Diesel Exhaust Treatment Using Catalysts/Zeolites-II

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16. Abstract
Catalytic converters have become a viable post-treatment system for reducing emissions from on-highway diesel engines. This investigation attempted to develop and test a catalyst (copper ion-exchanged ZSM-5 zeolite) system for its ability to effectively treat diesel exhaust gas. During the first phase of this investigation (UTCA project 02201), catalyst/zeolites were used in a laboratory scale plug flow reactor system to treat synthetic diesel exhaust gas maintaining operating temperature at 200-300°F (93.3-148.9°C), pressures at 6 and 12 psig, and the space velocity through the reactor at ~8000 hr⁻¹. The exhaust gas composition was monitored before and after passing through the catalyst system using gas chromatography techniques. Despite relatively low operating temperature, the hydrocarbons (particularly methane) removal efficiency was fairly good, ranged from 30 percent to 80 percent depending upon the variation in the composition of the catalyst samples/zeolite structures. Therefore this catalyst system seemed promising for large reduction of hydrocarbons from the diesel exhaust.

Two modified catalysts were prepared which involved incorporating CeO₂ and ZrO₂ as the external coating on the previously made Cu-ZSM-5 catalysts. The size and shape of new catalysts were changed to help minimize pressure drop as well as catalyst loss from the system at high back pressure. The conversion efficiency of methane was tested using both catalysts for temperatures in the range from 200 to 800°F (93.3-426.7°C) at four different space velocities (ranging from ~10,000 to ~25,000 hr⁻¹) and the conversion efficiency of butane was tested at the same temperature range and the space velocity of ~30,000 hr⁻¹. The new catalysts showed very good performance for hydrocarbon conversion and efficiencies up to 100 percent were achieved. Results of removal of synthetic diesel fuel (using methane and butane gas separately) for two different catalysts at different operating conditions are presented to support the conclusions of this research work.

A sample of the developed catalyst was delivered to the University of Alabama Internal Combustion Engines Lab and tested by passing diesel engine exhaust through a canister containing the catalyst. The eight engine test conditions used were identified to simulate the federal medium and heavy duty diesel test cycles. Exhaust hydrocarbon reductions from 6 to 25 percent were measured, with an overall weighted average of 16 percent reduction, for canister space velocities of about 19,300 hr⁻¹ for canister temperatures of 325-350°C (617-662°F).
# Table of Contents

Technical Report Documentation Page ................................................................. ii
Table of Contents ...................................................................................................... iii
List of Tables ........................................................................................................... v
List of Figures .......................................................................................................... vi
Executive Summary ................................................................................................. vii
1.0 Introduction ........................................................................................................ 1
  1.1 Introduction ...................................................................................................... 1
  1.2 Background ..................................................................................................... 2
  1.3 Objective of the Study ..................................................................................... 4
  1.4 Work Plan ....................................................................................................... 5

2.0 Methodology/Experimental Procedure ........................................................... 7
  2.1 Chemicals Used ............................................................................................. 7
  2.2 Equipment Used ........................................................................................... 7
  2.3 Accessories Used ......................................................................................... 8
  2.4 Fabrication of Canister ................................................................................ 10
  2.5 Experimental Layout ................................................................................... 10
  2.6 Experimental Procedure and Analysis, Tasks 1 – 4 ....................................... 11
  2.7 Fabrication of Diesel Engine Testing System, Task 5 .................................. 11
  2.8 Experimental Procedure and Analysis, Task 5 ............................................. 12

3.0 Equipment Calibration ...................................................................................... 15
  3.1 Introduction ................................................................................................... 15
  3.2 Calibration of Tube Furnace ......................................................................... 15
  3.3 Calibration of Canister Inlet/Outlet Temperature with Oven ....................... 17
  3.4 Calibration of Reactor Bed Temperature with Oven ..................................... 18
  3.5 Measurement of Gas Flow Rates ................................................................. 20
  3.6 Statistical Analysis ....................................................................................... 20

4.0 Results and Discussion .................................................................................... 21
  4.1 Process of Research Investigation ................................................................. 21
  4.2 Effect of Catalyst Temperature .................................................................... 22
  4.3 Effect of Space Velocity ............................................................................... 26
  4.4 Arrhenius Plot (Reaction Rate Constant, K versus T\(^{-1}\)) .......................... 26
  4.5 Comparison of the Efficiency of the CeO\(_2\)/Cu-ZSM-5 Catalyst at Different Operating Conditions ............................................................. 29
  4.6 Comparison of the Efficiency of the ZrO\(_2\)/Cu-ZSM-5 Catalyst at Different Operating Conditions ................................................................. 30
  4.7 Comparison of the Efficiency of the CeO\(_2\)/Cu-ZSM-5 and the ZrO\(_2\)/Cu-ZSM-5 Catalysts at Different Operating Conditions .......................... 31
  4.8 Statistical Analysis ....................................................................................... 35
  4.9 Results of Task 5, Testing of Catalyst on Diesel Engine Exhaust ................. 36
## List of Tables

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-1</td>
<td>Diesel test conditions to simulate the transient FTP test</td>
<td>14</td>
</tr>
<tr>
<td>4-1</td>
<td>Permutations and combinations of experiments performed with methane gas</td>
<td>21</td>
</tr>
<tr>
<td>4-2</td>
<td>Permutations and combinations of experiments performed with butane gas</td>
<td>21</td>
</tr>
<tr>
<td>4-3</td>
<td>Comparison of the methane conversion efficiency by the CeO&lt;sub&gt;2&lt;/sub&gt;/Cu-ZSM-5 catalyst at different operating conditions</td>
<td>23</td>
</tr>
<tr>
<td>4-4</td>
<td>Comparison of the methane conversion efficiency by the ZrO&lt;sub&gt;2&lt;/sub&gt;/Cu-ZSM-5 catalyst at different operating conditions</td>
<td>24</td>
</tr>
<tr>
<td>4-5</td>
<td>Comparison of the methane conversion efficiency by the CeO&lt;sub&gt;2&lt;/sub&gt;/Cu-ZSM-5 and ZrO&lt;sub&gt;2&lt;/sub&gt;/Cu-ZSM-5 catalysts at different operating conditions</td>
<td>32</td>
</tr>
<tr>
<td>4-6</td>
<td>Comparison of the methane conversion efficiency by the CeO&lt;sub&gt;2&lt;/sub&gt;/Cu-ZSM-5 and ZrO&lt;sub&gt;2&lt;/sub&gt;/Cu-ZSM-5 catalysts at different operating conditions</td>
<td>32</td>
</tr>
<tr>
<td>4-7</td>
<td>Comparison of the butane conversion efficiency by the CeO&lt;sub&gt;2&lt;/sub&gt;/Cu-ZSM-5 and ZrO&lt;sub&gt;2&lt;/sub&gt;/Cu-ZSM-5 catalysts at different operating conditions</td>
<td>35</td>
</tr>
<tr>
<td>4-8</td>
<td>Diesel exhaust results from January 13, 2005 tests</td>
<td>37</td>
</tr>
<tr>
<td>4-9</td>
<td>Diesel exhaust results from January 23, 2005 tests</td>
<td>38</td>
</tr>
<tr>
<td>4-10</td>
<td>Average unburned hydrocarbon reduction results</td>
<td>38</td>
</tr>
</tbody>
</table>
List of Figures

2-1 Schematic diagram of the catalyst/zeolite canister ...................................................... 9
2-2 Schematic diagram of experimental set-up of the catalyst/zeolite system .................. 10
2-3 Canister housing with sampling ports and band heater for diesel engine tests ........... 13
2-4 Schematic diagram of the catalytic test set-up for diesel engine testing .................... 14
3-1 Flow chart for calibration experiments ...................................................................... 15
3-2 Oven temperature with graduation of controller (for Observation No. 1) ............... 16
3-3 Temperature of canister inlet at different oven graduations .................................... 18
3-4 Temperature of reactor bed at different oven graduations ....................................... 19
3-5 Comparison of temperature of canister inlet and reactor bed at different oven graduations ........................................................................................................ 19
3-6 Graph showing gas flow rate as a function of the applied pressure ......................... 20
4-1 Effect of temperature on the conversion efficiency of methane using CeO2/Cu-ZSM-5 catalyst at different operating conditions ...................................................... 22
4-2 Effect of temperature on the conversion efficiency of methane using ZrO2/Cu-ZSM-5 catalyst at different operating conditions ...................................................... 23
4-3 Mean removal efficiency of catalyst/zeolite of set I and set II at pressure 6 psig versus mean removal efficiency of catalyst/zeolite of set I and set II at pressure 12 psig ........................................................................................................ 24
4-4 Effect of temperature on the conversion efficiency of butane using CeO2/Cu-ZSM-5 catalyst at 15 psig pressure .......................................................... 25
4-5 Effect of temperature on the conversion efficiency of butane using ZrO2/Cu-ZSM-5 catalyst at 15 psig pressure .......................................................... 25
4-6 Effect of space velocity on the conversion efficiency of methane using CeO2/Cu-ZSM-5 catalyst at different operating conditions ................................................. 26
4-7 Effect of space velocity on the conversion efficiency of methane using ZrO2/Cu-ZSM-5 catalyst at different operating conditions ................................................. 27
4-8 Arrhenius plot (ln K vs. 1/T) for methane conversion reaction using the CeO2/Cu-ZSM-5 catalyst at different pressures/space velocities .................................. 27
4-9 Arrhenius plot (ln K vs. 1/T) for methane removal reaction using the ZrO2/Cu-ZSM-5 catalyst at different pressures/space velocities .................................. 28
4-10 Arrhenius plot (ln K vs. 1/T) for butane removal reaction using the CeO2/Cu-ZSM-5 catalyst at ~30,000 hr⁻¹ space velocity ................................................. 28
4-11 Arrhenius plot (ln K vs. 1/T) for butane removal reaction using the ZrO2/Cu-ZSM-5 catalyst at ~30,000 hr⁻¹ space velocity ................................................. 29
4-12 Comparison of the conversion efficiency of methane using CeO2/Cu-ZSM-5 catalyst at different operating conditions ...................................................... 30
4-13 Comparison of the conversion efficiency of methane using ZrO2/Cu-ZSM-5 catalyst at different operating conditions ...................................................... 31
4-14 Comparison of the methane conversion efficiencies of CeO2/Cu-ZSM-5
and ZrO₂/Cu-ZSM-5 catalysts at 6 psig pressure ......................................................33
4-15 Comparison of the methane conversion efficiencies of CeO₂/Cu-ZSM-5
and ZrO₂/Cu-ZSM-5 catalysts at 12 psig pressure ................................................33
4-16 Comparison of the methane conversion efficiencies of CeO₂/Cu-ZSM-5
and ZrO₂/Cu-ZSM-5 catalysts at 18 psig pressure ................................................34
4-17 Comparison of the methane conversion efficiencies of CeO₂/Cu-ZSM-5
and ZrO₂/Cu-ZSM-5 catalysts at 24 psig pressure ................................................34
4-18 Comparison of the butane conversion efficiencies of CeO₂/Cu-ZSM-5
and ZrO₂/Cu-ZSM-5 catalysts at 15 psig pressure ................................................35
Executive Summary

Catalytic converters have become a viable post-treatment system for reducing emissions from on-highway diesel engines. This investigation attempted to develop and test a catalyst (copper ion-exchanged ZSM-5 zeolite) system for its ability to effectively treat diesel exhaust gas. During the first phase of this investigation (UTCA project 02201), catalyst/zeolites were used in a laboratory-scale plug flow reactor system to treat synthetic diesel exhaust gas maintaining operating temperatures at 200-300°F (148.9°C), pressures at 6 psig and 12 psig, and the space velocity through the reactor at ~8000 hr⁻¹. The exhaust gas composition was monitored before and after passing through the catalyst system using gas chromatography techniques. Despite the relatively low operating temperature, the hydrocarbons (particularly methane) removal efficiency was fairly good, ranging from 30 percent to 80 percent depending upon the variation in the structure and/or composition of the catalyst samples/zeolites. Therefore, the Cu-ZSM-5 catalyst showed promise for large reduction of hydrocarbons from the diesel exhaust.

