

Urea-SCR in automotive applications

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Stricter emission legislation for diesel vehicles will make exhaust after-treatment mandatory in the near future. Urea-SCR has been chosen for NO_x reduction on trucks and busses. Since its effectiveness in reducing NO_x is great, and since there is a trade-off between NO_x emissions and fuel consumption, engines can be adjusted on fuel efficiency. This review article deals with subjects such as the description of SCR catalysts, catalytic systems, system performance, choice of reducing agent and durability.

KEY WORDS: urea; SCR; deNO_x; truck; no_x; vanadium; zeolites; urea hydrolysis; modelling.

1. Introduction

Nitrogen oxide is always emitted if fossil or other fuels are combusted and vehicles are no exception. NO_x from gasoline engines is reduced by means of three-way catalyst. However, this technology cannot be used on diesel engines due to its lean mode of operation. SCR has for more than a decade been mentioned as a promising technology to reduce NO_x on diesel engines in automotive applications. The legislation has now become stringent to the extent that engine management alone is not enough to make engines compliant with the regulations, and exhaust gas after-treatment in one form or another must be introduced. The feature with Urea-SCR is summarised in a publication by ACEA [1], the European Automobile Manufacturers Association. The conclusions drawn are that there is a possibility that fuel optimised engines combined with a Urea SCR system could reduce fuel consumption by 7% and running cost by 3% compared to today's engine technology. The benefit compared to other alternative technologies is 5%. In a global perspective, transportation could be carried out with less CO₂ emitted, which is what many countries in Europe strive for in order to comply with the CO₂ levels they signed up to in the Kyoto protocol. The unique feature with a Urea-SCR after-treatment system is that, since it allows the engine to be optimised on fuel consumption, it will have a pay back time on a heavy-duty truck. A cost assessment made by Warren [2] showed that the payback time for a Urea-SCR system could be as low as one to two years in a long haul application. This is of course dependent on the fuel price, urea price, device price and the mileage travelled.

The technology was firstly developed for NO_x reduction in stationary application such as boilers, incinerators and stationary diesel engines. One of the first articles describing such a system for automotive use was

published by Held *et al.* [3], who suggested that urea should be used as a reducing agent. The technology is rather complex and requires a precise control of the reducing agent, urea. However, under transient operation, it has over the years developed to be mature enough to be implemented onboard vehicles. The challenges ahead are to reduce size and to develop the low temperature performance of the current catalyst types.

2. Technologies and system performance

There are two different routes for applying SCR catalysts. The first route is to use one single full catalyst, which has a channel wall made of catalytic material. The other route is to use wash-coated metallic or cordierite substrate. These substrates carry less active amount of catalysts and, therefore, possess less low-temperature performance than that of full catalysts. However, the low temperature performance can be enhanced by increasing the relation between NO and NO₂ to about 50/50 over a base metal type of catalyst as reported by Anderson [4] and over a zeolitic catalyst as reported by Brandin *et al.* [5].

Gieshoff *et al.* [6] compared two systems based on coated cordierite substrates. The basic system consisted of a hydrolysis catalyst, and an SCR catalyst with or without pre-oxidation catalyst. The SCR catalyst had a volume of 9.2 L, the pre-oxidation catalyst 2 L and the hydrolysis catalyst 4 L. On a 4-L diesel engine they found that the activity was enhanced when a pre-oxidation catalyst, containing 90 g Pt/ft³, was used. Results from ESC test cycles showed that the overall conversion efficiency could be increased by 30%, when a pre-oxidation catalyst was used with the same SCR catalyst volume.

Walker *et al.* [7] demonstrated a system consisting of a pre-catalyst, an SCR-catalyst and an ammonia slip oxidation catalyst, but also combined with a soot filter. The total volume of the system active in the SCR reaction was in the range of 36 L. The system showed a

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rather good low-temperature performance, enhanced by the pre-oxidation catalyst.

Gekas *et al.* [8] compared the performance over three different catalytic systems, pure SCR systems, with slip oxidation catalyst and with a pre-oxidation catalyst. By using a pre-oxidation catalyst, they measured an enhanced low-temperature performance of the catalyst, but the effect was limited, and by replacing the pre-oxidation catalyst with the same volume of SCR catalyst, they reached similar conversion efficiencies, but with a less complex system. Gekas *et al.* [8] also showed an improved catalyst performance when the cell density was increased from 130 to 300 cpsi leading to the fact that the catalyst volume could be reduced by 1/3 for the same conversion efficiency.

