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SILVER ALUMINA CATALYST PERFORMANCE WITH LIGHT ALCOHOLS AND OTHER REDUCTANTS

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ABSTRACT

A number of light alcohols and other hydrocarbons were used in experiments to map their NO_x reduction performance with a Ag-Al_2O_3 catalyst. Experiments were aimed at identification of compounds that could be candidates for fuel-borne reductants in a compression ignition fuel, or could be produced by some workable method of fuel reforming. A second goal was to improve understanding of reaction mechanisms and other phenomena that influence performance of this SCR system. Test results revealed that diesel engine exhaust NO_x emissions can be reduced by more than 80%, utilizing ethanol as the reductant for a space velocity near 50,000/h and catalyst temperatures between 330 and 490°C. Similar results were observed for 1-propanol, 2-propanol and 1-butanol, with a desirable shift in good performance to a lower temperature range for the primary alcohols. Heavier alcohols and other oxygenated organics gave less desirable levels of performance. Non-oxygenated hydrocarbons, cyclohexanol and tert-butanol proved to be very poor reductants. Some discussion concerning the possible mechanisms behind the results is offered.

INTRODUCTION

The use of hydrocarbons (HC) to reduce diesel exhaust NO_x emissions via selective catalytic reduction (SCR) is potentially a very attractive option for transportation applications. The exhaust stream is continuously oxygen rich under normal conditions and a ready supply of hydrocarbons is available on-board. However, the HC-SCR option is often viewed as less viable than lean NO_x traps and urea-based SCR technology. This view comes from reported NO_x reduction efficiencies for HC-SCR systems that are significantly lower than those achieved with these other technologies.[1-3] Alumina supported silver (Ag-Al_2O_3) catalysts are among the most promising of HC-SCR catalysts that have been examined in the open literature.[2,3]

Because of the drawbacks for urea SCR and lean NO_x traps, it would be attractive to develop a HC-SCR system that could effectively utilize compression ignition fuel, reformed fuel, a fuel-borne additive or a reformed fuel additive as the reducing agent. As a result, investigators continue to pursue development of HC-SCR based systems with the hope of developing a viable technology.

SILVER-ALUMINA HC-SCR

SCR catalysts utilizing HC reductants in oxygen-rich gas streams have been studied for at least two decades. There is a sizable body of literature relevant to HC-SCR including Ag-Al_2O_3 catalysts. Most published work has been bench-scale research using simulated exhaust. Two notable literature reviews were published in 2002, giving valuable interpretation to the results reported by many researchers. One review was commissioned by the Coordinating Research Council,[2] to evaluate the state of SCR technology as applied to vehicles, and another was carried out by a team at Queen's University Belfast,[3] which looked closely at fundamental mechanisms. Of the HC-SCR systems evaluated, certain Ag-Al_2O_3 catalyst formulations have been identified as being particularly active and selective,[2,3] and therefore may yet be promising as a NO_x control technology.

Some generalization concerning Ag-Al_2O_3 catalyst performance can be made from the published research. Successful reducing agents include heavier paraffins, certain alcohols and aldehydes. Catalyst formulations with 1.2% to 2% Ag are seen to lower the temperature at which alumina is active and selective.[2,3] Silver loadings near 10% can yield excessive levels of N_2O.[3] Some experiments resulted in conversion levels greater than 80% and demonstrated good resistance to water and SO_2 inhibition.[2,3] Sliver sulfate is active and responsible for good performance reported with some reductants in the presence of SO_2.[3] In the presence of water, polar oxygenates seem to have quite an advantage. Inhibition by water is probably due to competitive surface adsorption between water and key reactants. Highly polar oxygenates probably have a greater ability to compete with water in comparison to non-polar hydrocarbons.[2,3]

There are significant hurdles to development of a robust Ag-Al_2O_3 system applicable to on-road diesels.[2,3] Diesel fuel and many components of diesel fuel do not appear to be good reductants. This leads to fuel-borne and fuel-derived/reformed reductants as a possible approach. Efficient use of reductants to minimize the "fuel penalty" is also an issue.

