



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

CRC Project No. AVFL-7

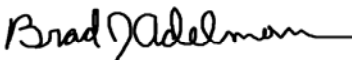
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Final Report for Project AVFL-7

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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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1. INTRODUCTION:

As the effects of anthropogenic emission on the environment are becoming better understood, governments have acted to minimize this impact. Current legislation imposes limits on the emissions from internal combustion engines. These limits have been set for the release of carbon oxides (CO, directly, and CO₂, indirectly by fuel economy limits), hydrocarbons and nitrogen oxides (NO and NO₂ referred to as NOx). For diesel engines, the mass of particulate matter is also legislated. Sulfur emissions, though not directly legislated, are limited so that H₂S is not formed as it has a strong, pungent odor. The formation of sulfates and SO₃ is also limited as they readily adsorb onto the particulate matter and thus impart an increase in total particulate mass. Nitrous oxide is not currently a regulated emission. It is, however, a potent greenhouse gas and may become a regulated compound if vehicle emissions of N₂O are deemed to be significant. Of all these emissions, the most difficult to remove from vehicle emissions is NOx. This task becomes even more difficult for compression ignition vehicles (diesel) than spark ignition (gasoline).

For several decades, spark Ignition (SI) engines have employed three-way catalytic converters (TWC). The technology is called "three-way" since hydrocarbons and carbon monoxide are oxidized to CO₂ and H₂O while NOx is simultaneously reduced to N₂. These catalysts have been proved to yield high conversion efficiencies at temperatures above 250°C provided that the exhaust gas is at or near the stoichiometric point (enough oxygen present to combust all reductants to CO₂ and H₂O). As lambda (a measure of stoichiometry) deviates from stoichiometry ($\lambda = 1$), the efficiency of the TWC rapidly decreases. Decreasing lambda (exhaust gas becomes net rich) permits significant hydrocarbon and CO emissions as not enough oxygen is present for combustion. Increasing lambda (exhaust gas becomes net lean) permits significant NOx emissions as the catalyst sites responsible for NOx reduction are saturated with oxygen preventing dissociative adsorption of NOx, the first step in NOx reduction on a TWC. In order to maintain exhaust gas streams at stoichiometry, engine control units monitor the exhaust gas lambda values and constantly adjust fueling and air flow to the engine. Moreover, TWCs also employ an oxygen storage component (OSC) to the catalyst formulation. The OSC is capable of buffering the exhaust gas composition. When excess O₂ is present, the OSC stores oxygen. When excess reductants are present, the OSC releases oxygen.

Unfortunately for compression ignition (CI) technologies such as diesel, it is not possible to buffer the exhaust gas so that the catalyst technology operates near the stoichiometric point. This would require an excessive amount of fuel and thus remove a primary advantage of CI engines; i.e., significantly improved fuel economy. Therefore, CI engines require an alternate technology.

1.1 Alternate Technologies To TWC

Several technologies have demonstrated promise. Lean NOx Traps (LNT) remove the NOx from the gas stream and store them as metal nitrates such as barium nitrate. Once the barium sites for NOx adsorption are saturated, these catalytic sites must be regenerated by converting the exhaust stream from net lean to net rich. During the regeneration cycle, the nitrate is reduced and NO is released. The resultant NO is further reduced to N₂ over a metal site (preferably Rh). By limiting the duration and frequency of the rich regeneration, the fuel penalty caused by creating the rich gas stream can be minimized. This tends to result in large catalyst volumes which can be several times greater than the cylinder displacement of the

engine. Another drawback to LNT is that they are sulfur intolerant. Since the NO_x adsorption reaction is an acid-base reaction, materials capable of NO_x adsorption also demonstrate significant sulfur uptake in the form of surface sulfate groups. These sulfate groups are significantly more stable than the adsorbed nitrates. While the sites present as nitrates can readily be regenerated (< 400°C), those present as sulfates require higher temperatures (>550°C) and longer regeneration events (minutes).

Selective Catalytic Reduction of NO_x with ammonia (SCR-NH₃) is currently employed as a NO_x removal technology for stationary power sources. SCR-NH₃ is based on the reaction of NO_x from the engine reacting with injected NH₃ to produce N₂ and H₂O. The injected quantity of NH₃ must be controlled to prevent excess ammonia from being released into the environment. This is called “NH₃-slip”. Contrarily, insufficient NH₃ will result in NO_x release into the environment. The use of a ‘clean-up’ catalyst downstream of the SCR-NH₃ catalyst prevents NH₃-slip by oxidizing any excess NH₃, though this yields NO_x. Conversion efficiencies for SCR-NH₃ have been reported to be above 90%. In order to apply SCR-NH₃ to mobile sources, NH₃ must be stored on the vehicle or produced onboard. Owing to the health and safety issues of storing NH₃, it will need to be produced onboard. Since NH₃ is not a significant engine emission, the source for producing NH₃ will need to be stored in the vehicle. There are two main compounds that can be used for NH₃ formation: urea and ammonium carbamate. Urea, present as a ~35% wt solution, readily hydrolyzes to form NH₃ and H₂O at temperatures above 180°C. There are a few limitations to using urea as the NH₃ source. One is that 65% of the urea solution is water and therefore, does not add to performance. This becomes wasted mass. There currently is no infrastructure present in North America for urea distribution. Moreover, since the urea tank will require frequent refilling, no mechanism is in place on the vehicle which would ensure that the tank never becomes empty. A concern among government regulator is that without this precaution it would be possible to defeat the SCR-NH₃ by not refilling the urea tank. Added to this are concerns about the various byproducts (cyanuric acid, ammeline, etc.) formed during urea pyrolysis. Ammonium carbamate, present as a solid, has cost, distribution and handling issues which makes it an unattractive source for producing ammonia on board.

Selective Catalytic Reduction of NO_x with hydrocarbons (SCR-HC) has the advantage that the catalyst utilizes hydrocarbon species present in the exhaust stream for NO_x reduction. The reaction can be supplemented with additional hydrocarbons either via secondary injection of fuel in the cylinder or direct injection into the exhaust stream. The former has the advantage that diesel fuel will partially combust to yield lighter hydrocarbons which tend to have performance benefits over raw diesel fuel injected over the catalyst. SCR-HC, also known as active deNO_x, requires minimal hardware and uses the diesel fuel as the reductant. This avoids the need for an additional reagent tank. As a result of its simplicity, SCR-HC would be the desired technology to attain future legislated NO_x emission limits.

1.2 Requirement For Light-Duty Diesel (LDD) Applications

Within the publicly available information, there exists a large body of data concerning the performance of SCR-HC technologies. The breadth of catalyst formulations, test operating conditions and reductant used make it difficult to compare these data and assess the potential for SCR-HC. It is the purpose of this report to assess SCR-HC as a feasible emission control technology (ECT) for light-duty applications. The legislated emission target is US TIER 2 Bin 5 with a NO_x emission limit of 0.07g NO_x/mi. Catalyst activity over the FTP cycle directly affects

the engine out NO_x limits. For example, a catalyst which converts 90% of NO_x emissions during the FTP cycle can tolerate engine out levels of 0.70 g NO_x/mi. and still achieve the Bin 5 target of 0.07g/mi. A catalyst with 50% efficiency requires engine out NO_x to be no greater than 0.14 g/mi. For the purpose of this discussion a conversion efficiency target of 70% has been used. This corresponds to engine out NO_x levels no greater than 0.23 g/mi. Based on literature values, these engine out targets are somewhat aggressive but achievable.

The actual temperature trace for the FTP cycle is engine dependant and varies with the relationship between engine size and vehicle mass. The larger the engine is with respect to the vehicle, the lower the inlet temperature to the catalyst will be. **Figure 1** gives a simulated temperature trace for two engine/mass scenarios: the higher engine-to-mass ratio yields the lower thermal trace. Based on the two thermal traces, effective SCR-HC catalysts for LDD application would need to have peak performance between 200-300°C. Catalysts that demonstrate significant NO_x reduction capabilities only at higher temperatures are not likely to be effective, as exhaust gases for LDD applications rarely exceed 350°C. These traces demonstrate that engine parameters will play a large role in achieving the legislated emission targets.

Additionally, the amount of hydrocarbon required for effective (>70% removal) will need to be low in order to minimize the fuel penalty. For the purpose of this study, an attempt to correlate hydrocarbon used to an exact fuel penalty has not been performed. It is assumed that the lower the C/NO_x ratio (normalized value of the hydrocarbon based on equivalent C1 units versus the quantity of NO_x) the lower the fuel penalty. None of the data points were excluded based on an elevated C/NO_x ratio.

2 LITERATURE IDENTIFICATION

The selection of the papers presented in this study was performed as follows.

Six different databases, which cover the wide range of the Selective Catalytic Reduction domains, were chosen. Their particularities are described in the Appendix. A search was conducted using the following keywords:

- Selective Catalytic Reduction (SCR)
- NO_x Reduction
- Diesel exhaust
- Lean
- DeNO_x
- Non urea/ammonia

A pre-selection, based on the article title and abstract, has been applied to eliminate the papers which were not related to the subject. From this search, 289 papers have been selected.

The abstract papers were studied and the papers were classified on an excel database. The classification fields were

- Type of papers (General, Laboratory test, Modeling, Review...)
- Catalyst
- Reductant
- Application
- Interest for this study

122 papers were ordered for detailed reading. These papers are listed in the Appendix .

3 ROLE OF THE SUPPORT MATERIAL

The bulk of this study will be divided into three sections: the role of the support, the role of the active metal center and the role of the reductant. In each section the representative data will be presented and discussed with respect to the section topic. The first topic is the role of the support material. Several support materials have been shown to be active supports for SCR-HC. The most prominently studied supports are zeolites. Zeolites are crystalline arrays of oxygen-bridged silica tetrahedra. When some of the silica (Si^{4+}) centers are replaced with alumina (Al^{3+}) the result is a net negative charge to the framework of the zeolite. The negative charge is compensated with a cation. Upon synthesis the cation is generally sodium or ammonium. This cation can readily be exchanged with other cations, thus imparting many opportunities for new catalyst formulations. The first section will list some of the more actively studied zeolite-based formulations along with those zeolite-based catalysts which show the greatest potential for application in LDD emission control technologies.

In addition to zeolites, amorphous oxide supports have also been demonstrated to be active supports. The best of these is alumina. Amorphous alumina has high surface area which is important in dispersing active metal sites. Moreover, it has greater hydrothermal stability than zeolites. Alumina can also possess acidic or basic properties based on the preparation method. For most of the references, the alumina supports were provided from an industrial source. As a result, little characterization data are presented. Attempts will be made to identify differences in performance of similar catalyst formulations based on the synthesis method of the support material or catalyst.

Similar to alumina, several other oxide supports have been proven active supports for SCR-HC. These supports can be mixed metal oxides (MMO) such as pillared clays or oxides such as silica and zirconia. Catalyst preparation with these types of supports can include incipient wetness where the minimum amount of water is used in order to cover the support surface. This tends to form bulk oxides. As this preparation employs dilute metal solutions, it limits the metal loading achievable. Co-precipitation is another catalyst preparation method. Unlike incipient wetness, co-precipitation uses a solution containing the support material mixed and the active metal. The solution pH is gradually increased with a combustible base such as urea or ammonia. As the pH rises, the solution forms a gel. Upon calcination, the resultant powder will possess highly dispersed active metal sites.

When possible, these differences will be assessed with respect to catalytic performance.

3.1 Zeolite-Based Catalysts

The first SCR-HC catalyst of significant interest is Cu/ZSM-5. In independent studies Iwamoto and Held demonstrated enhanced NO_x reduction of copper ion-exchanged zeolites when an excess of oxygen is present. NO_x reduction begins around 300°C and reaches a maximum between 400-450°C. The shape of the conversion graphs have been shown to be dependant on reductant type and concentration as well as on space velocity. The experimental conditions did not include H₂O or SO₂ which are ubiquitous in real diesel exhausts. When these components are included in the feed, NO_x reduction is inhibited. For short duration, the inhibiting effect of H₂O is reversible while extended exposure to water vapor irreversibly deactivates Cu/ZSM-5 catalysts. This effect is accelerated at elevated temperatures. The Cu/ZSM-5 system remains a popular catalyst for academic studies and continues to elucidate new features of heterogeneous catalysis. It will, however, never meet the rigors for industrial application in LDD emission control technologies.

An almost Edisonian approach has been employed to screen potential catalyst formulations. **Figures 2 and 3** show a very small sample of the various exchange metals tested for SCR-HC activity. Since ZSM-5 has been the most actively studied support, those formulations using ZSM-5 have been presented in a separate graph (**Figure 2**) in an attempt to create a more facile comparison. Though the number of points is small, a good representative sample has been presented.

As evidenced in **Figure 2** most of the catalysts possess peak NO_x conversion either at temperatures which are higher than expected for LDD applications or at conversion levels too low to meet future legislative standards. There are four samples which possess sufficient conversion at the proper temperatures. Two of the catalysts are supported platinum catalysts and the other two are supported cerium catalysts. Another set of six catalysts possess sufficient conversion but the peak temperatures are slightly higher than desired. Of these, four are supported copper catalysts. The other two are supported iron catalysts, one which is promoted by lanthanum. Since the focus of this report is to assess the potential of various catalyst formulations as emission control technologies on LDD applications, all of the other samples will not be considered except in the case when these inferior catalysts are of similar composition to those which have displayed adequate performance. It will be critical to reconcile these differences in order to fully understand the potential of the adequate technologies.

Of all the references selected for this project, the most frequent formulation studied is Cu/ZSM-5. These results can be summarized as follows. Supported copper catalysts have high NO_x conversion levels usually at temperatures above 350°C when the reductant is C₃ or higher hydrocarbon. For ethene, moderate conversion occurs between 200-300°C though it is not significant enough (~40%). It is interesting to note that for lighter hydrocarbons (C₆ or lower), the presence of water vapor leads to significant catalytic inhibition while heavier hydrocarbons such as C₈ show moderate water vapor tolerance though peak NO_x conversion occurs at 350°C with normal octane and 500°C with *iso*-octane. Most of the differences in Cu/ZSM-5 performance can be traced to the hydrocarbon employed. Though heavier hydrocarbons maintain catalytic activity over Cu/ZSM-5 even in the presence of water vapor, the formulation on the whole possesses flaws which prevent its use in LDD applications. Extended hydrothermal exposure leads to irreversible loss of catalytic activity. The presence of SO₂ also leads to permanent deactivation. Though it may be possible to avoid SO₂ with the use of synthetic diesel (Fischer Tropsch), water and heat present in diesel exhaust are enough to deactivate Cu/ZSM-5 eventually.

As has been readily discussed in the literature, Cu/ZSM-5 remains as a reference catalyst even though there is no potential for this formulation to have industrial success.

There are seven conversion levels reported for supported Pt catalysts in **Figure 2**. Of the seven, only two are deemed suitable with respect to conversion level and temperature of maximum conversion. All of these catalysts are represented in **Figure 2A** and are summarized as follows. Supported platinum catalysts have been shown to be ineffective when ethane is used as the reductant. At high space velocities, the conversion peak is diminished and shifted to higher temperatures. Ion-exchanged samples are less effective than bulk impregnated samples. This difference implies that larger platinum ensembles are required for effective NO_x removal and not intimate interaction between Pt and the zeolite pores. Of the seven samples, only the ion exchanged ones were tested in the presence of water vapor or SO₂ but the same generalization can be applied to all Pt/ZSM-5 catalysts. There is only a mild inhibition (<5%) from the presence of water vapor. In the presence of SO₂ the conversion window is shifted slightly to higher temperatures (+25°C) and is also slightly broader (+50°C). Therefore, under

realistic conditions, Pt/ZSM-5 has a high likelihood of meeting the future emission legislation. Unfortunately, Pt/ZSM-5 possesses a serious limitation. For all of the catalysts, a significant fraction of NO_x reduced resulted in the formation of N₂O. Though N₂O is not currently a regulated emission, it is a strong greenhouse gas. The use of an emission control technology which produces N₂O in significant quantities would not be welcomed and would most likely prompt government legislation. In order for Pt/ZSM-5 to achieve industrial interest, the discovery of a Pt formulation that does not form N₂O or catalyst that removes N₂O concomitantly with NO_x reduction is required. Currently no such catalyst exists though Rh on ZSM-5 or Al₂O₃ show promise for N₂O decomposition, attaining light-off between 250°C and 300°C.

