Perspektiven der mobilen SCR-Technik
Perspectives on Mobile SCR Technology

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Zusammenfassung

Zur Minderung der NO_x-Emissionen von Dieselmotoren wurden seit ca. 1990 sowohl durch innermotorische Maßnahmen als auch durch Abgasnachbehandlung mit der SCR-Technik große Fortschritte erzielt. Bei den motorischen Maßnahmen kommt der Abgasrückführung (AGR) große Bedeutung zu, bei der Nachbehandlung der Abgase ist die Harnstoff-SCR-Technik zur effizientesten Art der NO_x- Reduktion bei mager laufenden Verbrennungsmotoren herangereift. Bei Nfz-Motoren erfolgt seit 2005 Serieneinsatz für die Euro V-Stufe. Hierbei werden Motoren ohne Abgasrückführung (AGR) eingesetzt, deren Abgas aber die Katalysatoren mit relativ hohen NO_x- und Harnstoff- Konzentrationen belastet. Im Pkw-Bereich ist durch innermotorische NO_x-Minderung mit AGR die Katalysatorbelastung ca. fünfmal geringer. Hohe Aktivität, Selektivität und Dauerstabilität (bei > 500 °C) von neuentwickelten SCR-Katalysatoren auf Eisenzeolith-Basis ermöglichen die Vorschaltung von Dieselpartikelfiltern. Die Technologie der Zukunft wird auf einer drastischen Absenkung der NO_x-Bildung im Motor basieren und damit die spezifische Belastung der Katalysatoren mit NO_x und Harnstoff signifikant verringern. So wird man auch künftigen sehr niedrigen NO_x-Limits entsprechen können. Bei Nfz wird man durch Einführung der innermotorischen NOx-Verminderung mit AGR eine Angleichung der SCR-Technik an die der Pkw erhalten. Dem SCR-Katalysator wird ein Voroxidationskatalysator und Filter vorgeschaltet. Als wichtiger technischer Fortschritt wird die Einführung „turbulenter“, radial offener Katalysatoren und von Festharnstoff als Reduktionsmittel beschrieben.

Abstract

Since 1990 NO_x emissions from diesel engines have come down dramatically because of engine-based measures and selective catalytic reduction (SCR) aftertreatment. Among these engine-based measures exhaust gas recirculation (EGR) plays the most important role. Urea SCR was developed as the most efficient method of reducing NO_x emissions in the exhaust of lean-running engines. Serial applications that meet the Euro V standard were introduced in commercial vehicles at the beginning of 2005. These systems are based on non-EGR engines and consequently expose the catalysts to high NO_x and urea concentrations. In passenger car applications that are currently being developed the catalyst load is smaller by a factor of approx. 5. However, the diesel particulate filter (DPF) located upstream from the SCR system requires a significantly higher permissible operating temperature for the SCR catalysts in these applications. This paper examines the prospects of mobile SCR technology, which is being developed to meet future ultra-low NO_x emission

limits. Future SCR technology for trucks is expected to become more similar to the approach currently applied to cars, following the implementation of engine-based NO_x reduction through EGR and pre-oxidation catalyst/filters, which will result in a lower specific catalyst load of NO_x in high-EGR engines. The introduction of “turbulent”, radially open catalysts and solid urea as a reducing agent represents an important technical breakthrough.

1 Introduction

1.1 Motivation

An exhaustive range of measures to reduce NO_x emissions, i.e. through a combination of engine-based technology such as EGR and exhaust gas aftertreatment, will have to be implemented to meet future, very strict emission standards for commercial vehicles (Euro VI, US 2010) and for passenger cars with lean-running engines (to bring their emissions in line with those of lambda 1 petrol engines). These measures must also ensure compliance with an average NO_2 immission limit of 40 $\mu g/m^3$ per annum, which is to be introduced in the EU in 2010. The preferred method of reducing NO_x levels in the exhaust gas is selective catalytic NO_x reduction because it includes the following features:

- Continuous reduction using ammonia from precursors, especially AdBlue®,
- High NO_x conversion rates in the entire engine map,
- NO_2 is more reactive than NO and can therefore be reduced more easily,
- Aging- and sulphur-resistant catalysts are available.