OBJECTIVE OF CURRENT WORK

A primary goal guiding this effort was to compare the effectiveness of various reductant candidates with the Ag-Al_2O_3 catalyst under realistic engine conditions. It could be viewed as a (partial) reductant "screening" study for this particular catalyst. Interesting reductants could be examined in follow-on studies, which might look more closely at performance, the composition of slip compounds, and the feasibility of the reductant to be fuel-borne or fuel-derived.

A second important goal was to increase understanding of chemical mechanisms and other physical processes governing the performance and selectivity of this HC-SCR system. Observing the relative performance of differing organic functional groups and other reductant properties values was expected to assist in gaining such understanding.

MATERIALS AND EQUIPMENT

EXPERIMENTAL FACILITY

The experimental effort was conducted at the Oak Ridge National Laboratory, National Transportation Research Center. A Cummins 5.9 liter ISB diesel engine (1999 model, 24 valve) was used as the test engine. This engine is refitted to be a "near-2004" emissions engine, having unique controls and calibration, cooled exhaust gas recirculation (EGR), fuel system and turbocharger. Control of the EGR valve can be governed by independent control. The engine was coupled to a General Electric direct current motoring dynamometer capable of absorbing 224 kW (300 hp).

The HC-SCR system layout and sample locations are shown schematically in Fig. 1. Gaseous emissions were sampled from the engine-out and catalyst-out raw exhaust streams and directed to standard emission benches to provide measurements of NO_x, THC, CO, CO_2, and O_2.

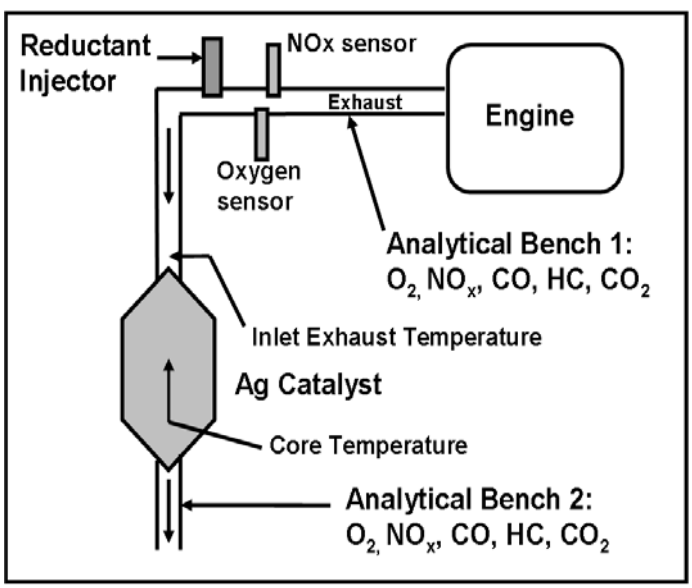

Fig. 1. Schematic diagram showing layout of HC-SCR components and sampling locations.

Caterpillar, Inc. provided the 7.0 liter Ag-Al_2O_3 catalyst to ORNL. The catalyst has a cell density of 31 cells/cm^2 and measured 24.1 cm in diameter by 15.2 cm long. No other catalysts or particulate traps were used for this investigation. This catalyst was de-greened and tested for over 80 hours in previous studies.[1]

TEST FUELS AND REDUCTANTS

The fuels used to operate the engine were BP ECD-1 and BP-15. Both are high cetane number, ultra-low sulfur diesel fuels (< 15 ppm mass sulfur) and are viewed as essentially identical for the purposes of this study. The ethanol used in this study was denatured with gasoline and contained a corrosion inhibitor; pertinent specifications are listed in Table 1. The other reductants used in this work, listed in Table 2, were chemical-grade compounds, with the exception of 2-propanol which was 70% 2-propanol with 30% water.

Some reasoning behind the 13 reductants chosen (listed in upper portion of Table 2) for the test matrix is offered. The objective was to see if a trend existed going from lighter to heavier primary alcohols and how secondary and tertiary alcohols responded. The diols were chosen to see whether there was a benefit from a higher abundance of OH groups. Cyclic compounds (cyclohexane, cyclohexanol) were deemed interesting due to their potential abundance in Canadian oil-sand derived fuels. An acetate and ketone were chosen to look at oxygenates with alternative functional groups. Admittedly, testing many other compounds could reasonably be justified. The compounds listed in the lower portion of Table 2, were chosen because they are fuels or fuel components.