Two modified catalysts were prepared that involved incorporation of CeO₂ and ZrO₂ as the external coating on the previously made Cu-ZSM-5 catalysts. CeO₂ and ZrO₂ were found to have oxygen storage capacity that broadens the conversion efficiency during rich/lean perturbations in the exhaust system. The size and shape of new catalysts were modified to help minimize the pressure drop as well as catalyst loss from the system at high back pressures. The conversion efficiency of methane was tested using both catalysts for temperatures in the range of 200 to 800°F (93.3 – 426.7°C) at four different space velocities (from ~10,000 hr⁻¹ to 25,000 hr⁻¹). The new catalysts showed very good performance for methane conversion, and efficiencies as high as 100 percent were achieved for the CeO₂/Cu-ZSM-5 catalyst at a lower temperature range of ~500°F (260°C), while the maximum hydrocarbon removal efficiency obtained for ZrO₂/Cu-ZSM-5 catalyst was 87 percent at 800°F. The conversion efficiency of butane was also tested using both catalysts for temperatures in the range of 200 to 800°F (93.3 – 426.7°C) at the space velocity of ~30,000 hr⁻¹. Results of hydrocarbon (methane and butane) removal efficiency for these two different catalysts at different operating conditions are presented to support the conclusion of this research work.

A sample of the developed catalyst was delivered to the University of Alabama Internal Combustion Engines Lab and tested by passing diesel engine exhaust through a canister containing the catalyst. The eight engine test conditions used were identified to simulate the federal medium and heavy duty diesel test cycles. Exhaust hydrocarbon reductions from 6 to 25 percent were measured, with an overall weighted average of 16 percent reduction, for canister space velocities of 19,300 hr⁻¹ for canister temperatures of 325 - 350°C (617 – 662°F).
1.0 Introduction

1.1 Introduction

Diesel-powered vehicles represent a significant portion of the vehicle market worldwide. In the U.S., the market share of diesel passenger cars is expected to grow even higher in the years ahead. Compared to gasoline-powered vehicles, diesel vehicles offer better fuel economy and engine durability. As diesel passenger cars become more popular both in the U.S. and elsewhere, emissions reduction is an increasingly urgent issue. In fact, regulations passed by the Environmental Protection Agency (EPA) for model year 2007 and later calls for a 92 percent reduction of nitrogen oxides (NOx) emissions (0.20 g/bhp-hr) and 93 percent reduction of non-methane hydrocarbon (NMHC) emissions (0.14 g/bhp-hr) compared to the EPA standards for model year 2004 (NOx emissions level of 2.4 g/bhp-hr and NMHC emissions level of 2.0 g/bhp-hr) [EPA Regulatory Announcement, 2000]. For some vehicles, it will be difficult to meet the EPA emission standards for 2007 or later targets by engine improvement alone. It may be impossible to meet the regulations without highly efficient after-treatment technologies [Zelenka, et al., 1996].

The pollution emitted by diesel engines contributes greatly to America's continuing air quality problems. The noxious fumes from the tailpipes of trucks and buses is not only an assault to the sense of smell, it is also toxic, especially to children and their developing lungs. Although trucks and buses account for less than 6 percent of the miles driven by highway vehicles in the United States, they are responsible for the following [California Air Resources Board, 2004]:

- One-quarter of the smog-causing pollution from highway vehicles;
- More than half of the soot from highway vehicles;
- The majority of the cancer threat posed by air pollution in some urban areas;
- 6 percent of the nation’s global warming pollution; and
- More than one-tenth of America’s oil consumption.

Even with more stringent heavy-duty highway engine standards set to take effect from 2007, these engines will continue to emit large amounts of nitrogen oxides and particulate matter, both of which contribute to serious public health problems in the United States. These problems include premature mortality, aggravation of respiratory and cardiovascular disease, aggravation of existing asthma, acute respiratory symptoms, chronic bronchitis, and decreased lung function [EPA Environmental News 2000]. Numerous studies also link diesel exhaust to an increased incidence of lung cancer. According to the EPA, diesel exhaust is likely to be carcinogenic to humans by inhalation, and this cancer hazard exists for occupational and environmental levels of exposure [EPA Environmental News, 2001]. The EPA established a comprehensive national control program on March 19, 2001, that is now regulating heavy-duty vehicles and their fuel as a single system. As part of this program, new emission standards will begin to take effect in
model year 2007 and will apply to heavy-duty highway engines and vehicles [EPA Regulatory Announcement, 2000]. These standards are based on the use of high-efficiency catalytic exhaust emission control devices or comparably effective advanced technologies. Because these devices are damaged by sulfur, the EPA is also taking steps to significantly reduce the level of sulfur (from 500 ppm to 15 ppm) in highway diesel fuel by mid-2006.

It is estimated that heavy-duty trucks and buses today account for about one-third of nitrogen oxides emissions and one-quarter of particulate matter (PM) emissions from mobile sources. In some urban areas, the contribution is even greater. The new legislation will reduce particulate matter and oxides of nitrogen emissions from heavy-duty engines by 90 percent and 93 percent below current standard levels, respectively. PM, NOx, and NMHC emission standards are set for heavy-duty vehicles at 0.01 g/bhp-h, 0.20 g/bhp-h, and 0.14 g/bhp-h, respectively, for model year 2007 [EPA Regulatory Announcement, 2000]. In order to meet these more stringent standards for diesel engines, the program also calls for a 97 percent reduction in the sulfur content of diesel fuel. As a result, diesel vehicles will achieve gasoline-like exhaust emission levels.

The clean air impact of this program will be dramatic when fully implemented. By 2030, this program will reduce annual emissions of NOx, NMHC, and PM by a projected 2,600,000, 115,000 and 109,000 tons, respectively [EPA Environmental News, 2001]. It has been estimated that 8,300 premature deaths, 5,500 cases of chronic bronchitis, and 17,600 cases of acute bronchitis-I in children can be prevented annually. The EPA estimates that these reductions and the resulting significant environmental benefits of this program will come at an average cost increase of about $2,000 to $3,200 per new vehicle in the near term and about $1,200 to $1,900 per new vehicle in the long term, depending on vehicle size. In comparison, new vehicle prices today can range well over $100,000 for larger heavy-duty vehicles. EPA also estimates that when fully implemented, the sulfur reduction requirement will increase the cost of producing and distributing diesel fuel by about five cents per gallon. The benefits of the action outweigh costs by 16 to 1 [EPA Environmental News, 2001].

All these efforts, rules, and regulations demand innovative breakthroughs in the field of exhaust emission control technology to comply with the 2007 heavy duty (HD) rule. Various efforts have been taken to reduce the greenhouse gas emissions and soot from vehicle tail pipes. This problem can be solved through the application of high-efficiency emissions control technologies, which can result in large emissions reductions, especially through the use of catalytic emission control devices installed in the vehicle’s exhaust system and integrated with the engine controls. For the technology to be feasible and capable of meeting the standards, it will require diesel fuel with sulfur content at or below the 15 ppm level.

1.2 Background

Diesel exhaust is a complex mixture of gases, vapors, and fine particles. The gaseous fraction is composed primarily of typical combustion gases such as nitrogen, oxygen, carbon dioxide, and water vapor. In addition, the gaseous fraction also contains air pollutants such as carbon monoxide (CO), sulfur oxides (SOx), NOx, volatile hydrocarbons (HC), and low-molecular-weight polycyclic aromatic hydrocarbons (PAHs) and PAH derivatives. At least 40 components, including suspected human carcinogens benzo[a]pyrene, 1,3-butadiene, and formaldehyde, are
listed by the EPA as hazardous air pollutants and by the Air Resources Board (ARB) as toxic air contaminants. If exhaust gases containing these harmful components are emitted into the air without any treatment, pollution and environmental degradation will occur. Therefore, exhaust gases containing these harmful components are emitted into the air after treatment by a device such as a catalyst system. The catalyst converts NO\textsubscript{x}, HC, and CO contained in exhaust gases into innocuous nitrogen, carbon dioxide (CO\textsubscript{2}), or water (H\textsubscript{2}O).

It is key to use catalyst compositions, including those commonly referred to as three-way conversion catalysts, to treat the exhaust gases of internal combustion engines. Catalysts, containing precious metals such as platinum, palladium, and rhodium, have been successful in promoting the oxidation of unburned HC and CO and promoting the reduction of NO\textsubscript{x} in exhaust gas, provided that the engine is operated around balanced stoichiometry for combustion ("combustion stoichiometry"; i.e., between about 14.7 and 14.4 air/fuel volumetric ratio). However, fuel economy and global CO\textsubscript{2} emissions have made it desirable to operate engines under lean-burn conditions, where the air-to-fuel ratio is somewhat higher than combustion stoichiometry, to realize a higher benefit in fuel economy [Eastwood, 2000].

Diesel and lean-burn gasoline engines generally operate under highly oxidizing conditions (i.e., using much more air than is necessary to burn the fuel), typically at air/fuel ratios greater than 14.7 and generally between 19 and 35. Under these highly lean conditions, typical three-way catalysts exhibit little activity toward NO\textsubscript{x} reduction, as their reduction activity is suppressed by the presence of excess oxygen. Therefore the three-way catalyst technology, which is widely used in gasoline cars, is not operational in diesel vehicles. A key factor in achieving maximum results in reducing the emission of CO, HC, and NO\textsubscript{x} is to control the air/fuel ratio of the diesel engine within a narrow window at all times. If the engine is operated close to the stoichiometric air:fuel ratio, then CO, HC, and NO\textsubscript{x} could be simultaneously converted [Eastwood, 2000].