The remaining two catalyst formulations of interest are supported iron catalysts. The iron only parent catalyst shows 75% NO_x conversion at 350°C when *iso*-butane is the reductant. It is remarkable to note that the presence of 10% water vapor does not inhibit conversion. By adding 0.9wt% lanthanum to the parent catalyst, the conversion increases to 83% and has a larger conversion window though shifted to higher temperatures. The promotional effect of adding 0.9wt% lanthanum is not inhibited by the presence of water vapor. For most of the supported iron catalysts, water vapor actually increases catalytic performance at lower temperatures. This presumably is a result in removal of coke precursors which would otherwise block catalytically active sites. Unlike the Pt/ZSM-5 catalysts, Fe/ZSM-5 yields N₂ only. Moreover, after 100 hours time-on-stream, conversion only decreases by 10%. This effect is reversible by removing water vapor from the feed and heating to 500°C though it is unlikely that this regeneration event will occur under real conditions. It is important to note that another Fe/ZSM-5 sample with similar iron composition has been reported using the same feed composition. However, with this catalyst, peak NO_x conversion is shifted to 500°C. The presence of 150 ppm SO₂ did not affect NO_x conversion levels.

The origin in the different performances most likely originates in the catalyst preparation method. The first two samples have been prepared by solid-gas exchange (chemical vapor reaction). The parent zeolite present as the protonic form is exposed to FeCl₃. The proton reacts with FeCl₃ to form cationic iron (FeCl₂)⁺ complexes at exchange sites and HCl. The HCl is removed from the zeolite pore structure by the diluent gas. The residual chloride is removed via washing resulting in the removal of HCl and the formation of [HO-Fe-O-Fe-OH]²⁺. The Fe/Al atomic ratio achieved from this procedure reaches unity. Since the exchange ion is Fe³⁺, the calculated exchange level is 300%. The lanthanum promoted sample is made by exposing the thus formed Fe/ZSM-5 sample to a dilute La solution. Cobalt catalysts prepared by chemical sublimation have also been shown to possess lower temperatures for maximum NO_x conversion than samples formed via aqueous ion-exchange. The Fe/ZSM-5 which has a maximum NO_x conversion at 500°C utilizes a different preparation procedure. This sample is made by exposing a Na/ZSM-5 parent zeolite powder to a saturated ferrous oxalate solution in the absence of oxygen. The resultant catalyst possess a Fe/Al atomic ratio equal to 0.9. Since the exchange material is Fe²⁺, the calculated exchange level is 190%. Therefore, the difference in reported ion-exchange levels is a bookkeeping issue and not based on composition. A more accurate comparison of the two catalysts is the Fe/Al atomic ratios which are nearly identical. Fe/ZSM-5 catalysts prepared via incipient wetness and convention ion exchange result in lower iron loading and significantly inferior performance presumably from the formation of iron oxide particles. The Fe/ZSMZ-5 catalysts formed via FeCl₃ sublimation or FeC₂O₄ exchange show great promise though their preparation procedure is difficult.

The unique preparation procedures are deemed necessary for Fe/ZSM-5. For aqueous ion-exchange, ferrous (Fe²⁺) ions are desired. Proton sites exchange with [FeOH]⁺ complexes

up to a Fe/Al ratio equal to unity. Unless the exchange occurs in the presence of excess FeC_2O_4 and the absence of O_2 , ferrous ions readily oxidize to ferric (Fe^{3+}) complexes such as FeOOH . FeOOH will not exchange with the zeolite protons but rather form non-framework iron oxide particles. These oxide particles are not active for NO_x reduction. With the solid/gas reaction, FeCl_3 reacts with one zeolite proton to form HCl_{gas} and FeCl_2^+ complexes. Upon exposure to H_2O $[\text{Fe}(\text{OH})_2]^+$ complexes are formed and HCl is washed from the zeolite. Calcination of the thus prepared sample yields $[\text{HO-Fe-O-Fe-OH}]^{2+}$ complexes. All of the steps involved in the solid/gas preparation allow iron to be exchanged into the zeolite until a Fe/Al ratio of unity is reached. This is similar to the result during aqueous ion-exchange in the presence of FeC_2O_4 . The resulting iron complex formed after both preparations is $[\text{HO-Fe-O-Fe-OH}]^{2+}$ which is the active site for de NO_x catalysis. This complex allows iron to undergo a redox cycle ($\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+}$) but prevents further reduction to Fe^0 . When iron is reduced to the metallic state, it allows the formation of iron oxide particles and zeolite protons which in turn deactivates the catalyst. This does not occur even under reaction conditions with catalysts prepared via these two methods. There still remains, however, some degree of controversy around the Fe/ZSM-5 catalysts. Further investigation is required to determine the origin for observed differences in performance from lab to lab as well as if alternate, industrially-friendly procedures are possible.

In **Figure 3**, the performance of several metal ion-exchanged zeolite catalysts are presented. In this graph, the zeolite support material is not ZSM-5. Of the six supported platinum catalysts, two have conversion levels that are both significant and within the desired temperature window. The two with significant conversion but at high temperatures use methane as a reductant. When methane is the reductant, the conversion peak temperatures are shifted higher as a result of the higher activation energy for C-H bond rupture of methane compared to higher paraffins. The results with methane as the reductant will be discussed in **Section 5.2**. There are two catalysts which have peak NO_x conversion within the desired temperature window but whose maximum is too low. These catalysts are similar in composition (each are 1wt%Pt/USY) to those with higher conversion maxima. The difference in performance arises from a lower reductant to NO_x ratio (4.5 versus 0.6) as well as a mixture of propene, a selective reductant, with propane, a nonselective reductant. The lower carbon/ NO_x ratio coupled with the presence of propane result in these lower conversion levels. This indicates that a higher fuel consumption penalty would be required in order for a supported platinum catalyst to give the desired conversion levels. Again, one should note that all of the zeolite supported platinum catalysts mentioned in this section produce a significant quantity of N_2O . In order to utilize this family of catalysts, either a catalyst capable of concomitant N_2O removal needs to be developed or a method (via catalyst additive or use of a unique reductant) for avoiding N_2O production is required.

There are two supported sodium and three supported barium catalysts with conversion in the desired temperature window. All of these catalyst are on Y zeolite. The two supported sodium catalysts show a moderate NO_x conversion level even in the presence of 2% water vapor. Unfortunately, the levels are too low for further consideration other than to note that the reductants are alcohols. For the supported barium catalysts, significant NO_x conversion is achieved when an oxygenated reductant is used. When 500ppm of acetaldehyde and 200ppm NO_2 are used, 85% NO_x removal is achieved even in the presence of 2% water vapor. By substituting higher aldehydes but keeping the C/ NO_x ratio constant, the conversion levels remain high but are decreased slightly (80% with propionaldehyde, 75% with butyraldehyde). Slightly lower conversion levels have been reported when the NO_2 is replaced by NO . This suggests that a dominant role of the plasma in non-thermal plasma (NTP) assisted catalysis is the partial oxidation of the hydrocarbon to form an aldehyde and not solely the oxidation of NO

to NO_2 . If *n*-octane is used, 70% NO_x removal is achieved but only if NO_2 is already in the feed. When NO is present, conversion drops to below 50%. The zeolite-supported barium catalysts have become of interest with the recent application of NTP towards emission control technologies. The role of the NTP will be discussed in **Section 6**. Moreover, the ability of oxygenated reductants to demonstrate significant NO_x conversion in the presence of water vapor will be discussed in **Section 5.3**. Both NTP and the use of oxygenated reductants show great promise for achieving the required NO_x conversion within the desired temperature window for LDD applications.

One of the catalysts of promise is a Na/Y supported gold catalyst (brown dot). Unfortunately, the high NO_x conversion is achieved under a net reducing atmosphere and is therefore not applicable to this study. It is important to note that several supported gold catalysts have been reported in the literature though none meet the requirements for LDD applications.

3.2 Alumina-Based Catalysts

The next set of catalyst formulations that have received great interest has been alumina-based catalysts. A composite of the NO_x conversion levels for several different catalyst compositions has been collected in **Figure 4**. Again a significant number of formulations possess adequate NO_x conversion levels but at temperatures outside the desired range for LDD applications. Most of the alumina only catalysts have high conversion levels but above 400°C , thus making them unacceptable for LDD applications. High temperature performance is observed when light olefins and paraffins are used as the reductant.

Over the metal-free support, ethanol and methanol have also been proven as selective reductants over alumina only catalysts. Ethanol tends to yield maximum NO_x conversion at slightly higher ($400\text{--}450^\circ\text{C}$) temperatures than desired. Methanol yields maximum NO_x conversion around $300\text{--}435^\circ\text{C}$. The temperature for maximum conversion seems to be effected by the C/ NO_x ratio with higher C/ NO_x ratios yielding lower peak temperatures. Unfortunately, none of the alumina samples presented have been tested in the presence of water vapor. It is assumed that NO_x conversion will be significantly inhibited when light paraffins or olefins are used as the reductant as water readily displaces adsorbed nitrogen oxide complexes on the surface which are responsible for hydrocarbon activation. It is likely that oxygenated reductants will prove to be water tolerant as they can compete with water for active sites. With respect to the effect of sulfur, none of these samples have been tested in the presence of SO_2 but two have been tested after exposing the catalysts to SO_2 for extended periods. In the case where propane is the reductant, the peak temperature is shifted from 550°C to 650°C and conversion is lowered from 76% to 20%. Sulfate complexes block the sites responsible for paraffin activation and thus inhibit NO_x reduction. This in turn supports the concept that propane performance would be inhibited by water vapor in a similar fashion to sulfur poisoning. In the case where methanol is the reductant, there is only a mild shift in peak temperature (300° to 325°C) and conversion is only mildly lowered from 99% to 95%. Though alumina catalysts with methanol as the reductant remain an attractive catalyst formulation, it still remains unclear how methanol could be efficiently produced on-board so as to avoid the difficulties inherent in using a secondary tank for the reductant. Another limitation to the use of methanol is the propensity to form dimethyl ether at lower temperatures. This volatile organic compound is both a greenhouse gas as well as a contributor to ground level photochemical smog.

There has been significant interest in alumina supported silver catalysts. There are fourteen examples of $\text{Ag}/\text{Al}_2\text{O}_3$ catalysts presented in **Figure 4**. Of these only one has a peak

temperature which falls in the desired temperature and conversion range while four are close. Six have sufficient conversion but they occur at too high a temperature to be of use for LDD applications. In order to better understand the origin for these vast differences in performance, the data have been collected in **Figure 4A**. Two clear statements can be made about supported silver catalysts; neither methanol nor methane is a selective reductant. By plotting only the peak temperatures, one misses the large conversion window observed when higher hydrocarbons are used. The arrow bars included in **Figure 4A** highlight the greater than 80% conversion window for several of the catalysts. The 2wt% supported Ag catalysts tested with 2% and 12% water vapor represent two separate formulations tested. For the latter the catalysts have been prepared via impregnation of a dilute AgNO₃ solution onto alumina while the former have been prepared via hydrolysis of an aluminum isopropoxide - silver nitrate gel. With the exception of the performance with *n*-octane, the catalysts demonstrate very similar performance behaviors even though the space velocity of impregnated catalysts are four times greater and the water content is six times greater. The differences in *n*-octane performance may be a result of silver cluster size or experimental conditions. Overall, there is a correlation between the different experimental studies. It should be noted that the presence of water vapor enhances NO_x conversion when higher paraffins are used as the reductant. This can be ascribed to hydrolysis or gasification of coke and coke precursors which would otherwise deactivate the catalyst in dry streams.

In short, the performance data strongly suggest that an alumina supported catalyst could provide sufficient NO_x conversion for LDD applications. It should be noted that alumina catalysts are susceptible to sulfur poisoning. As stated above, the NO_x conversion performance is strongly inhibited for metal-free catalysts shifting to higher temperatures upon sulfating the surface of the alumina. When propane is used as the reductant in dry streams, the conversion is shifted from a maximum of 76% conversion at 550°C for the fresh catalyst to 20% at 650°C for the sulfated catalyst. In the case of alumina supported silver catalysts, the effect of sulfur is less pronounced. A 4.6wt% supported silver catalyst has been tested using ethanol as the reductant in the presence of 10% water vapor. Greater than 95% NO_x conversion is observed over a wide temperature window (300°C to 500°). The addition of 80 ppm SO₂ shrinks the temperature window yielding a maximum conversion of 85% at 475°C. Simulated aging in a dry, elevated SO₂ environment results in a further decrease in conversion to 70% though the peak temperature is still at 475°C. The formation of Ag₂SO₄ is believed to cause the inhibition. However, this inhibition is not catastrophic like in the metal-free case. A better understanding of the effect on NO_x conversion performance over alumina supported silver catalysts when higher hydrocarbons are used as the reductant is needed.

In addition to supported silver catalysts, supported platinum catalysts have been of significant interest as a potential emission control technology. In **Figure 4B**, five examples are presented. These catalysts containing 1wt% platinum have been tested using propene as the reductant. All yield peak NO_x removal at 250°C. There is a slight space velocity effect where the catalysts at low (5k/h) and high (60k/h) rate show slightly inferior performances to that at a moderate rate (20k/h). Again, as with zeolite-supported platinum catalysts, significant quantities of N₂O are formed as a product. Two examples with a platinum-rhodium alloy are also presented. With a 2wt% Pt:Rh (1:1 mass ratio) catalyst, only 35% of the NO_x is converted though the selectivity towards N₂ is high. The lower conversion is ascribed to enhanced direct oxidation of propene with oxygen and the enhanced selectivity is ascribed to the presence of rhodium. With a 1wt% Pt:Rh (3:1 mass ratio) catalyst, 60% NO_x removal is observed and though the N₂ selectivity is greater than a 1wt% Pt only catalyst, the N₂:N₂O ratio is near unity.

Higher Rh loadings result in lower NO_x conversion and therefore addition of Rh will not address the N₂O issue with supported Pt catalysts. A 0.3wt% Pt catalyst has been tested using *n*-octane as the reductant. Though the results show poor NO_x conversion (38%), the selectivity towards N₂ is high. It has been demonstrated that the N₂:N₂O ratio is strongly dependant on the reductant used with higher hydrocarbons favoring the formation of N₂ presumably owing to their ability to create larger Pt ensembles and thus increasing the likelihood of two N adatoms reacting to form N₂.

3.3 MIXED-METAL OXIDES (MMO) BASED CATALYSTS

During the course of this program, several other catalyst formulations have been discovered which do not rely on zeolites or alumina as the support material. Those data are collected in **Figure 5**. Silica, titania and pillared clays are inferior supports. Only two examples possess significant NO_x conversion levels. Two platinum catalysts tested have demonstrated significant NO_x removal at low temperatures. The silica-supported catalyst has a very high selectivity towards N₂O formation. On the other hand, the zirconia based catalyst (a La₂O₃ – ZrO₂ mixed metal oxide with a 1:1 mass ratio of La:Zr formed via co-precipitation) shows 65% NO_x conversion at 200°C even in the presence of 12% water vapor with low N₂O formation. At lower temperatures, this catalyst forms the most N₂O (20% at 150°C) while at higher temperatures this value decrease (8% at 250°C) and eventually N₂O formation ceases (at 300°C). Another conversion product is NO₂ which becomes significant above 200°C and reaches a maximum of 10% at 300°C. At 200°C, NO conversion equals 70% of this N₂ accounts for 55%, N₂O for 10% and NO₂ for 5%. Granted the N₂ values are lower than desired; however, of all the non-zeolite, non-alumina supported catalysts, this is the only example which might merit further investigation. Moreover, this formulation shows promise as a route to avoid N₂O formation with Pt-based catalysts.

3.4 REACTION MECHANISMS

3.4.1 ORGANIC SURFACE INTERMEDIATES PATHWAY

For all of the zeolite-supported catalysts, two dominant reaction pathways have been proposed. One involves the formation of organic surface intermediates the other invokes a decomposition pathway which is facilitated by the hydrocarbon reductant. For the surface intermediate pathway, the first step towards NO_x reduction is actually NO oxidation to NO₂. The thus formed NO₂ is adsorbed onto the active metal site either as a NO₂ (nitro or nitrito) ligand or is further oxidized to form a surface nitrate. The adsorbed complex is sometimes referred to as a NO_y group to distinguish it from the NO_x in the gas phase. These NO_y groups are capable of hydrocarbon activation which usually precedes via the abstraction of a H atom to form a hydrocarbon free-radical. This free-radical can combine with another free-radical such as NO (or NO₂) to form a nitroso alkane or other C_xH_yN₂O complex (e.g., acetone oxime which is an isomer of 2-nitrosopropane). These intermediates react with a gas phase NO (or NO₂) to yield N₂ and a partially oxidized hydrocarbon. It is also possible that the C_xH_yN₂O intermediate can undergo reaction steps to form complexes such as nitriles and isocyanates. In all cases, there is strong evidence from isotopically labeled ¹⁵NO experiments that N₂ formation involves the reaction of an organic-bound nitrogen complex on the catalyst surface with a NO molecule from the gas phase. Experiments where organic-bound nitrogen complexes (such as oximes, nitriles,

isocyanates...) are present on the surface and are exposed to ^{15}NO yield exclusively an isotopically mixed N_2 product.

