

## **Original Research Article**

### MECHANISTIC STUDIES OF CATALYTIC REDUCTION OF NITROGEN OXIDES FROM DIESEL ENGINE EXHAUST OVER MANGANESE AND CERIUM OXIDE BASED CATALYSTS

#### **Abstract**

Finding a catalyst system that is effective and consistent for the selective reduction of NO<sub>x</sub> during lean exhaust conditions has been a predominant challenge to both industrial and research institutions, despite the large number of reported catalysts tested. The selective catalytic reduction of NO + NO<sub>2</sub> (NO<sub>x</sub>) with CO and C<sub>3</sub> hydrocarbons at low temperatures (175-225 °C) is investigated over manganese and cerium catalysts with and without the presence of a precious metal. 1% Pt/Mn/Al catalysts show promising results for the reaction, with continuous NO<sub>x</sub> conversions well more than 35% in the period extending beyond 170 hours. The synthesis technique of the catalyst and the reaction temperature greatly effects the reaction. There is no evidence of the presence of other nitrogen oxides in the products except for a very small quantity of N<sub>2</sub>O only at the beginning of the reaction. Mechanistic studies reveal manganese to be the major catalytic sites, while the platinum plays a secondary role. Mn/Ce/Al also show continuous deNO<sub>x</sub> activity with NO<sub>x</sub> conversions of 28-35%.

**Key words:** *Manganese oxide, cerium oxide, platinum, lean burn deNO<sub>x</sub>, diesel exhaust.*

## 1. Introduction

Nitrogen oxides, or NO<sub>x</sub> comprise one of the main groups of air pollutants that contribute largely to a variety of environmental and health problems. The major source of nitrogen oxides is the combustion of fossil fuels, of which more than 50% comes from burning petroleum in the engines of vehicles and airplanes. The combustion processes are so fast that the thermodynamic equilibrium is not reached in these cases. For this reason, the exhaust gases contain products of incomplete combustion such as carbon monoxide, hydrogen and lighter hydrocarbons. Nitrogen oxides are formed at the higher temperatures resulting from the combustion reactions. Nitrogen monoxide (NO) accounts for 95% of all NO<sub>x</sub> emissions. [1,2]

Table 1 Approximate automobile exhaust compositions.

	Content (vol.%)		
	Rich -gasoline	Diesel	Our working cond.
CO	0.3-1.0	<3.0	0.11
H <sub>2</sub>	0.1-0.3	-	-
O <sub>2</sub>	0.2-0.5	3-14	15
NO	0.05-0.15	0.005-0.200	0.015
Hydrocarbon	0.03-0.08	0.01-0.03	0.045
CO <sub>2</sub>	~12	varies	3.4
H <sub>2</sub> O	~13	varies	3.5
N <sub>2</sub> (or He)	~74	varies	~77
Temperature (°C)	>500	150-400	200

Since the emergence of noble metal based three-way catalysts (TWC), it has been possible to meet the standard emission level of NO<sub>x</sub> emitted from gasoline engines, which operate under close stoichiometric conditions[3-5]. Unfortunately, these catalysts

are not effective for NO<sub>x</sub> reduction under oxidizing conditions. Selective catalytic reduction (SCR) using ammonia or hydrogen as the reducing agent [6-8], works well with stationary diesel engines, but is not practical with mobile engines. SCR with hydrocarbons has been extensively studied using precious metals, metal zeolites and metal oxides as catalysts. However, these catalysts have not showed significant, continuous activity in reducing NO<sub>x</sub> in diesel engine exhausts, at low temperature.

Diesel engines that operate under a lean condition with higher air to fuel ratios produce less NO<sub>x</sub>. The exhaust temperature of a diesel engine is lower and there are less hydrocarbons and more oxygen remaining in the exhaust compared with a gasoline engine.[9-14]

However, strict and tightening exhaust emission limits worldwide for diesel engines and diesel vehicles require more and more extraordinary development efforts to reduce both engine out emissions by improved combustion processes and tailpipe emissions by new exhaust gas after-treatment systems.[10,15]

It is well known that almost all types of known conventional catalysts are poisoned with respect to NO reduction in excess oxygen by accumulation of either adsorbed oxygen atoms or adsorbed NO<sub>2</sub> which is formed by NO oxidation. Therefore, no effective, long lasting, NO<sub>x</sub> control technology has been implemented yet for diesel engines that operate under a full lean condition with higher A/F ratios. [1,9,11]

Catalytic oxidation of carbon monoxide is reported to occur on supported metals of the platinum group and base metals like copper oxides. In the later case, the reaction most probably proceeds through a redox cycle of the surface metals, whereas on platinum catalysts the reaction follows a Langmuir-Hinshelwood type mechanism. Here carbon

monoxide molecules condense along with oxygen molecules on the metal surface and the two types of molecules interact forming  $\text{CO}_2$ . The adsorption energy for carbon dioxide is very low and hence, once it is formed it will rapidly leave the surface.