HC conversion is strongly influenced by temperature and is generally carried out at temperatures greater than 300\textdegree C. The catalyst for purifying exhaust gases is heated by exhaust gases. As is common practice, catalysts used to treat the exhaust of internal combustion engines are less effective during periods of relatively low temperature operation, such as the initial cold-start period of engine operation, because the engine exhaust is not at a temperature sufficiently high for efficient catalytic conversion of noxious components in the exhaust. To this end, an adsorbent material is included as part of a catalytic treatment system in order to adsorb gaseous pollutants, usually hydrocarbons, and retain them during the initial cold-start period. As the exhaust gas temperature increases, the adsorbed hydrocarbons are driven from the adsorbent (desorbed) and subjected to catalytic treatment at the higher temperature. Besides, immediately after an engine starts exhaust gases contain a large amount of HC, and the ratio of HC in the emission is large. Accordingly, it is a critical problem to suppress HC emission from a catalyst when the catalyst has a low temperature.

Over the past thirty years, the emphasis of regulations has shifted from one pollutant to another, but the overall trend has been towards stricter emission control on all types of motor vehicles [White, 1982]. In particular, NO\textsubscript{x} emissions from heavy-duty diesel-powered vehicles have been the target of aggressive regulation during the last decade [Schimek, 1998].
NO\textsubscript{x} emissions from mobile sources occur as a result of physical conditions in an internal combustion engine that enable chemical processes to form nitric oxide (NO). Generally, ambient air consists of 3.76 moles of nitrogen (N\textsubscript{2}) for every mole of oxygen (O\textsubscript{2}) [Schafer and van Basshuyen, 1995]. The combustion process results in sufficient temperatures and pressures to allow the N\textsubscript{2} and O\textsubscript{2} in the air drawn into a vehicle’s engine cylinder to combine to form two moles of NO. This phenomenon is represented by the “Zeldovich mechanism” and is shown below [Schafer and van Basshuyen, 1995].

\[
\begin{align*}
N_2 + O &\rightarrow NO + N \\
O_2 + N &\rightarrow NO + O
\end{align*}
\]

For this reason, NO\textsubscript{x} emissions are not particularly sensitive to changes in fuel types or chemical compositions and require exhaust treatment technologies for their reduction as previously discussed [Schafer and van Basshuyen, 1995; Sawyer et al., 2000].

Studies have shown that heavy-duty trucks contribute a significant portion of the overall mobile source emissions of NO\textsubscript{x} [Sawyer et al., 2000; Nelson et al., 1991]. In many cases, diesel-powered heavy trucks constitute a significant percentage of total traffic volumes [Bureau of Transportation Statistics, 1998]. In addition, truck traffic continues to increase in total vehicle-miles traveled, implying that heavy-duty vehicles have an increasingly important role in the emission of ozone precursors.

Studies have shown that diesel-powered heavy duty vehicles account for greater NO\textsubscript{x} emissions per vehicle than gasoline-powered passenger cars due to the relatively high combustion temperatures and pressures associated with diesel engines [TRB, 1995; Sawyer et al., 2000; Guensler, 1991]. The mobile source emissions model developed by the EPA, MOBILE5, reports that NO\textsubscript{x} emission rates for trucks are seven times greater than those of passenger cars [Schimek, 1998].

Several studies of ozone formation have indicated that mobile source emissions are capable of contributing to ozone levels around 120 ppbv [Winner and Cass, 2000; Proyou et al., 1998; Harley et al., 1997]. To date, there has been considerable effort devoted to the reduction of emissions from heavy-duty diesel engines. For example, techniques such as selective catalytic reduction using ammonia have been studied at Oak Ridge National Laboratory and NO\textsubscript{x}Tech is working to develop an after-treatment device to further reduce NO\textsubscript{x} emissions from diesel exhaust. In response to increasing concerns and stricter environmental regulations on vehicle emissions, this project searched for a cost-effective catalytic treatment technique that can effectively handle and treat diesel emissions from heavy-duty diesel-powered vehicles, both for retrofit of older engines and as a supplemental device to achieve further NO\textsubscript{x} reductions from post-2007 engines.

1.3 Objective of the Study

The objective of this study was to develop and test an oxidation catalyst/zeolite system for its ability to effectively treat synthetic diesel exhaust (containing mainly hydrocarbons).
1.4 Work Plan

The project involved the following tasks:

- **Task 1** – Investigation of several additional catalysts in addition to copper nitrate. Potential catalysts examined included copper, platinum, rhodium, palladium, silver, and vanadium pentoxide. The active component was incorporated onto the zeolite support using the ion exchange technique. Argonne National Laboratory provided assistance in the selection and optimization of the catalysts used in this study.

- **Task 2** – Investigation of the catalytic activities of the developed catalysts using methane gas at different operating conditions.

- **Task 3** – Investigation of the catalytic activities of the developed catalysts using butane gas at different operating conditions.

- **Task 4** – Comparison of the two newly developed catalysts as well as the catalysts used in the preliminary investigation of this project [UTCA Project No. 02201].

- **Task 5** – Testing of the best catalyst on actual diesel exhaust at conditions typical of medium and heavy duty diesel engine operation.

In Task 1, the active components for the catalyst/zeolite system were identified in consultation with Argonne National Laboratory. During the first phase of this research, UTCA Project 02201, “Diesel Exhaust Treatment Using Catalyst/Zeolites,” the catalysts (Cu-ion impregnated onto different structured zeolites) showed decreased efficiencies for hydrocarbon conversion in presence of water vapor [Gill, 2003; Peters et al., 2004]. A review of recent literature on auto catalysts suggested that incorporation of CeO2 and/or ZrO2 onto the metal ion-exchanged zeolites improves the hydrocarbon conversion efficiency in the presence of water vapor [Eastwood, 2000]. As a follow-up to the first phase of the research (UTCA project 02201), two modified catalysts were prepared, which involved incorporating CeO2 and ZrO2 as the external coating on the previously made Cu-ZSM-5 catalysts. The sizes and shapes of the new catalysts were also modified to minimize pressure loss as well as catalyst loss from the system at high back pressures.

In Task 2, a plug-flow reactor system was used for laboratory tests. Exhaust gas, as represented by methane gas, was passed through the canister and treated by the catalysts in a packed-bed arrangement. Sensors were used to monitor the system performance in near real-time conditions. The gas samples collected from the inlet and outlet ports were analyzed in the gas chromatography (GC) system for measuring the conversion of hydrocarbons. The activities of the catalysts at different operating temperatures (200 to 800°F; 93.3 – 426.7°C) and space velocities (~10,000 hr⁻¹ to ~30,000 hr⁻¹) are included in the Results and Discussion section.

In Task 3, the catalytic activities of two different catalyst samples for the butane conversion reaction were monitored using two catalyst samples while maintaining the temperatures from 200 to 800°F (93.3 to 426.7°C) at a space velocity of ~30,000 hr⁻¹.

In Task 4, the catalytic activities of the two modified catalysts were compared to each other and to those used in the preliminary investigation, UTCA Project 02201 [Gill, 2003; Peters et al., 2004].
Task 5 was carried out in the Internal Combustion Engines Laboratory at the University of Alabama using a single-cylinder 3400 series Caterpillar engine. A standard five-gas emissions bench was used to measure the concentrations of CO, CO₂, O₂, NOₓ and unburned hydrocarbons in exhaust gas samples collected both before and after passage through the catalyst canister. Canister space velocities of 19,200 hr⁻¹ and temperatures of 325 to 350°C (617 – 662°F) were employed. The test conditions used were eight steady-state speed/load combinations that, when the measured results are weighted properly, simulate the Transient Federal Test Procedure.
Section 2.0
Methodology/Experimental Procedure

2.1 Chemicals Used

The chemicals used in this study are discussed below:

- Argonne National Laboratory provided two samples of zeolites/catalysts to the University of Alabama at Birmingham (UAB) for this research project. Copper ion (Cu\(^{2+}\)) exchanged zeolite externally coated with CeO\(_2\) and zirconia (ZrO\(_2\)) were obtained having a nominal weight of 5.00 gm each. The compositions of the two catalysts are given below:

  Sample ID: 2060-88-A
  Mixture Composition: 16.7% CeO\(_2\), 83.3% Cu-ZSM-5
  Zeolite Composition: 0.9% Cu (50% exchanged, 0.25 Cu/Al) SiO\(_2\)/Al\(_2\)O\(_3\) = 50

  Sample ID: 2060-88-B
  Mixture Composition: 18.7% ZrO\(_2\), 81.3% Cu-ZSM-5
  Zeolite Composition: 0.9% Cu (50% exchanged, 0.25 Cu/Al) SiO\(_2\)/Al\(_2\)O\(_3\) = 50

- Silicon carbide (SiC) was provided by Electro Abrasives, Inc. (Buffalo, NY). Four pound samples of silicon carbide of the following mesh sizes were used: 24, 150, and 240. The SiC served as the inert packing material above and below the catalyst/zeolite material.
- Two cylinders of methane gas were obtained from BOC Group, Inc. Each gas cylinder had the gas composition of 52.2 ppm methane and the balance being air.
- Three tanks of compressed butane gas were obtained from BOC Group, Inc.
- Compressed air, hydrogen, and helium gases from BOC Group, Inc., were used for operation of the gas chromatograph.

2.2 Equipment Used

The following equipment was used in Tasks 1 – 4 of this investigation:

- Tube furnace – to provide heat to the experimental equipment (copper tube and canister);
- Variable auto transformer – to control the heat input for the canister and preheat the inlet line to the canister;
- Thermocouples – to monitor temperature before and after the canister containing catalyst/zeolite matrix;
- Digital indicators – to display the temperature measured by the thermocouples;
• Pressure gauges and capillary tubes – to measure the pressure difference (ΔP) between the inlet and outlet of the canister;
• Sieves/Meshes – to size the pelletized catalyst/zeolite samples;
• Crushing equipment – to crush the pelletized catalysts into mean particle size range of 725 μm; and
• Gas chromatograph (Agilent model 6890N) – to analyze the composition of hydrocarbon (methane) before and after treatment with the plug flow canister containing the catalysts/zeolites.

The following equipment was used in Task 5 of this investigation:

• A single-cylinder 3400 series Caterpillar lubricant testing engine.
• A General Electric cradled-DC dynamometer capable of absorbing 100 hp and motoring at 75 hp.
• A Richmond Instruments five-gas emissions bench that employed an automatic gas divider for calibration and Rosemount gas analysis instruments for measurement of NOx and unburned hydrocarbons in the “wet” condition (not passed through a moisture trap), and measurement of CO, CO2 and O2 in dried gas samples.
• A custom-built test rig for diverting a controlled flow of exhaust gas, cleaning it of soot/particles, passing it through a heated system that contained the catalyst test canister, and provided for collecting gas samples before and after the catalyst. The canister temperature was controlled by electric heaters regulated using an electronic temperature controller.
• Thermocouples, pressure gauges and transducers, rotameter, valves and fittings as needed to measure and control pressures, temperatures and flow rates.