For these reaction pathways, one major limitation is that the hydrocarbon must be activated via a NO_y surface complex. As most of these studies have been performed in the absence of water vapor, the NO_y complexes readily form. However, in the presence of water vapor, water acts as a competitor for these adsorption sites and will readily displace the NO_y to form an aquo complex. This is borne out by the strong inhibition water vapor has when Cu/ZSM-5 employed as the catalyst. This inhibition is strongest when light paraffins are used as the reductant. For heavier paraffins, it is possible for the reductant molecule to condense on the surface of the catalyst and thereby permit hydrocarbon activation via alternate routes. Conversely, when olefins are used, it is possible to activate the hydrocarbon via direct reaction of the carbon-carbon double bond with NO_x to create an organic-bound nitrogen complex which subsequently reacts with NO_x to form N_2 . Olefins are also prone to partial oxidation reactions which can create oxygenated reductants. These reductants are able to compete for active sites even in the presence of water vapor. Once the hydrocarbon is bound to the surface (either via reaction between a carbon-carbon double bond or an oxygen atom with the active sites) subsequent reaction will form a nitrogen containing organic complex on the surface of the catalyst. This complex will then react with a gas phase NO_x molecule to form N_2 . The role of oxygenated reductants and their effect on the reaction mechanism will be discussed in further detail in **Section 5.3**.

3.4.2 **NO_x DECOMPOSITION PATHWAY**

Excessively exchanged Cu/ZSM-5 ($\text{Cu}/\text{Al} > 0.5$) has been shown to decompose NO to N_2 . This discovery led to the great interest in zeolite supported catalysts for NO_x abatement and eventually led to the discovery that many zeolite supported catalysts are active for NO_x reduction. Cu/ZSM-5 remains unique in its ability to decompose NO to N_2 at relatively low temperatures. It has been postulated that the requirement that the catalyst be excessively exchanged results in the formation of adjacent copper sites which are capable of adsorbing/desorbing oxygen. The two main limitations to the applicability of Cu/ZSM-5 as a decomposition catalyst in LDD emission control technologies are the presence of water vapor and oxygen in the exhaust streams. Both are known to significantly inhibit the decomposition mechanism. Since both will always be present in the diesel engines exhaust this catalyst will not be successful. In order for a decomposition catalyst to be successful the reaction pathway must be different than that the pathway over Cu/ZSM-5. In other words, it must not be sensitive to either water vapor or residual oxygen both of which will always be present in LDD exhaust streams.

Another reaction pathway involves the dissociative adsorption of NO onto transition metal clusters. This is the main pathway for NO_x reduction over supported platinum group metal (PGM) catalysts. This process is known to be enhanced in the presence of a reductant. The role of the reductant is to remove oxygen from the PGM surface. The reductant needs to clear a patch of exposed metal atoms which is large enough for a NO molecule to adsorb dissociatively. The thus formed N adatom can combine with another N adatom to desorb associatively forming N_2 . This process is often called "hydrocarbon assisted NO decomposition". It is also possible, however, that the N adatom reacts with an impinging NO molecule resulting in the formation of N_2O . Under the lean conditions employed for these experiments as well as the low temperatures observed in LDD exhausts, a significant fraction of the N adatoms react with NO to form N_2O with Pt-based catalyst formulations. Supported platinum catalysts are not active for N_2O

decomposition at the same temperatures where NO_x reduction occurs. Since N₂O decomposition/reduction is difficult under conditions expected for LDD applications, a preferred catalyst would be one that does not form N₂O in the first place.

There is some evidence that in the presence of higher hydrocarbons such as *n*-octane or toluene, the quantity of N₂O formed can be minimized or even completely suppressed. Such a selective reductant would therefore be a molecule capable of creating a patch of exposed Pt atoms which is large enough for dissociative adsorption of NO. It remains to be proven if these non-N₂O forming reductants will maintain the high N₂ selectivity in the presence of nonselective reductants such as propene which will always be present in the exhaust.

4 ACTIVE METALS – SUMMARY

4.1 SUPPORTED PLATINUM CATALYSTS

The data for the supported platinum catalysts are compiled in **Figure 6**. Most of the data have been discussed in the previous sections and have been collected here for a thorough discussion of Pt-based catalysts. The two ferrierite (FER) supported Pt catalysts are different from the others on two counts. These catalysts are actually bimetallic with the platinum present mainly for NO oxidation to NO₂. Therefore, the performance of these two catalysts are more indicative of the co-cation (Co or In). Also methane is used as the reductant. As will be discussed in **Section 5.2**, methane catalyst can provide sufficient NO_x conversion levels but almost exclusively at temperatures outside the desired range. The carbon supported catalyst uses propene as the reductant. The peak NO_x conversion temperatures are much higher than most other supported platinum catalysts using propene; there is a strong indication that the support material is participating in the reduction process. Carbon supports are not desirable for LDD applications since exhaust temperatures would frequently reach conditions that could facilitate the combustion of the support material.

With the exception of one point, all other supported platinum catalyst show peak NO_x conversion at or below 300°C with reductants other than methane. Ultra-stable Y zeolite (USY) supported catalysts convert over 90% of the NO_x when propene is the reductant. If the C/NO_x ratio is lowered (from 4.5 to 0.65) and part of the propene is replaced with propane, then the conversion level is strongly impacted with conversion levels falling to below 25% and peak temperature shifting from 200°C to 300°C. Subsequent addition of 10% water vapor and 300 ppm SO₂ has little impact though since the conversion levels are already strongly inhibited water and sulfur tolerance should not be inferred. Alumina-supported catalysts also display significant NO_x reduction at low temperatures. As stated in **Section 3.3**, the addition of rhodium favors N₂ formation but lowers the conversion level. When testing catalysts with Pt loadings around 1wt%, most reductants yield between 50-70% NO_x conversion provided that the C/NO ratio is two or greater. Most catalysts provide sufficient NO_x removal when the platinum is present as large crystals as this provides enough space for ensembles of platinum atoms to become exposed to the gas phase after reaction with a hydrocarbon. Bulk impregnation of a platinum salt onto the support will create an active catalyst.

The limitation for all supported platinum catalysts is the high propensity to form N₂O. This can be mitigated by employing specific hydrocarbon reductants. Heptane and propene have N₂O/N₂ yields ≥ 1 . Toluene, conversely, has 100% N₂ selectivity. It is difficult to envision on-board production of toluene and, the selectivity of streams with mixed reductant feeds (e.g., toluene/propene) has not been studied. It is likely that these feeds will yield N₂O. Therefore

preventing the formation of N_2O will most likely not arise from employing a unique selective reductant. It is therefore necessary that a catalyst formulation modification that prevents the formation of N_2O or a novel catalyst that concomitantly removes the thus formed N_2O must be discovered. A large number of catalysts have been tested for direct decomposition of N_2O . Most possess light-off temperatures that are greater than the desired temperature window for LDD applications. Rhodium exchanged zeolites and Al_2O_3 supported Rh catalysts have been shown to decompose N_2O at low temperatures; e.g., Rh/ZSM-5 achieves 50% conversion at $275^\circ C$. While addition of O_2 only slightly inhibits catalysis, the effect of H_2O addition is not currently known. The reaction temperature is still slightly too high for LDD applications.

Further research is needed into N_2O avoidance or mitigation for Pt-based catalysts. Until of these limitations can be overcome, supported platinum catalysts will not be the catalyst of choice for LDD applications.

4.2 SUPPORTED SILVER CATALYSTS

Conversion data for supported silver catalysts are presented in **Figure 7**. Methane and methanol have been proven to be nonselective reductants. When a ZSM-5 supported silver catalyst is doped with ceria, the resulting catalyst has greatly enhanced performance (from 28% to 80%) with methane as the reductant. The peak conversion temperature is lowered from $600^\circ C$ to $500^\circ C$. This is attributed to ceria catalyzing NO oxidation to NO_2 . Still, the performance is not within the desired temperature window. There are a series of promoted zirconia supported catalysts which contain silver and copper as the active sites. Though these catalysts do not possess sufficient activity for LDD application, they do demonstrate a trend that higher hydrocarbons are better for NO_x removal.

Alumina supported silver catalysts are the best performers. Conversion levels are high and there is a broad temperature window where conversion is greater than 80%. Higher paraffins and many alcohols are very active for NO_x reduction and are not inhibited by the presence of water vapor. The effect of SO_2 is not well documented though it clearly is not as catastrophic as is the case with the metal-free alumina catalysts.

There are two main routes for alumina supported silver catalyst synthesis, incipient wetness and hydrolysis of a silver ion - aluminum alkoxide gel. Incipient wetness is the simplest procedure. A dilute silver salt solution is carefully added to a dehydrated alumina sample. The volume of solution is just sufficient enough to fill the pores and cover the surface of the alumina powder. A dilute solution is required to promote metal dispersion and the minimum volume is used in order to prevent ion migration while the sample is dried. The silver salt employed must have high solubility and must be combustible. In other words, the anion must decompose or burn during the calcination step thus leaving silver oxide clusters on the surface. In addition to its simplicity, this procedure also ensures that all of the silver will be either on the exterior of the alumina crystal or within the pore structure. This in turn ensures that the exterior of each silver cluster will be accessible to the gas phase. One disadvantage is that dispersion drops as the weight loading increases. This procedure tends not to be used for the synthesis of high metal loaded catalysts.

The hydrolysis procedure uses a silver salt dissolved in an aluminum alkoxide gel. Aluminum *iso*-propoxide is the most common aluminum salt used. The silver - aluminum gel is usually made with an alcohol such as ethanol. Upon addition of water, the *iso*-propoxide is displaced to form hydroxyl bridges between aluminum and silver atoms; this creates a silver-aluminum hydroxide precipitate. *iso*-propanol is formed as a byproduct. The precipitate is washed to remove any ions present that were not incorporated into the precipitate as well as to

remove residual alcohol. Calcination at 500°C creates the finished catalyst. The resultant catalyst has high metal dispersion even at high metal loadings. In addition to being more complex than simple impregnation techniques, hydrolysis also creates silver sites which are buried within the crystal structure. These sites are not accessible to the gas phase and therefore are inactive. On the whole, hydrolysis tends to produce better catalysts than incipient wetness techniques.

4.3 SUPPORTED COPPER CATALYSTS

Ever since Cu/ZSM-5 was identified as an active catalyst for both the direct decomposition of NO and SCR-HC, supported copper catalysts have been the main focus for deNO_x catalysis research. A large body of data exists for Cu/ZSM-5 in SCR-HC catalysis. Unfortunately, the majority of the data available for Cu/ZSM-5 catalysts have been collected in the absence of water vapor or SO₂. For the purpose of this study, the data can be condensed into the following statements. Though Cu/ZSM-5 is active for NO_x reduction with hydrocarbons, the inherent properties of this catalyst formulation make it unsuitable as an emission control technology for LDD applications. The presence of water vapor displaces surface NO_y complexes responsible for light hydrocarbon activation. As a result, direct oxidation of the hydrocarbon by O₂ becomes the dominant and, therefore, non-selective reaction. NO_x reduction becomes strongly inhibited by the presence of water vapor. This inhibition is reversible if water exposure is brief. Heavier hydrocarbons (C₈₊) have demonstrated high NO_x conversion even in the presence of water vapor. Unfortunately, extended hydrothermal exposure leads to irreversible catalyst deactivation regardless if light or heavy hydrocarbons are employed as the reductant. In addition to the well documented water inhibition, Cu/ZSM-5 also possesses a strong sensitivity towards SO₂ arising from the formation of CuSO₄.

Owing to the ubiquitous nature of water vapor from internal combustion engines, Cu/ZSM-5 will never have use in LDD emission control technologies. Copper catalysts in general exhibit strong water and sulfur sensitivities and will not be of interest for further study.

5 EFFECT OF THE REDUCTANT – SUMMARY

5.1 LIGHT OLEFINS AND PARAFFINS

Many of the catalysts which are active for NO_x reduction with light olefins or paraffins as the reductant display a strong inhibition in the presence of water vapor, Cu/ZSM-5 is chief among these. This is unfortunate as these reductant species form via in-cylinder, incomplete combustion. There are a few catalysts such as Fe/ZSM-5 that show promise. Catalyst synthesis involves a solid-gas exchange reaction between FeCl₃ and the zeolite protons to produce active iron sites and gaseous HCl or via ion-exchange of FeC₂O₄ under anaerobic conditions. This complex synthesis route is required as catalysts prepared via a traditional ion-exchange route are significantly less active. It is also the origin for the performance discrepancies reported in the literature. As a result, Fe/ZSM-5 may have limited industrial interest. In comparison to catalysts formed via the traditional ion-exchange method, Co/ZSM-5 formed via solid-gas exchange synthesis demonstrates improved NO_x conversion levels at lower temperatures with light olefins or paraffins used as the reductant. Again, the complexity of catalyst synthesis will limit interest in these formulations.

Supported platinum catalysts are active in the desired temperature window for NO_x reduction. Unfortunately, when light olefins are used, there is a strong propensity to form N₂O.

Light paraffins are not selective and are directly oxidized by O_2 forming CO_2 and H_2O . Higher paraffins such as *n*-octane are active and these higher hydrocarbons form less N_2O than when light olefins are used as the reductant.

No catalyst formulation is known which efficiently uses the reductants readily produced in-cylinder (light olefins and light paraffins) in realistic exhaust atmospheres. Many catalysts are efficient for NO_x reduction but only in the absence of water vapor and SO_2 .

5.2 METHANE

Methane as a NO_x reductant has received considerable attention in the stationary power industry where it is a common fuel source. The conversion efficiencies for several catalyst with methane as the reductant are presented in **Figure 8**. As evidenced in the graph, most catalysts exhibit NO_x conversion at elevated temperatures which are significantly greater than those desired for LDD applications. Therefore, methane-based solutions will not be successful for LDD applications.

5.3 OXYGENATED REDUCTANTS

Increasingly, oxygenated hydrocarbons have been investigated as selective reductants for NO_x removal. Initial results are quite promising. NO_x conversion efficiencies with oxygenated reductants are presented in **Figure 9**. Several points are borne out by these data. Supported silver catalysts are active when the support material is alumina but not with titania or silica. Alumina-supported silver catalysts are not active with methanol but metal-free alumina catalysts are active. With higher alcohols, conversion is high for alumina-supported silver catalysts. Small dispersed silver sites are more active and have peak NO_x conversion at lower temperatures than large silver clusters. It is important to note that the conversion windows for these systems are rather large with $> 80\%$ conversion occurring over a $125^\circ C$ range. Moreover, surface sulfation has only a minor impact on metal-free alumina catalyst performance with methanol as the reductant. When propane is the reductant, severe inhibition is observed over the metal-free alumina catalysts upon surface sulfation. Surface sulfation has significantly less of an impact on supported silver catalysts. Highly dispersed alumina supported silver catalysts show promise for LDD applications.

Another catalyst formulation which is gaining significant interest is Ba/Y zeolite. In a simulated exhaust stream with 500 ppm C_2H_4O , 200 ppm NO_2 , 8% O_2 , 2% H_2O balance N_2 , significant NO_x reduction is observed. Conversion levels are similar when C_3H_6O or C_4H_8O (at constant C/ NO_x) is used as the reductant. Conversely, CH_2O does not react over Ba/Y zeolite under these conditions. Over the metal-free alumina catalysts, conversion levels are significantly improved when NO_2 is present in the feed gas. This difference is not observed when Ba/Y zeolite is the catalysts.

Though Ba/Y zeolite presents a catalyst formulation with significant NO_x conversion within the desired temperature range two issues must be addressed prior to a successful application of this technology for LDD applications. First, the desired reductant needs to be provided. One option is to use a separate tank though this removes the key benefit of SCR-HC: on-board production of reduction. The other option is to form the oxygenates upstream of the catalysts. A partial oxidation catalyst could be employed for this. Recently, the use of non-thermal plasma has shown great promise.

6 POTENTIAL OF NON-THERMAL PLASMA (NTP)

Non-Thermal Plasma (NTP) has been investigated as an enabling technology for SCR-HC. Dielectric Barrier Discharge (DBD) devices have been commercially available for over 100 years. In general, a gas flow is passed through parallel plates covered with a dielectric barrier (commonly alumina). Upon application of a high voltage alternating current, a corona is created between the plates. A DBD device placed upstream of a catalyst has shown promise as part of an emission control technology. An alternate design uses wire placed inside a metallic tube. A pulsed, high voltage creates a plasma plume which is propagated through the cylinder. The pulse must be on the order of tens of nanoseconds in order to prevent arcing. The metallic cylinder can be filled with catalyst beads allowing catalysis to occur within the plasma plume. Similar NO_x conversion performances have been reported for both configurations. This demonstrates that catalysis is not contingent upon the short-lived species such as ·OH, e⁻ or O₃ formed in the corona.

