COMPARISON OF VARIOUS OXIDATION CATALYST/ZEOLITE SYSTEMS FOR TREATING DIESEL EXHAUST FROM MOBILE SOURCES

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ABSTRACT

Catalytic converters have become a viable post treatment system for reducing emissions from on-highway diesel engines. This investigation attempts 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, catalyst/zeolites were used in a laboratory scale plug flow reactor system to treat synthetic diesel exhaust gas at an operating temperature of 200-300°F, 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% to 80% depending upon the variation in the composition or structure of the catalyst samples. Taking into account the drawbacks from the preliminary work, two modified catalysts were prepared which involved incorporating CeO_2 and ZrO_2 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 pressures. The conversion efficiency of methane was tested using both catalysts for temperatures in the range from 200 to 800°F at four different space velocities (from ~10,000 to ~30,000 hr^{-1}). The conversion efficiency of butane was also tested at the same temperature range and space velocity ~30,000 hr^{-1}. The new catalysts showed very good performance for hydrocarbon conversion and efficiencies up to 100% were achieved. The catalyst coated with CeO_2 showed much better performance for removing hydrocarbons from exhaust gas than that of ZrO_2 coated Cu-ZSM-5. The hydrocarbon reduction efficiency did not decrease significantly, up to a space velocity of ~30,000 hr^{-1}.

INTRODUCTION

The pollution emitted by diesel engines contributes greatly to America's continuing air quality problems. 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 [1]. 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, engine durability and the resultant benefits of reduced CO_2 emission. 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 EPA for Model Year 2007 and later are calling for a 92% reduction of NO_x emissions (0.20 g/bhp-hr) and 93% reduction of nonmethane hydrocarbons (NMHC) emissions (0.14 g/bhp-hr) compared to the EPA emission standards for Model Year 2004 (NO_x emissions level of 2.4 g/bhp-hr and NMHC emissions level of 2.0 g/bhp-hr) [2]. For some vehicles, it will be difficult to meet the EPA emission standards for Model Year 2007 and later targets by engine improvement alone. This problem can be solved through the application of high-efficiency emissions control technologies, resulting 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.

BACKGROUND

Diesel exhaust is a complex mixture of gases, vapors, and fine particulates. 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 (SO_x), nitrogen oxides (NO_x), volatile hydrocarbons, and low-molecular weight polycyclic aromatic hydrocarbons (PAHs) and PAH derivatives. Exhaust gases containing these harmful components are emitted into the air after purification of the exhaust using a catalyst. The catalyst converts NO_x, HC and CO contained in exhaust gases, into innocuous nitrogen, carbon dioxide or water by the catalyst metal.

Diesel and lean-burn gasoline engines generally operate under highly oxidizing conditions, 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_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 the gasoline cars, is not operational in diesel vehicles [3].

Diesel exhaust has high particulate content compared to gasoline engine exhaust and these particulates mainly consist of elemental carbon, unburnt hydrocarbons and oxides. HC conversion in the catalytic converter is strongly influenced by temperature and is generally carried out at temperatures exceeding 300°C (572°F). 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.

In this project, catalyst compositions for oxidizing gaseous pollutant (hydrocarbon) from diesel engine exhaust has been studied. The goal of the research work involved using oxidation catalysts comprising copper ion (Cu^{2+})-exchanged zeolite (ZSM-5) coated with high surface area ceria or zirconia to treat synthetic diesel exhaust. The experimental procedure of the research work involved passing methane (52.2 ppm, balance air) and butane gas (6% butane, balance air), separately through the plug flow canister system.

OBJECTIVE

The objective of this study was to develop and test oxidation catalysts/zeolites for their ability to effectively treat synthetic diesel exhaust (containing mainly hydrocarbons).

EXPERIMENTAL PROCEDURE

A plug flow canister containing the catalysts/zeolites was prepared for testing the removal efficiencies of hydrocarbons (methane and butane) in the laboratory. Two catalyst samples, obtained from Argonne National Laboratory, were tested at different operating conditions to compare the effectiveness of each catalyst/support media matrix. Sampling ports were on both sides of the canisters to enable gas samples to be collected by gas tight syringes and analyzed to determine the system performance as a function of the gas throughput and operating temperature. Two different catalysts were used: (i) Sample A – composition: 16.7% CeO_2, 83.3% Cu-ZSM-5, and (ii) Sample B – composition: 18.7% ZrO_2, 81.3% Cu-ZSM-5. Two different compositions for the synthetic diesel exhaust were used: (i) 52.2 ppm methane (CH_4), and (ii) 6% butane, with the balance being air. A schematic diagram of the experimental set-up of the catalyst/zeolite canister system is provided in Figure 1.

