# High Performance Catalysts for Storage and Reduction of NOx in Diesel Engine Exhaust

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## ABSTRACT

*Diesel engines offer fuel efficiency and reliability in its operation but they also cause many adverse environmental effects, especially due to the emission of nitrogen oxides (NOx) and particulate matter in the form of soot. Selective catalytic reduction of NOx is a well-proven method to get rid of NOx in diesel engine exhaust gases. A number of catalysts have been developed in which the active phases are different metallic oxide such as oxides of Mn, Co, Cu and noble metals. The common catalyst supports being evaluated for this application are such as vanadia, titania, ceria, zirconia and lanthana. The reduction of NOx has been generally found to take place over as fairly narrow temperature range. The catalysts used for NOx storage comprise combinations of noble meals for oxidation and reduction purposes and barium oxide/carbonate as the storage materials as the nitrogen oxides are chemically bound as surface nitrates. The NOx is then released from the catalyst when shorter lean periods were used while very rich purges of reductant is fed. Potassium-loaded catalysts have been found to show high activity in soot combustion. This metal can play the role due to its high mobility to consequently increase the effective contact between the oxidation catalyst and the soot particle. The activity can be further improved by introducing barium as the promoter. The contact between the soot and the catalyst strongly affects the reaction rate. By a proper combination of active metals, a catalyst suitable for the NSR process, while showing lower tendency to be deactivated by soot can be obtained.*

*Keywords: Diesel exhaust, NOx, selective catalytic reduction, storage, soot oxidation.*

## 1 INTRODUCTION

The diesel engine owes its popularity to its fuel efficiency that results from its lean-burn operation, reliability, durability and relatively low fuel price [1-3]. However, diesel engine exhaust has many adverse environmental effects, due to the high concentration of nitrogen oxides (NOx), particulate matter in the form of soot and sulfur dioxide ($SO_2$). Emission of nitrogen oxides (NOx) and particulate matter (soot) from diesel engine vehicles is a major environmental concern, especially in view of the increasingly stringent limits worldwide. Legal limits for emissions of carbon monoxide, unburned hydrocarbons and nitrogen oxides (NOx) in automotive and stationary sources exhaust gases are becoming more and more strict. Emission standards for heavy duty vehicles in 2007 and beyond will require a 90 % reduction in total particulate matter and NOx from 2003 levels [3]. These standards place new demands on improved engine performance and catalytic converter technology. At the same time, there is a strong pressure to lower the fuel consumption for economic purposes and to lower the production of carbon dioxide, which is an important greenhouse gas [4,5]. Further developments of a diesel engine exhaust should be focused on the adverse effects on environment and health caused by NOx and sooth emissions. Unfortunately, measures to reduce particulate mass emission will often result in an increase in NOx emission and vice versa. This phenomenon is known as the NOx-PM trade-off.

## 2 SELECTIVE CATALYTIC REDUCTION (SCR) OF NOx

### 2.1 SCR Process and Reaction

Conventional process for deNOx of exhaust gases is by converting NOx via a reduction process by mainly ammonia or hydrocarbon (HC) component that present in the gas, to nitrogen ($N_2$) which is safe to the environment. In recent years, hydrocarbons have been studied in order to replace the current best control technology for reducing NOx emission stationary sources that employ ammonia as reducing agent [6,7]. The main advantage of the reaction between NOx and hydrocarbons in post-combustion processes is the use of gas mixture similar to that found in the exhaust. The lean-burn conditions of diesel combustion, which yielded higher combustion temperature and improved efficiency, produced an exhaust gas containing an excess of oxygen. This complicates conventional approaches to chemically reduce NOx to $N_2$ as the reducing components such as carbon monoxide (CO), hydrocarbon (HC) and hydrogen ($H_2$) are preferably oxidized by oxygen [5]. Selective catalytic reduction using a hydrocarbon as a reducing agent has been widely proposed as one of the promising techniques to get rid of NOx in the exhaust gas. The reaction involves is;

$$a\mathrm{NO} + b\mathrm{HC} + c\mathrm{O}_2 \qquad\qquad d\mathrm{N}_2 + e\mathrm{CO}_2 + f\mathrm{H}_2\mathrm{O} \qquad (1)$$

The catalytic reduction of NOx has been generally found to take place over a fairly narrow temperature range. However, diesel exhaust temperature varies from 200°C to 600°C [7]. Thus, to obtain the needed reduction over a wide range of operating temperatures, more than one catalyst could be used.