CO-SCR of NO therefore requires a catalytic system that preferably undergoes CO oxidation via a redox cycle on the catalyst surface that also involves NO reduction and not direct catalytic oxidation by the oxygen in the reaction medium.

This study is an effort to identify a suitable catalytic system that could reduce nitrogen oxides in lean burn diesel engine exhausts under specific conditions (150 ppm NO, 1100 ppm CO, 450 ppm propane and 15%  $\text{O}_2$ ) for a prolonged period of time. It also includes mechanistic studies of de- $\text{NO}_x$  reaction on manganese and cerium oxide catalysts. Noble metals were coupled with the above-mentioned metal oxides to get CO and HC-SCR at an effective level at a low temperature.

## 2. Experimental

### 2.1 Catalyst Preparation

Grafting of manganese oxide on  $\gamma$ -alumina was done using manganese ethoxide prepared according to a literature method [15,16] with few modifications, in ethanol. The support material ( $\gamma$ -alumina, surface area,  $235 \text{ m}^2/\text{g}$ ) was dried at  $110^\circ\text{C}$ . The support was introduced to the alkoxide at  $60^\circ\text{C}$  under  $\text{N}_2$  in a Schlenk line and the reaction was maintained at the same temperature for 24 hours. The grafted catalyst was washed, dried overnight at  $110^\circ\text{C}$  and then calcined at  $500^\circ\text{C}$  for 10 hours.

Manganese(II) nitrate dissolved in THF was used for the impregnation of manganese oxide onto the alumina support at room temperature ( $25^\circ\text{C}$ ). The solvent was gradually

evaporated off and the catalysts were dried overnight at 110 °C and calcined at 500 °C for 10 hours.

Ceria was grafted on alumina using cerium methoxy ethoxide in methoxy ethanol under the protection of a flux of N<sub>2</sub>. The reaction was maintained at room temperature or 60°C for 24 hours. The grafted catalyst was filtered, washed, hydrolyzed for 24 hours, dried overnight at 110 °C and then calcined at 500 °C for 10 hours. Impregnation of cerium oxide was done using cerium nitrate in THF following the same procedure used for loading manganese oxide. Introduction of Pt and Pd was done using platinum acetylacetonate or palladium acetylacetonate respectively, dissolved in acetonitrile acidified to ~0.5 pH using nitric acid and the catalyst was added to the solution and kept overnight. The solvent was then evaporated off in a rotary evaporator and the catalysts were dried at 110 °C in an oven for 4-5 hours. Then the catalysts were calcined at 500 °C in air. Catalysts were reduced with hydrogen at 500 °C for 4 hours and then flushed with He at the same temperature for at least one hour followed by one hour at 200 °C before use.

## 2.2 Catalytic Testing

All catalytic reactions were carried out in a quartz tubular packed reactor at atmospheric pressure. The quartz tubular reactor was placed in a tube furnace (Lindberg/blue) equipped with an inbuilt temperature control unit. The reactant gases NO, CO, O<sub>2</sub>, propane or propene were mixed with He to get the required gas compositions. The total flow rate was maintained in the range of 100-105 mL/min to give a space velocity of 50,000 h<sup>-1</sup>, except in a few experiments where the reaction conditions

are specified. The gas composition was 150 ppm NO, 1100 ppm CO, 450 ppm propene or propane, 15% O<sub>2</sub> with He making the balance. Silicon carbide was mixed with 0.1 g of catalyst and placed on the catalytic bed, sandwiched between two SiC pellet layers.

The effluents were analyzed mainly by FT-IR (Thermo-Nicolet-Nexus 670 FT-IR spectrometer) equipped with a TGA interface consisting of a one meter gas cell and a mass spectrometer (Stanford research systems-QSM 300 gas analyzer. The experimental conditions for FT-IR analysis were 8 scans with a resolution of 1 cm<sup>-1</sup> and collection time of 17 seconds. Samples were analyzed in the wave number range 400-4000 cm<sup>-1</sup> using a DTGS KBr detector. Mass spectroscopic data was only available for high feed concentrations due to background interference. The presence of CO and NO (both mass no.28) together also made the mass analysis of no significant use. GC was also of little help in detecting low concentrations of nitrogen species.

Temperature programmed reduction (TPR) analysis was carried out by flowing 50 mL/min of either 1% CO or 1% propene in He and raising the catalyst temperature from room temperature to 700 °C at 5 °C /min. The change in the CO or C<sub>3</sub> concentration was measured by a gas chromatograph (GC- 9AM Shimadzu gas chromatograph equipped with a C-R6A chromatopac plotter) equipped with a thermal conductivity detector (TCD). The CO<sub>2</sub> (and H<sub>2</sub>O in C<sub>3</sub> TPR) produced during the reaction was trapped in a 5 Å molecular sieve column prior to analysis.