In order to maintain the plasma, energy is required. Typically 20 to 60 J/L is required to reach maximum NO_x conversions. Higher energy input leads to negligible performance increases while contributing to increased fuel consumption. It is important to minimize the energy requirements of a NPT-based ECT as this will draw power from the vehicle resulting in an added fuel penalty.

For NO_x reduction, the pertinent chemistries are believed to be oxidation of NO to NO₂ without concomitant SO₂ to SO₃ oxidation and partial hydrocarbon oxidation. Within the corona plume, several free-radical species are believed to exist. At the exit of the DBD device, HNO₃, NO₂, CH₂O, C₂H₄O, CO and CO₂ have all been detected from initial streams with NO, O₂, C₃H₆ and H₂O. Nitro-alkanes have also been detected.

Though most of the catalyst formulations tested have been proprietary, three have been openly discussed in the literature, Na/Y zeolite, Ba/Y zeolite and γ Al₂O₃. Ba/Y yields 70-80% NO_x conversion at 200°C. Alumina catalysts show high conversion levels (70%) but only at elevated temperatures (525°C). Na/Y zeolite yields 70% conversion at 225°C. The performance of these catalysts are equivalent but the differences in temperature for maximum conversion makes Ba/Y zeolite the most promising formulation. By comparison to 'thermal' catalysis (without a plasma), recent data with Ba/Y zeolite using simulated diesel exhausts show that the likely benefit of NTP is the formation of C₂H₄O by partial oxidation of propene.

There are several limitations with NTP which must be solved prior to employing this technology in industrial applications. Some of the byproducts from the plasma are toxic. As stated above, aldehydes are formed in the plume. While acetaldehyde and higher aldehydes react over Ba/Y zeolite and other catalyst surfaces this does not occur for formaldehyde. In addition, hydrocyanic acid (HCN) formation has been detected. The use of an oxidation catalyst is required to combust the products that do not react over the Ba/Y zeolite catalyst. If this catalyst is platinum-based there is a strong likelihood that N₂O formation will occur. Even though the formaldehyde and hydrocyanic acid will be oxidized, the formation of N₂O represents its own litany of issues. In addition, NTP catalysts have a strong propensity to form organic deposits on the catalyst surface. These deposits will readily combust at higher temperatures even leading to the formation of N₂. It should be noted though that for extended operation at lower temperatures, it is possible to saturate the catalyst surface and thus strongly inhibit catalysis. The NTP unit itself is another issue. Cost effective production of DBD devices and plasma durability remains to be demonstrated.

7 ENGINE PARAMETERS AND OTHER VARIABLES

SCR-HC will not achieve the legislated emission targets of 0.07g/mi (TIER II Bin 5) by improved catalyst formulation alone. Several parameters need to be optimized in order for this technology to reach the future goals. First and paramount is thermal management of exhaust temperatures. Most of the SCR-HC catalysts display NO_x conversion within a narrow temperature window. Even with alumina supported silver catalyst using oxygenated reductant, the catalyst must reach a minimum temperature (light-off) rapidly and must be maintained within that range. If temperatures are too low, then the hydrocarbon does not react; too high, O₂ directly oxidizes the hydrocarbon. For LDD applications, exhaust gas temperatures are below 150°C for a significant fraction of the legislated drive cycle. The catalyst temperature can be increased via combustion of additional fuel. Considering the time exhaust gas temperature is below 150°C, the quantity of fuel required to maintain the catalyst within the desired range would be cost prohibitive. An alternate approach is required.

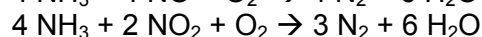
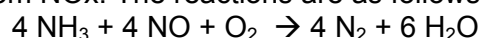
One of the keys to thermal management is to size properly the engine to vehicle weight ratio. The smaller the ratio, the higher the exhaust temperatures. Using too large an engine forces significant constraints of the efficiency and cost of the emission control technology. Another technique to increase exhaust gas temperatures is cylinder deactivation. During low load operation, cylinder deactivation will be a useful technique to maintain the catalyst operating in the optimum temperature window. This will be important as a significant fraction of the FTP drive cycle has exhaust temperatures that would normally be below 200°C. Cylinder deactivation will minimize this percentage. It is unlikely that a catalyst technology will be discovered that is capable of reducing NO_x to N₂ at temperatures below 150°C.

By minimizing engine out NO_x concentrations, the burden on the ECT is thusly reduced. The use of exhaust gas recirculation (EGR) greatly reduces engine out NO_x concentrations. Over the light-duty modal test, engine out NO_x concentration has been decreased from 3.7 g/mi to 0.27 g/mi by the introduction of cooled EGR to a 7.3L V8 engine (MY 2000). This is a 93% decrease. As a result, a further 74% reduction in NO_x is required. Unfortunately, EGR leads to a concomitant increase in particulate matter mass. This will necessitate the use of a particulate filter trap.

In order to meet the legislated emission targets, 'enabling' technologies such as EGR and thermal management strategies will be required in order for SCR-HC to be effective.

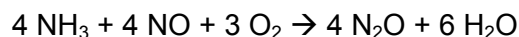
8 COMPARISON TO SELECTIVE CATALYTIC REDUCTION WITH NH₃

SCR-NH₃ is currently used in many industrial NO_x emission control applications, most notably in the stationary power generation industry. This process relies on the reaction of an ammonia molecule with a NO_x molecule to form N₂ in a process similar to the decomposition of NH₄NO₂ and NH₄NO₃ which form N₂ and N₂O, respectively. Over V₂O₅/TiO₂ catalysts, greater than 80% NO_x conversion is observed at 350°C. By incorporation of WO₂ into the formulation, the light-off temperature is reduced by over 100°C with 80% NO_x conversion attained at 225°C. Isotopically labeled experiments have shown that one nitrogen atom originates from a NH₃ while the other is from NO_x. The reactions are as follows:



Since the NH₃/NO_x ratio depends on the oxidation state of NO_x, there is a potential for either excessive or insufficient NH₃ addition thus yielding either NH₃ or NO_x slip, respectively. To

prevent NH₃ slip, the use of an oxidation catalyst downstream of the SCR unit is common. Though this converts NH₃ to NO_x, it eliminates NH₃-slip. As the incoming NO_x concentrations vary during the drive cycle, predicting the required dose of NH₃ is difficult. Another reaction to consider is:



This non-desirable reaction needs to be avoided as N₂O is a strong greenhouse gas. These three reactions are not inhibited by the presence of water vapor or SO₂. Though it is possible to form NH₄NO₃ or (NH₃)₂SO₄ on the catalyst surface, these compounds readily decompose below 300°C.

Other formulations such as supported Pt catalyst and zeolite supported catalyst have been proven very efficient for SCR-NH₃. Supported Pt catalysts are active at lower temperatures (150° to 350°C) though these formulations are more prone to N₂O formation than others. Zeolite supported catalysts are active at higher temperatures (350°C to 600°C). For LDD applications, supported Pt and promoted V₂O₅/TiO₂ catalysts are ideal.

For stationary power generators, the storage of large quantities of toxic NH₃ is less of an issue compared to mobile applications such as LDD. As a result, compressed NH₃ is not the desired source for the reductant. Two other compounds have been investigated: urea and ammonium carbamate. Urea is stored as a 30-36wt% solution while ammonium carbamate is a solid. Based on lower cost and ease of use, urea is the preferred source for the SCR-NH₃ reductant. During catalysis, urea is injected up stream of the catalysis. At temperatures above 160°C, urea readily undergoes hydrolysis to form 2 NH₃ and CO₂. Urea also decomposes to NH₃ + HNCO. There are additional byproducts (cyanuric acid, biuret, ammeline, ammelide, melamine, etc.) formed during urea decomposition. These byproduct may prompt government legislation which strongly deters the use of urea as the on-board source of NH₃. Urea injection is stopped when the exhaust gas temperature is below 160°C to minimize urea decomposition and avoid urea crystals forming on the injector. The injection equipment is complex so as to ensure proper atomization and to prevent urea crystallization. Though urea injection is stopped when the exhaust gas temperature is below 160°C, these catalysts are capable of storing NH₃ at the Lewis acid sites. These stored NH₃ complexes account for a significant amount of NO_x removal at lower temperatures.

There are two major limitations preventing widespread use of SCR-NH₃. The first is logistics. Currently, there is not a nationwide infrastructure for urea distribution nor is there a clear method to achieve this. Second, this technology requires the urea tank to be replenished. In order to ensure that the system is working properly, an on-board diagnostic is needed which prevents the driver from circumventing urea refills. Since urea is not require to operate the engine, it is facile to avoid refilling the urea tank. These two issues are significant obstacles preventing widespread use of urea-based SCR-NH₃ and demonstrate the benefits that SCR-HC possess as a potential ECT for LDD applications.

9 SUMMARY AND PROPOSAL FOR FUTURE WORK

Despite the large body of literature pertaining to SCR-HC, the vast majority of these studies failed to include realistic diesel exhaust gas constituents; namely, water vapor and SO₂. As a result, it is difficult to determine which, if any, technology is a potential ECT for LDD applications. The most studied catalyst, Cu/ZSM-5, is irreversibly deactivated in the presence of water vapor and SO₂ and therefore is not a viable candidate. Most of the catalyst formulations

studied either demonstrate too low NO_x conversions or have peak conversions at temperatures above the desired window for LDD applications. For this study, a potential catalyst has been defined as one that converts at least 70% NO_x at or below 300°C.

Supported platinum catalysts show significant NO_x conversion within the desired temperature range. Catalysis is not inhibited by water vapor or SO₂. Unfortunately, significant N₂O formation is observed with this formulation. The N₂/N₂O product ratio depends on the reductant employed. Light olefins tend to produce a large N₂O fraction while heavier reductants (such as toluene or *n*-octane) produce less or none. Light paraffins such as propane are non-selective reductants as they lead to direct oxidation via O₂. In order for supported Pt catalyst to achieve greater acceptance as part of an ECT, either a Pt formulation which does not form N₂O or a novel catalyst formation which concomitantly removes N₂O needs to be discovered.

Of all the zeolite-supported catalysts, only Fe/ZSM-5, produced via a solid-gas exchange or anaerobic aqueous exchange of FeC₂O₄ processes, shows promise. The best catalyst from this group is formed by solid-gas exchange which displays 75% NO_x removal at 350°C. This catalyst is tolerant to water vapor and SO₂. Fe/ZSM-5 catalysts produced via the traditional metal-in-solution ion exchange route are significantly less active. Therefore, the complex procedure is required. A more direct, simpler synthesis route is needed prior to Fe/ZSM-5 receiving greater industrial interest.

Alumina supported silver catalysts show the greatest promise. The use of heavier reductants (*n*-octane or higher) as well as the use of oxygenates (C₂₊ alcohols or aldehydes) have been proven rather effective for NO_x removal. Moreover, alumina supported silver formulations demonstrate a broad temperature window with > 80% NO_x conversion occurring over a 125°C range. The presence of water vapor does not inhibit the reaction. In fact, water vapor inhibits catalyst deactivation when heavy paraffins are employed as the reductant. The effect of SO₂ appears to be minimal; further investigation is required. The support material affects silver-based catalyst performance with alumina being active while those formed with titania or silica are inactive. The incipient wetness technique or hydrolysis of an aluminum alkoxide - silver salt gel are both successful catalyst preparation routes. Higher loaded catalysts formed via incipient wetness lead to lower NO_x conversion with the maxima at higher temperatures. This is ascribed to the formation of large silver clusters which do not form with the gel process. In order for alumina supported silver catalysts to achieve success as an ECT for LDD applications, a method for forming oxygenated reductants *in-situ* is required.

Non-Thermal Plasma is of increasing interest for LDD applications. The use of a DBD device upstream of a catalyst provides the catalyst with the required reactants: NO₂ and oxygenated reductants such as formaldehyde and acetaldehyde. Catalysts such as Ba/Y zeolite (80% at 200°C) and Na/Y zeolite (70% at 225°C) have been proven efficient for NO_x reduction at low temperatures. There are several limitations with NTP. First, these catalysts tend to form significant quantities of organic surface deposits on the catalysts at lower temperatures. It is possible to saturate the surface and thereby deactivate the catalyst if an engine operates at low speed and load for extended periods. Second, the plasma produces several toxic byproducts such as HCN and CH₂O which do not react over Ba/Y zeolite or Na/Y zeolite. An oxidation catalyst is therefore needed. The use of supported platinum catalysts yields N₂O formation which entails its own issues. Third, the NTP unit requires energy input which decreases the fuel economy and the DBD device has not been proven to be durable for this application though several groups (industrial and government) are actively pursuing this technology.

It is unlikely that catalyst formulations will be discovered which actively reduce NO_x to N₂ at temperatures below 150°C. Unfortunately, exhaust gas temperatures are below 200°C during

a significant fraction of the FTP drive cycle. Therefore techniques which increase exhaust gas temperatures will facilitate SCR-HC becoming a viable route to achieve US TIER 2 Bin 5 NOx emission targets of 0.07g/mi. This can include reduced engine to vehicle weight ratios or engine management (cylinder deactivation) which both will increase exhaust temperatures. Another route would include a method for storing NOx emissions during cool exhaust conditions and later re-injecting the stored NOx once the ECT has achieved light-off conditions.

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 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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2 DATABASES SEARCHED

2.1. Ricardo Powerlink Database

Ricardo's own database of around 70,000 references to a wide variety of public domain material, dated from 1994-2002. Material includes SAE papers, conference papers, manufacturers' literature, journal articles, reference books, etc. Topics covered include all aspects of powertrain and vehicle systems technologies.

2.2. Compendex

Produced by Engineering Information, Inc., provides coverage of the world's significant engineering and technological literature. Contains technical reports, books, conference papers etc. Sources include 4,500 journals, publications of engineering societies, reports and monographs. Compendex contains a total of more than 2 million references.

2.3. INSPEC

Corresponds to the three print publications Physics Abstracts, Electrical and Electronic Abstracts, and Computer and Control Abstracts. Source material includes 4100 serials and journals, conference proceedings, books, reports and dissertations. Updated twice a month, the Database includes around 3,750,000 references.

2.4. NTIS (National Technical Information Service)

Summaries of US Government-sponsored research, development and engineering, plus analyses prepared by Federal agencies or their contractors. Agencies covered include NASA, DOD, DOT etc. The Database also provides access to government-sponsored research outside the US, in countries such as the UK, Japan, France and Germany. Around 2 million records, currently.

2.5. CAB Abstracts

Online version of Chemical Abstracts. Covers all aspects of chemistry, including analytical and physical, applied, organic and inorganic, and chemical engineering. Contains over 11 million references, updated biweekly.

2.6. CHEMWEB – Catalysis Forum

Web-based service focusing on catalysis issues. Databases available from this service include Beilstein Abstracts, Catalysis Patents, Chemical Engineering and Biotechnology Abstracts.