2.3 Accessories Used

Accessories used to perform this research included the following:

• A flow meter was used to measure the flow rate of gases.
• Gas regulators for the compressed hydrogen, helium, and air lines were used in the operation of the GC system to control the flow rates. Each regulator had a pressure rating of 3000 psig.
• A gas regulator with a pressure rating of 2000 psig was used to control the flow of methane gas through the canister system.
• A gas regulator with a pressure rating of 2000 psig was used to control the flow of butane gas through the canister system.
• Six drierite (calcium sulfate) laboratory gas drying units were used to remove residual moisture from the compressed gas feed lines (hydrogen, helium, and air) for operating the GC.
• Hamilton gastight syringes (100 mL) were used to grab gaseous samples during an experiment and inject them into the GC system (see Figures 2-1 and 2-2). Hamilton Series 1000 Gastight Syringes (from Fisher Scientific International, Suwannee, GA), available in microliter capacities, were used.
- A check valve was used in the air flow line to control the flow of air.
- A filter was used in the air flow line.

Figure 2-1. Schematic diagram of the catalyst/zeolite canister
2.4 Fabrication of Canister

The canister was fabricated at UAB’s machine shop and was used for the laboratory demonstration phase of this project. The unassembled catalyst/zeolite canister system is shown schematically in Figure 2-1.

A manifold system was fabricated and attached to the top and bottom of the canister to provide taps to measure temperature and pressure before and after the canister system. The manifold system was equipped with sample collection ports (involving septa), for direct injection of gastight syringes into the GC system for analysis.

2.5 Experimental Layout

A plug flow canister having a packed bed of embedded media with the catalyst was prepared for testing the removal efficiencies of methane/butane gas in the laboratory. Two samples of catalysts obtained from Argonne National Laboratory were tested at different operating conditions to compare the effectiveness of each catalyst/support media matrix. There were sampling ports on both sides of the canisters for collection of gas samples by gastight syringes (100 µL) and for analysis to determine the system performance as a function of the gas throughput and operating temperature.

Methane/butane flow rates were regulated using a gas regulator. The temperature of the tube furnace was controlled with a variable auto transformer (Variac system), thereby regulating the temperature of the reactor. The portion of the canister which contained the catalysts was placed inside the tube furnace. Thermocouples were inserted at the inlet and in the catalyst bed of the canister system to monitor the temperature within the bed. Additionally, the pressure drop through the packed-bed canister was monitored during the course of the experiment. A schematic diagram of the experimental set-up of the catalyst/zeolite canister system is shown in Figure 2-2.
2.6 Experimental Procedure and Analysis, Tasks 1 – 4

The procedure for conducting the experimental runs and analysis of the gaseous samples is summarized in the following steps, from the catalyst/zeolite synthesis to catalyst fabrication.

- Two samples of catalysts/zeolites were synthesized at Argonne National Laboratory, according to the “ion-exchange” approach as described in Appendix A.
- The catalyst samples were pelletized. The pelletized catalysts were then lightly crushed and sized using U.S. standard sieves sizes 20, 30, 40 and 50.
- A canister of stainless steel was fabricated at UAB’s machine shop. A schematic diagram of the canister system is shown in Figure 2-1. A manifold system was fabricated to attach at the top and bottom of the canister to provide sample collection port and ports for monitoring temperature and pressure.
- Before all the equipment was set up, the canister was partially filled with a mixture of catalyst/zeolite and silicon carbide. One part of the catalyst was mixed with two parts of silicon carbide (both had the same size range of 725 µm), and the mixture was placed inside the plug-flow reactor/canister. After packing the canister, the manifolds were attached to it.
- The tube furnace was placed horizontally and connected to a variable auto transformer to control the temperature of the furnace. It had a maximum temperature of 1400°F (760°C).
- The reactor bed was filled with the catalyst/zeolites and placed inside the oven. The upstream and downstream sides of the canister system were connected with pressure gauges and thermocouples. The upstream manifold was connected to the methane gas cylinder, and gas flow was regulated with the help of the gas regulators.
- Once the entire assembled unit was placed in the ventilation hood, the oven around the reactor bed was regulated by the variable auto transformer. After reaching the desired temperature, methane butane gas was passed through the canister at four different pressures (6, 12, 18 and 24 psig); temperatures at the inlet and reactor bed of the canister were measured with thermocouples and displayed on digital indicators in °F. Pressures at the inlet and outlet of canister were measured with pressure gauges to record the pressure drop across the canister, and determine whether there was any cake formation inside the reactor bed.
- Once the gaseous samples were collected with gastight syringes, they were manually injected into the Agilent gas chromatograph, model 6890N (GC/FID), to analyze their composition.

2.7 Fabrication of Diesel Engine Testing System, Task 5

The system for performing tests of the catalyst with actual diesel engine exhaust was designed and fabricated at the University of Alabama. First, a large container was designed to hold the catalyst canister, allow heating of the canister, filtration of the diesel particulates, and control of flow through the system. A major problem associated with the UAB laboratory canister system was that it was designed for an operating temperature range of 90-150°C (194 – 302°F) and the gaskets were made of Teflon. Teflon gaskets can be used up to ~230°C (446°F). During actual engine tests, the operating temperature range is 325-350°C (617 – 662°F). Therefore, a copper
A compact canister housing was designed to filter particulate matter and help maintain a uniform temperature in the canister, as shown in Figure 2-3. The housing consisted of an outer cylinder, which enclosed the canister. The annulus between the outer cylinder and the canister was divided into two partitions and filled with steel wool (#00 - #0000). Bypass exhaust gases from the engine entered one partition and passed through the steel wool, exited from the other partition. This process filtered the particulate matter and helped to maintain the temperature of the canister. The temperature and pressure of the filtered exhaust gases were measured, and a part of the exhaust gases was drawn for the emissions measurements. The filtered exhaust gases are then let into the canister. The gases leaving the canister were subjected to measurements of temperature and pressure and passed to the emissions bench for measuring the same exhaust gases mentioned above. The overall length of the cylindrical housing is about 8.9 cm and the diameter is 10.2 cm, per the design (Figure 2-3). The outer cylinder was machined from a piece of 4 inch OD stainless steel pipe. The circular disks upon which the canister rested were machined out of 0.19 inches thick steel plate. The partitions are also made out of 0.19 inch thick steel plate. Stainless steel Swagelok connectors were used to connect the removable sampling ports.

Although the bypass exhaust gases that circulate over the canister directly heat it, the relatively small volumetric flow was probably not sufficient to allow the catalyst to reach its light-off temperature quickly, thereby reducing its efficiency. A 3-in wide and 4-in OD Watlow band heater addressed this problem. The band heater was mounted around the outer cylinder. The temperature of the system was maintained between 325 and 375°C (617 and 707°F) by an electronic temperature controller (WATLOW 93AA-1DA0-00RG). The complete assembled system was mounted to a bypass off the main exhaust line leading from the Caterpillar test engine, as shown in Figure 2-4. A portion of the engine exhaust was diverted to the test system using an adjustable valve (not shown) in the main exhaust line. The diverted exhaust flow could be passed through the canister contained in the heated canister container for testing, or the exhaust flow could be bypassed around the canister when setting up, warming up, calibrating, but not collecting data.

2.8 Experimental Procedure and Analysis, Task 5

To simulate the varying operating conditions experienced by automotive diesel engines, a test matrix was identified from the engine literature. The test conditions represent the “Transient Federal Test Procedure,” as discussed by Cartellieri et al. [1992] and Greeves and Tullis [1993]. The intake pressure and temperature for each test conditions were obtained by interpolating the test conditions from the operating map of a commercial version of the test engine (Caterpillar 3406), as discussed by Montgomery and Reitz [1996]. The test matrix is shown in Table 2-1.

The experiments were carried out using 10 g of catalyst (supplied by Argonne National Laboratory) in the canister. The temperature of the canister and, therefore, the catalyst was maintained at about 350°C (662°F). Flow rates corresponding to 19,300 hr⁻¹ space velocities were used. The experimental data were recorded using a LabVIEW data acquisition system. The
experiments were repeated twice and the average data values were adopted for calculations and plotting.

Figure 2-3. Canister housing with sampling ports and band heater for diesel engine tests
Figure 2-4. Schematic diagram of the catalytic test set-up for diesel engine testing

Table 2-1. Diesel test conditions to simulate the transient FTP test

<table>
<thead>
<tr>
<th>Mode Number</th>
<th>Speed, (Rev/min)</th>
<th>Torque, (Nm)</th>
<th>Power, (kW)</th>
<th>Tin, (°C)</th>
<th>Pm, (kPa)</th>
<th>Pexh, (kPa)</th>
<th>Weight, (% of total)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>750</td>
<td>0.0</td>
<td>0.0</td>
<td>26</td>
<td>100</td>
<td>100</td>
<td>41.67</td>
</tr>
<tr>
<td>2</td>
<td>865</td>
<td>59.3</td>
<td>5.4</td>
<td>29</td>
<td>108</td>
<td>108</td>
<td>7.54</td>
</tr>
<tr>
<td>3</td>
<td>970</td>
<td>149</td>
<td>15.2</td>
<td>30</td>
<td>148</td>
<td>148</td>
<td>3.46</td>
</tr>
<tr>
<td>4</td>
<td>1086</td>
<td>199</td>
<td>22.7</td>
<td>31</td>
<td>168</td>
<td>167</td>
<td>3.97</td>
</tr>
<tr>
<td>5</td>
<td>1800</td>
<td>42.7</td>
<td>8.1</td>
<td>29</td>
<td>132</td>
<td>137</td>
<td>10</td>
</tr>
<tr>
<td>6</td>
<td>1747</td>
<td>94.9</td>
<td>17.4</td>
<td>31</td>
<td>148</td>
<td>148</td>
<td>12.44</td>
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<tr>
<td>7</td>
<td>1747</td>
<td>164</td>
<td>30.0</td>
<td>34</td>
<td>173</td>
<td>163</td>
<td>12.15</td>
</tr>
<tr>
<td>8</td>
<td>1684</td>
<td>225</td>
<td>39.8</td>
<td>40</td>
<td>239</td>
<td>220</td>
<td>8.73</td>
</tr>
</tbody>
</table>
Section 3.0
Equipment Calibration

3.1 Introduction

Prior to performing the experiments on the catalyst/zeolite canister system, several calibrations were performed on the equipment. Figure 3-1 shows the flow chart of calibration experiments conducted during the course of the project.