These features of SCR technology and their potential for future developments are discussed below. Secondary issues, such as diagnostics and control systems (OBD, sensors, actuation), simulation and software development (CFD and numerical modelling, dosing algorithms) have not been considered.

1.2 History of development

Since its introduction in the 1980s the selective catalytic reduction of NO_x using ammonia (ammonia SCR) has developed into a mature technology for reducing NO_x emissions from power stations and industrial facilities. The fundamental chemical principles behind this catalytic process are already known [Kö92].

SCR processes in mobile applications have undergone continuous development since 1989 as part of FVV and VFI research projects. The main challenges included the improvement of the process to enable it to cope with dynamic operating modes, the use of urea in an aqueous solution or in solid form instead of NH_3 as a reducing agent, the widening of the exhaust gas temperature range, the improvement of volume-specific activity, and vehicle-specific application. A summary of the work and the research reports will be published in October 2006 [Mü06b].

Since 1992 MAN Nutzfahrzeuge AG, DaimlerChrysler AG (then: Daimler-Benz AG) and Siemens AG have been at the forefront of the development of SCR technology for commercial vehicle engines using urea as a reducing agent (urea SCR). As early as 1992 NO_x emissions from an MAN Euro 0 engine (raw emissions: 10 g/kWh NO_x) were successfully reduced to the later Euro V limit of 2 g/kWh NO_x through exhaust gas aftertreatment based on an SCR process using urea water as a reducing agent in a steady-state cycle (ESC) [Ja93,03]. The SCR process proved to be very effective in reducing NO_x emissions, which has made it the preferred method among European commercial vehicle manufacturers of ensuring that their non-EGR engines meet Euro V limits. The progress made in the development of SCR technology has been the subject of several papers [Ja98,00,03,04a/b,06]. A special feature of the technology employed by MAN Nutzfahrzeuge AG is the use of auxiliary catalysts, which increase the system's efficiency in practical applications while reducing its overall size. At present, urea decomposition and ammonia slip catalysts keep the size of the SCR catalyst in MAN's Euro V vehicles relatively small.

2 Mobile SCR: State-of-the-art technology and prospects

2.1 Reducing agents (ammonia precursors)

2.1.1 Summary

Ammonia is the only known chemical compound able to reduce NO_x on reactant and product-selective catalysts (SCR catalysts) in the presence of oxygen (a stronger oxidation agent than NO) to form nitrogen. Ammonia in pressurised containers represents a safety risk when carried onboard a vehicle. Ammonia precursors are used instead since they can be decomposed in the vehicle's exhaust gas system to form ammonia.

A eutectic solution of 32.5% urea in water (AdBlue®) whose quality is specified by an ISO standard was chosen as a suitable NO_x reducing agent that would be available across Europe for the SCR exhaust gas aftertreatment of European commercial vehicles in future. However, AdBlue® suffers from the following problems, which increase the complexity of its application and logistics:

- A freezing point of -11°C
- Formation of solid residues under delayed evaporation
- The active ammonia content is relatively low at 0.2 kg NH_3/kg

The search for alternative liquid and solid reducing agents for mobile SCR technology has therefore become an important subject of current research. The active ammonia content can be dramatically increased by using solids, such as ammonium carbamate or urea pellets. **Figure 1** shows four potential precursor compounds of ammonia with very different degrees of suitability. In order to illustrate the chemical relationship of these compounds the structures of two ammonium salts, ammonium carbamate (AC) and ammonium formate (AF), are shown on the left-hand side of **figure 1**. They can be both technically and actually converted to urea (HS) and methanamide (MA) (shown on the right-hand side of **figure 1**) by dehydration.