GRAPHS, FIGURES AND TABLES

Figure 1: Simulated Thermal Trace versus Engine to Mass Ratio

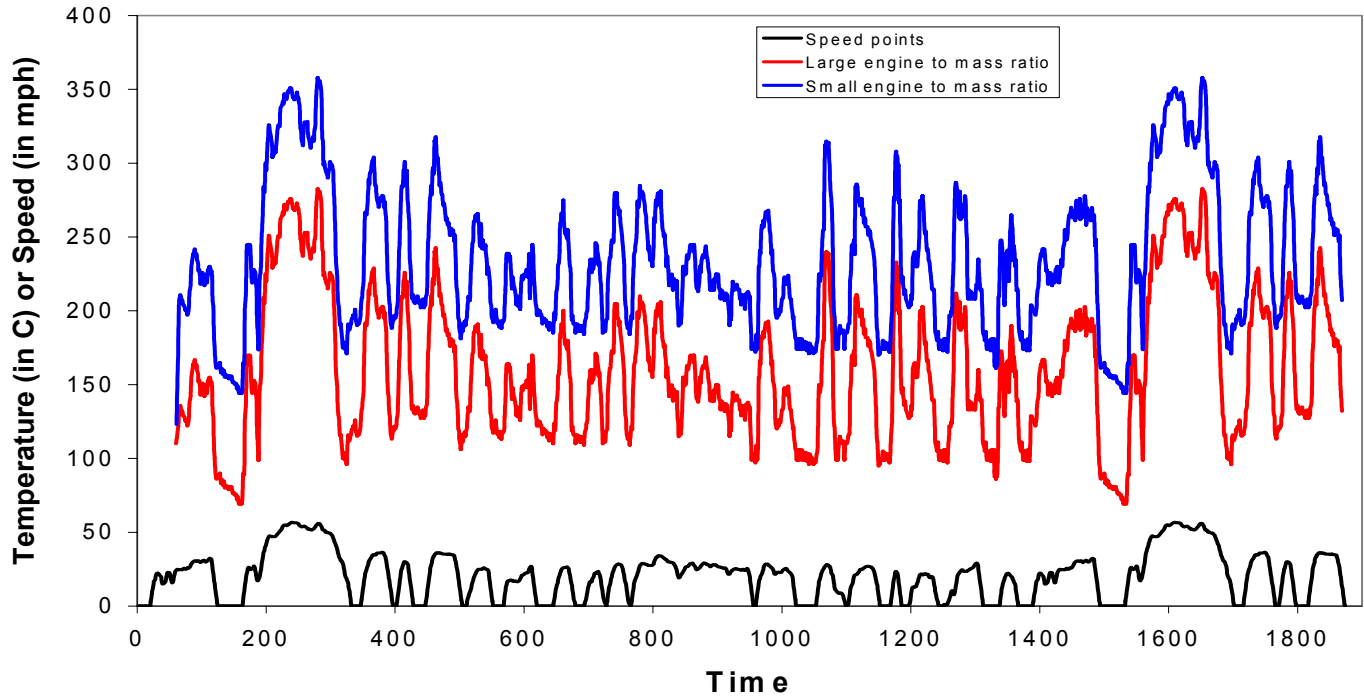


Figure 2: Peak NOx Conversion versus Temperature for ZSM-5 Supported Catalysts

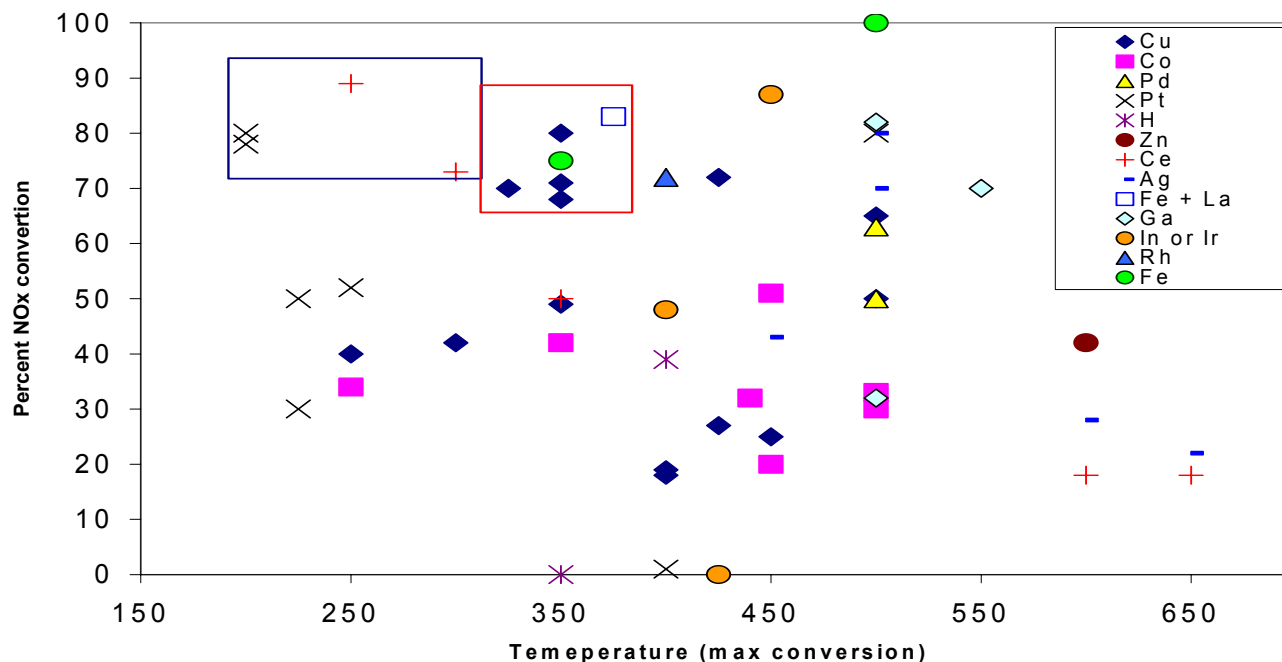
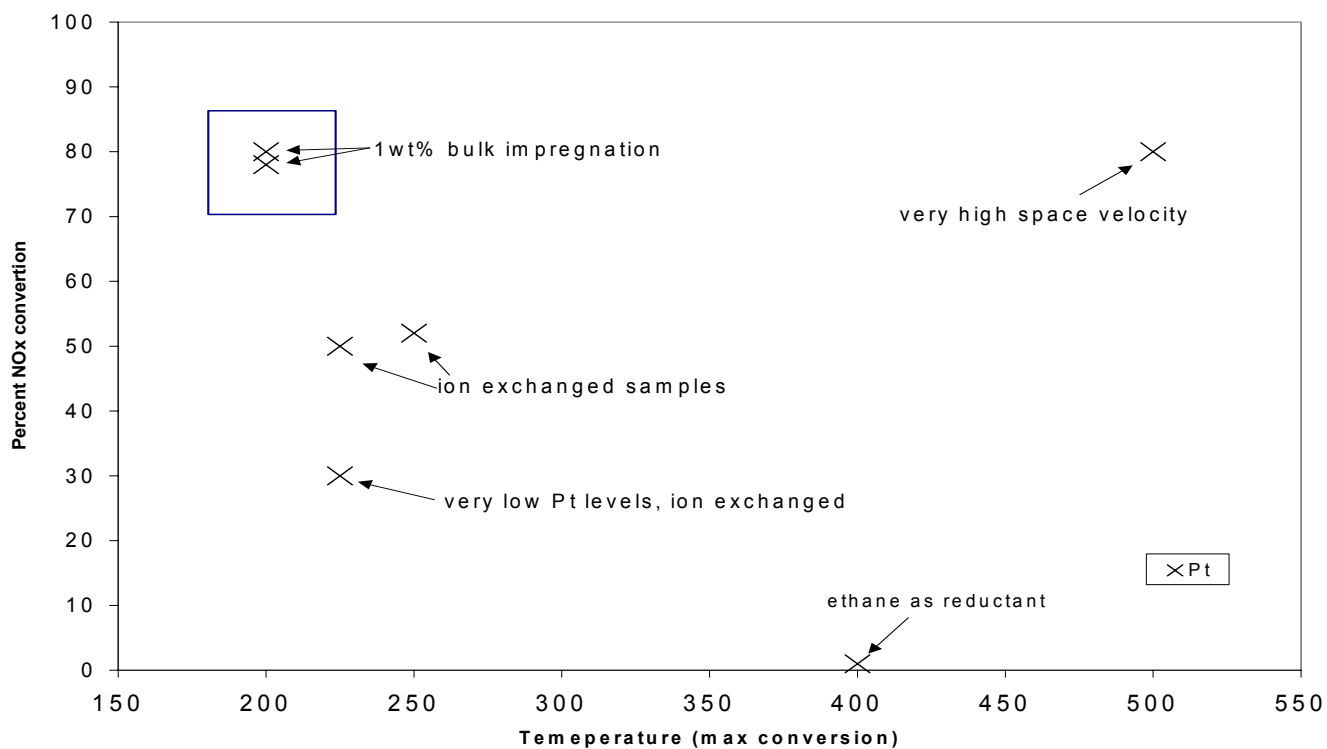
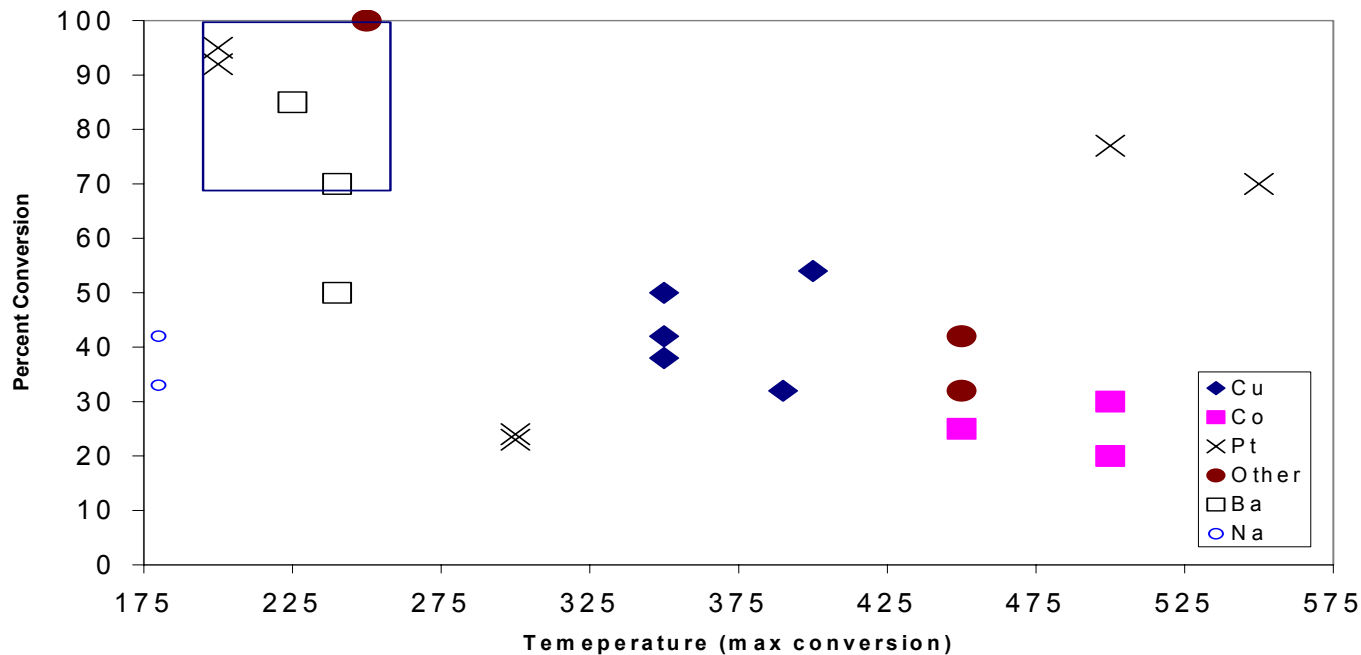


Figure 2A: Peak NOx Conversion versus Temperature for ZSM-5 Supported Pt Catalysts



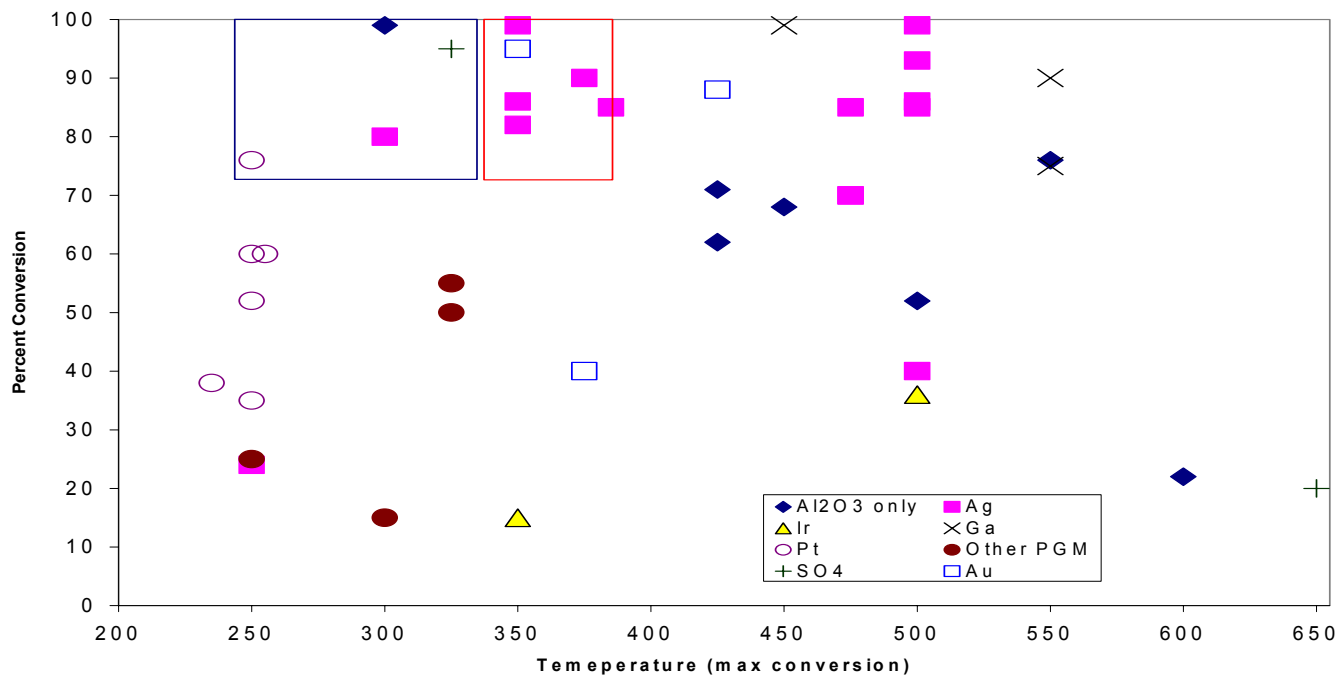
See Table 1 for data points.

Figure 3: Peak NOx Conversion versus Temperature for Other Zeolite Supported Catalysts



See Table 2 for data points.

Figure 4: Peak NOx Conversion versus Temperature for Alumina Supported Catalysts



See Table 3 for data points

Figure 4A: Peak NOx Conversion versus Temperature for Alumina Supported Pt Catalysts

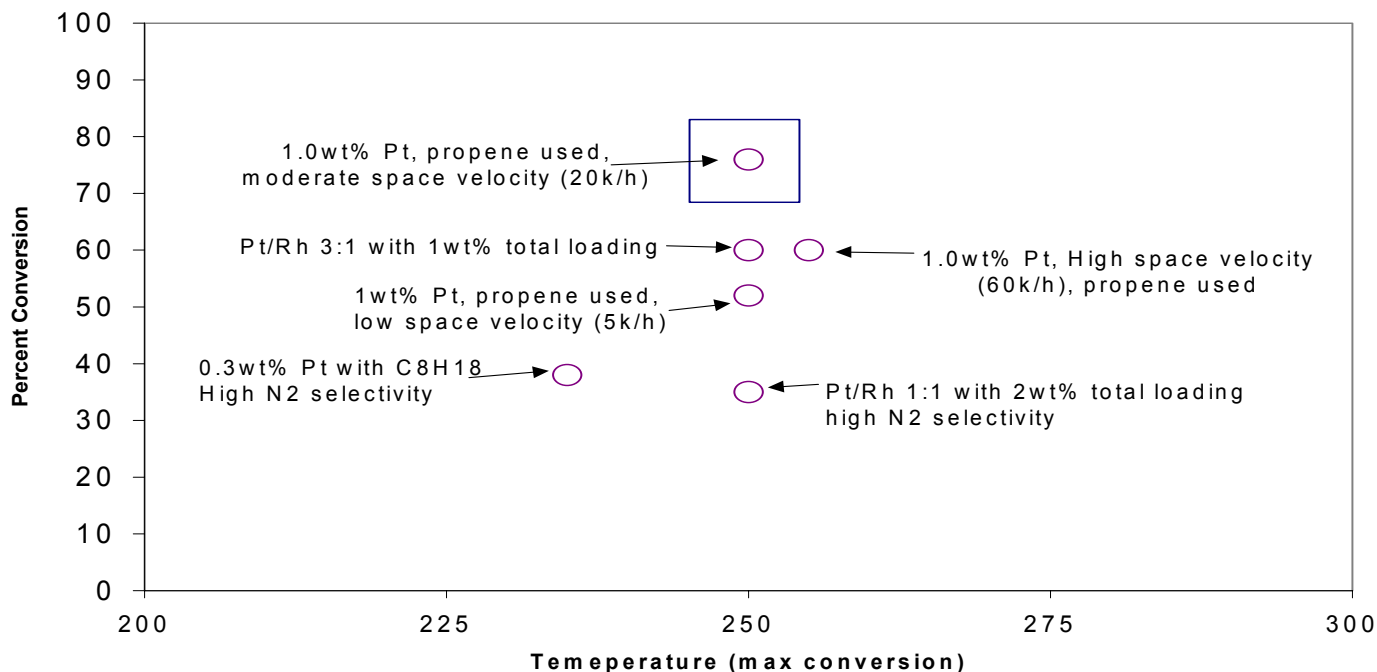


Figure 4B: Peak NOx Conversion versus Temperature for Alumina Supported Ag Catalysts