![Flow chart for calibration experiments](image)

3.2 Calibration of Tube Furnace

To heat the canister with the oven, the oven was calibrated. The oven was connected to a variable auto transformer, and the temperature inside the oven was obtained using two K-type thermocouples. After equilibration (one hour later), the temperature was read at different dial settings of the variable auto transformer, ranging from 10 percent to 70 percent of its maximum deliverable output voltage. Two observations were taken at each dial location to obtain the calibration curves. The room temperature was constant at 68°F (20°C), and the pressure was atmospheric. The results for the calibration are presented in Figures 3-2, 3-3, and 3-4.
Figure 3-2. Oven temperature with graduation of controller (for Observation No. 1)

Figure 3-3. Oven temperature with graduation of controller (for Observation No. 2)
3.3 Calibration of Canister Inlet/Outlet Temperature with Oven

Prior to the experiments on the catalysts/zeolites of the canister system, the canister was calibrated using the oven. The temperature of the canister inlet/outlet port was calibrated using the oven, the J-type thermocouples, and the temperature controller. As a precursor, the system was calibrated using ice water (32°F; 0°C) and boiling water (212°F; 100°C). The results for the calibration are shown in Figure 3-5.
3.4 Calibration of Reactor Bed Temperature with Oven

Prior to the experiments on the catalysts/zeolites of the canister system, the reactor bed was calibrated using the oven. The temperature of the reactor bed was calibrated using the oven, the J-type thermocouples, and the power supply received from Argonne National Laboratory. As a precursor, the system was calibrated using ice water (32°F; 0°C) and boiling water (212°F; 100°C). The results of the calibration are shown in Figures 3-6 and 3-7.

\[
y = 86.332e^{0.0227x} \\
R^2 = 0.9975
\]

\[
y = 49.155e^{0.0305x} \\
R^2 = 0.9993
\]
Figure 3-6. Temperature of reactor bed at different oven graduations

Figure 3-7. Comparison of temperature of canister inlet and reactor bed at different oven graduations
3.5 Measurement of Gas Flow Rates

The flow rate was measured by passing gas through a soap solution in a burette (6-in. diameter) at room temperature of 70°F. Compressed gas cylinders (95 percent Argon and 5 percent methane) were used. Two sets of data were collected at each pressure, and then the mean flow rate was calculated, as shown in Figure 3-8.

![Figure 3-8. Graph showing gas flow rate as a function of the applied pressure](image)

3.6 Statistical Analysis

Statistical t-tests were performed to determine whether the calibration curves obtained from increasing the voltage were statistically different or identical to those obtained from reversing the direction of applied voltage. By comparing the mean values of two variables, it was statistically concluded that the difference was not significant and temperature measured by increasing voltage or decreasing the voltage can be considered to be the same, i.e., the hysteresis effect was not significant [Lotus, 2004].
Section 4.0
Results and Discussion

4.1 Process of Research Investigation

Synthetic exhaust gas involving methane/butane was passed through two different catalysts packed in the canister system. Analysis of the exhaust gas was performed before and after it passed through the canister system. The sets of experiments conducted in this research investigation using methane gas and butane gas are shown in Tables 4-1 and 4-2, respectively.

This experimental study investigated the performance of two different catalyst samples. The compositions of the two catalysts are as follows:
(a) Sample ID: 2060-88-A; composition: 16.7 percent CeO$_2$, 83.3 percent Cu-ZSM-5
(b) Sample ID: 2060-88-B; composition: 18.7 percent ZrO$_2$, 81.3 percent Cu-ZSM-5.
Composition of methane gas: 52.2 ppm methane, balance air.
Composition of butane gas: 6 percent butane, 94 percent air.

Table 4-1. Permutations and combinations of experiments performed with methane gas

<table>
<thead>
<tr>
<th>Experimental Subset Number</th>
<th>Catalyst/Zeolite</th>
<th>Pressure, (psig)</th>
<th>Temperature, (°F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CeO$_2$/Cu-ZSM-5</td>
<td>6</td>
<td>200 to 800</td>
</tr>
<tr>
<td>2</td>
<td>CeO$_2$/Cu-ZSM-5</td>
<td>12</td>
<td>200 to 800</td>
</tr>
<tr>
<td>3</td>
<td>CeO$_2$/Cu-ZSM-5</td>
<td>18</td>
<td>200 to 800</td>
</tr>
<tr>
<td>4</td>
<td>CeO$_2$/Cu-ZSM-5</td>
<td>24</td>
<td>200 to 800</td>
</tr>
<tr>
<td>5</td>
<td>ZrO$_2$/Cu-ZSM-5</td>
<td>6</td>
<td>200 to 800</td>
</tr>
<tr>
<td>6</td>
<td>ZrO$_2$/Cu-ZSM-5</td>
<td>12</td>
<td>200 to 800</td>
</tr>
<tr>
<td>7</td>
<td>ZrO$_2$/Cu-ZSM-5</td>
<td>18</td>
<td>200 to 800</td>
</tr>
<tr>
<td>8</td>
<td>ZrO$_2$/Cu-ZSM-5</td>
<td>24</td>
<td>200 to 800</td>
</tr>
</tbody>
</table>

Table 4-2. Permutations and combinations of experiments performed with butane gas

<table>
<thead>
<tr>
<th>Experimental Subset Number</th>
<th>Catalyst/Zeolite</th>
<th>Pressure, (psig)</th>
<th>Temperature, (°F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CeO$_2$/Cu-ZSM-5</td>
<td>15</td>
<td>200 to 800</td>
</tr>
<tr>
<td>2</td>
<td>ZrO$_2$/Cu-ZSM-5</td>
<td>15</td>
<td>200 to 800</td>
</tr>
</tbody>
</table>
4.2 Effect of Catalyst Temperature

The removal efficiency of methane for both catalysts was monitored at temperatures ranging from 200 to 800°F (93.3 to 426.7°C) at an interval of 50°F (10°C) before the temperature exceeded T50, the temperature at which 50 percent removal of methane took place. Once that temperature was attained, the removal efficiency was monitored at an interval of 100°F (37.8°C) until the temperature reached 800°F (426.7°C) [Lotus, 2004]. Figures 4-1 and 4-2 show the effect of temperature on the conversion efficiency of methane for Cu ion-exchanged zeolite (Cu-ZSM-5) coated with CeO2 and ZrO2, respectively, at four different gas pressures. Tables 4.3 and 4.4 present the conversion efficiency data of methane for Cu ion-exchanged zeolite (Cu-ZSM-5) coated with CeO2 and ZrO2, respectively, at four different gas pressures.

Figure 4-3 shows the mean catalytic performances of the catalysts/zeolites used during the first phase of the project, “Diesel Exhaust Treatment Using Catalyst/Zeolites I,” at two different pressures (6 psig and 12 psig). From the graph, it can be seen that the conversion efficiency ranged from 29.3 percent to 72.8 percent, and for most of the catalysts, the conversion efficiency were below 60 percent [Gill, 2003; Peters et al., 2004].

Figures 4-4 and 4-5 show the mean catalytic performances of the two modified catalysts for the removal of butane gas in a fuel rich condition (6 percent butane and 94 percent air). Therefore, the modified catalysts showed much better performances than those catalyst/zeolites prepared during the preliminary investigation of this research work. It should be noted that in the previous studies, the catalysts were used in their powdered form rather than their pelletized/crushed form.

![Image of removal of methane using CeO2/Cu-ZSM-5 catalyst at different operating conditions]
Figure 4-2. Effect of temperature on the conversion efficiency of methane using the ZrO₂/Cu-ZSM-5 catalyst at different operating conditions

Table 4-3. Comparison of the methane conversion efficiency by the CeO₂/Cu-ZSM-5 catalyst at different operating conditions

<table>
<thead>
<tr>
<th>Temperature, (°F)</th>
<th>Conversion of methane at different space velocities, (%)</th>
<th>Decrease in conversion at 6 psig pressure from 24 psig pressure, (%)</th>
<th>Decrease in conversion at 12 psig pressure from 24 psig pressure, (%)</th>
<th>Decrease in conversion at 18 psig pressure from 24 psig pressure, (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>35.876, 37.545, 39.524, 42.854</td>
<td>16.283</td>
<td>12.388</td>
<td>7.770</td>
</tr>
<tr>
<td>300</td>
<td>40.764, 42.876, 43.674, 46.517</td>
<td>12.367</td>
<td>7.827</td>
<td>6.112</td>
</tr>
<tr>
<td>350</td>
<td>52.443, 54.459, 55.967, 60.387</td>
<td>13.155</td>
<td>9.817</td>
<td>7.319</td>
</tr>
<tr>
<td>400</td>
<td>80.221, 82.114, 87.496, 89.597</td>
<td>10.465</td>
<td>8.352</td>
<td>2.345</td>
</tr>
<tr>
<td>500</td>
<td>98.654, 96.832, 97.322, 99.783</td>
<td>1.1315</td>
<td>2.957</td>
<td>2.466</td>
</tr>
<tr>
<td>600</td>
<td>100, 100, 100, 100</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>700</td>
<td>100, 100, 100, 100</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>800</td>
<td>100, 100, 100, 100</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
Table 4-4. Comparison of the methane conversion efficiency by the ZrO₂/Cu-ZSM-5 catalyst at different operating conditions

<table>
<thead>
<tr>
<th>Temperature, (°F)</th>
<th>Conversion of methane at different space velocities, (%)</th>
<th>Decrease in conversion at 6 psig pressure from 24 psig pressure, (%)</th>
<th>Decrease in conversion at 12 psig pressure from 24 psig pressure, (%)</th>
<th>Decrease in conversion at 18 psig pressure from 24 psig pressure, (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10400 hr⁻¹</td>
<td>14,730 hr⁻¹</td>
<td>19,060 hr⁻¹</td>
<td>24,570 hr⁻¹</td>
</tr>
<tr>
<td>400</td>
<td>61.654</td>
<td>62.54</td>
<td>64.657</td>
<td>65.546</td>
</tr>
<tr>
<td>500</td>
<td>72.438</td>
<td>74.687</td>
<td>74.976</td>
<td>75.654</td>
</tr>
<tr>
<td>600</td>
<td>66.875</td>
<td>66.434</td>
<td>70.878</td>
<td>70.989</td>
</tr>
<tr>
<td>700</td>
<td>77.343</td>
<td>76.755</td>
<td>78.864</td>
<td>80.644</td>
</tr>
<tr>
<td>800</td>
<td>81.064</td>
<td>82.001</td>
<td>83.116</td>
<td>86.533</td>
</tr>
</tbody>
</table>

Figure 4-3. Mean removal efficiency of catalyst/zeolite of set I and set II at pressure 6 psig versus mean removal efficiency of catalyst/zeolite of set I and set II at pressure 12 psig [Gill, 2003].
Figure 4-4. Effect of temperature on the conversion efficiency of butane using the CeO₂/Cu-ZSM-5 catalyst at 15 psig pressure

Figure 4-5. Effect of temperature on the conversion efficiency of butane using the ZrO₂/Cu-ZSM-5 catalyst at 15 psig pressure
4.3 Effect of Space Velocity

Figures 4-6 and 4-7 show the effect of space velocity on the removal efficiency of methane of the CeO$_2$/Cu-ZSM-5 and ZrO$_2$/Cu-ZSM-5 catalysts, respectively. The space velocity ranged from ~10,000 hr$^{-1}$ to ~25,000 hr$^{-1}$.