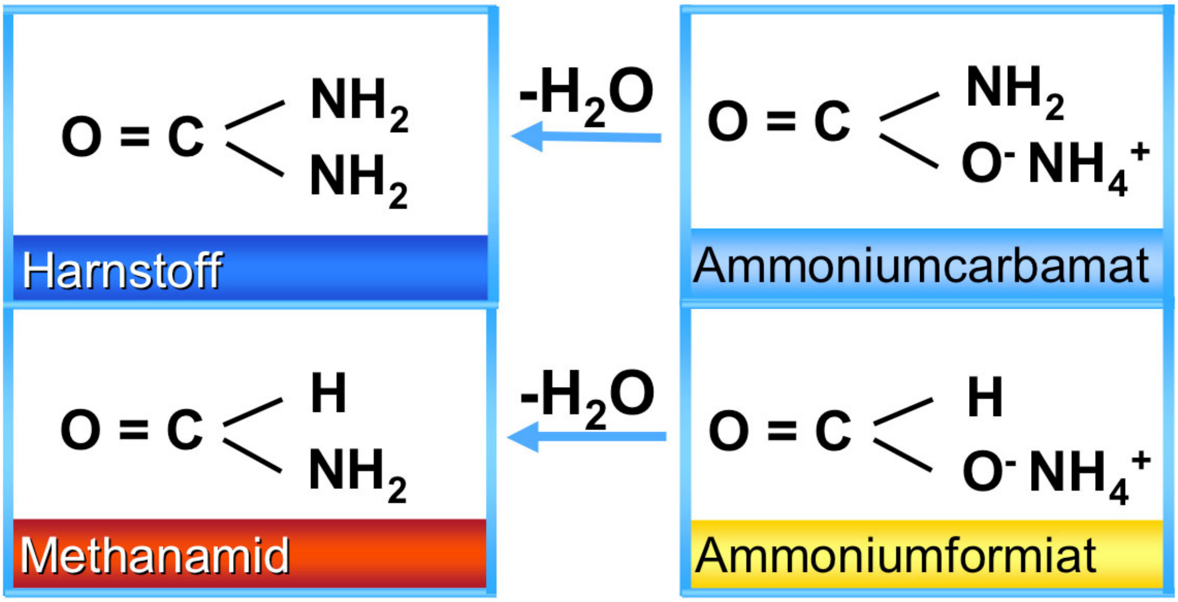

Abb. 1: Beziehungen zwischen den chemischen Strukturen verschiedener Ammoniakvorläuferverbindungen. Durch Wasserabspaltung entsteht HS aus AC und MA aus AF

Fig. 1: Chemical structure relationships of various ammonia precursors. AC forms HS and AF forms MA by dehydration

The chemical properties of these compounds are very different. AC is hydrolysed by water and so has to be handled under exclusion of moisture and readily breaks down to form ammonia and carbon dioxide when exposed to heat. The ammonia partial pressure of AC is approx. 3 bar at 80°C. Therefore AC used for the generation of ammonia must be handled in pressurised containers.

Ammonium formate (AF) breaks down on SCR catalysts above a temperature of 200-300°C to form ammonia and carbon monoxide. AF forms toxic methanamide (MA) by dehydration (toxicity similar to petrol due to its teratogenic effect). Urea (HS) is the only compound that can be classified as harmless in mobile applications. However, the production of ammonia from HS is far from simple since secondary reactions can take place during thermolysis and leave non-volatile residues and cause malfunctions.

2.1.2 Alternatives to AdBlue®

2.1.2.1 Liquid reducing agents

Ammonia precursor compounds used in a water-soluble state can be dispensed into the exhaust gas more easily than solids.

Ammoniakvorläufer-substanz (AV)	Fp [°C]	Zusammens. [Gew. -%]					Gehalt an aktivem Ammoniak	
		HS	AF	MA	AC	H_2O	pro Gewicht [kg/kg]	pro Volumen [kg/L]
AdBlue (HS)	-11	32,5				77,5	0,20	0,22
Ammoniumformiat (AF)	-35		40			60	0,13	0,14
Denoxium -30 (HS+AF)	-26/-30	20	26			54	0,20	0,22
Methanamid (MA)	-28			80		20	0,30	0,33
Ammoniumcarbamat (AC)					>99		0,44	
Harnstoff (HS)-Perlen Ø 2mm	133	>99					0,57	0,42

Tab. 1: Festpunkte, chemische Zusammensetzung und Ammoniakbildungspotential von wassergelösten und festen Ammoniakvorläuferverbindungen

Table 1: Freezing points, chemical composition and active ammonia content of solved and solid ammonia precursors

Since AdBlue® freezes at only -11°C the proportioning and delivery modules, the vehicle tank and the filling stations require heating to ensure the system's function in winter. Alternative liquid reducing agents have been proposed to avoid the extra costs involved.