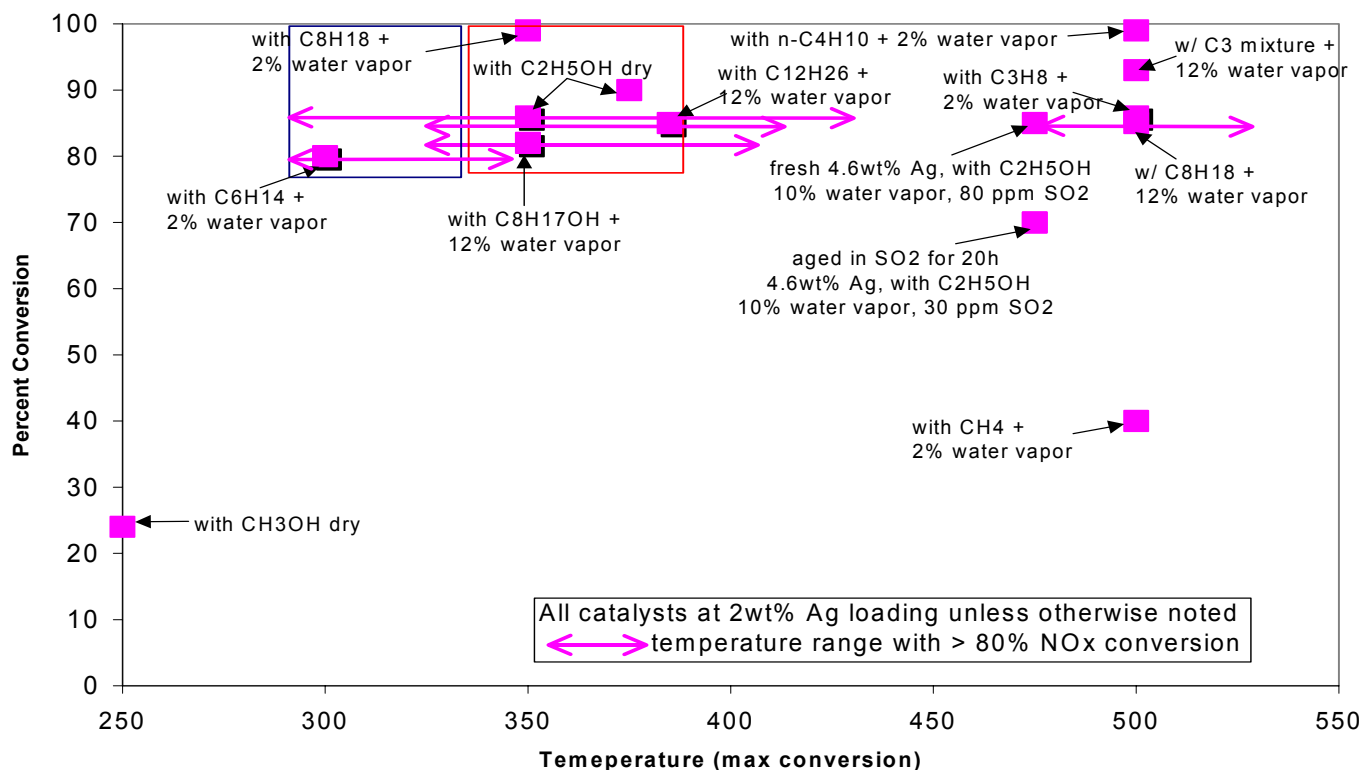
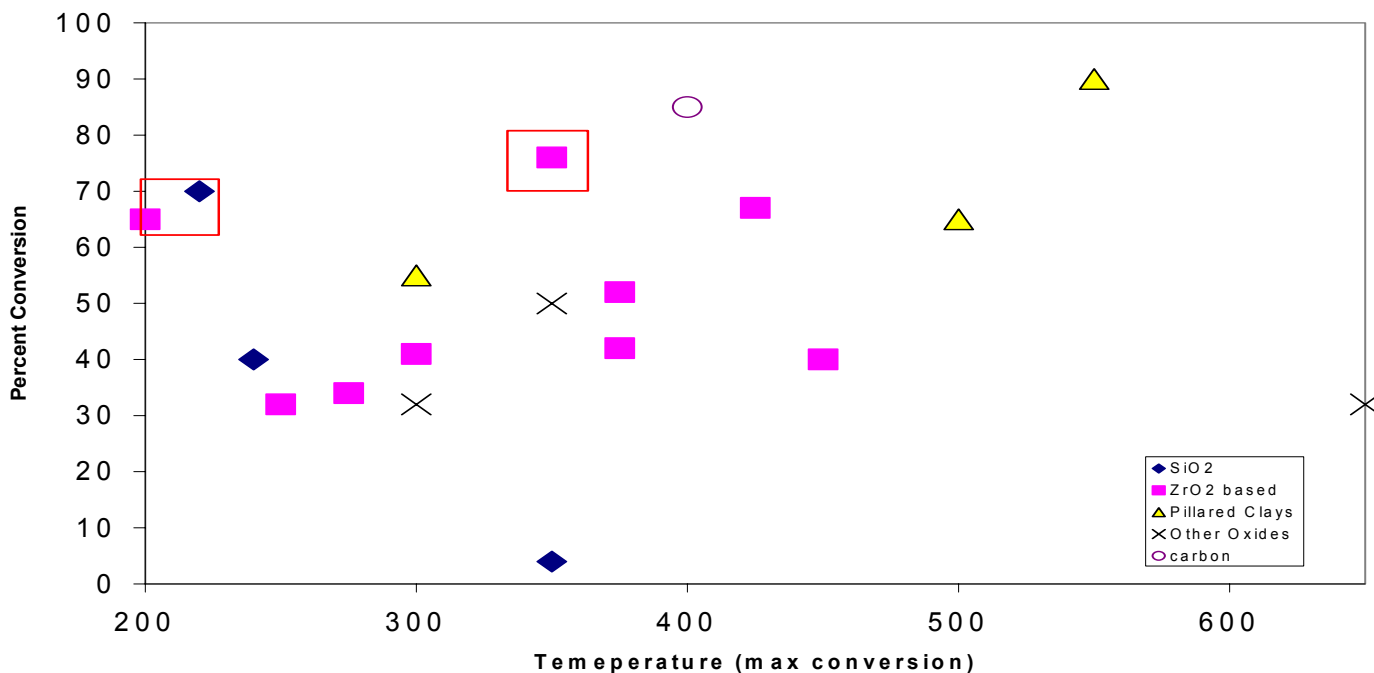
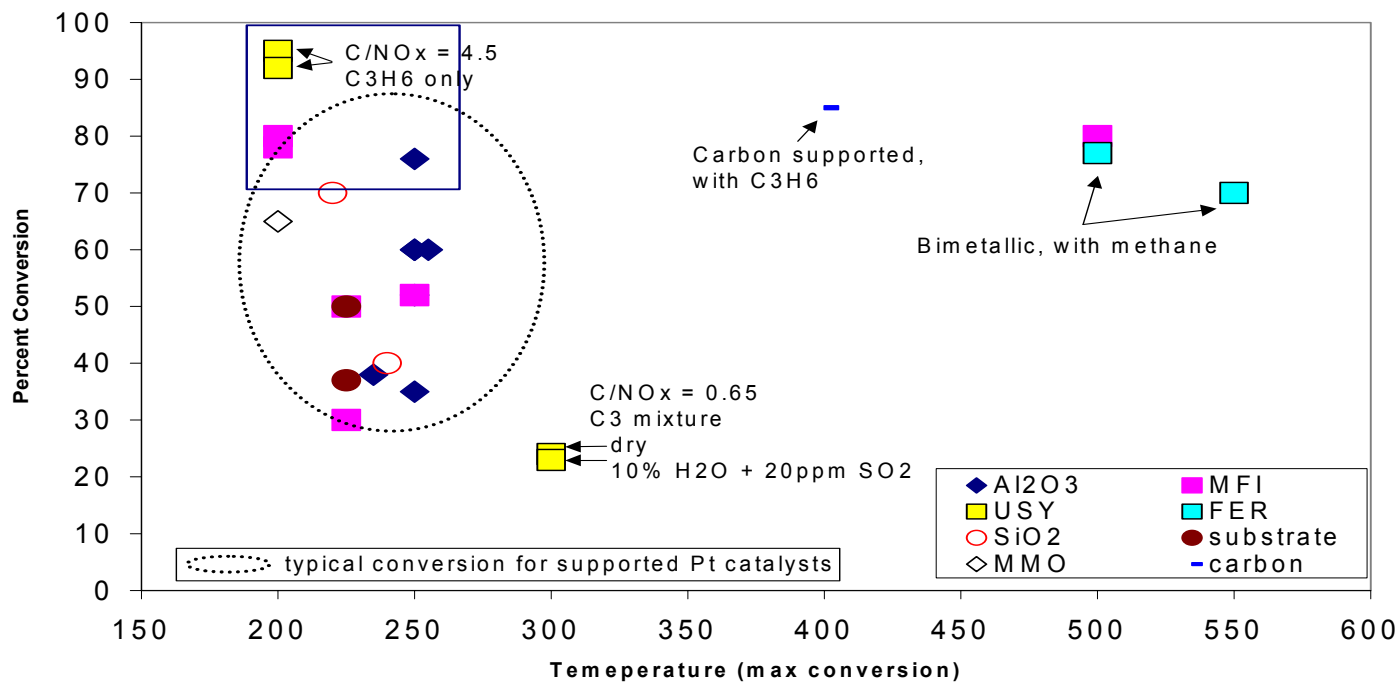


Figure 5: Peak NOx Conversion versus Temperature for Mixed-Metal Oxide Supported Catalysts



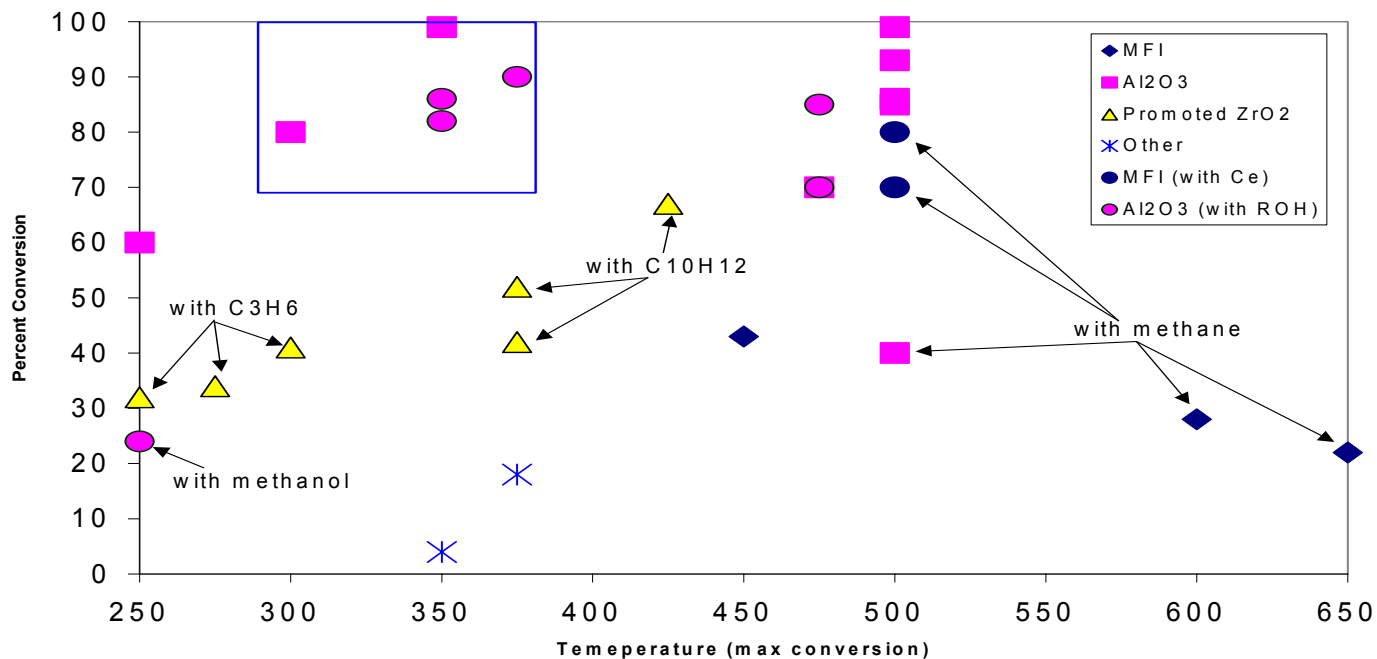
See Table 4 for data

Figure 6: Peak NOx Conversion versus Temperature for Supported Platinum Catalysts



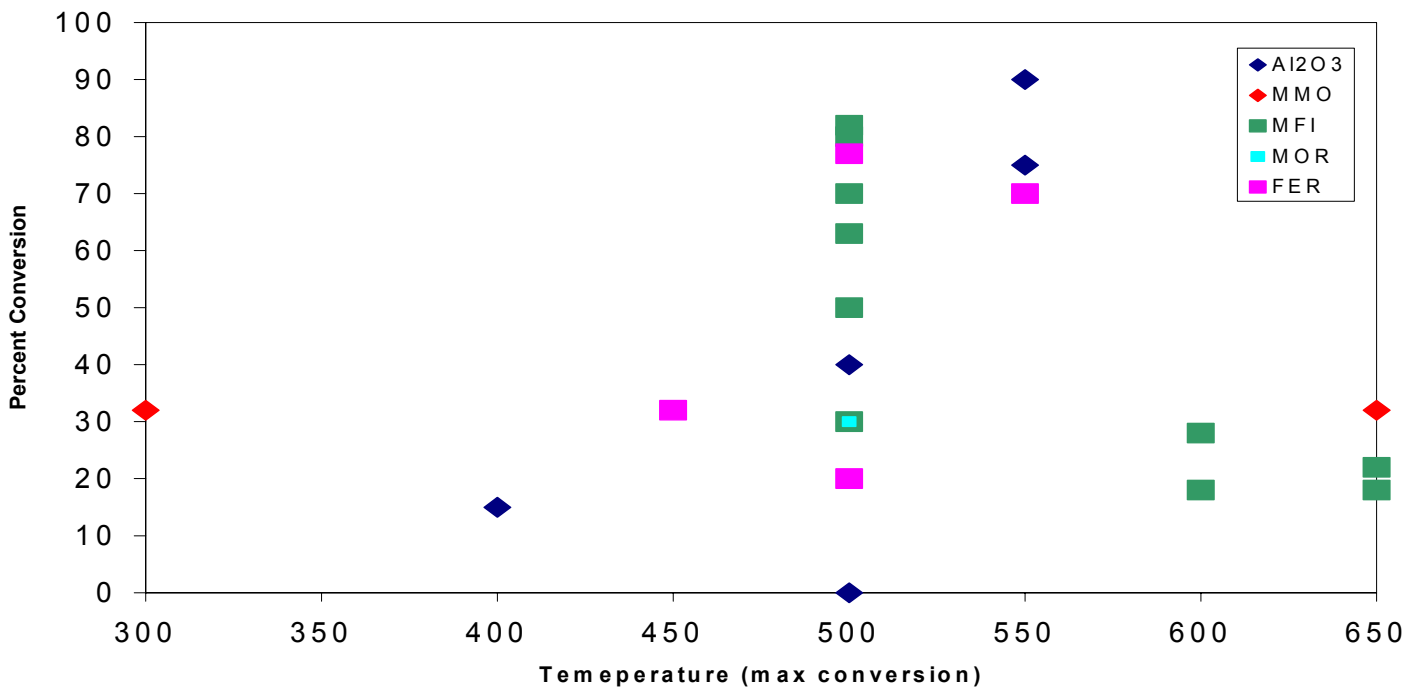
See Table 5 for data.

