F. Aftertreatment Catalysts Materials Research

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Objective

- Develop the knowledge and tools necessary to satisfy the U.S. Environmental Protection Agency (EPA) 2007 and 2010 diesel emissions regulations while minimizing the total cost of ownership.

Approach

- Develop reactors and test methods for understanding the fundamental behavior of catalysts.
- Evaluate novel base metal oxide catalysts for oxidation of diesel soot with conventional and microwave heating.
- Improve understanding of sulfation and desulfation of commercial nitrogen oxides (NO_x) reduction catalysts through reactor studies.

Accomplishments

- Evaluated the kinetics of desulfation on a commercial NO_x reduction catalyst.
- Demonstrated that microwave heating results in catalyzed soot oxidation rates substantially similar to those from conventional heating.

Future Direction

- Continue sulfation and desulfation studies with private funding.
- Continue the search for low-temperature soot oxidation catalysts.

Introduction

The 2007 and 2010 EPA regulations on particulate and NO_x emissions from diesel engines mandate significantly lower emissions than the current regulatory standards. These regulations are seen as aftertreatment-forcing by the diesel industry.

NO_x traps (also referred to as NO_x storage and release catalysts) are a primary path toward compliance with the 2007 and 2010 EPA regulations. However, the poisoning effects of sulfur reduce the efficiency of NO_x traps in capturing and destroying NO_x emitted from diesel engines. Even though sulfur levels will be reduced in future diesel fuels, any

amount of sulfur in fuel will be detrimental because the effect of sulfur on NO_x traps is cumulative. NO_x traps can be desulfated by high-temperature reduction. Desulfation, however, can require an extended time at high temperature. If the desulfation process requires 10 minutes for completion for light-duty applications, then desulfation will be impractical because the average time between engine start and stop for a light-duty vehicle is less than 10 minutes.

Catalysts commonly used for soot oxidation in catalyzed soot filters are based on platinum group metals and cerium oxides. The use of platinum group metals significantly increases the cost of catalyst systems. Base metal oxide catalysts, while typically less active than platinum group metal catalysts, are much less expensive. There have been reports in the literature that microwave heating accelerates soot oxidation in the presence of some base metal oxide catalysts more than conventional heating to a similar temperature accelerates oxidation. If true, this could allow very low-temperature regeneration of soot filters, significantly reducing the stress on the system and the cost of regeneration.

Approach

An Emerachem NO_x adsorber catalyst was selected for evaluation of sulfation and desulfation behavior. The impacts of desulfation temperature, reductant concentration, duration of exposure to reductant, and sulfur loading on desulfation rates and desorbed sulfur species were measured. The behavior of other NO_x adsorber catalysts will be similar to the behavior of this catalyst, although the temperature required for desulfation will likely be higher.

Using the microwave thermal gravimetric analysis (TGA) method developed under this program at Notre Dame University, microwave and conventional TGA was applied to several catalysts. Catalysts were selected based on other literature reports of accelerated activity in microwave heating and the principal investigators' knowledge of microwave heating and soot oxidation.

Results

Sulfation and Desulfation

A proprietary Emerachem catalyst was applied to a 3-in.-long 400-cpsi NGK extruded cordierite catalyst substrate. A core drill was used to separate 0.6-in.-diameter cores from the catalyzed substrate for use in a bench flow reactor. All cores were prepared for desulfation experiments using the degreening cycle detailed in Table 1. Before sulfation/desulfation testing, the performance of each catalyst core was evaluated at the conditions described in Table 2.

Table 1. Experimental conditions for degreening

Parameter	Lean	Rich
Time (sec)	300	300
Space velocity (1/h)	30,000	30,000
Temperature (°C)	575	575
NO (ppm)	300	0
SO_2 (ppm)	0	0
CO (%)	0	2.5
H_2O (%)	8	8
CO_2 (%)	8	8
O_2 (%)	8	0
N_2	Balance	Balance

Table 2. Experimental conditions for catalyst characterization before sulfation/desulfation.

Parameter	Lean	Rich
Time (sec)	56	4
Space velocity (1/h)	30,000	30,000
Temperature (°C)	Varied	Varied
NO (ppm)	300	0
SO_2 (ppm)	0	0
CO (%)	0	2.5
H_2O (%)	8	8
CO_2 (%)	8	8
O_2 (%)	8	0
N_2	Balance	Balance

For evaluation of temperature effects, a fresh core was used for each desulfation temperature. Conditions during sulfation and desulfation are listed in Table 3. It is important to note that no oxygen was included in the desulfation gas stream. This both aided in controlling the temperature of the cores during desulfation and eliminated the need to inject extra reductant to remove the oxygen.