Table 1 lists the properties and composition of HS, AF and MA solutions in water. The freezing point of these solutions should be guided by the cold filter plugging point (CFPP) of diesel fuel, which is -25°C for winter diesel in Central Europe.

Ammonium formate (AF) appears to be particularly suitable. A 40% solution of AF in water freezes at -35°C and does not form any residues even in case of slow evaporation. The decomposition of AF on different SCR catalysts was examined using a model gas system. The tests revealed a number of problems. As a result, AF cannot be recommended without reservation because the dissociation of AF produces formic acid at temperatures below 300°C and at high catalyst loads, especially in case of an overdose [Kr06c]. Other disadvantages of AF include its corrosion behaviour – the corrosive effects of formic acid are well known from chemical plant engineering – and the fact that its active ammonia content is 35% lower than that of AdBlue®. The active ammonia content of ammonium formate can be raised to the level of AdBlue® by adding urea. However, this inevitably leads to the formation of solid polymerisation products, as those found in urea. A solution of 24%

AF and 20% HS in water (freezing point -30°C) is sold as Denoxium-30. A dual system using AdBlue® in summer and Denoxium-30 in winter would eliminate the extra costs for making the system frost-resistant. The release of Denoxium-30 is subject to international standardisation, which is expected to take at least three years.

A solution of methanamide (MA) in an aqueous solution (freezing point -28°C) offers undecomposed long-term stability even at 100°C and can be evaporated easily without leaving any residue. On certain SCR catalysts it behaves in a similar way as ammonium formate. It also has a 50% higher active ammonia content than AdBlue® and is biodegradable (Water Hazard Class 1). Despite its otherwise perfect process-based suitability the use of this reducing agent in mobile applications is problematic because of its teratogenic properties even though to all intents and purposes the level of toxicity is similar to that of petrol [Ja05b].

2.1.2.2 Solid urea

By using solid urea the amount of onboard reducing agent can be cut by almost half compared to an aqueous urea solution (AdBlue®) (**table 1**). Solid urea also improves the system's low-temperature activity. In cars the urea tank does not have to be refilled between regular service intervals.

Solid urea can be thermally and catalytically produced by an electrically heated reactor in the auxiliary flow [Mü02] or in the main flow [Mü06b] of the exhaust gas. The auxiliary flow version requires an integrated catalyst for the hydrolysis of isocyanic acid; this can be dispensed with if the reactor is located in the main flow (**figure 2**).

Dosing is based on a cell wheel principle; the urea pellets are lifted out of the cells by a conveying air stream and carried through a tube to the reactor. **Figure 3** shows the change in NO and NO_2 concentrations for a stationary map point when the urea feed is spontaneously activated and deactivated. This discontinuous feed of urea pellets utilises the temperature-dependent ammonia storage properties of the SCR catalyst to achieve high conversion rates with minimum ammonia slip.

In contrast to thermal decomposition of an aqueous urea solution in the exhaust gas system, a solid urea system offers a number of important advantages because the pellets are decomposed in a reactor. In order to achieve comparable conversion rates in an MVEG cold engine test, much smaller amounts of reducing agent have to be stored in the SCR catalyst, which reduces the risk of ammonia slip accordingly. This advantage becomes even more important in view of future legislation on secondary emission limits (limit: 10 ppm ammonia).