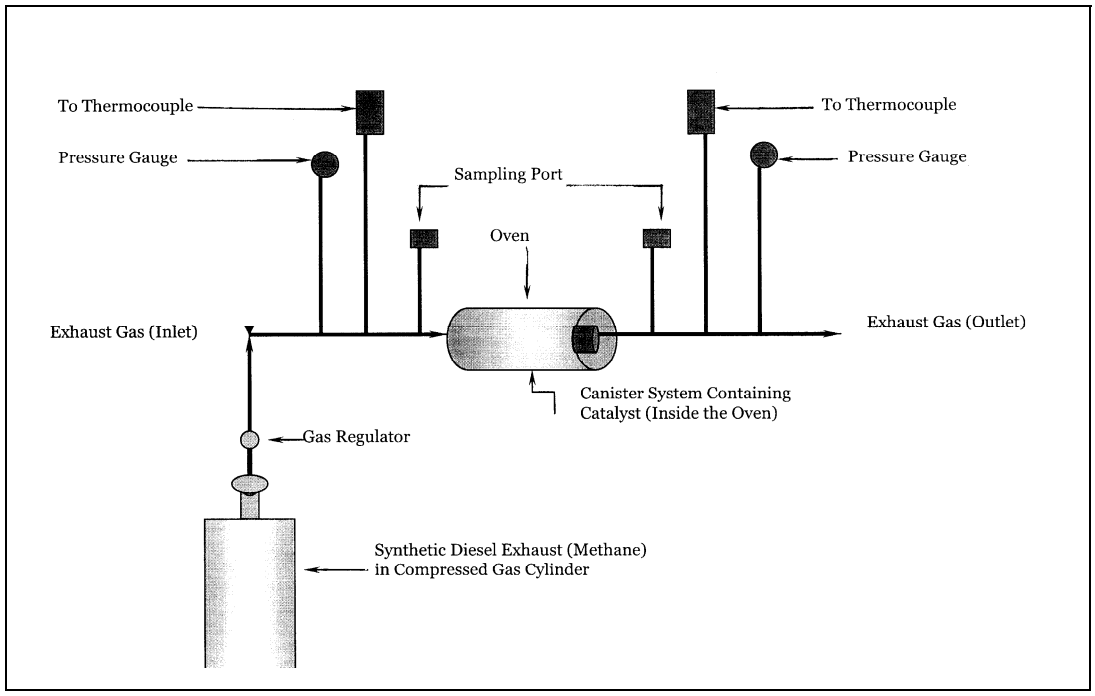

FIGURE 1. Schematic diagram of the experimental set-up of the catalyst/zeolite canister.

RESULTS AND DISCUSSIONS

Effect of Zeolite Structures. The methane removal efficiency by different zeolites was evaluated at the temperature range of ~200-300°F and pressure of 6 psig and 12 psig, respectively. Figure 2 shows the mean catalytic performance of the catalysts/zeolites used

during the first phase of the project. The methane removal efficiencies ranged from 29.3% to 72.8%, and for most of the catalysts/zeolites, the mean removal efficiency was below 60% [4]. However, the MFI (ZSM-5) structure showed good promise for hydrocarbon removal at low temperature range.

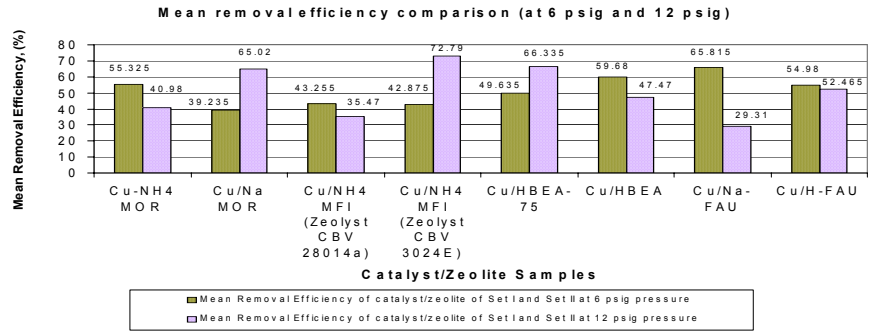

FIGURE 2. Mean removal efficiency of catalyst/zeolite at pressure 6 psig versus mean removal efficiency of catalyst/zeolite at pressure 12 psig [Gill, 2003].