Table 1. Specifications for fuel-grade ethanol supplied by Williams-Pekin, Inc.

Ethanol content, vol.%	92.1 min
Methanol content, vol.%	0.5 max
Denaturant content, vol.%	2 min, 5 max
Water content, mass%	~0.5

REDUCTANT INJECTION

The reductant delivery system featured a variable-speed dosing pump to inject reductant into an entrainment air stream and then through a spray nozzle into the exhaust. The injection point was at a bend in the exhaust 1.0 meter from the catalyst face. An experiment was performed measuring reductant dispersion at the catalyst face while injecting a number 2 diesel fuel. The face of the catalyst was traversed in two perpendicular directions with a probe to obtain a concentration map. Results indicated nearly constant concentration at a 28,000/h and 51,000/h SV condition. We assume that the (more volatile) reductants used in the current effort were well dispersed before reaching the catalyst face.

The injection system was calibrated for fluid volume delivered as a function of pump motor speed. The system was found to hold calibration very well, even with changes in fluid viscosity and injection air pressure. Calibrations were conducted with water, diesel fuel, and ethanol and for entrainment air pressures of 0 to 140 kPa above atmospheric pressure. "Spot checks" of the calibration were performed periodically.

Table 2. Reductants tested with Ag-Al_2O_3 catalyst.

Reductants used in 50,000/h SV test matrix		
Alcohols	**Molecular weight (amu)**	**Boiling Point or range (°C)**
fuel-grade ethanol	46.1	~ 79
1-propanol	60.1	97
2- propanol	60.1	82
1-butanol	74.1	117
tert-butanol	74.1	83
1-hexanol	102.2	157
cyclohexanol	100.2	67
1-octanol	130.2	196
ethylene glycol	62.1	196
1,3-propanediol	76.1	215
Other oxygenates		
ethyl acetate	88.1	77
acetone	58.1	56
hydrocarbon		
cyclohexane	84.2	81
Reductants used in miscellaneous tests		
low sulfur diesel fuel	C9-C20	185-350
low sulfur kerosene	Mostly C12-C15	175-325
iso-paraffin mixture		190-210
n-heptane	100.2	99

EXPERIMENTS

An experimental matrix was developed which would allow NO_x reduction performance comparisons of the various reductants over an applicable temperature range. A SV value of 50,000/h was chosen for most data.

The guidance for performing the experimental matrix for a given reductant is listed below.

- Space velocity: 50,000/h for most data; an optional test at 100,000/h to examine the role of SV.
- C/N range of at least 0 to 10, vary range as applicable. Collect data at several C/N values to define a meaningful curve.
- Engine out NOx concentration: 200 to 240 ppm.
- Catalyst inlet temperature range, 250°C to highest achievable with the engine system, ~460-470°C. Examine at least 5 temperatures in this range.

The method for testing at a given exhaust condition and reductant type, was to begin with no injection and to progress in discrete steps from a low to a high injection rate. Data was recorded at a given injection rate when a steady-state condition was observed. The data acquisition system gave real-time traces of temperatures, NO_x and HC concentrations, such that progression to steady state could be observed easily.

Typical test conditions used for an individual reductant are given in Table 3. Representative gas concentrations are given to show how the exhaust environment changes with test condition. The presence and concentration of O_2 and H_2O may change the behavior of the HC-SCR system somewhat.[2,3,4] The catalyst is continuously exposed to particulate matter (PM), but no measurements of PM were made. In some cases operating points "between" those listed for conditions 1-5 were also explored to obtain data at other temperatures. Condition 6 was only used with a few reductants.

Table 3. Approximate test conditions used to explore reductant performance.

Test Condi-tion	SV (1/h)	Catalyst inlet Temperature (°C)	O_2 conc. (%)	CO_2 conc. (%)	H_2O conc. (%)
1	50K	260	13.2	4.8	6.5
2	50K	295	12.3	5.4	7.1
3	50K	335	10.6	6.5	8.2
4	50K	390	8.5	7.8	9.6
5	50K	465	5.5	9.8	11.9
6	100K	380	10.5	6.5	8.2

SEPARATION OF FUEL-BORNE REDUCTANTS

A limited number of tests were performed examining how effectively reductants mixed with diesel fuel could be removed using a laboratory "mild" vacuum distillation method. If the laboratory method worked well, it would imply that an on-board device could be developed to carry out this function. Results show that light alcohols are easily removed by this method. More details are given in the Appendix.