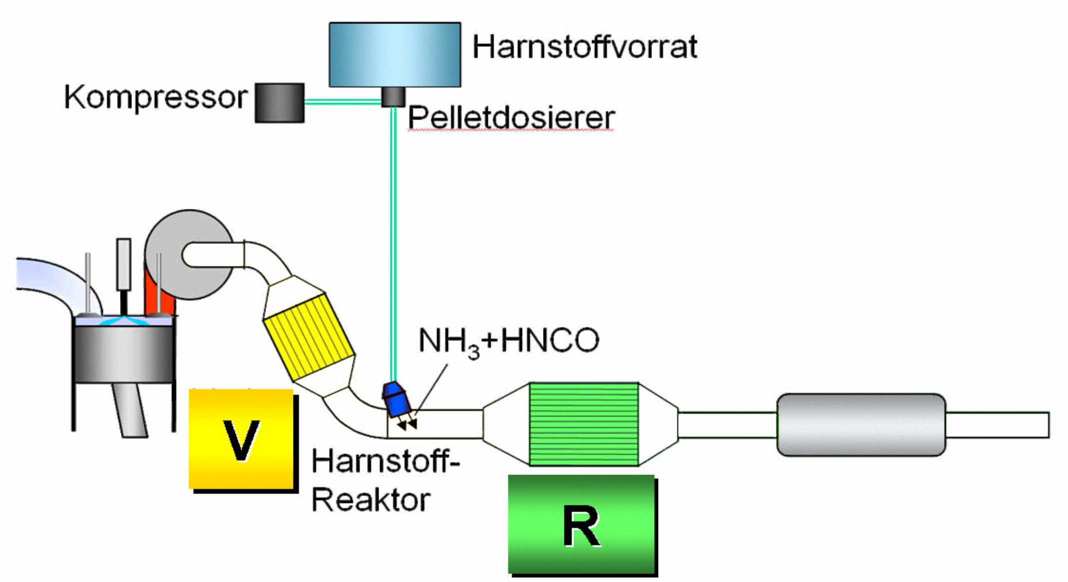

Abb. 2: Schema eines Festharnstoffsystems mit Reaktor im Abgashauptstrom [Mü06b]

Fig. 2: Diagram of a solid urea system with a reactor in the exhaust gas main flow [Mü06b]

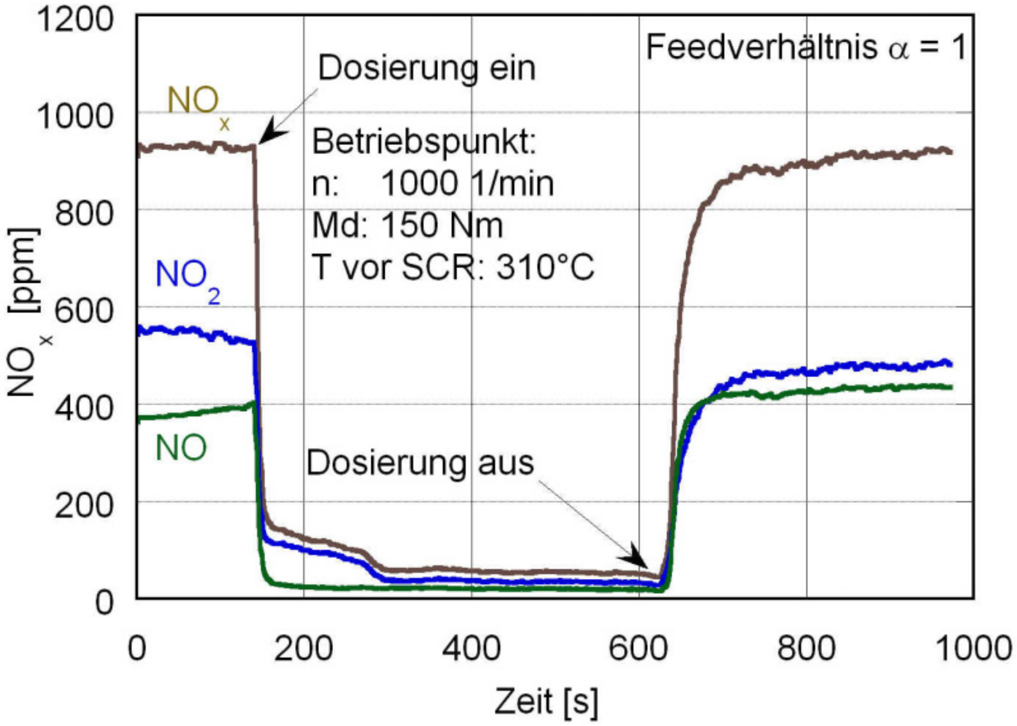

Abb. 3: NO_x-Umsatz und dynamisches Verhalten eines Festharnstoff-Systems [Mü06b]