Effect of Catalyst Temperature. CH_4 removal efficiency using both catalysts was monitored for temperatures ranging from 200 to 800°F. Figures 3 and 4 show the effect of temperature on the removal efficiency of CH_4 for Cu ion-exchanged zeolite (Cu-ZSM-5) coated with CeO_2 and ZrO_2 at different space velocities.

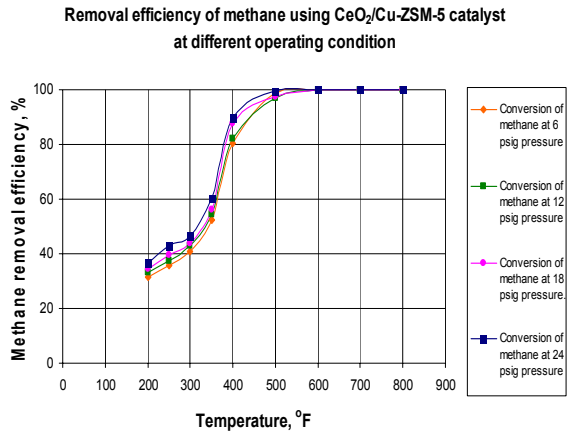

FIGURE 3. Methane conversion efficiency using CeO_2/Cu-ZSM-5 catalyst at different operating conditions.

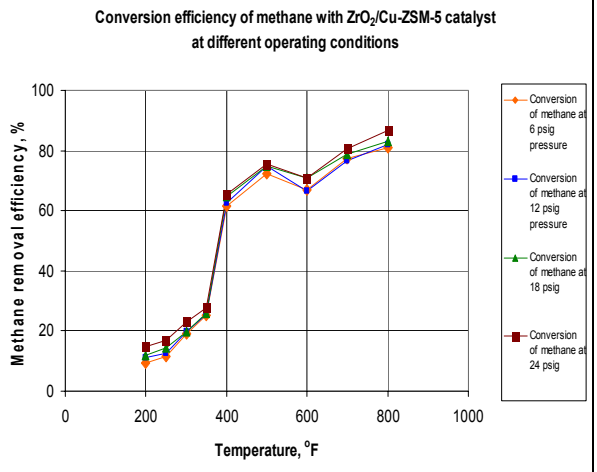

FIGURE 4. Methane conversion efficiency using ZrO_2/Cu-ZSM-5 catalyst at different operating conditions.

Figure 5 shows comparison of the removal efficiency of butane (6 wt % in air) using both the catalyst samples.

The conversion efficiency increased with increasing temperature for both catalysts and conversion efficiency was considerably higher for the CeO_2/Cu-ZSM-5 catalyst than that of the ZrO_2/Cu-ZSM-5 catalyst. For the CeO_2/Cu-ZSM-5 catalyst, the mean removal efficiency of methane was ~34% at the temperature of 200°F and the removal efficiency sharply increased to ~100% when temperature reached 500°F. On the other hand, for the ZrO_2/Cu-ZSM-5 catalyst, the mean methane removal efficiency was ~12% at the temperature of 200°F, at 500°F, the mean removal efficiency was ~74%, and the efficiency was increased up to ~83% as the temperature increased to 800°F. The butane removal efficiency also followed a similar trend with increasing temperature.

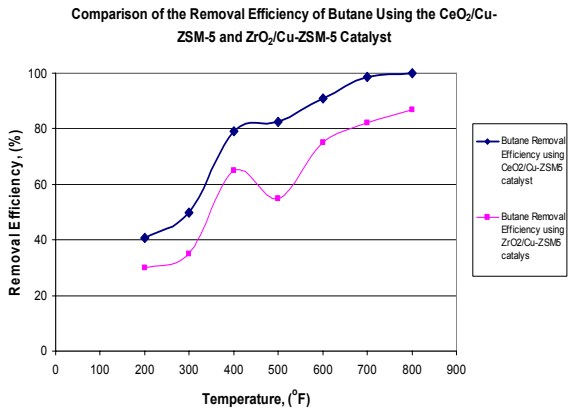

FIGURE 5. Comparison of butane conversion efficiency by the CeO_2/Cu-ZSM-5 and ZrO_2/Cu-ZSM-5 catalysts at different operating conditions

Effect of Space Velocity. Figures 6 and 7 show the effect of space velocities on the removal efficiency of methane using CeO_2/Cu-ZSM-5 and ZrO_2/Cu-ZSM-5 catalysts. The hydrocarbon removal efficiency was not significantly affected within the range of ~10,000 to ~25,000 hr^{-1}; the removal efficiency increased slightly as the space velocity increased.