The total sulfur release is shown in Figure 1. As shown in Figure 2, even a small portion of residual sulfur will adversely impact subsequent NO_x reduction performance. High-efficiency NO_x removal at lower temperatures in Figure 2 was due to the mildness of the NO_x performance cycle rather than to a lack of impact due to sulfur poisoning.

Table 3. Experimental conditions for sulfation/desulfation.

Parameter	Sulfation	Desulfation

Time (min)	37	15
Space velocity (1/h)	30,000	30,000
Temperature (°C)	550	Varied
NO (ppm)	0	0
SO_2 (ppm)	40	0
CO (%)	0	4.0
H_2O (%)	8	8
CO_2 (%)	8	8
O_2 (%)	8	0
N_2	Balance	Balance

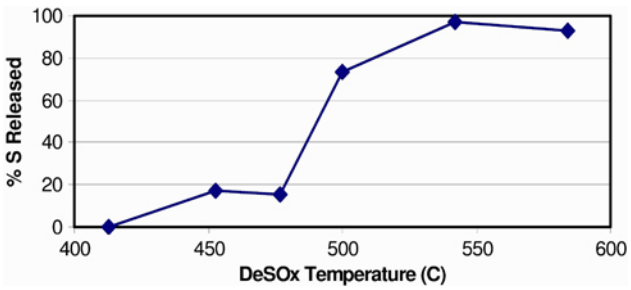

Figure 1. Total sulfur released during desulfation as a function of desulfation temperature.

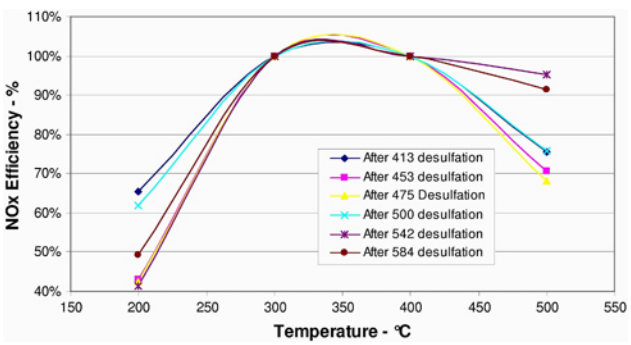

Figure 2. NOx performance after desulfation at various temperatures.

Similar degreening cycles and test methods were used in preparing fresh cores for evaluation of the impact of reductant concentration. The impact of reductant concentration on total sulfur release is shown in Figure 3. All cores were fresh except for the 0.25% CO core, which had been previously used for the 4% CO data. Temperature was 550°C for each of these experiments. The decrease in sulfur release with increasing reductant at low concentration was likely due to CO poisoning of the oxidation

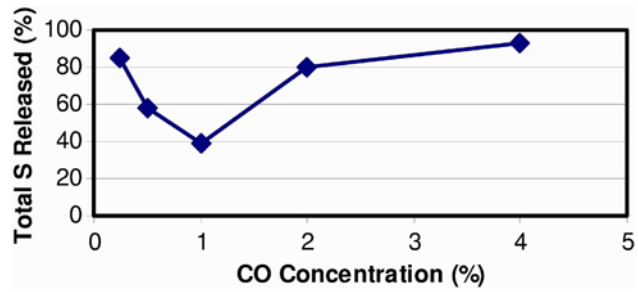

Figure 3. Total sulfur released during desulfation as a function of CO concentration at 550°C.

sites on the platinum catalyst. The high-temperature NO_x reduction performance of cores desulfated with 0.5% and 2% CO was similar, and both were better than the core desulfated at 1% CO.

The impact on desulfation of the sulfur quantity loaded on the catalyst was investigated at 550°C and at 2% CO. As total sulfur on the catalyst increased, sulfur released during desulfation increased nearly proportionally. Desulfation time effects were investigated at 550°C with 2% CO. As desulfation time increased, sulfur release increased and the release rate decreased (see Figure 4).

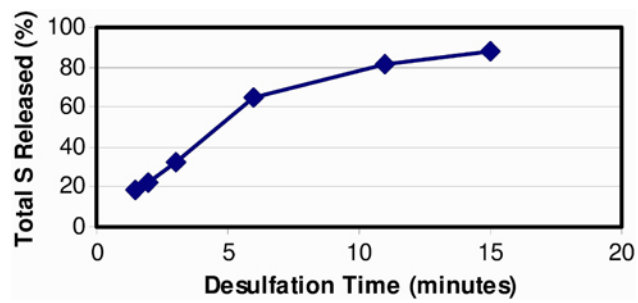

Figure 4. Total sulfur released during desulfation as a function of desulfation time at 550°C and 2% CO.