From the figures, it is seen that the hydrocarbon removal efficiency was not significantly affected within the space velocity range of ~10,000 hr$^{-1}$ to ~25,000 hr$^{-1}$. The removal efficiency increased slightly as the space velocity increased.

4.4 Arrhenius Plot (Reaction Rate Constant, K versus T$^{-1}$)

Figures 4-8 through 4-11 show the Arrhenius plot (semilogarithmic) of reaction rate constant K versus T$^{-1}$ (inverse temperature) for both catalysts. For the methane removal reaction using CeO$_2$/Cu-ZSM-5 catalyst, the mean activation energy within the temperature range of 200 to 400°F was found to be 13.67 kJ/mol-oK, and for the ZrO$_2$/Cu-ZSM-5 catalyst the mean activation energy in the same range of temperature was 17.74 kJ/mol-oK [Lotus, 2004]. For the case of butane conversion reaction, the values of the activation energy were 8.03 kJ/mol-oK for the CeO$_2$/Cu-ZSM-5 catalyst, and 9.79 kJ/mol-oK for the ZrO$_2$/Cu-ZSM-5 catalyst in the same temperature range [Lotus, 2004].
Effect of space velocity on the conversion of methane using ZrO₂/Cu-ZSM-5 catalyst at different operating conditions

Figure 4-7. Effect of space velocity on the conversion efficiency of methane using ZrO₂/Cu-ZSM-5 catalyst at different operating conditions

Natural logarithm of rate constant, ln K vs. 1/T for CeO₂/Cu-ZSM-5 catalyst at different pressures/space velocities

Figure 4-8. Arrhenius plot (ln K vs. 1/T) for methane removal reaction using CeO₂/Cu-ZSM-5 catalyst at different pressures/space velocities
Figure 4-9. Arrhenius plot (ln K vs. 1/T) for methane removal reaction using ZrO_2/Cu-ZSM-5 catalyst at different pressures/space velocities

Figure 4-10. Arrhenius plot (ln K vs. 1/T) for butane removal reaction using CeO_2/Cu-ZSM-5 catalyst at 30,000 hr^{-1} space velocity
Figure 4-11. Arrhenius plot (ln K vs. 1/T) for butane removal reaction using ZrO₂/Cu-ZSM-5 catalyst at ~30,000 hr⁻¹ space velocity.

For the temperature range of 400-800°F, the mean activation energy for the methane removal reaction using CeO₂/Cu-ZSM-5 catalyst was 1.21 kJ/mol-°K, and that for the ZrO₂/Cu-ZSM-5 catalyst was found to be 3.2 kJ/mol-°K [Lotus, 2004]. For the butane conversion reaction, the activation energies were 3.24 kJ/mol-°K and 4.74 kJ/mol-°K, respectively [Lotus, 2004]. Therefore, it can be concluded that the CeO₂/Cu-ZSM-5 catalyst lowered the activation energy for hydrocarbon combustion reaction more than the ZrO₂/Cu-ZSM-5 catalyst.

4.5 Comparison of the Methane Conversion Efficiency of the CeO₂/Cu-ZSM-5 Catalyst at Different Operating Conditions

A comparison of the CeO₂/Cu-ZSM-5 catalyst at different operating conditions is shown in Table 4-3 and Figure 4-12. At 200°F (93.3°C), the mean methane removal efficiency was 34 percent. The removal efficiency reached nearly 100 percent when the temperature reached 500°F (260°C) and remained the same up to temperature range of 800°F (426.7°C) (i.e., complete removal of methane). Although space velocity did not have much effect on the removal efficiency throughout the operating range, the removal efficiency increased slightly.
4.6 Comparison of the Methane Conversion Efficiency of the ZrO₂/Cu-ZSM-5 Catalyst at Different Operating Conditions

A comparison of the ZrO₂/Cu-ZSM-5 catalyst at different operating conditions is shown in Table 4-4 and Figure 4-13. For the ZrO₂/Cu-ZSM-5 catalyst, the mean methane removal efficiency ranged from ~12 percent to 83 percent within the temperature range of 200-800°F (93.3-426.7°C) and space velocity range of ~10,000 hr⁻¹ to ~25,000 hr⁻¹. The effect of space velocity was not significant. As the space velocity increased from ~10,000 hr⁻¹ to ~25,000 hr⁻¹, the conversion efficiency increased slightly. There was a drop in efficiency at ~500°F (260°C), but it increased at 600°F (315.6°C) and continued to increase until the temperature reached 800°F (426.7°C). At a lower temperature level, the removal of methane by the catalysts is due to their adsorptive capacity rather than typical catalytic activity [Heck and Farrauto, 2001]. When the temperature reached ~500°F (260°C), the adsorption sites of zeolites were saturated by methane, and the additional flow of methane decreased the removal efficiency or perhaps the desorption of methane from zeolite was the predominant phenomenon at that temperature. Again, as the temperature was further increased, the catalytic activity (through chemical reactions) increased, causing another increase in removal efficiency. Thus, it can be concluded that in the case of catalyst ZrO₂/Cu-ZSM-5, hydrocarbons adsorbed at low temperature were desorbed when the exhaust gas temperature increased.
4.7 Comparison of the Hydrocarbon Conversion Efficiency of the CeO$_2$/Cu-ZSM-5 Catalyst with ZrO$_2$/Cu-ZSM-5 Catalyst at Different Operating Conditions

A comparison of the methane removal efficiency of the CeO$_2$/Cu-ZSM-5 catalyst with the ZrO$_2$/Cu-ZSM-5 catalyst at different operating conditions is shown in Tables 4-5 to 4-6 and Figures 4-14 to 4-17. It is evident from these graphs that the conversion efficiency increased with increased temperature for both the catalysts, and conversion efficiency was considerably higher for the CeO$_2$/Cu-ZSM-5 catalyst than for the ZrO$_2$/Cu-ZSM-5 catalyst. For the CeO$_2$/Cu-ZSM-5 catalyst, the mean removal efficiency was ~34 percent at 200°F (93.3°C), and the removal efficiency sharply increased to ~100 percent when the temperature reached 500°F (260°C). On the other hand, for the ZrO$_2$/Cu-ZSM-5 catalyst, the mean removal efficiency was ~12 percent at 200°F (93.3°C); at 500°F (260°C), the mean removal efficiency was ~74 percent; and the efficiency was increased to ~83 percent as the temperature increased to 800°F (426.7°C). A comparison of the butane removal efficiency of the CeO$_2$/Cu-ZSM-5 catalyst with that of the ZrO$_2$/Cu-ZSM-5 catalyst at different operating conditions is shown in Table 4-7 and Figure 4-18.
Table 4-5. Comparison of the methane conversion efficiency by the CeO$_2$/Cu-ZSM-5 and ZrO$_2$/Cu-ZSM-5 catalysts at different operating conditions

| Temperature, (°F) | Nominal space velocity, 10,400 hr$^{-1}$ | | Nominal space velocity, 14,730 hr$^{-1}$ | | Decrease in efficiency, (%) | Decrease in efficiency, (%) |
|------------------|------------------------------------------|------------------|------------------------------------------|------------------|------------------|
|                  | Methane conversion efficiency, (%)      | CeO$_2$/Cu-ZSM-5 | ZrO$_2$/Cu-ZSM-5                      | CeO$_2$/Cu-ZSM-5 | ZrO$_2$/Cu-ZSM-5 |
| 200              | 31.665                                   | 9.496            | 70.011                                  | 33.232           | 10.996           | 66.911 |
| 250              | 35.876                                   | 11.462           | 68.051                                  | 37.545           | 12.456           | 66.823 |
| 300              | 40.764                                   | 19.154           | 53.012                                  | 42.876           | 19.873           | 53.650 |
| 350              | 52.443                                   | 25.141           | 52.060                                  | 54.459           | 25.433           | 53.298 |
| 400              | 80.221                                   | 60.654           | 24.391                                  | 82.114           | 62.540           | 23.837 |
| 500              | 98.654                                   | 72.438           | 26.573                                  | 96.832           | 74.687           | 22.869 |
| 600              | 100                                      | 66.875           | 33.125                                  | 100              | 70.434           | 29.566 |
| 700              | 100                                      | 77.343           | 22.657                                  | 100              | 76.755           | 23.245 |
| 800              | 100                                      | 81.064           | 18.936                                  | 100              | 82.001           | 17.999 |

Table 4-6. Comparison of the methane conversion efficiency by the CeO$_2$/Cu-ZSM-5 and ZrO$_2$/Cu-ZSM-5 catalysts at different operating conditions

| Temperature, (°F) | Nominal space velocity, 19,600 hr$^{-1}$ | | Nominal space velocity, 24,570 hr$^{-1}$ | | Decrease in efficiency, (%) | Decrease in efficiency, (%) |
|------------------|------------------------------------------|------------------|------------------------------------------|------------------|------------------|
|                  | Methane conversion efficiency, (%)      | CeO$_2$/Cu-ZSM-5 | ZrO$_2$/Cu-ZSM-5                      | CeO$_2$/Cu-ZSM-5 | ZrO$_2$/Cu-ZSM-5 |
| 200              | 34.517                                   | 11.753           | 65.950                                  | 36.731           | 14.662           | 60.082 |
| 250              | 39.524                                   | 14.345           | 63.706                                  | 40.854           | 16.945           | 58.523 |
| 300              | 43.674                                   | 19.899           | 54.437                                  | 44.517           | 22.874           | 48.617 |
| 350              | 55.967                                   | 25.943           | 53.646                                  | 57.387           | 27.655           | 51.809 |
| 400              | 87.496                                   | 64.657           | 26.103                                  | 85.597           | 65.546           | 23.425 |
| 500              | 97.322                                   | 74.976           | 22.960                                  | 98.113           | 75.654           | 22.891 |
| 600              | 100                                      | 68.878           | 31.121                                  | 100              | 70.989           | 29.011 |
| 700              | 100                                      | 78.864           | 21.136                                  | 100              | 80.644           | 19.356 |
| 800              | 100                                      | 83.116           | 16.883                                  | 100              | 86.533           | 13.467 |
Figure 4-14. Comparison of the methane conversion efficiencies of CeO$_2$/Cu-ZSM-5 and ZrO$_2$/Cu-ZSM-5 catalysts at 6 psig pressure

Figure 4-15. Comparison of the methane conversion efficiencies of CeO$_2$/Cu-ZSM-5 and ZrO$_2$/Cu-ZSM-5 catalysts at 12 psig pressure
Figure 4-16. Comparison of the methane conversion efficiencies of CeO$_2$/Cu-ZSM-5 and ZrO$_2$/Cu-ZSM-5 catalysts at 18 psig pressure

