Characterization of Adsorber Chemistry for LNT Catalysts, DOE Pre-Competitive Catalyst Research

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Objectives

- Quantify model LNT catalyst storage behavior between 150 and 400˚C to identify key reaction steps for simulation and engine optimization.
- Investigate regeneration behavior of model LNT catalysts.
- Inspect thermal deactivation effects with respect to NO_x capacity, surface area losses, and precious metal sintering.
- Investigate the poisoning effects of sulfur, the desulfation requirement of each model catalyst, and its relationship to thermal deactivation and overall catalyst aging.

Approach

- Effort is pre-competitive for easy dissemination of results across industry.
- Test model powder catalysts indicative of LNT technology
  - —$Pt/K/Al_2O_3$: 1% Pt, 8% K_2CO_3 on Al_2O_3
  - —$Pt/Ba/ Al_2O_3$: 1% Pt, 20% BaO on Al_2O_3
  - —50-100 g Pt/ft^3 equivalent
- Analyze surface species for validation of chemical behavior using ORNL's powerful Barrel Ellipse DRIFTS Reactor.
- Measure aging effects with respect to Pt size, catalyst surface area, NO_x capacity using high temperature treatments up to 900C while cycling between characteristic lean and rich conditions.
- Disseminate results openly to guide and validate modeling efforts and to immediately affect engine controls.

Accomplishments

- Full investigation of storage behavior at 150-450˚C; the results were immediately applied to ORNL's global model.
  - —Quantified DRIFT spectroscopy at all temperatures
  - —Identified kinetic limitations for LNTs at 150˚C
  - —Characterized thermodynamic limitations above 400˚C
- Identified limitations during catalyst regeneration and verified the importance of including H_2O in all valid simulated exhaust experiments.

- Developed unique reactor for simultaneous surface observation and kinetic measurements, which will be used to elucidate key steps of NO_x reduction to benign N_2.
- Developed testing procedure for measuring thermal deactivation that simulates 400,000 miles of operation in a 15-hour test.
  - —Demonstrated 65% less storage capacity for model catalysts at 760˚C.
  - —Demonstrated 50-90% loss in capacity at 900˚C.
- Demonstrated poisoning effects of sulfur in model LNT catalysts using a test procedure that simulates 126,000 miles of operation.
  - —Complete loss of capacity for both model catalysts.
  - —Desulfurization under rich conditions recovered 75% of capacity.

Future Directions

- Elucidate chemistry of catalyst regeneration with unique flow-through DRIFTS reactor. Include O_2 as a variable in regeneration investigation (2003 feedback)
- Elucidate Sulfur-based deactivation mechanisms and chemistry.
  - —Determine chemical form of sulfur-based species
  - —Elucidate the desulfation temperatures for each species
  - —Evaluate intermediate species formations to determine chemistry
- Establish DRIFTS reactor system to axial analyze washcoated substrate samples *in-situ*. Working with Englehard to use realistic systems that model a working channel of a catalyst.

Introduction

Under future vehicle regulations, the efficiency of a diesel engine system will also be correlated to the efficiency of the catalyst system since a fuel penalty is sustained to achieve the emissions requirements. Therefore, it is essential to have an efficiently functioning catalyst system in operation with a diesel engine. Modeling/simulating processes is an effective way to develop efficient systems, and basing the model on fundamental chemistry is critical for it to be transportable and broadly-useful to industry; parametric-based models will not fill the need.

The emphasis of this project is to improve detailed understanding of mechanisms limiting catalyst performance. Work closely with Catalyst-Industry representatives to identify and investigate pre-competitive catalyst-performance issues of broad relevance across the catalysis industry. Specific objectives are to improve the fundamental understanding of adsorption, reduction, poisoning processes and the influence of catalyst morphology. The objectives of this project are consistent with those of the Diesel Cross-Cut Team regarding details of sulfur poisoning and catalyst morphology effects.

Approach

Several efforts previously investigated under the Cummins/ORNL CRADA which are pre-competitive have been transferred to this project. This allows open dissemination of those research results, without confusing issues of CRADA protected information, and frees up CRADA funds to investigate protected topics. The transferred efforts are

primarily in the optical spectroscopy areas. Nevertheless, the two projects will continue to work closely to address both competitive and pre-competitive research issues.

