
Recent Advances in the Development of Urea-SCR for Automotive Applications

Manfred Koebel, Martin Elsener and Giuseppe Madia
Paul Scherrer Institute

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ABSTRACT

In the recent years, considerable progress has been achieved in the development of urea-SCR for nonstationary, mobile applications. Main challenges are the reduction of the catalyst volumes and the optimization of the dosing strategy to minimize transient ammonia emissions during load changes. Catalysts with increased cell density and enhanced intrinsic activity are one way to obtain smaller catalyst volumes. Another approach is the introduction of additional catalysts upstream and downstream of the SCR catalyst itself. Most effective is an oxidizing pre-catalyst that converts a part of NO to NO₂, thus allowing a faster SCR reaction to occur. However, such a system requires the use of fuel with reduced sulfur content.

Work performed at the Paul Scherrer Institute comprises of fundamental experiments in a laboratory scale reactor with synthetic exhaust gas and applied experiments on a diesel test stand. In addition to the evaluation of various commercial and proprietary catalysts, important problems of the process have been investigated as, for example, the fast SCR reaction, ammonia adsorption on the catalysts, the decomposition of urea, and catalyst aging.

INTRODUCTION

Forthcoming European and U.S. emission legislation for diesel vehicles calls for a significant reduction of both particles and NO_x. However, an important difference is the fact that in Europe an increasing number of passenger cars are equipped with diesel engines. Their maximum allowable emissions of particles and NO_x will be also subjected to stringent regulations. The present work focuses mainly on HD diesel vehicles.

Figure 1 shows the large gap between feasible raw emissions of HD diesel engines for trucks and forthcoming emission standards. It is now generally assumed that the EURO 4 emission standards proposed for the year 2005 will be no longer feasible by primary measures alone, but will require additional exhaust gas aftertreatment techniques. There exist two basic strategies to attain these future standards:

1. Optimize the combustion with respect to low NO_x emissions, leading to a high emission of unburned material (soot, CO, hydrocarbons). Then use a particulate filter in the aftertreatment to clean up the particulate matter.
2. Optimize the combustion with respect to low emissions of unburned material, leading to a high emission of NO_x. Use a DeNO_x process in the aftertreatment.

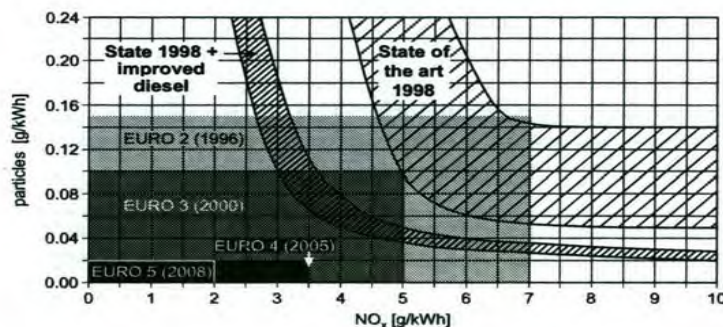


Figure 1: Trade-off between particulate matter and NO_x for HD truck engines and prospected EURO emission standards

The first strategy does not require a complicated chemistry, but leads to an increase in fuel consumption. If optimized fuel economy is an additional target, then the second strategy is the better choice. This calls for the selective catalytic reduction of NO_x in the presence of oxygen.

Various selective DeNO_x techniques have been proposed and studied in the last years. These include SCR (Selective Catalytic Reduction) with N-containing reducing agents like ammonia and urea [1, 2], the NO_x storage-reduction (NSR) catalyst [3, 4] and the so-called HC-SCR [5, 6]. In the latter process hydrocarbons are used to reduce nitrogen oxides. However, although much effort has been directed into the development of these catalysts, selectivity is still poor resulting in the preferential oxidation of oxygen that, in turn, increases the fuel consumption and the CO₂ emissions. The NSR

catalyst utilizes the ability of basic oxides to store NO_x as nitrates, but it is very prone to deactivation by sulfur oxides due to the higher stability of the corresponding sulfates.

In our opinion the SCR process using urea as selective reducing agent has the highest chances of maturing into a commercial technique for heavy duty diesel applications. Urea-SCR has been studied by various groups in the last ten years [2, 7-9]. The present paper resumes the challenges of this development and further reports some recent advances.

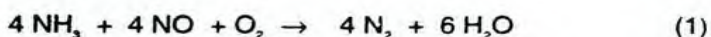
CHEMISTRY OF THE SCR PROCESS

It is well known that diesel exhaust contains the nitrogen oxides mainly in the form of NO (nitrogen monoxide, typically over 90 %) and only a minor fraction in the form of NO_2 (nitrogen dioxide). Therefore, the SCR process must mainly remove NO by reduction.