Figure 4-17. Comparison of the methane conversion efficiencies of CeO$_2$/Cu-ZSM-5 and ZrO$_2$/Cu-ZSM-5 catalysts at 24 psig pressure
Table 4-7. Comparison of the butane conversion efficiency by the CeO$_2$/Cu-ZSM-5 and ZrO$_2$/Cu-ZSM-5 catalysts at different operating conditions

<table>
<thead>
<tr>
<th>Temperature, ($^\circ$F)</th>
<th>Nominal space velocity, $\sim$30,000 hr$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Butane conversion efficiency, (%)</td>
</tr>
<tr>
<td></td>
<td>CeO$_2$/Cu-ZSM-5</td>
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<td>700</td>
<td>98.69</td>
</tr>
<tr>
<td>800</td>
<td>100</td>
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</table>

Figure 4-18. Comparison of the butane conversion efficiencies of CeO$_2$/Cu-ZSM-5 and ZrO$_2$/Cu-ZSM-5 catalysts at 15 psig pressure

4.8 Statistical Analysis

From the t-tests, it was concluded that the space velocity effect on the removal efficiency of methane with CeO$_2$/Cu-ZSM-5 and ZrO$_2$/Cu-ZSM-5 catalysts at the range of $\sim$10,000 hr$^{-1}$ to $\sim$25,000 hr$^{-1}$ was not statistically significant. The result of a t-test on the removal efficiency of methane with CeO$_2$/Cu-ZSM-5 and ZrO$_2$/Cu-ZSM-5 catalysts at different temperatures showed that the null hypothesis was rejected in each case (i.e., $\alpha < 0.05$). Therefore, it was concluded
statistically that temperature had a significant effect on the removal efficiency of methane for both catalysts.

The mean performance for the removal of methane gas using the two catalyst/zeolite matrices was evaluated using t-tests for the differences in mean values, assuming a confidence level at 95% ($\alpha = 0.05$). Comparison of the mean removal efficiency of CeO$_2$/Cu-ZSM-5 and ZrO$_2$/Cu-ZSM-5 catalysts at different space velocity/pressure conditions showed that the null hypothesis was accepted for every case (i.e., $\alpha > 0.05$), indicating that the mean removal efficiencies of the catalysts at different space velocity/pressure conditions were statistically the same [Lotus, 2004]. Comparison of the mean removal efficiency of the CeO$_2$/Cu-ZSM-5 and ZrO$_2$/Cu-ZSM-5 catalysts at different temperatures showed that the null hypothesis was rejected for every case (i.e., $\alpha < 0.05$) indicating that the mean removal efficiencies of the catalysts at different temperatures were statistically different.

4.9 Results of Task 5, Testing of Catalyst on Diesel Engine Exhaust

The single-cylinder Caterpillar 3400 engine was operated at the eight steady-state test conditions identified in the literature that, when appropriately weighted, yield results similar to the Transient FTP Test. Two sets of data were collected at each of the eight test conditions. At each operating condition, the reported measurements represent the average of measurements made over a 3-minute period after steady state operation had been achieved. This section reports the measurements made on diesel exhaust. Table 4-8 shows results from the first test run on January 13, 2005 at the eight engine conditions previously described in Table 3-1. Table 4-9 shows similar results for the second set of tests, performed on January 23, 2005. As can be seen in both Tables 4-8 and 4-9, the presence of the catalyst had a negligible effect on the concentration of the exhaust concentrations of CO, CO$_2$, O$_2$, and NO$_x$.

The primary interest in this study was the reduction of unburned hydrocarbons (UHC). Results for average values of UHC with and without the catalyst are presented in Table 4-10 for engine modes 1-8. The weight of each engine mode is also provided. These mode weights were used to calculate a weighted average of all modes that should provide a result similar to the Transient FTP test. The average percentage UHC reduction caused by the catalyst was also calculated for each engine mode. Finally, the product of the percent hydrocarbon reduction and the mode weight was reported for each engine mode, and the sum of these represents the weighted average hydrocarbon reduction for the two sets of measurements. An unburned hydrocarbons reduction of about 16 percent was obtained.

Tests performed for hydrocarbon reduction on actual diesel engine exhaust did not produce hydrocarbon reduction to the degree observed in the simulated exhaust experiments. There are several reasons this could be the case. First, the model hydrocarbons selected may not be representative of the complex mix of thousands of hydrocarbon species found in engine exhaust. Second, because of the late receipt of the catalyst sample, sufficient time was not available to optimize space velocities and the physical characteristics of the catalytic pellets. Considering that this was the first testing of the catalyst in actual diesel exhaust, the results should be viewed as a promising starting point for future development.
Table 4-8. Diesel exhaust results from January 13, 2005 tests

<table>
<thead>
<tr>
<th>Mode</th>
<th>Canister Temp., (°C)</th>
<th>Exhaust Gas Flow Rate, (mL/min)</th>
<th>Space Velocity, (hr⁻¹)</th>
<th>CO, (ppm)</th>
<th>CO₂, (%)</th>
<th>UHC, (ppm)</th>
<th>NOₓ, (ppm)</th>
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Table 4-9. Diesel exhaust results from January 23, 2005 tests

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<th>Exhaust Gas Flow Rate, (mL/min)</th>
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<th>CO(_2), (%)</th>
<th>UHC, (ppm)</th>
<th>NO(_x), (ppm)</th>
<th>O(_2), (%)</th>
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Table 4-10. Average unburned hydrocarbon reduction results

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<th>Weight x % Reduction</th>
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<td>8.73</td>
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Weighted Average Reduction: 15.7%
4.10 Summary

The modified catalysts showed much better performances than those catalyst/zeolites prepared in the absence of CeO₂ and ZrO₂ on Cu-ZSM-5 catalyst. The removal of methane using these catalysts exhibited an “S”-type behavior with increasing temperature. For the CeO₂-coated catalyst, nearly 100 percent removal of methane was achieved for temperatures exceeding 500°F (260°C); for the ZrO₂-coated catalyst, a maximum of 87 percent removal of methane was achieved at a temperature of 800°F (426.7°C); i.e., complete conversion of methane was not achieved using the ZrO₂-coated catalyst. The temperature T₅₀ at which 50 percent removal of methane occurred was at a temperature of ~340°F (171.1°C) and ~500°F (260°C) for the CeO₂-coated and ZrO₂-coated catalysts, respectively. For the ZrO₂-coated catalyst, a decrease in removal efficiency of methane was observed for a temperature of ~500°F (260°C), after which the removal efficiency again increased for temperatures exceeding ~600°F (315.6°C). At the lower temperature levels, the removal of methane by the catalysts was due to their adsorptive capacity rather than by catalytic activity. At ~500°F (260°C), the adsorption sites of the zeolites became saturated, causing additional flow of methane to decrease the removal efficiency of methane. Similar behavior was observed using butane as the fuel source. After reaching a temperature of 600°F (315.6°C), the methane effectively desorbed from the zeolite, resulting in a light-off. For space velocities ranging from ~10,000 hr⁻¹ to ~25,000 hr⁻¹, the hydrocarbon removal efficiency was not significantly affected.

For the methane removal reaction using CeO₂/Cu-ZSM-5 catalyst, the mean activation energy within the temperature range of 200 to 400°F (93.3 to 204.4°C) was found to be 13.67 kJ/mol-°K, and for the ZrO₂/Cu-ZSM-5 catalyst, the mean activation energy in the same temperature range was 17.74 kJ/mol-°K. For the temperature range of 400-800°F, the mean activation energy for the methane removal reaction using CeO₂/Cu-ZSM-5 catalyst was 1.21 kJ/mol-°K, and that for the ZrO₂/Cu-ZSM-5 catalyst was found to be 3.2 kJ/mol-°K. For the butane conversion reaction, the activation energies were 3.24 kJ/mol-°K and 4.74 kJ/mol-°K, respectively. It was concluded that the CeO₂/Cu-ZSM-5 catalyst lowered the activation energy for hydrocarbon combustion reaction more than the ZrO₂/Cu-ZSM-5 catalyst.

For the case of butane conversion reaction in the range of 200 to 400°F (93.3 to 204.4°C), the activation energies were ~8.03 kJ/mol-°K for the CeO₂/Cu-ZSM-5 catalyst, and 9.79 kJ/mol-°K for the ZrO₂/Cu-ZSM-5 catalyst in the same temperature range. For temperatures in the range of 400 to 800°F (204.4 to 426.7°C), the activation energies were 3.24 kJ/mol-°K and 4.74 kJ/mol-°K, respectively. As a result, for removal of both methane and butane, it was concluded that the CeO₂/Cu-ZSM-5 catalyst lowered the activation energy for hydrocarbon combustion reaction more than the ZrO₂/Cu-ZSM-5 catalyst.

Tests performed for hydrocarbon reduction on actual diesel engine exhaust did not produce hydrocarbon reduction to the degree observed in the simulated exhaust experiments. This may be the result of the model hydrocarbons selected may not be representative of the complex mix of thousands of hydrocarbon species found in engine exhaust, and due to insufficient time being available to optimize space velocities and the physical characteristics of the catalytic pellets.
Section 5.0
Project Conclusions and Future Recommendations

5.1 Conclusions

The performance of copper ion-exchanged ZSM-5 catalysts coated with CeO$_2$ and ZrO$_2$ for oxidation of hydrocarbon (methane and butane) was studied. Both catalysts exhibited substantial hydrocarbon removal performances over a wide temperature range in conditions similar to lean burn engine exhaust as well in fuel rich exhaust condition. The major conclusions from this research investigation are summarized below:

- The modified catalysts showed much better performances than those catalyst/zeolites prepared in the absence of CeO$_2$ and ZrO$_2$ on Cu-ZSM-5 catalyst.
- The removal of methane using these catalysts exhibited an “S”-type behavior with increasing temperature. For the CeO$_2$-coated catalyst, nearly 100 percent removal of methane was achieved for temperatures exceeding 500°F (260°C); for the ZrO$_2$-coated catalyst, a maximum of 87 percent removal of methane was achieved at a temperature of 800°F (426.7°C); i.e., complete conversion of methane was not achieved using the ZrO$_2$-coated catalyst.
- The temperature $T_{50}$ at which 50 percent removal of methane occurred was at a temperature of ~340°F (171.1°C) and ~500°F (260°C) for the CeO$_2$-coated and ZrO$_2$-coated catalysts, respectively.
- For the ZrO$_2$-coated catalyst, a decrease in removal efficiency of methane was observed for a temperature of ~500°F (260°C), after which the removal efficiency again increased for temperatures exceeding ~600°F (315.6°C). At lower temperature levels, the removal of methane by the catalysts was due to their adsorptive capacity rather than by catalytic activity. At ~500°F (260°C), the adsorption sites of the zeolites became saturated, causing additional flow of methane to decrease the removal efficiency of methane. Similar behavior was observed using butane as the fuel source. After reaching a temperature of 600°F (315.6°C), the methane effectively desorbed from the zeolite, resulting in a light-off.
- For space velocities ranging from ~10,000 hr$^{-1}$ to ~25,000 hr$^{-1}$, the hydrocarbon removal efficiency was not significantly affected.
- The CeO$_2$/Cu-ZSM-5 catalyst lowered the activation energy for hydrocarbon combustion reaction more than the ZrO$_2$/Cu-ZSM-5 catalyst.
- Tests performed for hydrocarbon reduction on actual diesel engine exhaust did not produce hydrocarbon reduction to the degree observed in the simulated exhaust experiments. This may be the result of the model hydrocarbons selected may not be representative of the complex mix of thousands of hydrocarbon species found in engine exhaust, and due to insufficient time being available to optimize space velocities and the physical characteristics of the catalytic pellets.