For adsorption-desorption studies, a gas mixture (150 ppm NO, 1100 ppm CO and 15% O<sub>2</sub> in He) was passed over the catalysts for a period of one hour, while the effluent gas mixture was monitored by FT-IR and a NO<sub>x</sub> chemiluminescence analyzer (Thermo electron -42C NO-NO<sub>2</sub>-NO<sub>x</sub> analyzer). The gas flow was then changed to pure He at the

same temperature for 15 minutes, making sure that all unattached gases are evolved with He. The temperature **was** then increased to 350 °C till the gases **were** desorbed and then increased to 500 °C. The individual reactant gases in He were also sent over the catalysts and the same experimental procedure was followed.

150 ppm NO in He was sent over the working catalysts and the component metal oxides on alumina for 30 minutes at 200 °C. The NO flow was stopped and He was sent over the catalyst for a period of 10 minutes. 1100 ppm of CO in He was sent at 200 °C over the catalyst for 15 minutes. The flow was then changed to pure He and the desorption experiment was carried out as above.

### **3. Results and Discussion**

#### **3.1 Continuous flow studies on Pt/Mn/Al Catalysts**

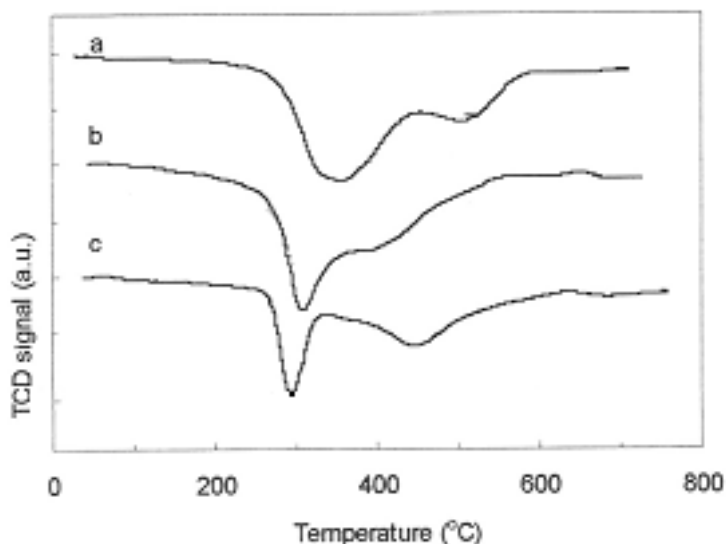
The catalytic activity of the synthesized catalysts was monitored mainly by FT-IR spectroscopy. The concentrations of the gases, CO, NO, NO<sub>2</sub>, CO<sub>2</sub>, N<sub>2</sub>O, propane, and propene were measured as a function of time. Initial studies carried out using ruthenium on vanadium and zirconium oxides supported on  $\gamma$ - alumina indicated that the noble metals are capable of altering the redox properties of the metal oxide making low temperature reductions possible. However, the Ru/V/Zr/Al catalysts could not perform continuous deNO<sub>x</sub> activity under the conditions applied.

Since manganese is known to be a good CO oxidant and an oxygen storage compound, impregnated 7%Mn/Al was tested for NO<sub>x</sub> reduction under lean burn conditions. 150 ppm NO, 1100 ppm CO and 15% O<sub>2</sub> in He over the catalyst at 200 °C showed 40-45% continuous oxidation of CO and NO<sub>x</sub> reduction well over 100 minutes. But the catalyst gradually deactivates with time. Sending CO with and without the

presence of oxygen over the catalyst in its oxidized state showed no CO oxidation taking place in the absence of oxygen but about 40% CO gets oxidized in 15% O<sub>2</sub>. This most likely indicates direct oxidation of CO on the surface of the catalyst. NO with 15% O<sub>2</sub> over the reduced catalyst showed reaction of NO<sub>x</sub> and desorption studies revealed that NO<sub>x</sub> reduction to nitrogen takes place on the reduced catalyst at 200 °C.

CO-TPR studies showed that CO reduction of manganese takes place in two steps starting at around 250 °C and the introduction of a precious metal makes it a one step reduction (Fig. 1). The two steps are Mn(III) reducing to Mn(II) via the more stable Mn(III)(II) intermediate (i.e. Mn<sub>2</sub>O<sub>3</sub>→Mn<sub>3</sub>O<sub>4</sub>→MnO). The added metal seems to influence the formation of the intermediate and also the reduction process, which is clearly seen by the CO reduction temperatures in CO-TPR. (However, no significant reduction peak is observed at 200 °C with or without the presence of ruthenium on Mn/Al, which leads to the deactivation of the 5% Ru/Mn(imp)/Al catalyst within two hours when 150 ppm NO, 1100 ppm CO and 15% O<sub>2</sub> in He is passed over it at 200 °C.) The CO oxidation was over 50% and continuous.