RESULTS AND DISCUSSION

The majority of results presented focus on NO_x conversion as a function of catalyst core temperature for reductant injection at a given C/N ratio. Data taken for reductant injection at relatively high C/N values is presented. The objective is to compare reductant effectiveness and identify those that demonstrate the most potential for good performance.

The result of a test matrix using ethanol as the reductant is shown in Fig 2. The best performance is seen at the 388°C catalyst inlet exhaust condition. All results are at the 50,000/h SV condition unless noted otherwise. This figure depicts the type of data set produced for each reductant tested.

Overall results in the form of NO_x reduction versus the catalyst core temperature are given in Figs 3-6, for C/N values of 9-12. The available data with C/N values nearest the middle of this range (10.5) were chosen for subsequent figures. Variation in the C/N values is due to the practicalities of engine operation and reductant injection. The range of C/N ratios vary from about 9-12, with some variation point to point for a given reductant and variation between reductants. Catalyst core temperature is measured by a small thermocouple in a central channel near the geometric center of the monolith.

The variation in C/N ratio would be problematic, but at this relatively high level of reductant injection, only small changes in performance occur over C/N values of 9 to 12, as seen in Fig. 2. This "diminishing returns" observation held true for all reductants except ethylene glycol, which behaved rather linearly in this range (but showed this diminishing returns trend for C/N ≥ 20). Analysis using detailed interpolation of the data (not reported in this paper) gave the identical trends, and was not found to be a particularly valuable exercise.

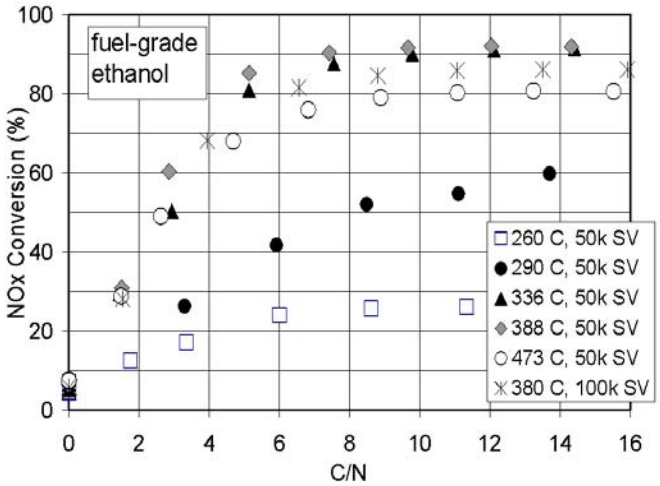

Fig. 2. Performance of fuel-grade ethanol for 50,000/h SV and five catalyst inlet temperatures. A 100,000/h SV case is included for comparison.

The most effective reductants tested are the light alcohols, as depicted in Fig. 3. 1-Propanol and 1-butanol both show a desirable shift toward effective NO_x reduction at lower temperatures. It appears that 2-propanol is slightly less effective than 1-propanol and 1-butanol. Because of the body of data generated in the previous study,[1] ethanol is a "base case" reductant and included in Figs. 4-6, along with 1-propanol which gave very favorable results.

Other alcohols - Performance results for 1-hexanol, 1-octanol, tert-butanol and cyclohexanol are given in Fig. 4. The heavier primary alcohols show significantly less NO_x reduction compared to the lighter alcohols, except at temperatures nearing 250°C where performance appears to be about the same. Both tert-butanol and cyclohexanol appear to have no value as a reductant with this catalyst.