### 2.2 Active Catalysts for SCR of NOx

The reduction of NOx in oxygen rich-conditions using hydrocarbon (HC) as reductant is a well proven technique for the removal of NOx from stationary sources and has become of increasing interest in recent years [1]. A number of catalysts have been developed in which the active phases are different metallic oxide such as manganese oxide [1], cobalt [2,8], copper [4,7] and noble metals [4,6,9]. The common catalyst supports being evaluated for this application are such as vanadia [10], titania [4], ceria [8], zirconia [9] and lanthana [2,8]. Several other catalyst systems and the observed results are summarized in Table 1. The reduction of NOx has been generally found to take place over as fairly narrow temperature range. However, the temperature of diesel exhaust varies from 200°C to 600°C. Thus, to obtain the needed reduction over a wide range of operating temperatures, more than one catalyst has to be used. The combinations of catalysts have been recently reviewed by Blanco *et al.* [6], who distinguishes two main types of systems: bifunctional catalysts, in which there is a cooperation of two catalytic species, and staging of two or more catalysts in line. Thus, the development of a multimetallic catalyst for improved performance over a wider temperature range is a worthwhile effort.

Table 1 Performance of Few Catalyst Systems Tested for NOx Reduction.

| Ref | Catalyst | Conditions | Remarks |
|---|---|---|---|
| [4] | Cu & Pt/$TiO_2$ | Real exhaust gas<br>1000 ppm NOx<br>260 ppm HC | Active for NOx reduction with diesel fuel as reductant. Stable with slight deactivation after 50 h in operation. |
| [11] | $[Fe(H_2O)]_{0.2}(VO)_{0.8}PO_4$ | 250-450°C<br>$t=9\times10^{-3}$ s<br>500 ppm $CH_4$ | NO conversion by $CH_4$ reached up to 60 % with small $N_2O$ production. $H_2O$ could suppress $N_2O$ formation. |
| [12] | Pd & Pt/<br>sulfated $ZrO_2$ | 350-500°C<br>150 ppm NOx<br>2,000 ppm $CH_4$ | Reached over 50 % conversion over 100 h operation in 9 % water vapor and 3 ppm $SO_2$. |
| [7] | Cu-ZSM-5 | 200°-350°C<br>500 ppm NOx<br>$NH_3$/NOx < 2.5 | Active catalyst for SCR of NOx with $NH_3$. Slight deactivation after 100 h of operation. |
| [9] | Pd/$ZrO_2$ | 300-600°C<br>500 ppm NO<br>5,000 ppm $CH_4$ | High activity for NO conversion with CH4. Amorphous zirkonium hydroxide was a more suitable starting material than crystalline $ZrO_2$. |

## 3 NOx STORAGE AND REDUCTION CONCEPT (NSR)

One current approach of deNOx process is the so-called NOx storage and reduction (NSR) concept based on storage of NOx in the catalyst for relatively long lean periods until saturation followed by interruption by rich spikes [8,9]. During the rich periods, the NOx stored in the lean periods is decomposed and subsequently reduced to nitrogen. The catalysts most commonly used for NOx storage applications comprise combinations of noble meals for oxidation and reduction purposes and barium oxide/carbonate as the storage materials [13]. It has been reported that the nitrogen oxides are chemically bound as surface nitrates. Unfortunately, affinity for nitrate formation also entails affinity for sulphation, which will lead to deactivation of the NOx storage capacity if sulfur is present in the exhaust. Kabin *et al.* [3] found that the NOx storage capacity of model NSR catalysts was as a function of temperature, oxygen ($O_2$), carbon dioxide ($CO_2$) and reductant concentrations. Amberntsson *et al.* [13] examined the influence of $O_2$ and $CO_2$ on the NOx release step. They found that $O_2$ inhibits the NOx release process by raising the desorption temperature while $CO_2$ promotes NOx release by forming barium carbonate ($Ba(CO_3)$). The NOx release was also minimized when shorter lean periods were used (translated as reducing the amount of NOx stored) and when very rich purges were fed (translated as providing excess reductant) [3].

The most popular metals being investigated for NOx reduction process are noble metals particularly platinum, palladium and rhodium [8,13] The metals seem to play several roles in the NOx storage and reduction cycles as well as for sulfur deactivation and for regeneration form the sulfur. Thus, it is of great importance to investigate their role in detail [8]. It was found that palladium-containing catalysts have a slightly higher NOx storage ability at lower temperatures compared to the platinum-loaded samples and that the NOx oxidation activity is much higher on platinum compared to palladium. The effect of addition of noble metals (palladium, platinum or rhodium) to a calcium oxide based NOx storage and reduction catalyst was studied by Amberntsson *et al.* [13] It was reported that rhodium provides better NOx storage ability for a $CaO/Al_2O_3$ catalyst compared to platinum due to higher formation of $NO_2$. However, the thermodynamic equilibrium concentration of $NO_2$ was never reached due to reduction of NOx with the hydrocarbon. The main function of the metals during the rich period of the NOx storage reduction cycle is the ability to reduce NO. The main drawback for the successful and practical use for noble metals are their high cost, that will limit its use, especially in this waste abatement process. Thus, efforts toward finding alternative and potential metals among transition metals that are available at lower cost should be further explored. Encouraging results have been reported by Pisarello *et al.* [8] by using cobalt (Co), Seijger *et al.* [7] by using copper and Blanco et al. [6] by using manganese. Complementary studies in this area should be focused on the understanding of the roles and interaction of the metals during the rich and lean periods of NOx storage and reduction processes.