A summary of the observations from the project is given below.
1. The copper ion-exchanged ZSM-5 zeolite catalyst showed good catalytic performance in reducing hydrocarbons from synthetic diesel exhaust gas, and the hydrocarbon reduction efficiency did not decrease up to a space velocity of \(~25,000\ \text{hr}^{-1}\). Therefore, the metal ion (Cu)-exchanged zeolite (ZSM-5) is a promising catalyst for removing hydrocarbons from diesel exhaust.

2. The incorporation of oxide additives such as CeO\(_2\) or ZrO\(_2\) onto Cu ion-exchanged zeolite (Cu-ZSM-5) enhanced the catalytic performance significantly.

3. The catalytic activity of Cu ion-exchanged zeolite (Cu-ZSM-5) differed noticeably with the oxide additive species. The catalyst coated with CeO\(_2\) showed much better performance for removing hydrocarbons from exhaust gas than did the ZrO\(_2\)-coated Cu-ZSM-5.

4. For the CeO\(_2\)/Cu-ZSM-5 catalyst, the mean conversion efficiency of methane ranged from 34 percent to 100 percent within the temperature range of 200-800°F (93.3-426.7°C) and space velocity range of \(~10,000\ \text{hr}^{-1}\) to \(~25,000\ \text{hr}^{-1}\). For the ZrO\(_2\)/Cu-ZSM-5 catalyst, the mean methane removal efficiency ranged from \(~12\) percent to 83 percent within the temperature range of 200-800°F (93.3-426.7°C) and space velocity range of \(~10,000\ \text{hr}^{-1}\) to \(~25,000\ \text{hr}^{-1}\).

5. The effect of space velocity on the removal efficiency for both catalysts was not significant. The removal efficiency increased slightly with the increasing space velocity within the range \(~10,000\ \text{hr}^{-1}\) to \(~25,000\ \text{hr}^{-1}\).

6. For the CeO\(_2\)/Cu-ZSM-5 catalysts, \(T_{50}\) (i.e. the temperature at which 50 percent removal of methane took place) was \(~340°F\ (171.1°C)\), while for the ZrO\(_2\)/Cu-ZSM-5 catalysts, \(T_{50}\) was \(~380°F\ (193.3°C)\). In the case of the CeO\(_2\)/Cu-ZSM-5 catalysts, 100 percent removal of methane was achieved at a temperature of \(~500°F\ (260°C)\), while for the ZrO\(_2\)/Cu-ZSM-5 catalyst, the mean removal efficiency of hydrocarbons at that temperature was \(~74\) percent. Complete removal of methane was not achieved for the ZrO\(_2\)/Cu-ZSM-5 catalyst within the operating conditions for this investigation, and the highest removal efficiency that could be attained was \(~87\) percent for a temperature of 800°F (426.7°C).

7. A decrease in removal efficiency of methane was observed at \(~500°F\ (260°C)\) temperature for the ZrO\(_2\)/Cu-ZSM-5 catalyst, and the removal efficiency again increased at temperature 600°F (315.6°C). The phenomenon can be attributed to the fact that, at a lower temperature level, the removal of methane by the catalysts is due to their adsorptive capacity rather than typical catalytic activity. When the temperature reached \(~500°F\ (260°C)\), as the adsorption sites of zeolites were saturated by methane already, the additional flow of methane decreased the removal efficiency, or perhaps the desorption of methane from zeolite was the predominant phenomenon at that temperature. Again, as the temperature was further increased, the catalytic activity (through chemical reactions) increased, causing another increase in removal efficiency. Thus, it was concluded that in the case of catalyst ZrO\(_2\)/Cu-ZSM-5, hydrocarbons adsorbed at low temperature were desorbed when the exhaust gas temperature increased. On the other hand, the CeO\(_2\)/Cu-ZSM-5 catalyst effectively reduced hydrocarbon emissions throughout the entire temperature range.

8. For the CeO\(_2\)/Cu-ZSM-5 catalyst, the mean conversion efficiency of butane ranged from 41 percent to 100 percent within the temperature range of 200-800°F (93.3-426.7°C) and space velocity range of \(~30,000\ \text{hr}^{-1}\). Again, for the ZrO\(_2\)/Cu-ZSM-5 catalyst, the mean butane removal efficiency ranged from \(~30\) percent to 87 percent within the temperature range of 200-800°F (93.3-426.7°C) and space velocity range of \(~30,000\ \text{hr}^{-1}\).
9. For the CeO$_2$/Cu-ZSM-5 catalyst, the mean activation energy for methane conversion reaction within the temperature range of 200 to 400°F (93.3 to 204.4°C) was found to be 13.67 kJ/mol-oK and for the ZrO$_2$/Cu-ZSM-5 catalyst the mean activation energy in the same range of temperature was 17.74 kJ/mol-oK.

10. For the CeO$_2$/Cu-ZSM-5 catalyst, the mean activation energy for the methane conversion reaction within the temperature range of 400 to 800°F (204.4 to 426.7°C) was 1.21 kJ/mol-oK and that for the ZrO$_2$/Cu-ZSM-5 catalyst was 3.2 kJ/mol-oK.

11. For the CeO$_2$/Cu-ZSM-5 catalyst, the mean activation energy for butane conversion reaction within the temperature range of 200 to 400°F (93.3 to 204.4°C) was found to be 8.03 kJ/mol-oK and for the ZrO$_2$/Cu-ZSM-5 catalyst the mean activation energy in the same range of temperature was 9.79 kJ/mol-oK.

12. For the CeO$_2$/Cu-ZSM-5 catalyst, the mean activation energy for the methane conversion reaction within the temperature range of 400 to 800°F (204.4 to 426.7°C) was 3.24 kJ/mol-oK and that for the ZrO$_2$/Cu-ZSM-5 catalyst was 4.74 kJ/mol-oK.

13. In contrast to the preliminary research work [Gill, 2003; Peters et al., 2004], pelletizing the powdered form of the catalyst significantly reduced the pressure drop through the canister. For the space velocity range of ~10,000 hr$^{-1}$ to ~25,000 hr$^{-1}$, the pressure drop through the canister was ~1.0 psi.

14. Tests performed of hydrocarbon reduction on actual diesel engine exhaust did not produce hydrocarbon reduction to the degree observed in the simulated exhaust experiments. There are several reasons this could be the case. First, the model hydrocarbons selected may not be representative of the complex mix of thousands of hydrocarbon species found in engine exhaust. Second, because of the late receipt of the catalyst sample, sufficient time to optimize space velocities as well as the physical characteristics of the catalytic pellets. Considering that this was the first run of the catalyst in actual diesel exhaust, the results should be viewed as a promising starting point for future development.

5.2 Recommendations for Future Work

Recommendations to pursue development of this technology are as follows:

1. Investigate other additives in addition to CeO$_2$ and ZrO$_2$ and make a comparison of their catalytic properties.
2. Investigate aging effects on both catalysts at different operating conditions.
3. Investigate the effect of temperature on both catalysts at temperatures above 800°F (426.7°C) as well as at smaller windows of temperature (e.g., 25°F (3.9°C) interval).
4. Investigate the effect of space velocities on the hydrocarbon removal efficiency up to the range of 120,000 hr$^{-1}$.
5. Modify the canister system, so that it can handle space velocities in the range up to 120,000 hr$^{-1}$.
6. Perform the experiments using honeycomb-structured industrial-grade catalysts.
7. Test the upgraded catalyst system on actual diesel exhaust at full exhaust flow using 2007/2010 very-low-sulfur diesel exhaust and diesel particulate traps now becoming commercially available.
5.3 Papers Presented at National Conferences

A number of technical papers, based upon the results obtained from this study, have been presented at national conferences. These papers are listed in Appendix B.


Appendix A
Preparational Procedure For CeO₂ AND ZrO₂ COATED Cu-ZSM-5: “Ion-Exchange” Approach

Ammonium forms of ZSM-5 (MFI) with SiO₂/Al₂O₃ = 50 were provided by Zeolyst International. To obtain the H-forms, the zeolite was calcined at 500°C for 4 hours in a vacuum furnace. Copper was ion-exchanged into the zeolite according to commonly used procedures. To obtain a 50% exchanged Cu-ZSM-5 sample (following the commonly used nomenclature where 100% exchanged stands for one Cu ion per every two Al sites), 100 mL of a 0.015 M Cu(NO₃)₂·2.5 H₂O (99.99% Aldrich) solution were stirred vigorously with 10 grams of H-ZSM-5 (SiO₂/Al₂O₃ = 50) for 2 hr before adjusting the pH dropwise to 8.0 using a 0.8 M NH₄OH (30%, AR, Mallinkrodt) solution while stirring. The slurry was kept under stirring for an additional 24-hr period. The solid was filtered, rinsed with water, and dried at 100°C. The sample was calcined for 4-hr at 450-500°C.

Metal oxides (CeO₂, ZrO₂) were added to the metal-exchanged zeolite by incipient wetness impregnation of a nanoparticle sol. For instance, to prepare a 20% CeO₂/Cu-ZSM-5 catalyst, where 20% stands for the added weight of ceria, 1.2 mL of CeO₂ sol (20%, Nyacol, 20 nm, acetate stabilized) were impregnated on 1.0 grams of Cu-ZSM-5 under constant mechanical mixing. After drying at 100°C, the solid sample was calcined at 500°C for 4 hr. 1.05 mL of ZrO₂ sol (20%, Nyacol, acetate stabilized) were used for the preparation of 23% ZrO₂/Cu-ZSM-5.
Appendix B
Papers Presented at National Conferences


Lotus, A.F., and R.W. Peters, 2004. “Study of an Oxidation Catalyst System for Diesel Exhaust Treatment”, Paper accepted for presentation at the Southern States Environmental Conference, Biloxi, Mississippi, (September 21), which was later cancelled due to the Hurricane Ivan.