Gekas *et al.* [9] demonstrated that a 12-L class, 400 horsepower engine, which was optimised on low fuel consumption and low soot particle emissions, could be compliant with future emission legislation, with 20 L of a 300 cpsi SCR catalyst alone (see Table 1).

Lambert *et al.* [10] tested an SCR system, consisting of a combination of base metals and zeolite type of catalyst, on a passenger car engine and found that the SCR system could reduce, on average, 83% NO_x in a US federal test cycle. This was carried out with an ammonia slip, which actually was lower than that for gasoline cars with three-way catalysts reported in other literature.

A graphical description of the different catalytic setups is seen in figure 1.

2.1. Reducing agents

Different ammonia precursors or reducing agents have been suggested. Liquefied NH₃ has been widely used in larger stationary installations, and has also been suggested for the use on vehicles as described by Funk *et al.* [12]. However, the safety is an issue when such a reducing agent is handled onboard vehicles, and lethal damages cannot be excluded since a rather large amount will need to be transported around to gas stations and also onboard the vehicles, where it is finally used.

Another suggested reducing agent is ammonium carbamate NH₄NH₂COO, which upon heating decomposes into urea (NH₂)₂CO and H₂O. In support of ammonium carbamate is that it is a solid which reduces the volume of the reducing agent which is needed onboard a vehicle compared to urea which is normally dissolved in water to give a 32.5% urea solution. The disadvantage of a solid reducing agent is that the injection system tends to be rather complex. It was suggested by Stieger and Weisweiler [13] that ammonium carbamate is dosed as powder in a bath of oil, in which it decomposes first to urea and later to NH₃. The ammonia gas was led into the exhaust gas manifold upstream of the SCR catalyst. Weisweiler and Buchholz [14] even suggested the use of solid urea, which is decomposed to reactive species by heat. There are a couple of drawbacks with such a system, one is that solid urea is hygroscopic and needs to be protected

Table 1

Urea-SCR system conversion efficiency over European test cycles, ETC (European transient test cycle) and ESC (European stationary test cycle), with a 12 litre class 400 hp heavy-duty diesel engine and 20 litres of Urea-SCR catalyst [9]. "EU V" refers to emission legislation which comes in to force in 2008

| Test-cycle | NO _x (g/kWh) | HC (g/kWh) | CO (g/kWh) | Particulate matter (g/kWh) | | | BSFC (g/kWh) |
|-------------|-------------------------|------------|------------|----------------------------|----------|----------|--------------|
| | | | | Insoluble | Lube oil | Fuel oil | |
| EU V limit | 2 | | | 0.02 ESC 0.03 ETC | | | |
| ESC w/o SCR | 9.0 | 0.28 | 0.30 | 0.007 | 0.020 | 0.010 | 194 |
| ESC w SCR | 1.4 | 0.05 | 0.48 | 0.009 | 0.003 | 0.004 | 194 |
| ETC w/o SCR | 8.5 | 0.26 | 0.38 | 0.015 | 0.014 | 0.010 | 198 |
| ETC w SCR | 1.5 | 0.04 | 0.61 | 0.013 | 0.002 | 0.005 | 197 |

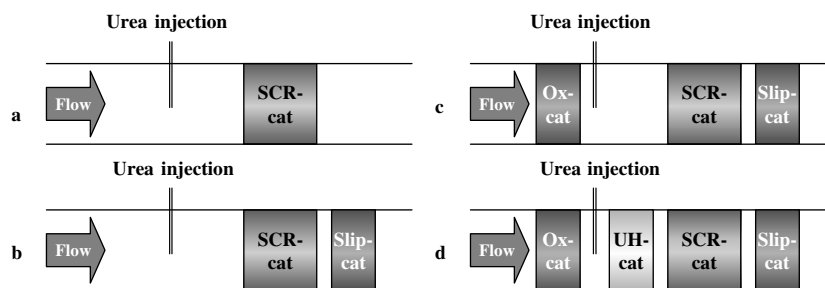


Figure 1. Different catalytic set ups: (a) single SCR catalyst [9]; (b) SCR and NH₃ slip oxidation catalyst [9]; (c) pre-oxidation, SCR and NH₃ slip oxidation catalyst [7]; (d) pre-oxidation, urea-hydrolysis, SCR and NH₃ slip oxidation catalyst [6,11]; Slip cat = ammonia oxidation catalyst, Ox-cat = oxidation catalyst, UH-cat = urea hydrolysis catalyst.

against humidity, another is that an even distribution of powder in the exhaust manifold could be difficult.