## 4 PARTICULATE MATTER (SOOT) REMOVAL

In diesel engines, soot particles are formed in the cylinder of the engines due to local shortage of oxygen [10,14]. The composition of diesel particulate depends on several factors such as engine load, speed and temperature [14]. Since NOx are formed in an oxygen-rich atmosphere at high temperatures and pressures, measures to reduce particulate mass emission will result in an increase in NOx emissions, and vice versa. This phenomenon is known as NOx-PM trade-off [7]

In a NSR application, soot is expected to cause serious deactivation to the catalyst. However, removing of soot from diesel engine exhaust gas is a challenging topic. The combination of a filter filled with oxidation catalysts appears to be the most plausible after-treatment technique to eliminate soot particles [8]. In this application, the soot-catalyst contact appears to be one of the most important problems to overcome [15]. Thus, something that is important in the catalyst formulation is to include active components with high mobility [2]. Any catalyst placed over the soot filter should possess high thermo-chemical stability and intrinsic oxidative properties to ignite reliably the soot as early as possible [14]. Potassium–loaded catalysts have been found to show high activity in soot combustion [2,8]. This metal can play the role due to its high mobility to consequently increase the effective contact between the oxidation catalyst and the soot particle [2]. The activity can be further improved by introducing barium as the promoter [8]. The contact between the soot and the catalyst strongly affects the reaction rate. By a proper combination of active metals, a catalyst suitable for the NSR process, while showing lower tendency to be deactivated by soot can be obtained.

## 5 STRUCTURED CATALYSTS

For a deNOx unit, pressure drop is a key issue [4,10]. In a car exhaust or a power plant flue gas system, the pressure drop should typically be below 10-20 mbar [7].

Additional demands comprise low sensitivity to dust and resistance to thermal shock. A suitable solution can therefore be provided by the implementation of a low-pressure drop structured catalyst packing. Structured packings, like ceramic and metal honeycombes and ceramic foams are gaining interest for application in low pressure drop reactors, membrane reactors and catalytic distillation units. Typical advantages of these open macroporous structures follow from their good internal accessibility due to their high porosity and low accumulation of dust due to the large size of the pores. These materials are also more abrasion resistant and have a high axial crushing strength. The specific surface area of most structured supports is below 1 $m^2/g$, which is too low for catalytic purposes. By washcoating with suitable microporous or mesoporous materials, the specific surface area can be enhanced up to about 40 $m^2/g$ [7]. An active and stable NSR monolithic catalyst with soot oxidizing ability and low pressure drop should appear to be an ideal catalyst for the deNOx of a diesel exhaust gas. In fact, it is already close to a practical application for the pollution abatement in a real diesel exhaust system.

## 6 CONCLUSIONS

Despite providing fuel combustion efficiency and reliability in operation, diesel engine has many adverse environmental effects, particularly due to the emission of NOx and particulate matter in the form of soot. Selective catalytic reduction (SCR) of NOx is a practical and efficient method to remove NOx in diesel engine exhaust gases. The active phases for SCR catalysts are different metallic oxide such as oxides of Mn, Co, Cu and noble metals. The common catalyst supports being evaluated for this application are such as vanadia, titania, ceria, zirconia and lanthana. The reduction of NOx has been generally found to take place over as fairly narrow temperature range. An innovative method to treat NOx using a so-called NOx storage and reduction (NSR) has been recently introduced. The catalysts used for NOx storage step comprise combinations of noble meals for oxidation and reduction purposes and barium oxide/carbonate as the storage materials as the nitrogen oxides are chemically bound as surface nitrates. The NOx is then released from the catalyst when shorter lean periods were used while very rich purges of reductant is fed. During this stage, the NOx will be reduced to $N_2$. Potassium–loaded catalysts have been found to show high activity in soot combustion. This metal can play the role due to its high mobility to consequently increase the effective contact between the oxidation catalyst and the soot particle. The activity can be further improved by introducing barium as the promoter. The contact between the soot and the catalyst strongly affects the reaction rate. By a proper combination of active metals, a catalyst suitable for the NSR process, while showing lower tendency to be deactivated by soot can be obtained.

## Acknowledgement

Research funding in the form of short term grant from Universiti Sains Malaysia to support this study is gratefully acknowledged.

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