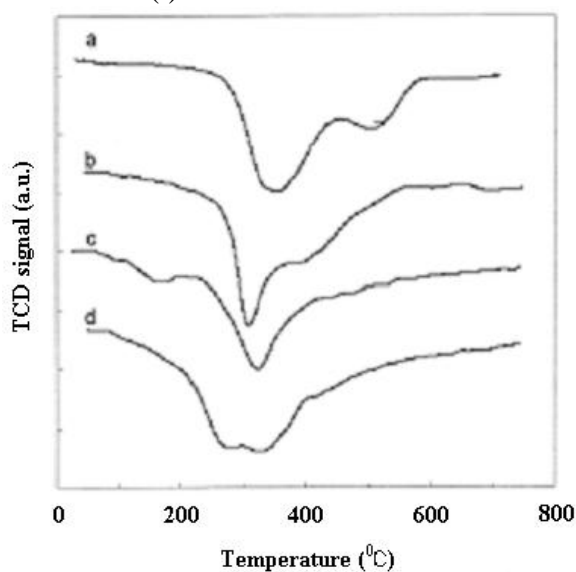
**Figure 1.** CO-TPR of (a) Mn(i)/Al, (b) 2.5%Ru/Mn(i)/Al and (c) 5%Ru/Mn(i)/Al.





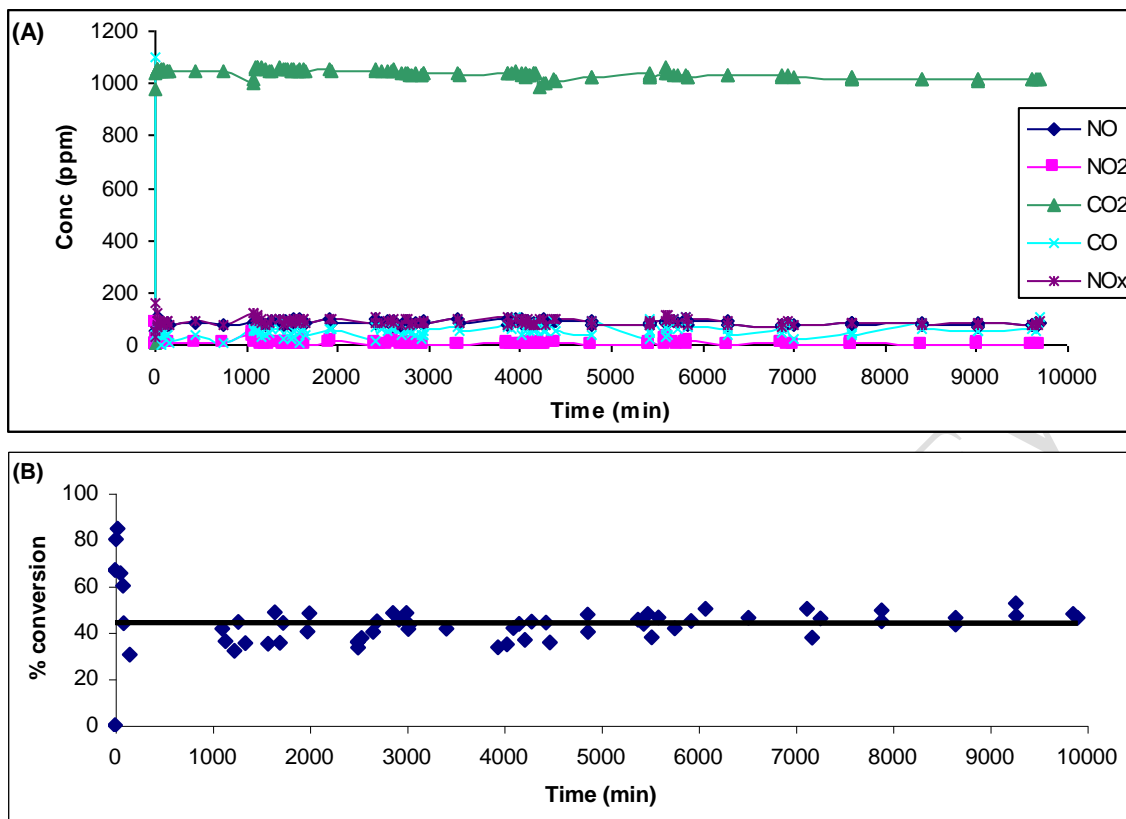
Substituting Ru with other metals that are commonly used in NO<sub>x</sub> reduction studies resulted in reduction of the catalyst at lower temperatures in CO-TPR studies (Fig. 2). Both platinum and palladium added to Mn/Al showed CO reduction even at 100 °C.

**Figure 2.** CO-TPR of (a) Mn(i)/Al, (b) 2.5%Ru/Mn(i)/Al, (c) 2.5%Pd/Mn(i)/Al and (d) 2.5%Pt/Mn(i)/Al.



A feed mixture of 150 ppm NO, 1100 ppm CO and 15% O<sub>2</sub> in He at 200 °C over 1%Pt/Mn(imp)/Al catalyst showed almost complete oxidation of CO (>95%) and continuous NO<sub>x</sub> conversions of 35-45% for a period of seven days (Fig. 3). The catalyst was active even at the time of shut off. This finding was significant as there are no reported catalysts that function under lean conditions even with 5% O<sub>2</sub>. Even the best reported short-lived catalysts show conversions below 30%.