Currently, the preferred choice is a solution of 32.5% urea in water, as described in a recent DIN norm. This is going to be the standard in Europe, when an infrastructure for the reducing agent is developed according to ACEA [15] which is also about to standardise the urea filling nozzle. Fang and DaCosta [16] studied the urea decomposition and found by mixing catalyst with urea and heating the mix above the melting point of urea, 135 °C, that it was possible to decompose urea with a higher rate when the urea catalyst mix was used. According to Fang the decomposition can be made in two stages of which the first stage starts after the melting point and the second above 300 °C. Melamine complexes are formed in the second stage, which could inhibit the catalytic reaction. Fang *et al.* also found that the nature of the urea spray had an influence on deposition in the front of the catalyst. A finer atomisation gave less deposition in the front of the catalyst. Larrubia *et al.* [17] studied the adsorption of urea on a V₂O₅-MoO₃-TiO₂ catalyst by FTIR and proposed a mechanism for the decomposition on the surface. According to them, the mechanism should be adsorption of an anionic urea species which further decomposes to ammonia and ammonium species and cyanate anions (N=C=O)⁻. The cyanate anion can be further decomposed to ammonia and CO₂ by hydrolysis with water. Ball [18] investigated the potential toxicity of urea and its degradation products and found no reasons for concern. However, since data for some compounds are poor, further investigations were recommended. Koebel *et al.* [19] compared performance for different reducing agents and found differences in the ability to reduce NO_x at the same stoichiometric ratio. The differences were most pronounced at high space velocities, where liquefied ammonia showed the highest activity.

2.2. Catalysts

2.2.1. Different types of monoliths for SCR catalysts

As mentioned above there are two different families of SCR monoliths, full or coated. The full catalyst could either be an extruded or corrugated structure. The extruded catalyst normally consists of about 700–1000 g/L of active material, while the corrugated structure is in

the range of 450–550 g/L. A coated monolith is based on a cordierite or a metallic substrate, which is washcoated with about 150–200 g of the active phase.

Koebel *et al.* [20] compared extruded catalysts, 300 cpsi, with coated catalysts of 400 cpsi, and found that a coated catalyst with 3% V₂O₅ on a cordierite substrate could have higher than or similar activity to an extruded catalyst. He also found that an extruded catalyst stored more ammonia than a coated catalyst at low temperatures, while it stored similar or less at high temperatures.

Kleeman *et al.* [20] investigated the ammonia adsorption capacity over an extruded and coated catalyst based on the same catalytic material, and found that the adsorption capacity was fairly similar for all coatings. However, there is a tremendous difference in the amount of active material in the two different types of catalysts. Since they carry different amounts of active material they also have different properties, see table 2.

The benefit of a high ammonia adsorption capacity is that it has a buffering property, it continues to reduce NO_x for several minutes after the injection is switched off as described by Kleeman *et al.* [21]. This means that the requirement for precision of reducing agent injection is lower than if a coated catalyst is used. However, the disadvantage of an extruded catalyst is that it is more difficult to control the ammonia slip if there is a sudden temperature increase in the system, because more ammonia is desorbed from the surface and this causes an ammonia slip.

2.2.2. Activity comparison

The different catalysts described above possess different activity in different temperature areas. The coated substrate has normally lower activity in the low temperature region from 170 to 250 °C than that of the full catalysts. The reason is that the reaction is more or less kinetically controlled, and therefore the activity is more or less dependent on the amount of catalyst. There are also differences between extruded and corrugated full catalysts. The extruded catalyst has a denser structure, which originates from the extrusion process, compared to the corrugated structure. This means that in an extruded catalyst the reaction is more limited by pore diffusion. However, in the high temperature area from 300 °C and upward, the reaction is more controlled by

Table 2
NH₃ storage capacity for different types of SCR catalyst [21]

| Catalyst type | Cpsi | Catalyst (g/L) | WO ₃ (%) | V ₂ O ₅ (%) | NH ₃ capacity (mg/g) | | NH ₃ capacity (mg/L) | |
|---------------|------|-------------------|------------------------|--------------------------------------|---------------------------------|--------|---------------------------------|--------|
| | | | | | 200 °C | 350 °C | 200 °C | 350 °C |
| Coated | 400 | 178 | 8 | 3 | 2.02 | 0.78 | 360 | 139 |
| Coated | 400 | 203 | 0 | 4 | 2.00 | 0.75 | 406 | 152 |
| Extruded | 300 | 955 | 10 | 3 | 1.78 | 0.46 | 1700 | 439 |

film mass transfer, and is therefore more dependent on the exposed surface area in channels within the monolith.

