Modeling of NO_x Storage on Pt/BaO/Al₂O₃ Catalysts: Pt Loading Effects,” *Appl. Catal. B. Environ.*, under review (June, 2010).

Paper 22. Kumar, A., M.P. Harold, and V. Balakotaiah, “Estimation of Stored NO_x Diffusion Coefficient in NO_x Storage and Reduction,” *I&EC Research*, 10.1021/ie100504q (2010).

Paper 23. Kumar, A., X. Zheng, M.P. Harold, and V. Balakotaiah, “Microkinetic Modeling of the NO + H₂ System on Pt/Al₂O₃ Catalyst Using Temporal Analysis of Products,” *J. Catalysis*, submitted for publication (August, 2010).

Conference and Other Presentations (from project start):

1. “Periodic NO_x Storage and Reduction (NSR) for Lean Burn Engines”, presented at AIChE Meeting, Cincinnati, 11/05 (with Manish Sharma and Vemuri Balakotaiah).
2. “TAP and Bench-Scale Reactor Studies of NO_x Storage and Reduction on Model Pt/BaO/Al₂O₃ and Pt/Al₂O₃,” presented at AIChE Meeting, Cincinnati, 11/05 (with Vinay Medhekar, presenter, Pranav Khanna, and Vemuri Balakotaiah).
3. Harold, M.P., CLEERS Conference, Mechanistic and Kinetics Studies of NO_x Storage and Reduction on Model Catalysts, Dearborn, MI, 5/06.
4. “Experimental Analysis and Mathematical Modeling of NO_x Storage and Reduction,” poster presented at the Spring 2006 Symposium of the Southwest Catalysis Society, Rice University, 5/06 (with Vinay Medhekar, presenter, and Vemuri Balakotaiah).

5. "Multiplicity in Lean NO_x Traps," poster presented at the International Symposium of Chemical Reaction Engineering, Berlin, Germany, 9/06 (with Manish Sharma, Robert Clayton, and Vemuri Balakotaiah, presenter).
6. "Modeling and Experimental TAP Studies on the Kinetics of NO_x Storage and Reduction over Pt/Al₂O₃ and Pt/BaO/Al₂O₃ Catalysts," presented at the AIChE National Meeting, San Francisco, CA, 11/06 (with Vinay Medhekar and Vemuri Balakotaiah).
7. "Steady State and Dynamic Studies of NO_x Storage and Reduction with H₂ on Pt/BaO/Al₂O₃ Monoliths," presented at the AIChE National Meeting, San Francisco, CA, 11/06 (with Robert Clayton, speaker, and Vemuri Balakotaiah).
8. "Modeling of NO_x Storage and Reduction in Catalytic Monolith Reactors," presented at the AIChE National Meeting, San Francisco, CA, 11/06 (with Jin Xu, speaker, and Vemuri Balakotaiah).
9. "Ammonia Formation During Steady-State and Cyclic Operation of the NO_x Trap with H₂ as the Reductant," Clayton, R., V. Balakotaiah, and M. Harold, NASCRE 2, Houston, TX, 2/07.
10. "Determination of the Microkinetics of NO_x Storage and Reduction on Pt/BaO/Al₂O₃ Catalysts Using TAP," Medhekar, V., V. Balakotaiah, and M. Harold NASCRE 2, Houston, TX, 2/07.
11. Harold, M.P., Department of Chemical Engineering, The University of Texas at Austin, *Multi-Functional Catalytic Reactors for NO_x Reduction and Hydrogen Generation*, 2/07.
12. "Ammonia and Nitrous Oxide Formation during NO_x Storage and Reduction on Pt/Ba Monolith Catalysts," North American Catalysis Society Conference, Houston, Texas, 6/07 (with Robert Clayton, presenter, and Vemuri Balakotaiah).
13. "Microkinetic Model Development of NO_x Storage and Reduction over Pt/BaO/Al₂O₃ Catalyst using Temporal Analysis of Product Reactor," North American Catalysis Society Conference, Houston, Texas, 6/07 (with Ashok Kumar, presenter, Vinay Medhekar, and Vemuri Balakotaiah).
14. Harold, M.P., Ford Motor Company, Corporate Research, *Spatio-Temporal Behavior of the Lean NO_x Trap*, Dearborn, MI 10/07.
15. Harold, M.P., Baker-Petrolite Inc., corporate Research, *Developments in Diesel Emission Control Technology at the University of Houston*, Sugarland, Texas, 10/07.
16. "Microkinetic Model Development for NO_x Storage and Reduction Over Pt/Ba/Al₂O₃ Catalysts Using Temporal Analysis of Products," presented at the AIChE National Meeting, Salt Lake City, UT, 11/07 (with Ashok Kumar, presenter and Vemuri Balakotaiah).
17. "Towards Optimal NO_x Trap Operation," presented at the AIChE National Meeting, Salt Lake City, UT, 11/07 (with Robert Clayton and Vemuri Balakotaiah).
18. "Low-Dimensional Models for Bifurcation Analysis of Catalytic Monolith Reactors," presented at the AIChE National Meeting, Salt Lake City, UT, 11/07 (with Saurabh Joshi, presenter, and Vemuri Balakotaiah).
19. "Microkinetic Modeling of Steady-State NO Reduction by H₂ on Pt/Ba/Al₂O₃ Monolith Catalysts," presented at the AIChE National Meeting, Salt Lake City, UT, 11/07 (poster; with Jin Xu and Vemuri Balakotaiah, presenter).
20. "Averaged Multi-Mode Models for Multiphase Catalytic Reactors," presented at the