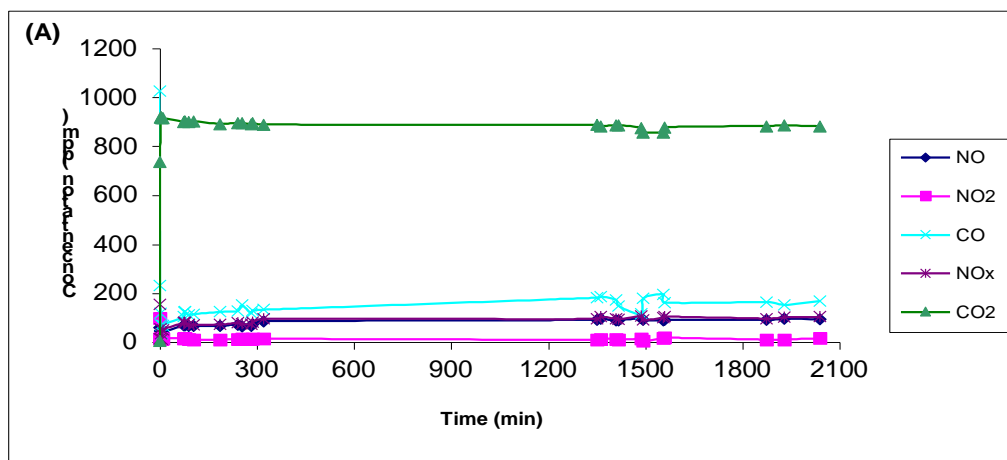
**Figure 3.** Change in concentrations (A) and NO<sub>x</sub> conversion for a feed of 150 ppm NO, 1100 ppm CO and 15% O<sub>2</sub> in He over 1%Pt/7%Mn(imp)/Al at 200 °C.



There were no nitrogen oxides observed in FT-IR except for NO and a very low concentration of NO<sub>2</sub> indicating that the reduced product is molecular nitrogen. This led us to believe that the active sites for NO<sub>x</sub> reduction are most probably not platinum sites because platinum reduction of NO<sub>x</sub> has almost always been reported to result in the formation of N<sub>2</sub>O.[17]

A grafted manganese analogue of the catalyst (1%Pt/Mn(g)/Al) also showed continuous reaction under similar reaction conditions, with approximately 90% CO oxidation and 30-38% NO<sub>x</sub> conversion (Fig. 4). The decreased NO<sub>x</sub> conversion is believed to be due to the low surface concentration of manganese (3%). Hence the catalyst is more active with respect to the manganese density on the surface.

**Figure 4.** Change in concentrations (A) and NO<sub>x</sub> conversion for a feed of 150 ppm NO, 1100 ppm CO and 15% O<sub>2</sub> in He over 1%Pt/3%Mn(g)/Al at 200 °C



However, the 1%Pt/3%Mn(imp)/Al also showed almost identical conversions under the same working conditions. This might be because 3% impregnated manganese oxide has well dispersed active sites on alumina and hence is exactly like a grafted manganese oxide catalyst as reported in the literature. [18]

Increasing the amount of platinum on the catalyst to 2.5% resulted in total conversion of CO to CO<sub>2</sub> but NO<sub>x</sub> conversions were lower (20-25%) than that seen for the 1% Pt loaded catalyst. This observation revealed very important information on the role of platinum in the de-NO<sub>x</sub> process over the catalyst. It is known that adsorption of the reactant gases on the catalytic surface is the main cause for deactivation of the catalyst. Adsorption of CO seems to be a very important step for the success of the catalyst, as it needs to be adsorbed on the active sites, which we believe is manganese for this class of catalysts, in order to reduce the catalyst. At the same time, CO adsorption should not be to an extent where the active sites are hindered for reaction. This makes the control of the amount of CO available very crucial and we think that the main role of platinum is the control of CO available to Mn. CO is known to be easily oxidized by molecular oxygen in the presence of platinum even at relatively very low temperatures.

1% Pt on the catalyst thus reduces the available CO by direct oxidation, but there is enough CO left that adsorb into and reduce manganese oxide on the surface, providing reduced sites for NO<sub>x</sub> reduction. Whereas direct oxidation on 2.5% Pt results in the removal of almost all CO in the feed resulting in lower de-NO<sub>x</sub> activity on the catalytic surface. According to CO-TPR studies platinum also enhances the redox activity of manganese, allowing reduction by CO at a lower temperature. The same feed mixture over 1%Pt/Al at 200°C shows almost 100% conversion of CO but only initial adsorption of NO<sub>x</sub> with no deNO<sub>x</sub> activity, proving manganese to be the active sites in the working catalysts.

Increasing the manganese content to 13% resulted in deactivation of the catalyst in terms of NO<sub>x</sub> reduction in less than an hour and loading of platinum without acidifying the solvent medium also resulted in a similar observation. Acidifying the solvent medium holding the platinum precursor is known to disperse the metal over the support material [3]. These observations make it clear that the platinum has to be well dispersed among the active manganese oxide sites for the catalyst to show continuous activity. This suggests that the role of platinum is not only reducing the amount of CO on the catalytic surface but also affecting the redox properties of manganese so that the de-NO<sub>x</sub> reactions take place under the experimental conditions used.