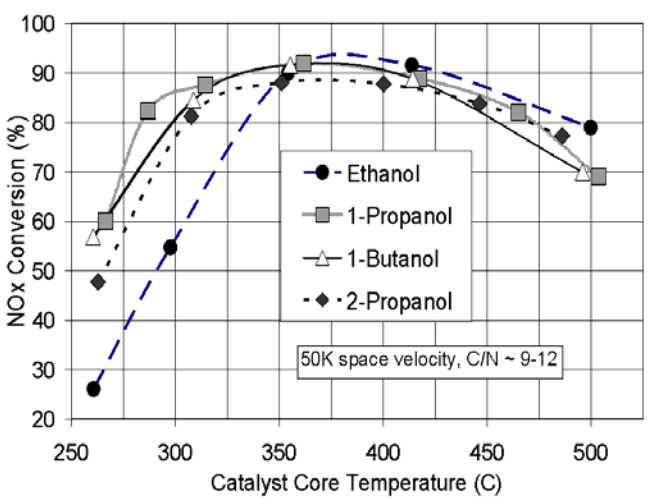

Fig. 3. Performance of light alcohols for 50,000/h SV and relatively high C/N ratio (reductant injection rate).

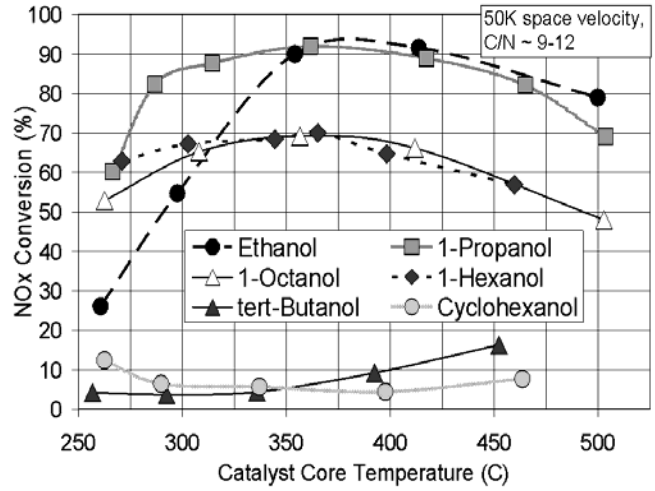

Fig. 4. Performance of 1-hexanol, 1-octanol, tert-butanol and cyclohexanol compared to ethanol and 1-propanol for 50,000/h SV and relatively high C/N ratio.

Diols - Results for 1,3-propanediol and ethylene glycol are summarized in Fig. 5. Interpolated data was used to better define the ethylene glycol curve (Fig. 5). A C/N value of 10.5 was chosen to be plotted. The 1,3-propanediol is seen to be moderately less effective as a reductant compared to the light alcohols, although it performs as well or better than ethanol at 250-300°C. Ethylene glycol appears similar to ethanol and 1,3-propanediol at 275°C, but is much less useful above 300°C.

Other non-alcohols - Figure 6 shows test results for the non-alcohol oxygenates, ethyl acetate and acetone, which seem to work relatively well as reductants near 400°C and above. Also shown is cyclohexane, which displays essentially no reductant capability with the tested system.

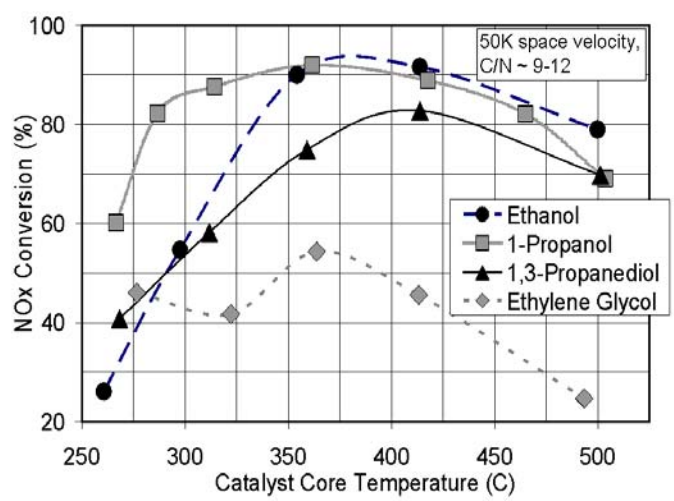

Fig. 5. Performance of diols compared to ethanol and 1-propanol for 50,000/h SV and relatively high C/N ratio. The ethylene glycol data is interpolated to give results for C/N = 10.5.

