



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

CRC Project No. AVFL-7

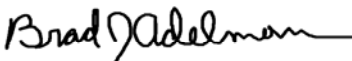
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Final Report for Project AVFL-7

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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 NO_x 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, NO_x Reduction, Diesel Exhaust, Lean, DeNO_x, 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 NO_x 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 SO₂. The most frequently sited catalyst, Cu/ZSM-5, is irreversibly deactivated upon extended exposure to water vapor and SO₂. Most of the ion-exchanged zeolite supported catalysts are not potential ECTs as they either suffer from one or more of the following: water/SO₂ inhibition, inferior conversion levels, elevated conversion temperature window. An Fe/ZSM-5 catalyst synthesized via a solid-gas exchange between FeCl₃ and H/ZSM-5 yields a very active catalyst which is water/SO₂ tolerant. The limitation of this formulation is the difficult procedure required for synthesis.

Supported platinum catalysts on many materials (e.g., Al₂O₃, SiO₂, zeolites, mixed metal oxides) demonstrate NO_x conversion levels within the desired temperature range. NO_x 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 N₂O:N₂ ratio of all reductants. Heavier hydrocarbons as well as oxygenates favor N₂ formation though most reductants still form some quantity of N₂O. Supported platinum catalysts are tolerant to water vapor and SO₂ in the exhaust gases though the oxidation of SO₂ to SO₃ occurs simultaneously with NO_x reduction. A catalyst technology for the concomitant removal of N₂O is required in order for supported platinum catalysts to achieve greater potential.

Alumina supported silver catalysts are active for NO_x reduction over a large temperature window. Selective reductants include higher paraffins and oxygenated organics (excluding methanol). These catalysts are resistant to water inhibition and SO₂ though the effects of SO₂ 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 NO₂ and partially oxidizes olefins to aldehydes. When a catalyst such as Ba/Y zeolite is downstream of a dielectric barrier discharge device, significant NO_x removal is observed at 200°C. This technology is tolerant to water vapor and SO₂; moreover, the oxidation of SO₂ to SO₃ 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 device requires energy input (20-60 J/L) which, in turn, will lower fuel economy. The durability of the DBD devices remains to be proven. Toxic byproducts such as CH₂O and HCN are produced within the NTP plumes. This requires the use of an oxidation catalyst which in turn has the potential to create N₂O.

Despite the large body of data for SCR-HC catalysts, very few formulations possess adequate NO_x 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 SO₂. 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 N₂O. 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 SO₂
- Pt-based formulations which do not form N₂O
- Novel catalyst formulations which decompose/reduce N₂O 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 FeC₂O₄
- 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 NO_x emissions during cool exhaust conditions followed by re-injection of the stored NO_x when the ECT has achieved light-off conditions.

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