- AICHE National Meeting, Salt Lake City, UT, 11/07 (poster; with Saurabh Joshi, presenter, and Vemuri Balakotaiah).
21. "Optimal Design of Three Way Catalytic Converters to Reduce Cold Start Emissions," presented at the AICHE National Meeting, Salt Lake City, UT, 11/07 (poster; with Divesh Bhatia, presenter, and Vemuri Balakotaiah).
 22. Harold, M.P., Department of Chemical Engineering, University of Florida, *Spatio-Temporal Behavior of the Lean NO_x Trap in Diesel Aftertreatment*, 3/08.
 23. Harold, M.P., Southwest Section of the North American Catalysis Society, *Elucidating Catalytic Chemistry and Spatio-Temporal Phenomena in the Lean NO_x Trap*, 4/08.
 24. "Spatio-Temporal Behavior of NO_x Storage and Reduction Monolith Catalysts," CLEERS Meeting, Dearborn, MI, 5/08 (with R.D. Clayton, A. Kumar, J. Xu, D. Bhatia, and V. Balakotaiah, speaker).
 25. "Bifurcation Analysis of CO and H₂ Oxidation on Pt/Al₂O₃ Monolith Reactors," ISCRE 20 Kyoto, Japan, 8/08 (poster; with D. Bhatia, presenter, V. Balakotaiah).
 26. "External and Internal Mass Transfer Coefficients in Washcoated Catalytic Monolith Reactors," ISCRE 20, Kyoto, Japan, 8/08 (poster; with S. Joshi, presenter, V. Balakotaiah).
 27. AICHE National Meeting, *Microkinetic Modeling of Steady-State NO/H₂/O₂ on Pt/BaO/Al₂O₃ NO_x Storage and Reduction Monolith Catalysts: The Role of NH₃*, Philadelphia, PA, 11/08 (with Jin Xu, presenter, V. Balakotaiah).
 28. AICHE National Meeting, *Elucidating the Role of the Pt/Ba Interface During NO_x Storage and Reduction on Model Pt/BaO/Al₂O₃ Catalyst*, Philadelphia, PA, 11/08 (with Ashok Kumar, presenter, V. Balakotaiah).
 29. AICHE National Meeting, *Bifurcation Analysis of CO and H₂ Oxidation on Pt/Al₂O₃ Monolith Reactors*, Philadelphia, PA, 11/08 (with Divesh Bhatia, presenter, V. Balakotaiah).
 30. AICHE National Meeting, *Modeling of Spatio-Temporal Effects in a Lean NO_x Trap Using Global Kinetics*, Philadelphia, PA, 11/08 (with Divesh Bhatia, presenter, V. Balakotaiah).
 31. Department of Mechanical Engineering, University of Houston, *Reduction of NO_x from Lean Burn Vehicle Exhaust: Technology Solutions from Simple to Complex*, 2/09.
 32. Division of Research, University of Houston, *Clean Diesel*, 2/09.
 33. CLEERS Conference, *Elucidating the Mechanism of NO_x Storage and Reduction*, Dearborn, MI, 4/09.
 34. North American Catalysis Society Meeting, *Experimental and Kinetic Investigations of NO_x reactions on Model Pt Catalysts*, San Francisco, CA, 6/09 (with D. Bhatia, speaker; R. McCabe, V. Balakotaiah).
 35. North American Catalysis Society Meeting, *Isotopic Studies of NO_x Storage and Reduction over Pt/BaO/Al₂O₃ using Temporal Analysis of Products*, San Francisco, CA, 6/09 (with A. Kumar, speaker; V. Balakotaiah).
 36. CLEERS Working Group, *Mechanistic and Kinetics Studies of NO_x Storage and Reduction on Model Catalysts, Isotopic Studies of NO_x Storage and Reduction over Pt/BaO/Al₂O₃ using Temporal Analysis of Products*, 6/09.