ORNL will perform analysis of selected model catalyst samples with a focus on in-situ measurements in bench-scale reactors catalyst chemistry. Emerachem will provide in-kind support to the project including catalyst sample preparation and personnel to co-direct the project.

Results

Based on the full analysis of DRIFTS data between 150 and 400˚C, a storage mechanism has been proposed. NO can adsorb onto K-LNT only through the initial formation of a nitrite (NO_2^-) on a K site near Pt. This nitrite can be further oxidized to form an ionic nitrate (NO_3^-). The NO storage route is only of significant below 200˚C where Pt activity for NO oxidation to NO_2 is low. This is graphically depicted in Figure 1a. Once NO is Oxidized to NO_2, it can adsorb readily on K-LNT; through a "spillover" step near a Pt site or through a two-step disproportionation reaction on the K-phase. Both of these steps are depicted in Figure 1b. These results have been used in the model being developed at ORNL.

To better understand the chemistry that occurs during the regeneration of the catalyst, the MIDAC DRIFTS system was modified to allow meaningful kinetic information to be gathered at the same time as surface spectra. The reactor is equipped with 3 inches of heated length that is exposed on the front edge for DRIFTS measurements as depicted in Figure 2. The plug flow reactor is a classical kinetic regime with well-defined rate equations. The combination of this reactor with the surface measurements provided by DRIFTS offers a powerful and unique tool for fundamental studies.

A full array of thermal deactivation experiments was performed. Model K- and Ba-based Lean NO_x Traps (LNT) were studied to determine the effects associated with exposing the catalyst to elevated temperatures. The catalysts were sequentially heated to 500˚C, 600˚C, 760˚C, and 900˚C with catalyst evaluation after each temperature. A 15h test at 760˚C represents approximately 400,000 miles of driving. The test procedure was based on the initial feedback of the industrial survey for the Rapid-Aging Protocol. The results of these experiments are shown in Figure 3a for the K-LNT and Figure 3b for Ba-LNT. It is evident that catalyst function can be maintained at a significant level after heating up to 760˚C for both catalysts, but the catalysts, the Ba-LNT in particular, incur dramatic losses after 900˚C.

A complete series of sulfur poisoning experiments on model $Pt/K/Al_2O_3$ and $Pt/Ba/Al_2O_3$ catalysts were fully quantified and analyzed. The catalysts were poisoned with 140 ppm SO_2 at 250˚C for 24 hours, and then desulfated up to 760˚C. This is an extreme sulfur condition, but represents an LNT that has been fully poisoned after approximately 100,000 miles of driving. Figure 4a displays the sulfur treatment causes the NO_x storage capacity to diminish by 97% and 99% for $Pt/Ba/Al_2O_3$ and $Pt/K/Al_2O_3$ respectively. Effects on Pt were also monitored (Figure 4b), and interestingly the Pt on the K-based LNT was affected by SO_2 but not on the Ba-based LNT. This suggests that the potassium

sulfate phase may grow to the point that it covers some of the Pt that is on the $Pt/K/Al_2O_3$ catalyst. Future DRIFTS experiments will help to elucidate this phase change effect.

Desulfation under rich conditions of the $Pt/Ba/Al_2O_3$ released a significant amount SO_2 between 250 and 500˚C, but virtually no H_2S was observed, as shown in Figure 5a. Post desulfation, the storage capacity was 25% less than the initial measurement. Desulfation of the $Pt/K/Al_2O_3$ occurred in two phases as indicated in Figure 5b. Most of the S was removed as SO_2 with peak at 435˚C, but a second peak of SO_2 was also observed between 500 and 760˚C, with a peak at 575˚C. In conjunction with the release of SO_2 was the formation of H_2S with an initial peak at 400˚C and a second more substantial peak at 650˚C. Post desulfation the storage capacity for $Pt/K/Al_2O_3$ also decreases by 27% of the initial measurement.