Figure 7: Peak NOx Conversion versus Temperature for Supported Silver Catalysts



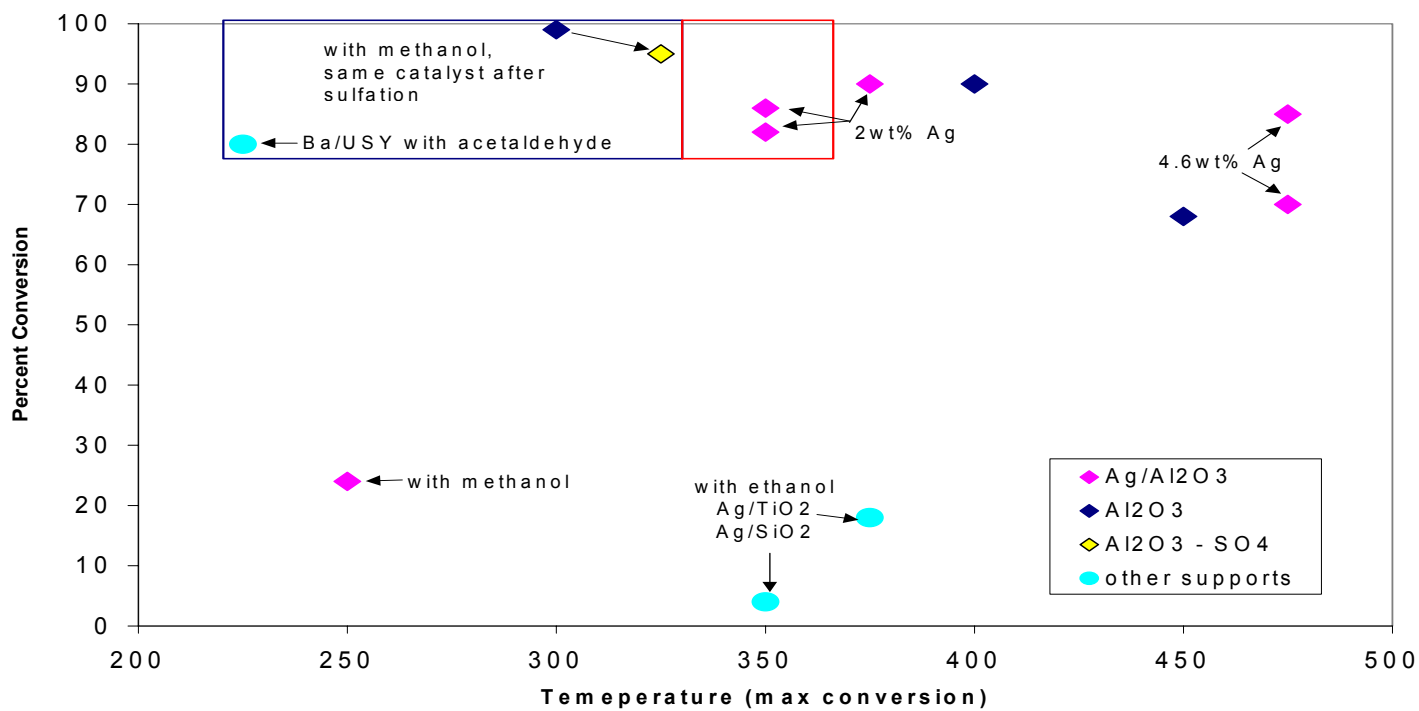
See Table 6 for data.

Figure 8: Peak NOx Conversion versus Temperature with Methane as the Reductant



See Table 7 for data.

Figure 9: Peak NO_x Conversion versus Temperature with Oxygenated Reductants



See Table 8 for data.



Table 1: NOx Conversion on ZSM-5 Supported Catalysts

Support	ZSM-5												
metal	% EL	HC type	HC conc	NO	O2 %	H2O	SOx	Tmax	%Conv max	GHSV (x 1000/h)	Ref	Other comments	
Cu	102	C2H4	250	1000	2.0	no	no	250	40	9	A		
Co	90	C2H4	250	1000	2.0	no	no	350	42	9	A		
H	100	C2H4	250	1000	2.0	no	no	400	39	9	A		
Ag	90	C2H4	250	1000	2.0	no	no	450-600	43	9	A		
Zn	96	C2H4	250	1000	2.0	no	no	600	42	9	A		
Ga	120	CH4	1000	1610	2.5	no	no	500	32	30	B	effected by 2% H2O vapor	
Co	NA	CH4	1000	1610	2.5	no	no	440	32	30	B	small effect of 2% H2O vapor	
Pt	0.9wt%	C2H4	1200	230	7.0	no	no	500	80	859	C	60% max conv at 450C with NO2	
Au	5.0wt%	H2	15000	1400	0.2	no	no	250	68	8	G	NOT LEAN	
Ce	15	C3H6	500	1000	2.0	no	no	350	50	10	I	0.5g Ce/MFI only	
Ce	16	C3H6	500	1000	2.0	no	no	300	73	10	I	50/50 mix with Ce2O3	
Ce	17	C3H6	500	1000	2.0	no	no	250	89	10	I	50/50 mix with Mn2O3	
Cu	0.7wt%	diesel	700	700	14.0	yes	no	425	27	17	J	~700ppm C3H6 added, sulfur free diesel	
Cu	100	n-C8H18	750	1000	6.7	2%	no	325-400	70	30	K	no effect of xtl size	
Cu	100	i-C8H18	750	1000	6.7	2%	no	500	65	15	K	shifted to higher temps for large xtls	
Pt	1.0wt%	C3H6	1500	1000	5.0	no	no	200-260	80	12	L	conv at 225C	
Cu	80	C10H22	300	1000	9.0	no	no	425	72	70	O		
Ag	77	CH4	5000	5000	2.5	no	no	600	28	7.5	Q	max conversion ~80% exchange	
Ce	21	CH4	5000	5000	2.5	no	no	600	18	7.5	Q	good for NO oxidation	
Ag Ce	67 54	CH4	5000	5000	2.5	no	no	500	80	7.5	Q	8.3% H2O inhibits reaction	
Ga	115	CH4	1000	1000	6.7	no	no	500	82	6	R	2.5% H2O strongly inhibits catalysis	
Ga	115	C3H6	1000	1000	6.7	no	no	550	70	12	R	C3H8 as slightly more active	
Fe	300	i-C4H10	2000	2000	3.0	10%	no	350	75	42	S	max exchange 1/1 Fe/Al = 300%EL	
La Fe	0.9 300	i-C4H10	2000	2000	3.0	10%	no	375	83	42	S	larger temp window than Fe only	
Cu	40	C3H6	800	800	4.0	no	no	500	50	15	T	1.4wt% Cu. Si/Al 11	
Cu	280	C3H6	800	800	4.0	no	no	350	49	15	T	1.4wt% Cu. Si/Al 100	
Cu	194	C3H8	470	750	2.4	no	no	350	68	20	U	Si/Al 17	
Cu	4.1wt%	C2H4	1000	1000	2.0	no	no	300	42	15	V		
Cu	5.4wt%	C3	400	1850	1.0	no	no	450	25	40	AA	3:1 C3H6:C3H8	
Cu	5.4wt%	C3	400	1850	1.0	10%	20	400	19	40	AA	3:1 C3H6:C3H8	
Pd	0.4wt%	CH4	2000	1000	10.0	10%	no	500	50-5	30	CC	conversion decreases from 50% to 5%	
Pd Co	0.4 3.3	CH4	2000	1000	10.0	10%	no	500	63	30	CC		
Cu	102	n-C6H14	1000	1000	6.7	2%	no	350-450	80	30	DD	no xtl size effect	
Cu	102	2,2 DMB	1000	1000	6.7	2%	no	350	71	30	DD	large xtl has much lower conversion	
Co	106	CH4	4000	4000	4.0	no	no	500	30	60	GG		
Pt	1wt%	C3H6	1500	1000	10	no	no	200	78	20	II	3:1 N2O:N2 yield	
Ag	77	CH4	5000	5000	2.5	no	no	650	22	7.5	JJ		
Ce	21	CH4	5000	5000	2.5	no	no	650	18	7.5	JJ		
Ce Ag	24 78	CH4	5000	5000	2.5	no	no	500	70	7.5	JJ	reached max with Ag EL ~ 80	
H	100	C3H6	1200	1500	3.0	no	no	-	-	30	KK	conversion <7%	
Co	60	C3H6	1200	1500	3.0	no	no	450	20	30	KK		
CoOx	5wt%	C3H6	1200	1500	3.0	no	no	250	34	30	KK		
In	4wt%	CH4	1000	1000	10	no	no	400	48	30	MM	with NO2 in feed conversion similar to In/Ir/MFI	
Ir	1wt%	CH4	1000	1000	10	no	no	-	-	30	MM		
In Ir	4% 1%	CH4	1000	1000	10	no	no	450	87	30	MM		
Co	1.7wt%	C2H6	1000	1000	2.5	no	no	450	51	60	NN		
Rh	1.7wt%	C2H6	1000	1000	2.5	no	no	400	72	60	NN	deactivates 50% with TOS another 50% with 2% H2O	
Pt	1.0wt%	C2H6	1000	1000	2.5	no	no	400	1	60	NN		
Cu	3.0wt%	C2H6	1000	1000	2.5	no	no	400	18	60	NN		
Fe	183	iC4H10	2000	2000	3	20	150	500	100	42	QQ	Cu/ZSM-5 53% initial dry act. goes to 0 complex synthesis route	
Pt	7	C2H4	500	500	10	10	no	225	30	72	SS	2:1 N2O:N2 ratio	
Pt	97	C2H4	1000	1000	2	8.6	no	225	50	72	TT	3:2 N2O:N2 ratio. Only slight H2O effect	
Pt	97	C2H4	1000	1000	2	no	300	250	52	72	TT	3:2 N2O:N2 ratio. SO2 effect: broader N2 conversion peak	
Co		CH4	1015	820	2.5	2	no	500	33	30	UU	significant deactivation w/ H2O below 500C	
Mn		CH4	1015	820	2.5	2	no	500	36	30	UU	deactivation w/ H2O below 500C	
Ni		CH4	1015	820	2.5	2	no	450	19	30	UU	slight H2O inhibition	
H		CH4	1015	820	2.5	2	no	-	-	15	UU		



Table 2: NOx Conversion on Zeolite (non ZSM-5) Supported Catalysts

Support	other zeolites												
metal	% EL	HC type	HC conc	NO	O2 %	H2O	SOx	Tmax	%Conv max	GHSV (x 1000/h)	Ref	Other comments	zeolite
Au	5.0wt%	H2	15000	1400	0.2	no	no	250	100	8	G	NOT LEAN	NaY
Pt	1.0wt%	C3H6	1500	1000	5.0	no	no	200	95	12	L	conv at 200C	USY
Ir	1wt%	C3H6 CO	2000 500	1000	10	no	no	450	42	25	N	conversion affected by pretreatment N2 formation only with C3H6 + CO	NaY
Cu	198	C10H22	300	1000	9.0	no	no	390	32	70	O		H/Beta
Cu	113	C10H22	300	1000	9.0	no	no	400	54	70	O		Na/Beta
Cu	60	C3H6	800	800	4.0	no	no	350	42	0.15	P	Si/Al = 21 from H form	MOR
Cu	60	C3H6	800	800	4.0	no	no	350	38	0.15	P	Si/Al = 21 from Na form	MOR
Cu	20	C3H6	800	800	4.0	no	no	350	50	0.15	P	Si/Al = 6 from Na form. H form slightly less	MOR
Co	34	CH4	1000	1000	6.7	no	no	500	30	8	X	CH4 combustion accelerated with NO	MOR
Pt	1.2wt%	C3	400	1850	1.0	no	no	300	24	40	AA	3:1 C3H6:C3H8 high N2O yield	USY
Pt	1.2wt%	C3	400	1850	1.0	10%	20	300	23	40	AA	3:1 C3H6:C3H8 high N2O yield	USY
Pt	1wt%	C3H6	1500	1000	10	no	no	200	92	20	II	2:1 N2O:N2 yield. C3H8 nonselective	USY
Co	1.38wt%	CH4	1000	1000	2.0	2%	no	500	20		LL		FER
In	0.52wt%	CH4	1000	1000	2.0	2%	no	450	32		LL		FER
Pt Co	0.5 1.8	CH4	1000	1000	2.0	2%	no	550	70		LL	requires prereduction step	FER
Pt In	0.5 0.5	CH4	1000	1000	2.0	2%	no	500	77		LL		FER
Co		CH4	1015	820	2.5	2	no	450	25	30	UU	deactivation w/ H2O below 500C	MOR
Ba		CH3CHO	500	200	8	2	no	225	80	12	XX	~ with NO or NO2; C2>C3>C4 aldehydes	USY
Na		C8H18	100	200	8	2	no	240	70	12	XX		USY



Table 3: NOx Conversion on Alumina Supported Catalysts

Support	Al2O3												
metal	% EL	HC type	HC conc	NO	O2 %	H2O	SOx	Tmax	%Conv max	GHSV (x 1000/h)	Ref	Other comments	
-	-	C2H4	250	1000	2.0	no	no	600	22	9	A		
-	-	C2H5OH	884	1094	10.0	no	no	450	68	10	F	all listed as conversion to N2	
-	-	CH3OH	3000	500	5.0	no	no	300	99	15	W	significant DME formation at low temp	
-	-	CH3OH	1500	1000	10	no	no	425	62	10	EE		
-	-	C2H5OH	900	1000	10	no	no	425	71	10	EE		
-	-	C3H6	1000	1000	10	no	no	500	52	10	EE		
-	-	C3H8	1000	500	5.0	no	no	550	76	15	W	not sulfur tolerant see next entry	
-	-	CH3CHO	500	200	8	2	no	400	90	12	XX	NO2 (90) much higher than NO (50)	
Ag	2.0wt%	C2H5OH	884	1094	10.0	no	no	350	86	10	F		
Ag	4.6wt%	C2H5OH	1565	800	10.0	10%	80ppm	475	85	36	H	without SO2 ~100% conv. 300-500C	
Ag	4.6wt%	C2H5OH	1565	800	10.0	10%	30ppm	475	70	90	H	slight deactivation aged 20h w/high SO2	
Ag	2wt%	C3	1000	500	6.0	12%	no	500	85	60	Y	2:1 C3H8:C3H6	
Ag	2wt%	C8H17OH	375	500	6.0	12%	no	350	82	60	Y	octanol ~ O-containing reductants	
Ag	2wt%	C8H18	375	500	6.0	12%	no	500	86	60	Y	octane ~ iC8 ~1C8ene	
Ag	2wt%	C12H26	500	500	6.0	12%	no	250-500	60+	60	Y	dodecane ~ > MK1 diesel. significant conversion observed (=>60%) with engines	
Ag	2wt%	CH4	6000	1000	10	2%	no	500	40	2	BB		
Ag	2wt%	C3H8	2000	1000	10	2%	no	500	93	15	BB	narrow conversion window	
Ag	2wt%	n-C4H10	1500	1000	10	2%	no	500	99	15	BB	wide conversion window	
Ag	2wt%	n-C8H18	650	1000	10	2%	no	300-450	80	15	BB	wide conversion window	
Ag	2wt%	n-C8H18	650	1000	10	2%	no	350-400	99	15	BB	wide conversion window	
Ag	2wt%	CH3OH	1500	1000	10	no	no	250	24	10	EE		
Ag	2wt%	C2H5OH	900	1000	10	no	no	375	90	10	EE		
Ag	2wt%	C3H6	1000	1000	10	no	no	475	70	10	EE		
Ir	1.0wt%	C3H6	870	995	5.0	no	no	350	15	5	J		
Ir	1wt%	C3H6	2000	1000	10	no	no	500	36	25	N	conversion affected by pretreatment	
Ga	27wt%	CO	500									N2 formation only with C3H6 + CO	
Ga	48	CH4	1000	1000	6.7	no	no	550	90	6	R	supported Ga2O3 on Al2O3	
Ga	48	CH4	1000	1000	6.7	no	no	550	75	6	R	mixed metal oxide (co ppt)	
Ga	27wt%	C3H6	1000	1000	6.7	no	no	450-550	99	12	R	C3H8 slightly less active	
Pd	1.0wt%	C3H6	870	995	5.0	no	no	250	25	5	J		
Pt	1wt%	C3H6	1500	1000	10	no	no	250	76	20	II	3:1 N2O:N2 yield	
Pt	0.3wt%	n-C8H18	1000	500	5.0	no	no	235	38	60	D	NO conv zero order above 500ppm HC	
Pt	1.0wt%	C3H6	1000	500	5.0	no	no	255	60	60	E	High N2O selectivity. No conv with C3H8	
Pt	1.0wt%	C3H6	870	995	5.0	no	no	250	52	5	J	Pt disp 41%	
Pt/Rh	3:1	C3H6	870	995	5.0	no	no	250	60	5	J	1/3 N2, 2/3 N2O	
Pt/Rh	1:1	C3H6	870	995	5.0	no	no	250	35	5	J	N2 level ?	
Rh	1.0wt%	C3H6	870	995	5.0	no	no	325	50	5	J	double the PGM loading (2wt%)	
Ru	1.0wt%	C3H6	870	995	5.0	no	no	325	55	5	J	mostly N2 formed	
Rh	1wt%	CH4	6700	2000	5.0	no	no	300-500	15	12	M	83% N2 selectivity	
SO4		C3H8	1000	500	5.0	no	no	> 600	20	15	W	max conversion above 600	
SO4		CH3OH	3000	500	5.0	no	no	325	95	15	W	significant DME formation at low temp	
all		CH4	1000	1000	2.0	2%	no	-	-	-	LL	all Al2O3 samples inhibited with H2O	
Au	0.17wt%	C3H6	1000	1000	5.0	10%	no	425	88	20	OO		
Au Mn2O3	0.17wt%	C3H6	1000	1000	5.0	10%	no	350-450	95	20	OO	mechanical mixture Au/Al2O3 with Mn2O3	
Mn2O3	19:1	C3H6	1000	1000	5.0	10%	no	375-500	40	20	OO	@ 19:1. 90% conversion @ 120K GHSV	
Ga	30wt%	C3H6	900	900	10	9.1%	90	450	76	75	RR	mechanical mixture Al2O3 with Mn2O3 sublimation > co precip > incipient wet Ga2O3 non reactive	