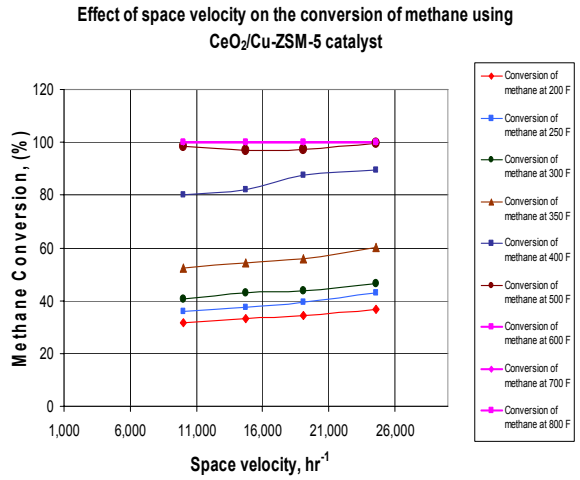

FIGURE 6. Effect of space velocity on the conversion efficiency of methane using CeO_2/Cu-ZSM-5 catalyst.

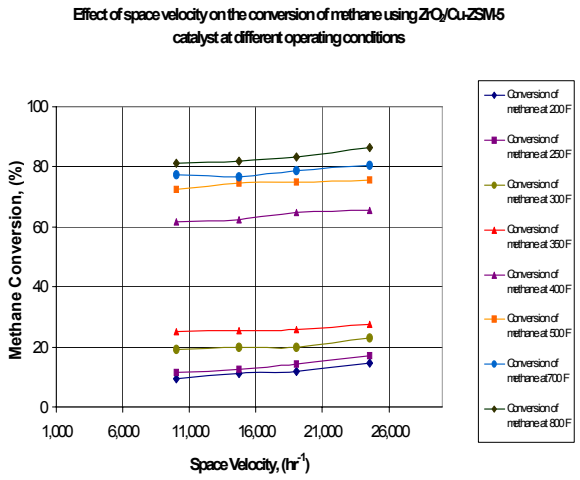

FIGURE 7. Effect of space velocity on the conversion efficiency of methane using ZrO_2/Cu-ZSM-5 catalyst.

Arrhenius Plot (Reaction Rate Constant, ln K versus T^{-1}). Figures 8 and 9 show Arrhenius plots of ln K versus T^{-1} for methane conversion reaction using both catalysts. For the 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-°K compared to 17.74 kJ/mol-°K for the ZrO_2/Cu-ZSM-5 catalyst. The mean activation energy within the temperature range of 400 to 800°F is 1.21 kJ/mol-K for the CeO_2/Cu-ZSM-5 catalyst, compared to 3.2 kJ/mol-°K for the ZrO_2/Cu-ZSM-5 catalyst.

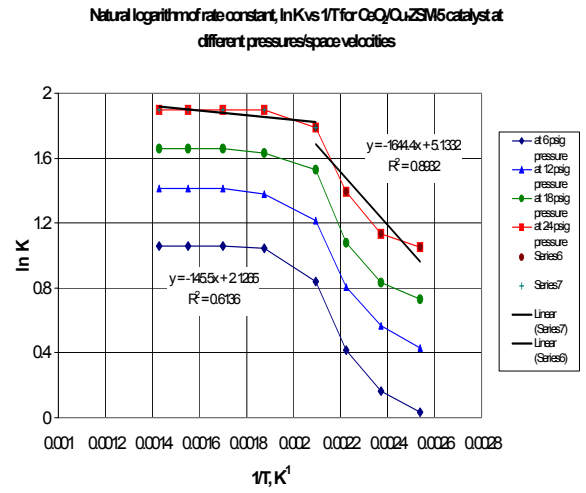

FIGURE 8. Arrhenius plot (ln K vs. 1/T) for CeO_2/Cu-ZSM-5 catalyst at different pressure/space velocities.

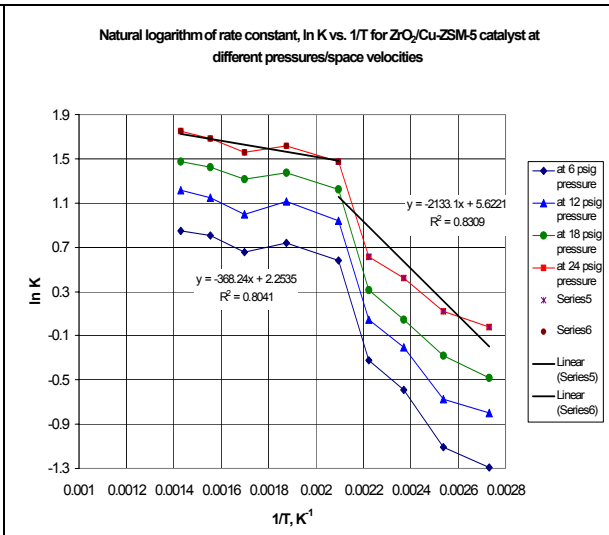

FIGURE 9. Arrhenius plot (ln K vs. 1/T) for ZrO_2/Cu-ZSM-5 catalyst at different pressure/space velocities.