These results from the deactivation studies correspond well with the observations from engine work. This suggests that a detailed kinetic and chemical analysis of the model catalysts will correspond well with real catalyst-engine. The continuing effort in FY2005 will focus on identifying the pathway that leads to deactivation of these representative model catalysts.

Conclusions

- DRIFTS measurements at 150-450˚C led to significant mechanistic findings for NOx storage
  - —NO is only significantly adsorbed on sites near Pt
  - —NO_2 is not adsorbed as a nitrite
  - —NO_2(g) can adsorb readily with/without Pt present
- At an equivalence of 400,000 miles, exposure of the catalyst at 760˚C results in a 65% loss in capacity, and about a 50% loss in precious metal surface area.
- 900˚C must be avoided due to extreme degradation of capacity (50-90%) and a 90% loss of precious metal surface area.
- Sulfur is a severe catalyst poison that if unchecked may render the catalyst inoperable after 100,000 miles.
- Extreme thermal treatments in rich conditions can reverse the poisoning effects of sulfur, but losses will be incurred as demonstrated in the thermal deactivation experiements.

FY 2004 Publications/Presentations

1. TJ Toops, DB Smith, WS Epling, JE Parks, WP Partridge, “Quantification of the *in-situ* DRIFT Spectra of Pt/K/gamma-Al_2O_3 NO_x Adsorber Catalysts”, Applied Catalysis B Environmental, in print.

2. TJ Toops, DB Smith, WS Epling, JE Parks, WP Partridge, “Quantified NO_x adsorption on Pt/K/gamma-Al_2O_3 and the Effects of CO_2 and H_2O”, Applied Catalysis B Environmental, in print.

3. TJ Toops, DB Smith, WP Partridge, "NO_x Adsorption of $Pt/K/Al_2O_3$ in the Presence of CO_2 and H_2O: an *in-situ* DRIFTS Study", National Laboratory Catalysis (NLCat)

Conference, Oak Ridge, Tennessee, October 22-24, 2003.

4. TJ Toops, DB Smith, WS Epling, JE Parks, WP Partridge, P6-076: "Lean NO_x Trap Chemical Behavior and Thermal Deactivation Effects ", 2004 DOE Advanced Combustion Review, May 18-20, 2004.

5. TJ Toops, DB Smith, WP Partridge, "Lean NO_X Trap Chemical Behavior and Thermal Deactivation Effects", Seventh DOE Crosscut Workshop on Lean Emissions Reduction Simulation (CLEERS), June 16-17, 2004.

6. TJ Toops, DB Smith, WS Epling, JE Parks, WP Partridge, P6-076: "*In-situ* DRIFTS Study of NO_X Storage on $Pt/K/Al_2O_3$", 13th International Congress on Catalysis, Paris, France, July 11-16, 2004.

Acronyms

ORNL – Oak Ridge National Laboratory
LNT – Lean NO_x Trap
DRIFTS – Diffuse Reflectance Infrared Fourier-Transform Spectroscopy

Figure Captions

Figure 1. Key Steps in $Pt/K/Al_2O_3$ Storage. (a) Route of adsorption for NO that is not oxidized to NO_2, but requires an adjacent Pt-site; typically only significant below 200˚C. (b) Route of adsorption for NO_2 through either a “spillover” mechanism where it is adsorbed adjacent to a Pt site, or a disproportionation reaction where two molecules from a nitrate and desorb an NO molecule; these routes dominate above 200˚C.

Figure 2. Newly developed flow-through packed bed/plug flow DRIFTS reactor.

Figure 3. Thermal deactivation effects associated with operating (a) a K-based LNT and (b) a Ba-based LNT. NO uptake experiments were performed at 250˚C, total surface area was determine using liquid N_2 BET, and average Pt size was estimated with H_2-O_2 titration experiments at 25˚C.

Figure 4. Effect of SO_2 and its subsequent desulfation at 760˚C with respect to (a) NO_x storage capacity at 250˚C and (b) exposed Pt surface atoms.

Figure 5. Desulfation of (a) $Pt/Ba/Al_2O_3$ and (b) $Pt/K/Al_2O_3$ for heating up to 760˚C.