It is sometimes difficult to compare different catalysts. The reason is that the experimental conditions differ. Sometimes monolithic materials are used and other times fine powder in a packed bed of the same type of catalyst is used. Between those two materials, there is an immense difference in, for instance, mass transfer constants, while the powder catalyst more or less has an efficiency factor close to 1. The kinetics in a monolith are normally more or less outer film mass transfer limited at temperatures above 300 °C, while a powder is more or less kinetically controlled or controlled by pore diffusion.

An easy way to scale and compare the activity over a monolithic catalyst is to calculate a first order rate constant based on space velocity, K_{NHSV} .

$$K_{\text{NHSV}} = \frac{\ln(1-x) * F}{V_{\text{cat}}}$$

where x is the NO_x conversion, F is the flow in Nm^3/h and V_{cat} the catalyst volume in m^3 . K_{NHSV} is expressed in the unit, Nh^{-1} .

In table 3, the first order rate constant has been calculated. The pattern emerging from the data is that coated catalyst, as mentioned above, possesses a lower low-temperature performance and needs a higher level of NO_2 in the gas to reach the activity levels of the full catalysts. It is also possible to observe a pattern on which level the rate constant should be at the two temperatures, 200 and 350 °C, in order to reduce NO_x in a test cycle with a reasonable volume of catalyst. The rate constants should in this case be above 25,000 Nh^{-1} at 200 °C and above 130–150,000 Nh^{-1} at 350 °C. Applying a pre-oxidation catalyst upfront of the urea-SCR catalyst and its urea injector enhances the rate constant

of the coated type of catalysts. With rate constants above these levels it will be possible to achieve about 80% NO_x conversion in a European Transient Test Cycle, which is used for certification in the emerging European market. However, it should be pointed out that there are other markets, such as in the US, where certification test cycles run at lower temperatures and, therefore, these might need an even higher conversion efficiency at lower temperatures than described above.

The above calculations are a textbook example that should not be forgotten. It is apparent that many authors do not know the boundaries of the applicability of a catalyst, and that this should be used as guideline for what to look for in their research and to judge the importance of their results.

2.2.2.1. Experimental conditions

Having this opportunity one would also like to urge experimentalists in this area to be very careful with their experimental conditions. It is for instance quite surprising to see that some authors are running experiments without water. Such results can only be used for relative comparisons within the same research and it is difficult to estimate their usefulness in real life. An example of a real exhaust gas composition is given by Roudit *et al.* [26] and it could be regarded as an input for experimental conditions, see table 4.

The influence of SO_2 and CO_2 on the catalyst could be debated. A more reasonable goal for a synthetic gas mix could have less SO_2 in the gas, 1–2 ppm seems more reasonable, and would be in line with the emissions from future engines in Europe. However, one should bear in mind that future vehicles occasionally might need to go to a country where low sulphur fuel is unavailable, and therefore the catalyst might see considerably higher levels of sulphur than it normally does. This, sulphur tolerance, could be an issue, which at least for very new and

Table 3
Comparison of first order rate constant between different catalyst types

| Material | $K_{\text{NHSV}} (\text{Nh}^{-1})$ | | | References |
|---|------------------------------------|-----------------------------|--------------|--------------------------------|
| | 200 °C NO | 200 °C NO/ NO_2 | 350 °C NO | |
| “Low temp.” 400 cpsi, coated | ~51,300 | ~98,200 | ~33,700 | Blakeman <i>et al.</i> [22] |
| “High temp.” 400 cpsi, coated | ~3580 | ~64,500 | ~109,537 | Blakeman <i>et al.</i> [22] |
| $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ 400 cpsi, coated | ~15,000 | ~28,300 | ~182,000 | Koebel <i>et al.</i> [23] |
| $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ 300 cpsi, extruded | ~23,200 | N/A | ~182,341 | Koebel <i>et al.</i> [23] |
| $\text{V}_2\text{O}_5/\text{WO}_3/\text{TiO}_2$ 400 cpsi, coated | ~4200 | | N/A | Gieshof <i>et al.</i> [6] |
| Not specified 400 cpsi, coated | ~3500 | ~34,300 | ~64,377 | Winkler <i>et al.</i> [24] |
| 4.6% $\text{V}_2\text{O}_5/\text{TiO}_2$ 400 cpsi coated | ~8200 | N/A | N/A | Bukart <i>et al.</i> [25] |

unknown materials should be investigated. Another gas component, of which the presence is not negotiable, is water because the activity and selectivity are affected by it.

Odenbrand *et al.* [27] made experiments with and without water and found that the selectivity of formation of N_2O was heavily influenced by the presence of water. The temperature window for NO_x reduction changed to higher temperatures when 1% water was added to the stream, having as a result that the temperature had to be increased by 15–20 °C in order to obtain the same NO_x conversion with water and without.