For the butane removal reaction, the mean activation energy was found to be 8.03 kJ/mol-K and 9.79 kJ/mol-K using CeO_2/Cu-ZSM-5 and ZrO_2/Cu-ZSM-5 catalyst, respectively, in the temperature range of 200-400°F and 3.24 kJ/mol-K and 4.74 kJ/mol-K, respectively in the temperature range of 400-800°F (see Figures 10 and 11).

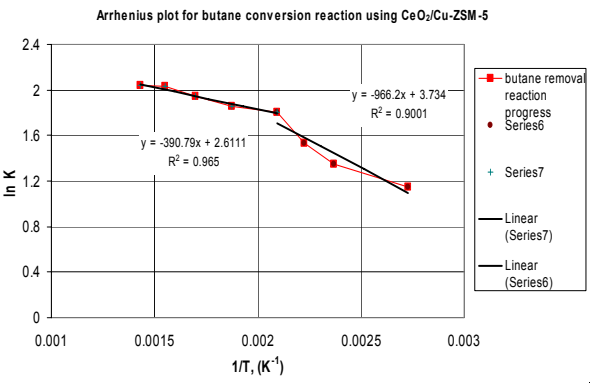

FIGURE 10. Arrhenius plot (K vs. 1/T) for butane conversion using CeO_2/Cu-ZSM-5 catalyst at space velocity~30,000 hr^{-1}.

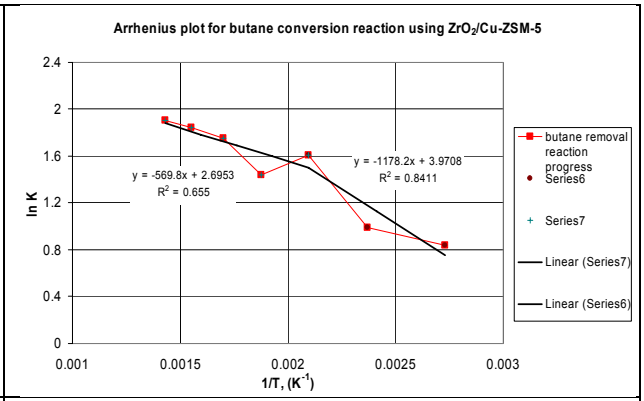

FIGURE 11. Arrhenius plot (ln K vs. 1/T) for butane conversion using ZrO_2/Cu-ZSM-5 catalyst at space velocity~30,000 hr^{-1}.

CONCLUSIONS

The performance of copper ion-exchanged ZSM-5 catalysts coated with CeO_2 and ZrO_2 for oxidation of hydrocarbon (methane and butane) in an oxidizing atmosphere has been studied. Both catalysts exhibited substantial hydrocarbon removal performance in a lean burn engine exhaust like condition over a wide temperature range. The conclusions from this investigation are summarized below:

- 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 significantly, up to a space velocity of ~30,000 hr^{-1}. Therefore, the metal ion (Cu) exchanged zeolite (ZSM-5) is a promising catalyst for removing hydrocarbon from diesel exhaust.
- Incorporation of oxide additives such as CeO_2 or ZrO_2 onto Cu ion-exchanged zeolite (Cu-ZSM-5) enhanced catalytic performance significantly. The catalyst coated with CeO_2 showed much better performance for removing hydrocarbons from exhaust gas than that of ZrO_2 coated Cu-ZSM-5.
- In the case of catalyst ZrO_2/Cu-ZSM-5, hydrocarbons adsorbed at low temperature were desorbed when the exhaust gas temperature increased as it is evident by the drop in methane removal efficiency at ~600°F. On the other hand, CeO_2/Cu-ZSM-5 catalyst effectively reduced hydrocarbon emissions throughout the entire temperature range.
- In contrast to the research work of Gill (2003), pelletizing the powdered form of catalyst reduced the pressure drop through the canister significantly. 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.

ACKNOWLEDGEMENTS

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