Fig. 3: NO_x conversion and dynamic behaviour of a solid urea system [Mü06b]

In contrast to aqueous urea solutions, pellets do not require a complex heating system since they cannot freeze so that the function of the reducing agent system is guaranteed when starting the vehicle.

The operational reliability of the solid urea system was demonstrated in tests carried out on engines and on a roller test bench. A road test covering approx. 20,000 km also confirmed the system's basic suitability for vehicle applications.

NO_x conversion rates of 60% were achieved in a European driving cycle without any catalyst heating. This figure rose to 90% after the system had reached its operating temperature. A conversion potential of this magnitude is required in order to comply with future, very strict NO_x limits. On the basis of current technology, and especially at high engine loads, these rates can only be achieved with SCR systems that use ammonia as a reducing agent.

A luxury car with Euro 2 emission levels was found to require a quantity approx. 9.5 kg or 13 litres of bulk volume for a distance of 40,000 km in order to comply with the Euro 4 limit.

In order to meet the extremely strict EPA 2010 and Euro VI limits in commercial vehicles, the reduction of NO_x through exhaust gas aftertreatment will have to be accompanied by a similar cut in raw emissions through the implementation of engine-based measures. This combination of measures limits the quantity of solid urea that has to be carried onboard to somewhere in the region of 10 litres for a driving distance of 10,000 km. Based on the future AdBlue® infrastructure, the use of solid urea in commercial vehicles in the EU will become a practical solution only after solid urea has actually proven its effectiveness in cars over a period of several years. In other countries, e.g. the US, the introduction of solid urea as a reducing agent should generally be considered the preferred option.

Meanwhile, the availability of highly stable and uniform ball-shaped urea granules (urea beads) has significantly improved the chances of implementing solid urea technology. The standardisation of solid urea is to start in 2006.

In conclusion, a solid urea system for the use in vehicles offers a number of advantages over a liquid option (AdBlue®), including a smaller size, frost resistance, better properties regarding the dosing of reducing agent and the absence of ammonia slip. System costs will be competitive primarily because of the absence of frost protection and of ammonia slip. Solid urea is expected to offer great potential for future applications: “Solid urea is a more sensible solution than AdBlue®” [Pi06c].

An alternative solids dispensing system was developed on the basis of ammonium carbamate (AC) [He02, Wi06]. However, the large-scale production of AC, the filling of small, pressurised containers and the safety aspect present some problems.

2.2 Activity and selectivity of SCR catalysts and auxiliary catalysts

2.2.1 “Turbulent” catalyst substrates

2.2.1.1 Turbulence and catalyst activity

The effective reaction rate on catalysts is determined by the following sequential steps:

- Mass transfer of the reactants from the core flow of the catalyst channel, and film diffusion through the stagnant thin layer of gas to the external catalyst surface (external mass transfer),
- Mass transfer of the reactants into the pore system of the washcoat, onto the internal surface (“pore diffusion”),
- Chemical reaction on the active centres, i.e. the actual catalyst (“reaction kinetics”),
- Mass transfer of the reaction products from the pore system to the external surface,
- Mass transfer of the reaction products from the catalyst surface, and film diffusion through the stagnant thin layer of gas into the gaseous phase of the catalyst channel.