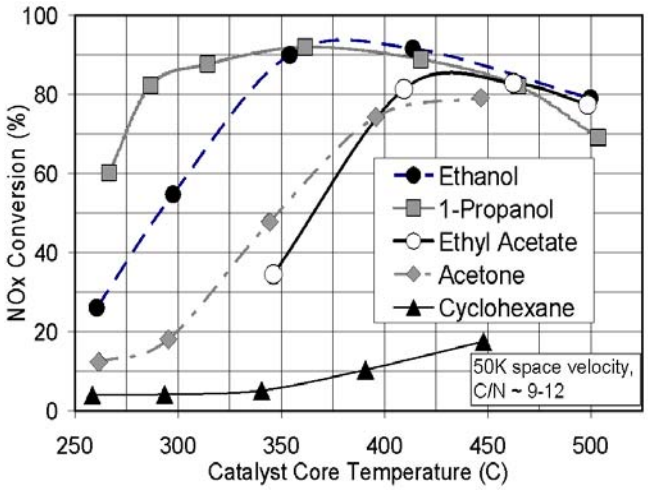

Fig. 6. Performance of ethyl acetate and acetone does not compare well to light alcohols, especially at the lower end of the temperature range. Cyclohexane shows little activity as a reductant.

RELATED EXPERIMENTAL EFFORT

Some data is available from a separate, but related effort using the same HC-SCR system. The major practical difference is the SV and NO_x levels were not held at 50,000/h and 200-240 ppm values used for the main body of data. Results for a low sulfur number 2 diesel fuel, a low sulfur kerosene, an iso-paraffin mixture and fuel grade ethanol are compared in Fig. 7. The compounds other than ethanol are rather ineffective as reductants. A single test using heptane at 100,000/h SV and 350°C exhaust temperature (not shown) gave only a few percent NO_x conversion. Including the cyclohexane results discussed earlier, the non-oxygenated reductants tested in this study all gave relatively poor results. These potential reductants were alkanes or contained a large amount of alkanes compounds. Other types of non-oxygenates may give different results.

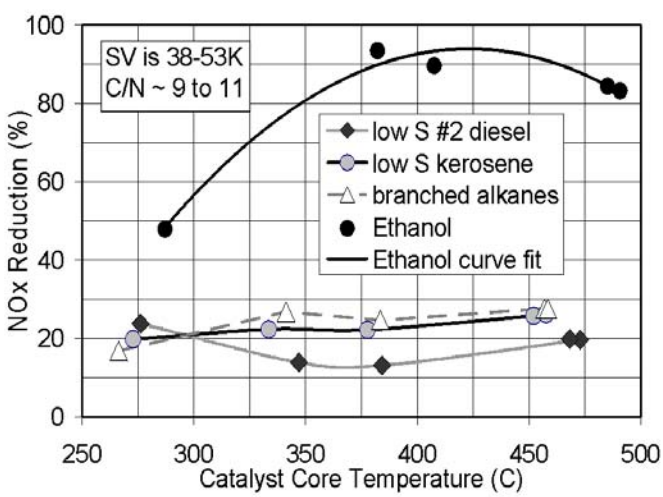

Fig. 7. Data comparing fuel-grade ethanol to relatively heavy hydrocarbon reductants.

DISCUSSION OF REDUCTANT PERFORMANCE

Some descriptions and explanations are offered addressing the hierarchy in performance among reductants tested.

Aldehyde formation - There is experimental evidence that ethanol, and 1-propanol undergo oxidation to form acetaldehyde and propionaldehyde, respectively.[1,4] It is likely that 1-butanol also forms a corresponding aldehyde. The aldehydes, which are thought to be good reductants, break down further as part of the reduction process.[1,4,5] It is proposed that 2-propanol forms acetone[4] which then breaks down further. We note that 2-propanol was quite superior as a reductant compared to acetone, especially at low temperatures, so this explanation may not be fully satisfactory. In forming either an aldehyde or ketone, the alcohol donates two H atoms, which presumably enhance in the overall reduction process. Tert-butanol would not be expected to form an aldehyde or a ketone and proved to be relatively unreactive for the tested system.