Hydrocarbons are another component with which one should be careful. Gieshoff *et al.* [6] tried different levels of *n*-decane in the gas mix and found that the activity window below 300 °C was changed by 50 °C to the higher end, when 10 ppm of *n*-decane was used which is 100 ppm C_1 . Since different hydrocarbons have different effects, it is suggested that the hydrocarbons are excluded in laboratory experiments, or that at least a reference comparison with and without hydrocarbons is made.

2.2.3. Catalytic material

Before starting to work in the field of SCR, one has to read an article by Bosch and Jansen [28]. The article is an extensive review of the area of SCR. Among other things it deals with topics like formation of NO_x , catalyst preparation and testing and kinetic mechanisms. It is also a source of inspiration not only about how to carry out experiments and prepare catalyst but also because many different catalytic materials are listed and referenced.

2.2.3.1. Base metal oxide catalysts

Base metal oxide catalysts are still the most common commercial types of catalyst for SCR and the predominant active ingredient is vanadium on a carrier of titanium oxide. Tungsten or molybdenum is used to increase the catalyst acidity. For the temperature stability a catalyst with WO_3 or MoO_3 holds a higher activity and is active in a broader temperature window, according to Forzatti *et al.* [29], due to the formation of more acid Brønsted sites and OH-groups on the surface. These are the sites with which NH_3 coordinates and becomes activated before it reacts with NO_x from the gas phase. Koebel *et al.* [30] compared three different vanadium-based catalysts, extruded 200 and 300 cpsi and coated 400 cpsi monoliths and found that the 300

and 400 cpsi catalysts exhibited the best activities. He also found that the 400 cpsi catalyst had a sharper boundary for the appearance of ammonia slip. Madia *et al.* [31] tried the thermal stability of coated catalyst with 173 g catalyst/L on a 370 cpsi substrate. The catalyst was based on a WO_3 - TiO_2 carrier, which was impregnated with 1, 2 and 3% V_2O_5 . Three ageing procedures were tested, “100 h @ 550 °C”, “100 h @ 550 °C + 30 h @ 600 °C” and “100 h @ 550 °C + 30 h @ 600 °C + 15 h @ 650 °C”. They found that the 3% V_2O_5 catalyst was most sensitive to high temperature, and its conversion efficiency went down during all the different ageing procedures. However, the 2% V_2O_5 catalyst remained stable up to 600 °C but lost activity going to 650 °C. The 1% V_2O_5 catalyst gained activity in the two first ageing procedures, but its initial activity was low in relation to the other two catalysts. The more dramatic effect on the 3% V_2O_5 catalyst at 650 °C was due to loss of anatase surface in the TiO_2 structure, which was induced by the vanadium loading. The vanadium-based system is not very active below 200 °C. A catalyst with low temperature performance that could be of interest is the MnO_x - CeO_2 system, which recently was described by Qi *et al.* [32]. Except for its low-temperature activity, the catalyst has robustness to high temperatures and is reversibly deactivated, when sulphur is used in the gas. The drawback with low-temperature active catalysts is that they are too active at higher temperatures and therefore burn off the ammonia instead of reducing NO_x .

2.2.3.2. Zeolitic catalysts

There are only few articles on zeolites and urea SCR. Two of those describe the use of zeolites in an engine application, Gieshoff *et al.* [33] and Lambert *et al.* [34], where the catalyst shows a good performance. However, the long-term stability and the sulphur tolerance are not discussed in these papers.

Sullivan *et al.* [35] compared a Cu-ZSM5 zeolite with traditional vanadium-based catalyst and found that the Cu-ZSM5 catalyst was active in a broader temperature window. One can have some concern about the experimental conditions, since they were carried out with 0.6% NH_3 and NO_x in the gas, which could be regarded as rather high. They also saw a promoting effect when water was used, which goes in the opposite direction to what is expected. The conversion efficiency was enhanced at low temperatures when water was added to

Table 4
Diesel exhaust gas composition according to Roudit *et al.* [26]

| P | NO | NO ₂ | HC ₁ | CO | CO ₂ | O ₂ | H ₂ O | SO ₂ | N ₂ |
|------|-------|-----------------|-----------------|-------|-----------------|----------------|------------------|-----------------|----------------|
| (kW) | (ppm) | (ppm) | (ppm) | (ppm) | (%) | (%) | (%) | (ppm) | |
| 890 | 1020 | 115 | 30 | 490 | 7,1 | 10,5 | 4–5 | 30 | Bal. |

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