Microwave-heated Catalytic Soot Oxidation

As discussed in the previous annual report, a microwave TGA was constructed and calibrated so that microwave effects on catalyzed oxidation of soot could be investigated. Calibration to conventional TGA results was done with a microwave susceptor supporting the soot specimen so that heating of the soot was primarily though conduction and convection (see Figure 5). The presence of the susceptor allowed heating of the specimen without

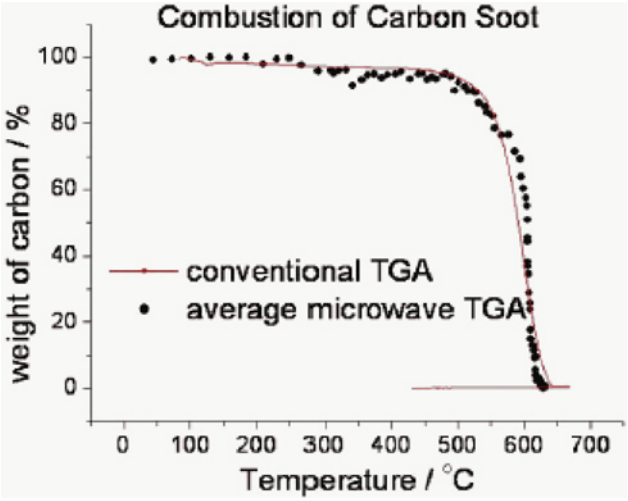

Figure 5. Comparison of microwave and conventional TGA results for uncatalyzed soot oxidation.

significant thermal gradients; but in the absence of a susceptor, thermal gradients were present.

Figure 6 shows the result of heating a mixture of CuO and carbon with microwaves on a quartz (non-suscepting) specimen support. Each specimen in the photograph was heated for a longer time than the specimen immediately to its left. The specimen on the left was not heated. The specimen in the middle has a mottled color, indicating that carbon has been oxidized. Note that the lighter colors are present toward the center of the pile of powder in the basket. (CuO alone is a red-brown color.) The specimen on the right is entirely red-brown in the middle of the pile, while the edges remain black. This indicates that the temperature gradients measured through infrared thermography (Figure 7) are indicative of where the soot is burning.

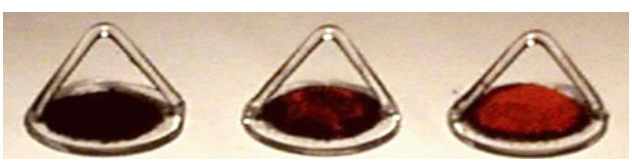

Figure 6. Mixtures of CuO and soot heated to various temperatures in microwave TGA.

It is not surprising that the edges of the specimens are cooler because of the higher surface area there relative to the mass available to absorb microwaves. Because of this effect, the fraction of soot burned (when no susceptor other than the soot is

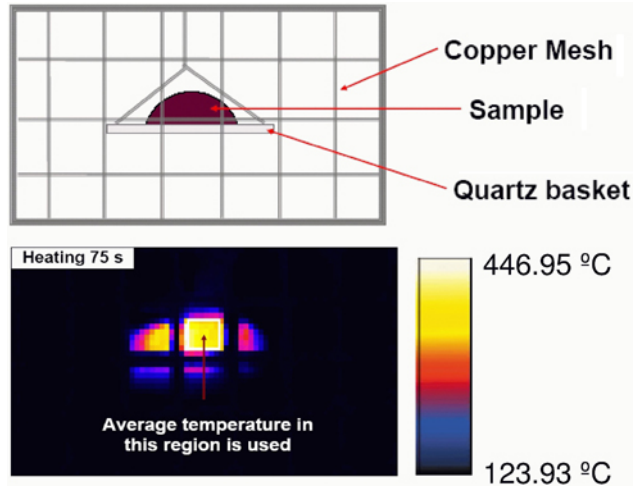

Figure 7. Thermography of specimen during heating in microwave TGA.

present) is a function of the soot present at the beginning of the experiment. (See Figure 8.)

