LITERATURE SURVEY TO ASSESS THE STATE-OF-THE-ART OF SELECTIVE CATALYTIC REDUCTION OF VEHICLE NOx EMISSIONS

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Final Report for Project AVFL-7

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EXECUTIVE SUMMARY

Ricardo has been commissioned by Coordinating Research Council to perform a comprehensive search of several scientific databases in order to assess the state-of-the-art of selective catalytic reduction of NOx using hydrocarbons as the reductant source. The objective is to identify potential catalyst formulations which show promise as emission control technologies to be used in LDD applications. To this end, Ricardo Powerlink™, Compendex, INSPEC, NTIS, CAB Abstracts and CHEMWEB – Catalysis Forum have been searched using the following key words: Selective Catalytic Reduction, SCR, NOx Reduction, Diesel Exhaust, Lean, DeNOx, Non urea/ammonia. From this search, 289 papers have been identified from which 122 have been selected for detailed reading. A catalyst formulation is defined as a potential ECT if the peak NOx conversion occurs below 300°C and the conversion levels are greater than 70%. The subsequent reading lead to the following observations.

Most of the literature available for SCR-HC omits key exhaust gas components, namely water vapor and SO_2. The most frequently sited catalyst, Cu/ZSM-5, is irreversibly deactivated upon extended exposure to water vapor and SO_2. Most of the ion-exchanged zeolite supported catalysts are not potential ECTs as they either suffer from one or more of the following: water/SO_2 inhibition, inferior conversion levels, elevated conversion temperature window. An Fe/ZSM-5 catalyst synthesized via a solid-gas exchange between $FeCl_3$ and H/ZSM-5 yields a very active catalyst which is water/SO_2 tolerant. The limitation of this formulation is the difficult procedure required for synthesis.

Supported platinum catalysts on many materials (e.g., Al_2O_3, SiO_2, zeolites, mixed metal oxides) demonstrate NOx conversion levels within the desired temperature range. NOx conversion levels vary from 30-95% between 200°C to 300°C. Conversion depends on metal loading, reductant employed, support material and presence of other metals. Zeolites and alumina are generally selective supports when the platinum loading is 1wt%. Light paraffins are nonselective reductants while light olefins are selective. Light hydrocarbons yield the highest N_2O:N_2 ratio of all reductants. Heavier hydrocarbons as well as oxygenates favor N_2 formation though most reductants still form some quantity of N_2O. Supported platinum catalysts are tolerant to water vapor and SO_2 in the exhaust gases though the oxidation of SO_2 to SO_3 occurs simultaneously with NOx reduction. A catalyst technology for the concomitant removal of N_2O is required in order for supported platinum catalysts to achieve greater potential.

Alumina supported silver catalysts are active for NOx reduction over a large temperature window. Selective reductants include higher paraffins and oxygenated organics (excluding methanol). These catalysts are resistant to water inhibition and SO_2 though the effects of SO_2 are less documented. Catalyst preparation methods include incipient wetness and hydrolysis of aluminum alkoxide; i.e., silver salt gels with the hydrolysis method allowing improved dispersion at higher silver loadings. A method for producing the oxygenates on-board is required to avoid the need for an additional tank.

Recently, non-thermal plasmas have received much attention. This technology converts NO to NO_2 and partially oxidizes olefins to aldehydes. When a catalyst such as Ba/Y zeolite is downstream of a dielectric barrier discharge devise, significant NOx removal is observed at 200°C. This technology is tolerant to water vapor and SO_2; moreover, the oxidation of SO_2 to SO_3 does not occur. There are limitations to NTP. The catalysts tend to create significant quantities of surface deposits at low temperatures and it is possible that after extended low temperature operation the catalysts could become deactivated. The DBD devise requires energy input (20-60 J/L) which, in turn, will lower fuel economy. The durability of the DBD devises remains to be proven. Toxic byproducts such as CH_2O and HCN are produced within the NTP plumes. This requires the use of an oxidation catalyst which in turn has the potential to create N_2O.

Despite the large body of data for SCR-HC catalysts, very few formulations possess adequate NOx conversion levels at temperatures observed with LDD applications. Moreover, most of the formulations tested have been done so in the absence of water vapor and SO_2. When these components of real diesel exhausts are added to the feed gases, many formulations which had been proven active are irreversibly deactivated. Cu/ZSM-5 is a classic example of this. Supported platinum catalysts are active but have a propensity to form N_2O. Fe/ZSM-5 is very active but its synthesis method is complex. Alumina supported silver catalysts hold promise. These formulation can be augmented by the use of non-thermal plasma. Plasmas are also quite active with Ba/Y zeolite and Na/Y zeolite catalysts.

Suggested areas of future research:

- All future research endeavors to include realistic diesel exhaust conditions: water vapor and SO_2
- Pt-based formulations which do not form N_2O
- Novel catalyst formulations which decompose/reduce N_2O below 300°C
- Facile synthesis routes to form Fe/ZSM-5 with equivalent performance and durability as those formed by the solid-gas or anaerobic aqueous exchange of FeC_2O_4
- On-board routes to form oxygenated reductants for silver-based catalysts
- Continued investigation into non-thermal plasma technologies
- Engine thermal management techniques to minimize exhaust conditions which are below 180°C – maintain catalyst within peak operating temperature window
- Techniques for storing NOx emissions during cool exhaust conditions followed by re-injection of the stored NOx when the ECT has achieved light-off conditions.

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