In all working catalysts there was no or very little NO<sub>2</sub> observed while the catalyst was reducing NO<sub>x</sub> and the amount of NO was less than that of the feed but was never completely absent. This suggests that the NO<sub>x</sub> reduction operates via NO<sub>2</sub> and it follows the mechanism known as “NO<sub>2</sub> reduction mechanism”.

Cerium oxide has been reported to be a good catalyst for the reduction of  $\text{NO}_2$  [19, 20]. However, the 1%Pt/7%Mn(imp)/5%Ce(imp)/Al catalyst showed only 25-33% conversion of  $\text{NO}_x$  even though the CO conversion was above 90%. Because of the success of the catalyst with platinum, 1%Pt/V:Zr(1:2)(g)/Al was also tested. 150 ppm NO, 1100 ppm CO with 15%  $\text{O}_2$  in He over the catalyst showed almost 100% CO conversion but  $\text{NO}_x$  reduction decreased with time and the catalyst was inactive in about 3 hours.

### 3.2 Adsorption-Desorption Studies on Pt/Mn/Al Catalysts

The effective temperature window for the 1%Pt/Mn(imp)/Al catalyst was found to be between 175-250 °C. The catalyst deactivates at lower and higher temperatures and this is thought to be mainly an effect of adsorption and desorption of NO and CO on the catalytic surface. Adsorption studies using a feed composition of 150 ppm NO with 15%  $\text{O}_2$  in He over the catalyst at various temperatures revealed the adsorption of  $\text{NO}_x$  to be minimum at 200 °C, which corresponds to the peak working temperature for the catalyst. The higher adsorption at lower temperatures is in accordance with the thermo-dynamics of adsorption that allows more adsorption as the temperature is lowered. The higher adsorption at higher temperatures is due to the shift of the equilibrium between NO and  $\text{NO}_2$  more towards  $\text{NO}_2$ .  $\text{NO}_2$  is known to be more strongly adsorbing onto metal surfaces than NO and this results in higher adsorption of  $\text{NO}_x$  onto the surface at higher temperatures. However, above 300 °C both NO and  $\text{NO}_2$  are desorbed from the surface.

Desorption studies were done on 1%Pt/Al and 7%Mn(imp)/Al by using a feed mixture of 150 ppm NO, 1100 ppm CO and 15%  $\text{O}_2$  in He to adsorb the gases onto the

surface at various reaction temperatures and then desorbing them by raising the temperature above 350 °C under a He flow. The results indicate that there is no significant adsorption on platinum below 150 °C and at 200 °C CO and NO<sub>x</sub> get adsorbed on the surface and NO is the major component while at 250 °C more NO<sub>x</sub> gets adsorbed but now NO<sub>2</sub> becomes the major component. A reduction of the amount of NO<sub>x</sub> adsorbed is seen at 300 °C. It's known that CO<sub>2</sub> adsorption on metal surfaces is very weak and also that CO adsorbs much more strongly to metals. However, CO was never seen desorbing from the surface. The reason might be that it is CO that gets adsorbed on to the surface but it leaves the surface as CO<sub>2</sub> removing lattice oxygens with it. This will therefore chemically reduce the surface. There was no significant adsorption seen on Mn/Al at lower temperatures either. The adsorption of NO<sub>x</sub> on manganese was prominent compared to that of platinum and NO<sub>2</sub> was always the major component increasing in ratio (NO<sub>2</sub>/NO) with temperature. CO<sub>2</sub> desorbed at 150 °C and 200 °C but was not observed at higher temperatures.

Adsorption-desorption studies done by sending NO and CO separately in He with and without the presence of oxygen over the catalyst and its components showed CO adsorbing on Pt and Mn and not on Al. NO<sub>x</sub> species mainly adsorb onto Mn sites with a lesser amount of NO<sub>x</sub> gases getting adsorb onto Pt and Al site. The major species adsorbed was NO in the absence of oxygen but with 15% O<sub>2</sub>, NO<sub>2</sub> becomes the major adsorbed species and it resides mainly on the Mn.