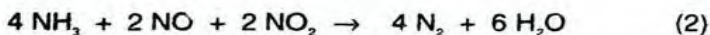
The selectivity of the process refers to the selectivity of the reducing agent, which should not reduce the excess oxygen typical to a lean exhaust. Experience has shown that N-containing reducing agents like ammonia, urea and cyanuric acid are outstanding for this purpose. Urea may be considered as a solid storage compound for ammonia and is produced commercially by reacting ammonia with carbon dioxide. The main advantages over ammonia are its negligible toxicity and its easier handling due to a negligible vapor pressure.

To facilitate the understanding of the main SCR reactions, we will firstly focus on ammonia as reducing agent. Only later we will present the reaction equations for the generation of ammonia from urea.

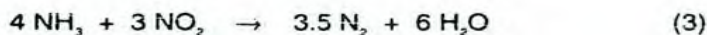
The main reaction between ammonia and NO on the usual SCR catalysts is:



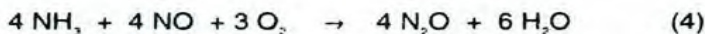
We will call this reaction subsequently "standard SCR". According to this reaction 1 mole of NO will consume 1 mole of NH_3 and $\frac{1}{4}$ mole of O_2 . Definitely faster than reaction (1), is the reaction of a 1:1-mixture of NO and NO_2 :



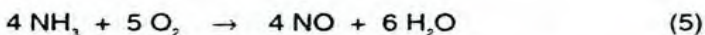
This reaction will be subsequently denoted "fast SCR". The increase of the reaction rate has been long known [10, 11] and it is now proposed as a practical measure to increase the performance of automotive DeNO_x systems. To increase the fraction of NO_2 in the exhaust, a strong oxidation catalyst (Pt-based) is placed upstream of the SCR catalyst. However, the fraction of NO_2 should not exceed 50% of NO_x because the reaction involving pure NO_2 is again slower than both reactions (1) and (2):



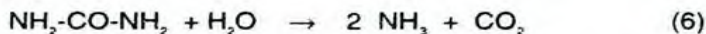
At high temperatures (>400°C) the commonly used SCR catalysts based on TiO_2 - WO_3 - V_2O_5 tend to form nitrous oxide (N_2O). One of the possible reactions leading to its formation is:



At still higher temperatures, the oxidizing properties of the catalyst get even more pronounced. This causes direct oxidation of ammonia to NO, thus limiting the maximum possible NO_x conversion:



In all these reactions ammonia may be substituted by urea and the above equations will change accordingly. The overall decomposition reaction of urea in the presence of water is:



This reaction involves both a thermal and a hydrolytic decomposition step. We will discuss the respective details further below.

IMPROVING SCR CATALYSTS

PROBLEM

Gas hourly space velocities (GHSV) typical to stationary SCR catalysts are around 10,000 h^{-1} (this means 10,000 volumes of gas at standard conditions per volume of catalyst and hour). On the other hand, the space velocities of three-way catalysts (spark ignited engines) are typically of the order of 100,000 h^{-1} , i.e. about ten times higher. The latter range of space velocities results in catalyst volumes similar to the cylinder volume of the gasoline engine.

Due to the limited space available onboard a vehicle, higher space velocities in the SCR catalyst are necessary, i.e. the volumetric activity of the SCR catalysts must be drastically increased. This requirement becomes even more important given the fact that the diesel engine has a widely varying range of exhaust gas temperatures. However, the catalysts based on TiO_2 - WO_3 - V_2O_5 have their maximum activity between 300 and 400°C, the activity decreasing rapidly with falling temperature. The following measures are useful to reduce the catalyst volume:

1. Increase the intrinsic activity of the SCR catalyst. If a high selectivity for N_2 -formation is to be kept, i.e. little formation of N_2O and NO_x at higher temperatures, the standard SCR catalyst systems based on TiO_2 - WO_3 - V_2O_5 or TiO_2 - MoO_3 - V_2O_5 are still the systems of choice. Their drawback is a limited activity, which is

particularly evident at the lowest loads/exhaust temperatures of the engine. The concentration of vanadia may be increased to boost the intrinsic activity, but concentrations above $\approx 3\%$ will lead to a loss of selectivity of these catalysts.

- Increase of the cell density of the monolith, i.e. the geometric surface-to-volume ratio of the catalysts. Increasing the cell density from 36 cpsi to 300 cpsi is accompanied by an increase of the volumetric surface from $\approx 770 \text{ m}^2/\text{m}^3$ to $\approx 2200 \text{ m}^2/\text{m}^3$. SCR extruded catalysts based on $\text{TiO}_2\text{-WO}_3\text{-V}_2\text{O}_5$ with cell densities up to 300 cpsi have been already developed by some manufacturers. Still higher cell densities can be realized by coating techniques using cordierite or metallic substrates. This is due to the fact that cordierite or metal foils have much better mechanical properties and, therefore, allow thinner walls of the monolith. In extruded catalysts the entire wall consists of $\text{TiO}_2\text{-WO}_3\text{-V}_2\text{O}_5$ plus admixtures of binders and glassfibers to increase the mechanical properties. Higher cell densities will be especially effective at high temperatures, where the SCR reaction proceeds mainly in the top layer of the catalyst.