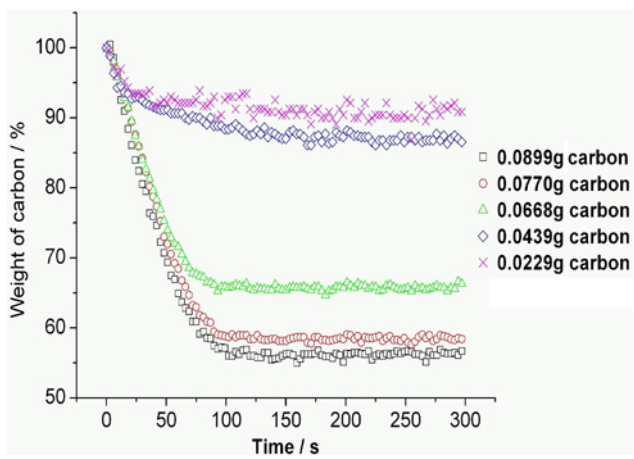

Figure 8. Soot oxidation vs. time for various soot loads in microwave TGA.

Despite this drawback of the microwave TGA system, it could be used for evaluating the usefulness of potential microwave catalysts because large effects were being looked for. Although a decrease in soot oxidation temperature of as little as 25 or 50°C would be useful in a real system, the added cost and complexity of microwave heating would be justified only by a much larger decrease in soot ignition temperature.

Figure 9 shows TGA results for mixtures of soot with CuO and $LiFe_5O_8$. Both oxides slightly

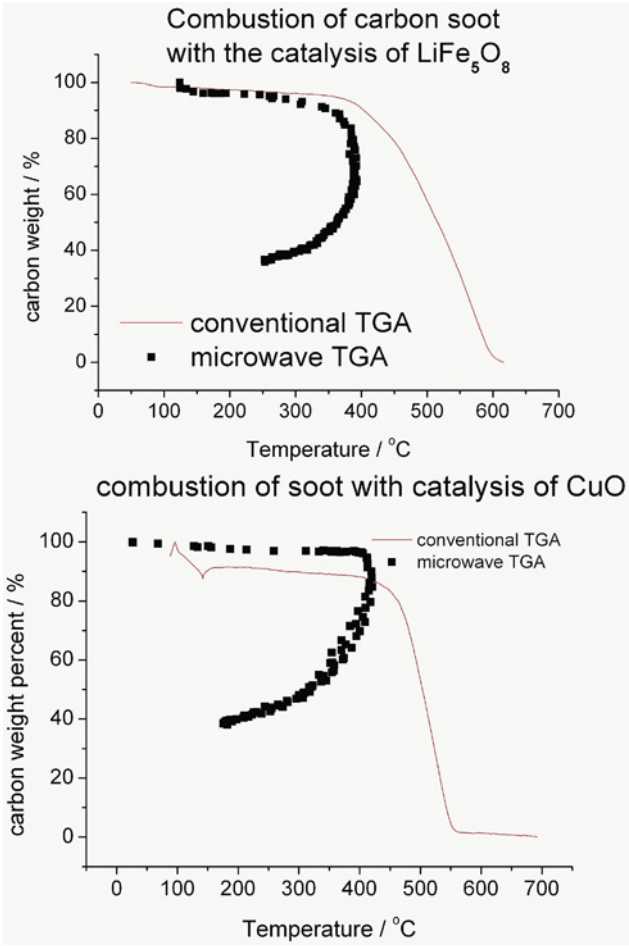

Figure 9. Catalyzed soot oxidation with microwave and conventional heating.

catalyze soot oxidation in conventional and microwave heating. It is important to note that in Figure 8, surface temperatures from microwave TGA are being compared with bulk temperatures from conventionally heated TGA. (Bulk temperatures in microwave heating can be substantially higher than surface temperatures.) The best point to compare the microwave and conventional results is at the beginning of oxidation. This best represents the temperature required for ignition.

While both CuO and $LiFe_5O_8$ lower soot oxidation temperatures relative to uncatalyzed oxidation, the difference between microwave and conventional temperatures required for ignition is less than 50°C. Taking into consideration the surface temperature measurement and temperature gradients likely present in the microwave TGA, these data provide no reasonable basis to believe that microwave heating significantly improves catalytic oxidation of soot.

Summary and Conclusions

An examination of the kinetics of desulfation on a commercial NO_x adsorber catalyst was begun. The information will be useful for designing desulfation control strategies. The impact of microwave heating on soot oxidation was investigated. Based on measurements made with microwave and conventionally heated TGA, it is not likely that microwave heating significantly lowers the temperature of catalyzed soot oxidation with the catalysts examined in this work.

Publications

Hongmei An, Caitlin Kilroy, and Paul J. McGinn, "An Examination of Microwave Heating to Enhance Diesel Soot Combustion," submitted to *Applied Catalysis B, Environmental*.

J. Kong, M. Henrichsen, and A. J. Shih, "Infrared Thermometry Measurement of Temperature Distribution in The Microwave Regeneration of Diesel Particulate Filters," *International Journal of Engine Research*, in press.