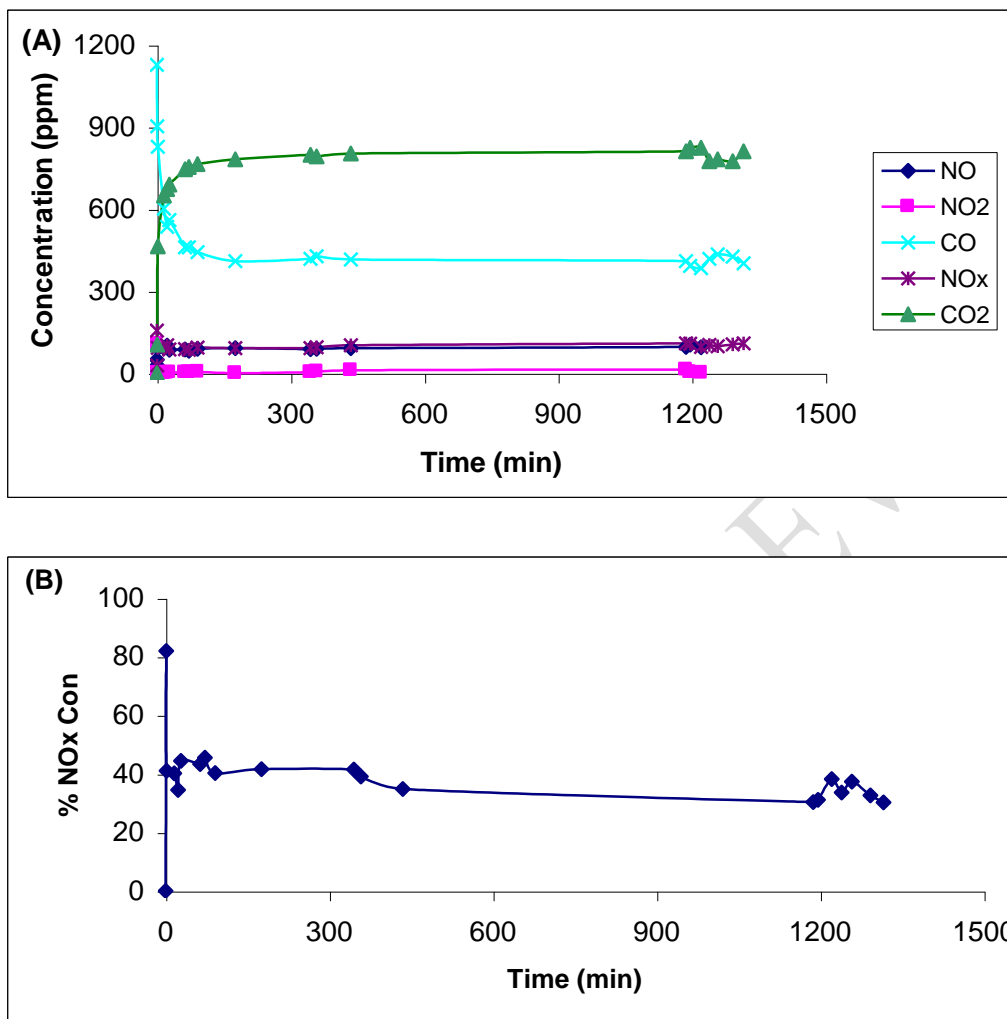
When the above experiment with NO was repeated, but sending CO in He just after adsorbing NO to the surface and then followed by desorption in He, pure alumina showed more or less the same desorption composition. However, over 1%Pt/Al a small

amount of CO<sub>2</sub> was observed when CO was passed and desorption showed a reduction in the amount of NO<sub>x</sub>. This indicates that CO is capable of reducing the adsorbed NO but not to a significant level. The same experiment carried on using Mn(imp)/Al shows a higher amount of CO<sub>2</sub> has been produced when CO is passed, clearly indicating that the deNO<sub>x</sub> reaction takes place on manganese sites. However, the amount of CO converted to CO<sub>2</sub> is greatly enhanced when 1%Pt/mn(imp)/Al is used showing the influence of Pt on the NO<sub>x</sub> reducing ability of Mn. In both catalysts with Mn, the introduction of CO resulted in desorption/production of some NO, which is thought to arise from partial reduction of NO<sub>2</sub> or as a result of adsorbed NO competing with CO for the same active sites. However, it is clear from these studies that the true reaction sites for the deNO<sub>x</sub> reaction are the Mn sites while Pt plays a supporting role by reducing the CO density on the catalytic surface and by influencing the redox properties of Mn. Pt and Al may also be playing a role by adsorbing NO<sub>x</sub>.

### 3.3 Mn/Ce/Al Catalysts

Another class of catalysts that was capable of reducing NO<sub>x</sub> to molecular nitrogen under lean burn conditions for a prolonged time was found in Ce(imp)/Mn(imp)/Al. Cerium oxide is known to reduce NO<sub>2</sub> to N<sub>2</sub> and with Mn in zeolite it has been used in NO<sub>x</sub> reduction studies.<sup>[19]</sup> When a feed mixture of 150 ppm NO, 1100 ppm CO with 15% O<sub>2</sub> in He was sent over 5%Ce(imp)/7%Mn(imp)/Al at 200 °C, continuous oxidation of CO (~55%) and NO<sub>x</sub> conversion of 28-35% was observed (Fig. 5).

**Figure 5.** Change in concentrations (A) and NO<sub>x</sub> conversion for a feed of 150 ppm NO, 1100 ppm CO and 15% O<sub>2</sub> over 5% Ce(i)/7%Mn(i)/Al at 200 °C.



But when Ce and Mn were co-impregnated, CO oxidation remained close to 50% but the NO<sub>x</sub> reduction ceased in about 3 hours. However, when Mn was impregnated on Ce/Al, the catalyst resulted in a lower CO oxidation (~35%) but the NO<sub>x</sub> conversion was continuous and between 30-40%. These observations were significant in the sense that the catalysts did not have a precious metal on it and this will be beneficial in the practical usage of the catalysts due to the role that it will play in cost reduction.