Reactivity – It is obvious that reductants that react or break down easily are likely to create "usable" reactive species, particularly at low temperatures. This might explain ethyl acetate and acetone looking like reasonable reductants at ~ 400°C, but not at low temperature, where they remain relatively stable. There was some expectation that the cyclohexanol could have some reactivity and behave somewhat like hexanol or the 2-propanol. Instead, cyclohexanol was completely unreactive with the tested system, likely due to the high stability of the six carbon ring structure.

Reactivity indications - Evidence of oxidation of reductants can be inferred from the measured CO_2, CO and HC levels and the temperature difference between the catalyst inlet and the catalyst core. The net reactions occurring appear to be quite exothermic. Unfortunately the CO_2 measurement is dominated by the engine-out values (~5-10%) and the increase derived from the reductants is about 0-2500 ppm in the range of interest. Furthermore the flame ionization detector for HC measurement used in this work gives useful information, but has a response that varies widely for many of the species likely present, and the actual slip species are not well characterized. It is not possible to compare and interpret the CO_2 and HC readings with confidence. However, a rise in CO and CO_2 is expected for the compounds that decompose and oxidize along with a relatively low HC reading, and the opposing trends are expected for compounds that are unreactive.

Analysis of the CO_2 "rise" data for C/N values of 9-12, gave somewhat crude and scattered results, but a few trends were seen. The poorest performing compounds, cyclohexane, cyclohexanol and tert-butanol, showed virtually no detectable CO and CO_2 formation except at the highest temperature condition where it is estimated 15-30% of the injected carbon ended up as CO and CO_2. These compounds also gave consistent and high HC readings (accounting for ~68-87% of the injected carbon, depending on the reductant) for the lower temperature conditions (conditions 1-4 in Table 3) with a modest drop in HC value for the highest temperature condition (condition 5 in Table 3). All other reductants gave much higher values for CO + CO_2 production, with increasing values for increasing temperature, and the opposing trend for the HC emissions. Ethylene glycol stood out as having the highest propensity to react to form CO + CO_2 at all temperatures (~ 80

% at the lowest temperature, and rising to ~ 100% at the highest temperature), followed by 1,3-propandiol and ethyl acetate. Ethylene glycol also displayed the highest degree of exothermic activity.

Polar compounds, water solubility - It is proposed that a distinct advantage is possessed by the more polar oxygenates, which can compete successfully with water for adsorption sites.[2,3] The environment of interest has abundant water which doubtlessly affects the catalytic process. This property favors the light alcohols and light asymmetric oxygenates. Note that the non-polar diols tested do have very high water-solubility, and may be less disadvantaged compared to low water-solubility compounds. Hexanol and octanol notably have lower water solubility than the lighter alcohols. The non-oxygenated compounds have very low solubility.

Molecular mobility - The ability of the compound to diffuse to make intimate contact with the catalyst surface and then be mobile on the surface, could affect the SCR process. This mobility property could be related to the molecular weight, boiling point (listed in Table 2) and other properties of the compound. No attempt to quantify this property is offered. Indirect evidence of a physical interference process, probably involving carbonizing (coking) of the reductant on the catalyst surface, was seen with octanol and compounds of higher molecular weight. The observation was that as injection quantity was increased, NO_x conversion began to decrease and would also slowly decrease with time at a given spray rate.

CONCLUSIONS

The tested HC-SCR system performed well with ethanol, 1-propanol, 2-propanol and 1-butanol as reductants over the range of conditions explored. These light alcohols gave greater than 80% NO_x reduction over a broad temperature range for C/N of 9 or greater and 50,000/h SV. A desirable shift toward effective NO_x reduction at 260-300°C, was seen for 1-propanol, and 1-butanol. Relatively good performance in the 260-300°C temperature range was also found for 1-hexanol and 1-octanol, but with reduced performance at higher temperatures compared to the lighter alcohols. The tested system gave > 50% NO_x reduction at 260-270°C for number of primary alcohols (1-propanol, 1-butanol, 1-hexanol, 1-octanol) for a C/N ratio of 9 or below.