RESULTS

We started to investigate coated SCR catalysts in 1996 [12]. The reason for this engagement was the fact that such catalysts were not available to us at that time. We expected superior performance in nonstationary applications due to the prospect of using higher cell densities and the lower mass of active material per volume. The latter reduces the problem of ammonia spikes following sudden load increases.

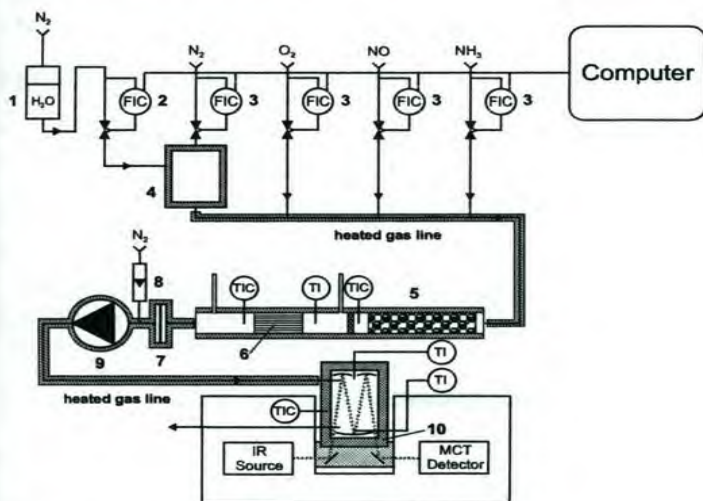


Figure 2: Laboratory test stand: 1, water reservoir; 2, liquid mass flow controller; 3, mass flow controller; 4, water evaporator; 5, reactor; 6, catalyst sample; 7, filter; 8, flow meter; 9, diaphragm pump; 10, gas cell

In the standard test, the catalysts are first tested in the laboratory test stand at a GHSV of $52,000 \text{ h}^{-1}$ (Fig. 2). The basic gas composition is adapted to a typical diesel exhaust containing 10% oxygen and 5% water with balance nitrogen. Standard tests are made with 1000 ppm NO and varying the concentration of NH_3 in the feed, i.e. varying the stoichiometric ratio $\text{NH}_3:\text{NO}$. Gas analysis is performed by FTIR spectroscopy (Nicolet Magna 560) allowing to measure simultaneously NO, NO_2 , NH_3 , N_2O .

In order to assess the performance of catalysts we opt to plot $\text{NH}_3\text{-slip} = f(\text{DeNO}_x)$, where DeNO_x denotes the conversion of NO_x in percent. For the practical use of a catalyst, the maximum possible DeNO_x at high ammonia slip is of no interest, the important issue being the lower DeNO_x at a limited ammonia slip (typically 10 ppm). Figures 3 to 5 compare the performance of three catalysts at various temperatures. The closer a curve is to the right lower edge of the graph, the better the catalyst is at this temperature. The strong improvement over the last years is evident from these figures. The basic properties of the three catalysts are resumed in Table 1.

Table 1: Properties of the three catalysts

property	units	D31	D42	K51
type	--	extruded	extruded	coated
production year	--	1995	1999	2000
cell density	cpai	200	300	400
$\text{V}_2\text{O}_5\text{-content}$	%	≈ 3	≈ 3	≈ 3

According to Fig. 3 catalyst D31 could hardly reach 30 % DeNO_x @ 10 ppm NH_3 . This is a commercial extruded catalyst with 200 cpsi. This cell density was already a strong improvement over the usual commercial catalysts available in 1995. Figure 4 shows the performance of D42, an extruded catalyst with 300 cpsi. This catalyst reaches almost 90 % DeNO_x at temperatures above 350°C . Still somewhat better results are obtained with the coated catalyst K51 from our own development (Fig. 5). Both the increased cell density and the higher intrinsic catalytic activity of K51 contribute to the better performance of this catalyst compared to D42.

However, an initial high activity is not the unique quality criterion for such a catalyst. We have found that thermal stability should also be tested. Figure 6 compares the activity of several coated catalysts with 400 cpsi cell density. For simplicity, only the DeNO_x at 10 ppm $\text{NH}_3\text{-slip}$ is given. Thermal aging was performed in this case during 100 hours at 550°C . More critical aging tests are performed at temperatures of 600°C and even 650°C . From these results it is evident that K99 is a much improved version of the earlier catalyst (K51). We have also found thermal stability to be a problem for some commercial catalysts.

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