150 ppm NO, 1100 ppm CO with 15% O<sub>2</sub> in He over 5% Ce(imp)/Al at 200°C did not result in any CO oxidation and the NO<sub>x</sub> reduction ceased in 50 minutes. This suggests that NO<sub>x</sub> reduction takes place on Ce or on both metals while reduction of the catalyst by CO takes place only on Mn sites. Therefore, for the catalyst to be functional there should be electronic communication between Mn and Ce sites. This makes the dispersion of the metal oxides on alumina very crucial for its activity. The Mn sites do not get poisoned by adsorbed reactants, mainly due to Ce adsorbing most of the NO<sub>x</sub> and O<sub>2</sub>.

The effective temperature window for the Ce(imp)/Mn(imp)/Al catalysts were also very narrow and found to be between 150-250 °C, and its again thought to be mainly due to an effect of adsorption and desorption of NO and CO on the catalytic surface.

Desorption studies done on 5% Ce/Al by using a feed mixture of 150 ppm NO, 1100 ppm CO and 15% O<sub>2</sub> in He to adsorb the gases onto the surface at various reaction temperatures ranging from 150-300 °C and then desorbing them by raising the temperature above 350 °C under a He flow, indicated that there is no significant adsorption of CO at any temperature and NO<sub>x</sub> adsorption is prominent only in the temperature range of 200-250 °C. NO<sub>2</sub> is the major adsorbed component at all temperatures.

Adsorption-desorption studies done by sending NO and CO separately in He with and without the presence of oxygen over the catalyst and its components showed CO adsorbing only on Mn containing catalysts. NO<sub>x</sub> adsorption was mainly on Ce with Mn and Al also adsorbing NO<sub>x</sub> but to a lesser extent. The major species adsorbed was NO<sub>2</sub> in

the presence of oxygen but both NO and NO<sub>2</sub> were seen adsorbed when no oxygen was present in the feed.

When the above experiment was repeated by sending NO, but sending CO in He just after adsorbing NO to the surface and then followed by desorption by increasing temperature under a He flow, no change was observed for 5% Ce/Al in the desorbed products in terms of components and amounts, from that desorbed during the experiment done without sending CO. However, the same experiment on 7%Mn(imp)/5%Ce(imp)/Al shows CO<sub>2</sub> is produced when CO is passed, indicating that the deNO<sub>x</sub> is taking place indicating that CO is capable of reducing the adsorbed NO<sub>x</sub> on the catalyst. However, the introduction of CO resulted in desorption/production of some NO, which is thought to arise from partial reduction of NO<sub>2</sub> or as a result of adsorbed NO competing with CO for the same active sites. It's not clear from these studies what the true reaction sites for deNO<sub>x</sub> reaction are. However, manganese is the only species that interacts and oxidizes CO.

#### 4. Conclusions

In the search for a catalyst that will reduce NO<sub>x</sub> in exhausts from lean burn diesel engines it was found that, like many metal/metal oxide catalysts reported in literature, Ru/V:Zr/Al catalysts were unable to show prolonged activity in terms of NO<sub>x</sub> conversion. The 1% Pt/Mn/Al catalysts were used with much more success giving almost 95% CO conversions and NO<sub>x</sub> conversions as high as 35-45%. The most promising finding is the durability of these catalysts. The 1% Pt/7%Mn(imp) /Al catalyst with a 150 ppm NO, 1100 ppm CO with 15% O<sub>2</sub> in He feed functioned well beyond 7 days at 200

°C. The analogous catalyst with 3% grafted manganese on  $\gamma$ -alumina gave continuous NO<sub>x</sub> conversions of 30-38% and with respect to conversion per manganese site, this catalyst is the best that is tested yet. It was also established that the manganese oxide sites on the surface function as the true NO<sub>x</sub> reduction sites, while platinum plays a supporting role. The role of platinum is thought to be reducing the CO density on the active sites via direct oxidation of CO and also altering the redox properties of Mn sites so they could function at the conditions used. Hence it was found that platinum has to be well dispersed among manganese oxide sites in order to show prolong NO<sub>x</sub> reduction activity, making the conditions/steps of the catalytic synthesis very important. The working temperature window for these catalysts was found to be very narrow (150-250 °C) and it is thought to be a function of adsorption and desorption of the reactant gases on the catalytic surface.

A second type of catalysts, Mn/Ce/Al catalysts, was also identified for the reduction of NO<sub>x</sub> in lean burn diesel engine exhausts. Even though the NO<sub>x</sub> conversions are lower (28-35%) than the Pt/Mn/Al catalyst, these catalysts are of interest due to the fact that they do not contain any precious metals. The sites of NO<sub>x</sub> conversions are not clear in these catalysts but it is thought to be both Ce and Mn oxide sites while CO oxidation takes place only on Mn oxide sites.

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