1,3-propanediol is seen to be less effective as a reductant compared to the light alcohols, although it performs as well or better than ethanol at 250-300°C. Ethylene glycol performed relatively well 275°C, but is a relatively poor reductant at higher temperatures.

Ethyl acetate, and acetone were both are seen to be good reductants at 400°C and above but not at lower temperatures. Potential reductant candidates that performed quite poorly include tert-butanol, cyclohexanol, cyclohexane, n-heptane, diesel fuel, kerosene and an iso-paraffin mixture.

Some overall patterns were observed from the testing of the 17 reductants with this particular SCR system. The results can be associated with certain chemical and physical properties of the reductants tested. Highly polar, water soluble compounds are thought to have a significant advantage, because they compete successfully with water for catalyst surface sites. Low molecular weight may be advantageous, allowing high diffusion rates and good surface mobility. High chemical reactivity in the appropriate temperature range is also desired. This may explain the superior performance of the light alcohols which have the previously mentioned attributes. The primary alcohols appear to readily form aldehydes while donating two protons per molecule in the process. In an analogous fashion, 2-propanol likely forms a corresponding ketone with the same desirable proton donation.

These concepts can be applied to the other reductants. The heavier primary alcohols tested, 1-hexanol and 1-octanol, did not perform as well as the lighter alcohols, probably due to being incrementally less polar and mobile. The diols tested were symmetric and non-polar, but appeared to be reactive. Testing a 3 or 4 carbon polar diol could shed more light on these contentions. Ethylene glycol stood out as being exceptionally reactive toward oxidation but was relatively poor at selective reduction of NO_x. This may apply to 1,3-propandiol but to a much lesser extent.

For the non-alcohol reductants we see that the oxygenates, ethyl acetate and acetone, are low molecular weight and polar, but are not reactive at lower temperatures. The non-oxygenated compounds are not water soluble, and probably have some difficulty competing for active surface sites. The relatively long-chain hydrocarbons showed more reactivity than n-heptane or cyclohexane, a general trend also seen in the literature.

More could be learned by examining the HC and nitrogen containing slip species and speices found at different positions within the catalyst through in-catalysts sampling. A follow-on effort of this type for selected reductants could be considered.

Another question to investigate is the feasibility of the successful reductants to be fuel-borne or fuel derived. Ethanol/diesel mixtures have been examined due to abundant and relatively inexpensive domestic ethanol production. Such fuel has several drawbacks including flammability/safety issues. More could be done to look into what other alcohols are feasible as either fuel-borne removable reductants, or that could be produced on-board from diesel fuel or a fuel-borne additives.

NOMENCLATURE

amu	atomic mass units
$Ag\text{-}Al_2O_3$	Catalyst composition of silver on an alumina substrate
C/N	Atomic ratio of carbon in the reductant to nitrogen in NO_x
E-diesel	A ethanol and diesel fuel mixture, usually containing a blending agent and mixed as a microemulsion
EGR	Exhaust Gas Recirculation
FTIR	Fourier Transform Infrared
HC	Hydrocarbon
HC-SCR	Hydrocarbon – Selective Catalytic Reduction
k	thousands
NO_x	Oxides of Nitrogen
NTRC	National Transportation Research Center
ORNL	Oak Ridge National Laboratory
PM	Particulate Matter
ppmv	parts per million by volume
SCR	Selective Catalytic Reduction
SV	Space Velocity referenced to 25 °C, units

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APPENDIX

A very limited number of tests were performed examining how effectively reductants mixed with diesel fuel could be removed using a laboratory "mild" distillation method. The distillation conditions were 90°C, 27 kPa vacuum.

It is seen that ethanol, 1-propanol and 1-butanol can be removed by this method. As might be expected, octanol with a boiling point of 196°C, was not recoverable. Hexane and heptane were partially recoverable.

Table A1. Results of mild distillation testing.

Fuel Additive	boiling Point (°C)	Mole-cular weight (amu)	Amount blended into ECD1 fuel (%)	Amount recovered by mild distillation (%)
Fuel-grade ethanol	~ 79	46.1	20	20
1-propanol	97	60.1	20	18
1-butanol	117	74.1	20	17.5
n-hexane	69	86.2	20	5
n-heptane	98	100.2	20	5
1-octanol	196	130.2	20	0