37. AIChE South Texas Section, *Catalytic Solutions to Achieve Clean Diesel Power*, 9/09.
38. International Conference on Structured Catalysts and Reactors, Ischia, Italy, *A Global Kinetic Model for NO_x Storage and Reduction on Pt/BaO/Al₂O₃ Monolithic Catalysts*, 9/09.
39. AIChE Annual Meeting, Nashville, TN, November, 2009, “Effects of Rh, CeO₂ and Regeneration Conditions during NO_x Storage and Reduction on Pt/BaO/Al₂O₃ Monolith Catalysts”, paper #547a (Y. Ren, R.D. Clayton, V. Balakotaiah and M. P. Harold).
40. AIChE Annual Meeting, Nashville, TN, November, 2009, “Modeling of Spatiotemporal Effects in a NO_x trap using Global Kinetics”, paper #547f (D. Bhatia, R.D. Clayton, V. Balakotaiah and M. P. Harold).
41. AIChE Annual Meeting, Nashville, TN, November, 2009, “Isotopic Studies of NO_x Storage and Reduction Over Pt/BaO/Al₂O₃ Monolith Catalysts”, paper #560c (A. Kumar, V. Balakotaiah and M. P. Harold).
42. AIChE Annual Meeting, Nashville, TN, November, 2009, “Modeling Studies on the Effect of Ceria on the Performance of a Lean NO_x Trap using H₂ as Reductant”, paper #487ak (with D. Bhatia, R.D. Clayton, V. Balakotaiah and M. P. Harold).
43. AIChE Annual Meeting, Nashville, TN, November, 2009, “Low-dimensional Models for Real Time Simulations of Catalytic Monoliths”, paper #487am (S. Y. Joshi and M. P. Harold and V. Balakotaiah).
44. AIChE Annual Meeting, Nashville, TN, November, 2009, “Internal Mass Transfer Coefficients for Modeling Multi-component Diffusion and Reaction in Washcoated Catalytic Monoliths”, paper #487an (S. Y. Joshi, M. P. Harold and V. Balakotaiah).
45. Harold, M.P., Catalysis Society of Michigan, *Catalytic Solutions to Achieve Clean Diesel Power*, 11/09.
46. Harold, M.P., Catalysis Club of Greater Chicago, *Catalytic Solutions to Achieve Clean Diesel Power*, 3/10.
47. Harold, M.P., Department of Chemical Engineering, University of Southern California, *Multifunctional Catalytic Reactors for Cleaner Energy and Air*, 4/10.

1. Special Recognitions & Awards/Patents Issued **Not applicable.**

Acronyms :

LNT = lean NO_x trap: The reactor which carries out NO_x storage and reduction (NSR).

TAP = Temporal Analysis of Products: Ultrahigh vacuum catalytic reactor system