Table 4: NOx Conversion on Mixed-Metal Oxide Supported Catalysts

Support	metal	% EL	HC type	HC conc	NO	O2 %	H2O	SOx	Tmax	%Conv max	GHSV (x 1000/h)	Ref	Other comments
SiO2	Pt	1.0wt%	C3H6	1000	500	5.0	no	no	220	70	60	E	High N2O selectivity. No conv with C3H8
TiO2	Ag	2.0wt%	C2H5OH	884	1094	10.0	no	no	375	18	10	F	Ag free sample no NOx conversion
SiO2	Ag	2.0wt%	C2H5OH	884	1094	10.0	no	no	350	4	10	F	
substrate	Pt	0.2wt%	diesel	700	700	14.0	yes	50	225	37	17	J	~700ppm C3H6 added
substrate	Pt/Rh	4:1	diesel	700	700	14.0	yes	50	225	50	17	J	~700ppm C3H6 added
carbon	Pt	1.0wt%	C3H6	1500	1000	5.0	no	no	400-500	85	12	L	conv at 200C support consumed during reaction
MMO			CH4	6700	2000	5.0	yes	no	300	32	12	M	MnLaSrCeOx 5/1/1/1 composition 4% H2O shifts max conv by 50C >90% N2 selectivity
laponite	Cu	2.6wt%	C2H4	1000	1000	2.0	no	no	550	90	15	V	Al2O3 pillared laponite
laponite	Cu	2.6wt%	C2H4	1000	1000	2.0	5%	500	500	65	15	V	550C not measured. n/n,H2O/n,H2O/SO2 81,78,65
bentonite	Cu	3.5wt%	C2H4	1000	1000	2.0	no	no	300	55	15	V	TiO2 pillard bentonite
La2O3 - ZrO2	Pt	1wt%	C3	330	500	6.0	12%	no	200	65	60	Z	2:1 C3H8:C3H6, 350ppm CO
ZrO2 CaO	Ag CuO	2% 5%	C10H22	500	1500	20.0	no	no	375	42	11.2	FF	Ag/Al2O3 max conv at 450C 30%
ZrO2 SrO	Ag CuO	2% 5%	C10H22	500	1500	20.0	no	no	375	52	11.2	FF	broad temp window
ZrO2 BaO	Ag CuO	2% 5%	C10H22	500	1500	20.0	no	no	425	67	11.2	FF	volcano shape conv
ZrO2 CaO	Ag CuO	2% 5%	C3H6	2000	2000	2.5	no	no	250	32	18	FF	
ZrO2 SrO	Ag CuO	2% 5%	C3H6	2000	2000	2.5	no	no	275	34	18	FF	
ZrO2 BaO	Ag CuO	2% 5%	C3H6	2000	2000	2.5	no	no	300-400	41	18	FF	broad temp window
Y2O3			CH4	4000	4000	4.0	no	no	650	32	60	GG	xtl size 17 nm
ZrO2	-		C3H6	948	1166	2.23	no	no	450-500	40	15	HH	mixed metal oxide (co ppt)
SnO2/ZrO2		45/55	C3H6	948	1166	2.23	no	no	350	76	15	HH	mixed metal oxide (co ppt)
SnO	-		C3H6	948	1166	2.23	no	no	350	50	15	HH	mixed metal oxide (co ppt)
SiO2	Pt	1wt%	C3H6	1500	1000	10	no	no	240	40	20	II	2:1 N2O:N2 yield



Table 5: NOx Conversion on Supported Platinum Catalysts

Support	% EL	HC type	HC conc	NO	O2 %	H2O	SOx	Tmax	%Conv max	GHSV (x 1000/h)	Ref	Other comments
MFI	0.9wt%	C2H4	1200	230	7.0	no	no	500	80	859	C	60% max conv at 450C with NO2
Al2O3	0.3wt%	n-C8H18	1000	500	5.0	no	no	235	38	60	D	NO conv zero order above 500ppm HC High N2 selectivity
SiO2	1.0wt%	C3H6	1000	500	5.0	no	no	220	70	60	E	High N2O selectivity. No conv with C3H8
Al2O3	1.0wt%	C3H6	1000	500	5.0	no	no	255	60	60	E	High N2O selectivity. No conv with C3H8 Pt disp 41%
Al2O3	1.0wt%	C3H6	870	995	5.0	no	no	250	52	5	J	1/3 N2, 2/3 N2O
Al2O3	3:1	C3H6	870	995	5.0	no	no	250	60	5	J	N2 level ? - Pt with Rh
Al2O3	1:1	C3H6	870	995	5.0	no	no	250	35	5	J	double the PGM loading (2wt%) - Pt with Rh
substrate	0.2wt%	diesel	700	700	14.0	yes	50	225	37	17	J	~700ppm C3H6 added
substrate	4:1	diesel	700	700	14.0	yes	50	225	50	17	J	~700ppm C3H6 added - Pt with Rh
Al2O3	1.0wt%	C3H6	1500	1000	5.0	no	no	250	60	12	L	all have low N2 selectivity <30%
MFI	1.0wt%	C3H6	1500	1000	5.0	no	no	200-260	80	12	L	conv at 225C
USY	1.0wt%	C3H6	1500	1000	5.0	no	no	200	95	12	L	conv at 200C
carbon	1.0wt%	C3H6	1500	1000	5.0	no	no	400-500	85	12	L	conv at 200C support consumed during reaction
La2O3 - ZrO2	1wt%	C3s	330	500	6.0	12%	no	200	65	60	Z	2:1 C3H8:C3H6, 350ppm CO
USY	1.2wt%	C3s	400	1850	1.0	no	no	300	24	40	AA	3:1 C3H6:C3H8 high N2O yield
USY	1.2wt%	C3s	400	1850	1.0	10%	20	300	23	40	AA	3:1 C3H6:C3H8 high N2O yield
USY	1wt%	C3H6	1500	1000	10	no	no	200	92	20	II	2:1 N2O:N2 yield. C3H8 nonselective
MFI	1wt%	C3H6	1500	1000	10	no	no	200	78	20	II	3:1 N2O:N2 yield
Al2O3	1wt%	C3H6	1500	1000	10	no	no	250	76	20	II	3:1 N2O:N2 yield
SiO2	1wt%	C3H6	1500	1000	10	no	no	240	40	20	II	2:1 N2O:N2 yield
FER	0.5 1.8	CH4	1000	1000	2.0	2%	no	550	70		LL	requires prereduction step - Pt with Co
FER	0.5 0.5	CH4	1000	1000	2.0	2%	no	500	77		LL	Pt with In

Table 6: NOx Conversion on Supported Silver Catalysts

Support	metal	% EL	HC type	HC conc	NO	O2 %	H2O	SOx	Tmax	%Conv max	GHSV (x 1000/h)	Ref	Other comments
MFI	Ag	77	CH4	5000	5000	2.5	no	no	600	28	7.5	Q	max conversion ~80% exchange
MFI	Ag Ce	67 54	CH4	5000	5000	2.5	no	no	500	80	7.5	Q	8.3% H2O inhibits reaction
Al2O3	Ag	2wt%	CH4	6000	1000	10	2%	no	500	40	2	BB	
MFI	Ag	77	CH4	5000	5000	2.5	no	no	650	22	7.5	JJ	
MFI	Ce Ag	24 78	CH4	5000	5000	2.5	no	no	500	70	7.5	JJ	reached max with Ag EL ~ 80
Al2O3	Ag	2wt%	CH3OH	1500	1000	10	no	no	250	24	10	EE	
MFI	Ag	90	C2H4	250	1000	2.0	no	no	450-600	43	9	A	
Al2O3	Ag	2.0wt%	C2H5OH	884	1094	10.0	no	no	350	86	10	F	
TiO2	Ag	2.0wt%	C2H5OH	884	1094	10.0	no	no	375	18	10	F	Ag free sample no NOx conversion
SiO2	Ag	2.0wt%	C2H5OH	884	1094	10.0	no	no	350	4	10	F	
Al2O3	Ag	4.6wt%	C2H5OH	1565	800	10.0	10%	80ppm	475	85	36	H	without SO2 ~100% conv. 300-500C
Al2O3	Ag	4.6wt%	C2H5OH	1565	800	10.0	10%	30ppm	475	70	90	H	slight deactivation aged 20h w/high SO2
Al2O3	Ag	2wt%	C2H5OH	900	1000	10	no	no	375	90	10	EE	
Al2O3	Ag	2wt%	C3H8	2000	1000	10	2%	no	500	93	15	BB	narrow conversion window
Al2O3	Ag	2wt%	C3	1000	500	6.0	12%	no	500	85	60	Y	2:1 C3H8:C3H6
ZrO2 CaO	Ag CuO	2% 5%	C3H6	2000	2000	2.5	no	no	250	32	18	FF	
ZrO2 SrO	Ag CuO	2% 5%	C3H6	2000	2000	2.5	no	no	275	34	18	FF	
ZrO2 BaO	Ag CuO	2% 5%	C3H6	2000	2000	2.5	no	no	300-400	41	18	FF	broad temp window
Al2O3	Ag	2wt%	C3H6	1000	1000	10	no	no	475	70	10	EE	
Al2O3	Ag	2wt%	n-C4H10	1500	1000	10	2%	no	500	99	15	BB	wide conversion window
Al2O3	Ag	2wt%	n-C6H14	650	1000	10	2%	no	300-450	80	15	BB	wide conversion window
Al2O3	Ag	2wt%	C8H17OH	375	500	6.0	12%	no	350	82	60	Y	octanol ~ O-containing reductants
Al2O3	Ag	2wt%	C8H18	375	500	6.0	12%	no	500	86	60	Y	octane ~ iC8 ~1C8ene
Al2O3	Ag	2wt%	n-C8H18	650	1000	10	2%	no	350-400	99	15	BB	wide conversion window
ZrO2 CaO	Ag CuO	2% 5%	C10H22	500	1500	20.0	no	no	375	42	11.2	FF	Ag/Al2O3 max conv at 450C 30%
ZrO2 SrO	Ag CuO	2% 5%	C10H22	500	1500	20.0	no	no	375	52	11.2	FF	broad temp window
ZrO2 BaO	Ag CuO	2% 5%	C10H22	500	1500	20.0	no	no	425	67	11.2	FF	volcano shape conv
Al2O3	Ag	2wt%	C12H26	500	500	6.0	12%	no	250-500	60+	60	Y	dodecane ~ > MK1 diesel. significant conversion observed (=>60%) with engines



Table 7: NOx Conversion with Methane as the Reductant

Support	metal	% EL	HC type	HC conc	NO	O2 %	H2O	SOx	Tmax	%Conv max	GHSV (x 1000/h)	Ref	Other comments
Al2O3	Rh	1wt%	CH4	6700	2000	5.0	no	no	300-500	15	12	M	83% N2 selectivity
MMO			CH4	6700	2000	5.0	yes	no	300	32	12	M	MnLaSrCeOx 5/1/1/1 composition 4% H2O shifts max conv by 50C >90% N2 selectivity
MFI	Ag	77	CH4	5000	5000	2.5	no	no	600	28	7.5	Q	max conversion ~80% exchange
MFI	Ce	21	CH4	5000	5000	2.5	no	no	600	18	7.5	Q	good for NO oxidation
MFI	Ag Ce	67 54	CH4	5000	5000	2.5	no	no	500	80	7.5	Q	8.3% H2O inhibits reaction
Al2O3	Ga	27wt%	CH4	1000	1000	6.7	no	no	550	90	6	R	supported Ga2O3 on Al2O3
Al2O3	Ga	48	CH4	1000	1000	6.7	no	no	550	75	6	R	mixed metal oxide (co ppt)
MFI	Ga	115	CH4	1000	1000	6.7	no	no	500	82	6	R	2.5%H2O strongly inhibits catalysis
MOR	Co	34	CH4	1000	1000	6.7	no	no	500	30	8	X	CH4 combustion accelerated with NO
Al2O3	Ag	2wt%	CH4	6000	1000	10	2%	no	500	40	2	BB	
MFI	Pd	0.4wt%	CH4	2000	1000	10.0	10%	no	500	50-5	30	CC	conversion decreases from 50% to 5%
MFI	Pd Co	0.4 3.3	CH4	2000	1000	10.0	10%	no	500	63	30	CC	
Y2O3			CH4	4000	4000	4.0	no	no	650	32	60	GG	xtl size 17 nm
MFI	Co	106	CH4	4000	4000	4.0	no	no	500	30	60	GG	
MFI	Ag	77	CH4	5000	5000	2.5	no	no	650	22	7.5	JJ	
MFI	Ce	21	CH4	5000	5000	2.5	no	no	650	18	7.5	JJ	
MFI	Ce Ag	24 78	CH4	5000	5000	2.5	no	no	500	70	7.5	JJ	reached max with Ag EL ~ 80
FER	Co	1.38wt%	CH4	1000	1000	2.0	2%	no	500	20		LL	
FER	In	0.52wt%	CH4	1000	1000	2.0	2%	no	450	32		LL	
FER	Pt Co	0.5 1.8	CH4	1000	1000	2.0	2%	no	550	70		LL	requires prereduction step
FER	Pt In	0.5 0.5	CH4	1000	1000	2.0	2%	no	500	77		LL	
Al2O3	all		CH4	1000	1000	2.0	2%	no	-	-		LL	all Al2O3 samples inhibited with H2O with NO2 in feed conversion similar to In/Ir/MFI
MFI	In	4wt%	CH4	1000	1000	10	no	no	400	48	30	MM	
MFI	Ir	1wt%	CH4	1000	1000	10	no	no	-	-	30	MM	
MFI	In Ir	4% 1%	CH4	1000	1000	10	no	no	450	87	30	MM	



Table 8: NOx Conversion with Oxygenated Reductants

Support	metal	% EL	HC type	HC conc	NO	O2 %	H2O	SOx	Tmax	%Conv max	GHSV (x 1000/h)	Ref	Other comments
Al2O3	-		C2H5OH	884	1094	10.0	no	no	450	68	10	F	all listed as conversion to N2
Al2O3	Ag	2.0wt%	C2H5OH	884	1094	10.0	no	no	350	86	10	F	
TiO2	Ag	2.0wt%	C2H5OH	884	1094	10.0	no	no	375	18	10	F	Ag free sample no NOx conversion
SiO2	Ag	2.0wt%	C2H5OH	884	1094	10.0	no	no	350	4	10	F	
Al2O3	Ag	4.6wt%	C2H5OH	1565	800	10.0	10%	80ppm	475	85	36	H	without SO2 ~100% conv. 300-500C
Al2O3	Ag	4.6wt%	C2H5OH	1565	800	10.0	10%	30ppm	475	70	90	H	slight deactivation aged 20h w/high SO2
Al2O3	-		CH3OH	3000	500	5.0	no	no	300	99	15	W	significant DME formation at low temp
Al2O3	SO4		CH3OH	3000	500	5.0	no	no	325	95	15	W	significant DME formation at low temp
Al2O3	Ag	2wt%	C8H17OH	375	500	6.0	12%	no	350	82	60	Y	octanol ~ O-containing reductants
Al2O3	Ag	2wt%	CH3OH	1500	1000	10	no	no	250	24	10	EE	
Al2O3	Ag	2wt%	C2H5OH	900	1000	10	no	no	375	90	10	EE	
Al2O3			CH3CHO	500	200	8	2	no	400	90	12	XX	NO2 (90) much higher than NO (50)
USY	Ba		CH3CHO	500	200	8	2	no	225	80	12	XX	~ with NO or NO2; C2>C3>C4 aldehydes



Table 9: References for the Data Points

A	Appl Catal 70 (1991) L1-L5
B	J Catal 145 (1994) 1-9
C	J Catal 178 (1998) 395-407
D	J Catal 176 (1998) 204-214
E	Catal Lett 43 (1997) 19-23
F	Catal Lett 51 (1998) 11-14
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