Each of these steps can determine the conversion rate. Under the typical conditions of a vehicle catalyst, reaction kinetics has a limiting effect only at low exhaust gas temperatures, whereas the effective reaction rate, and hence the reduction of emissions, is determined over a wide load range by the internal mass transfer in the pores and the external mass transfer through the boundary layer. The mass transfer coefficient can be increased by raising the flow rate, and thus the Reynolds number. Turbulent flows produce much better performance but they require higher flow rates, as the amount of pressure loss would otherwise become to great. The positive effects of turbulence can also be achieved by catalyst structures that induce turbulence in the flow due to their special geometry and thus significantly increase the mass transfer coefficient [Ma05]. These ideas can now be implemented due to the arrival of new production technologies, process technologies and materials. New coating processes adapted to structured metal substrate technologies were developed at the same time [Ja06]. These “turbulent” catalysts are already in production as three-way catalysts and diesel oxidation catalysts [Br06].

2.2.1.2. Mixing effects of MX/PE, LS/PE and PE/PE structures

MX/PE, LS/PE and PE/PE substrate structures (Fig. 4) are particularly suitable for SCR technology because apart from generating turbulent flow they also promote the homogenisation of the reducing agent in the exhaust gas due to their radial permeability, which enables the concentrations and pressures to be equalised [Br06, Ma05, St06a,b].

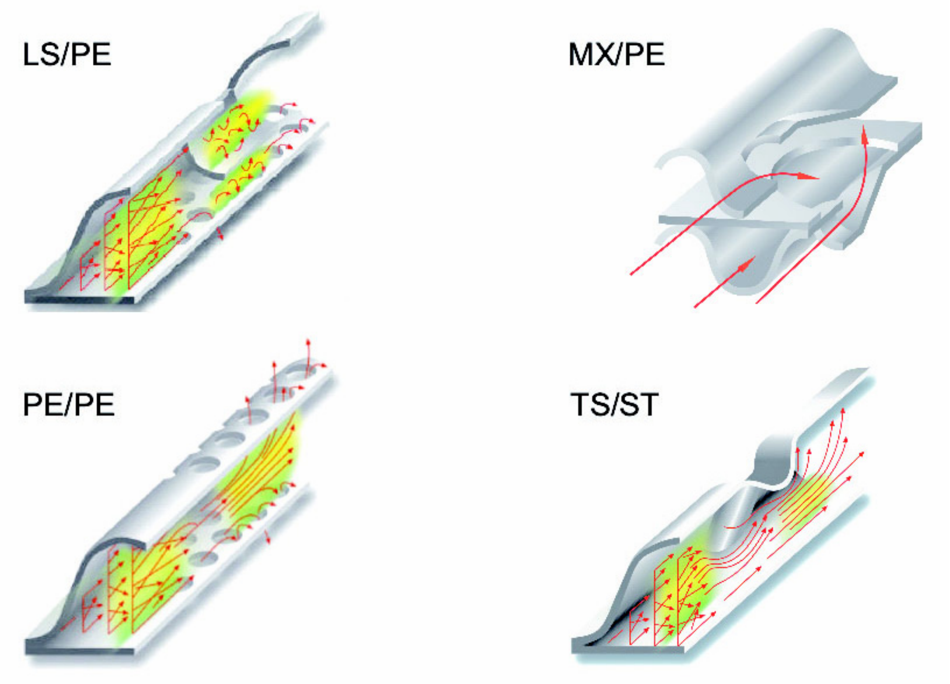

Abb. 4: Aufbau und Strömungsverhältnisse der untersuchten „turbulenten“, radial offenen Strukturen LS/PE, MX/PE, PE/PE und der geschlossenen Struktur TS/ST

Fig. 4: Setup and flow conditions of the tested “turbulent”, radially open LS/PE, MX/PE, PE/PE structures and the closed TS/ST structure

In order to determine the mixing effect between the catalyst channels for different substrate setups, a tracer gas was sprayed into a central single channel at the substrate end face and its radial dispersion was measured after it had flowed through the substrate. **Figure 5** shows the measurement result. **Figure 6** shows the mixing efficiency in relation to the exhaust flow rate as calculated with a 9-channel CFD model. A value of 0 means no mixture while a value of 1 represents the perfect distribution of the tracer gas. The trends correspond well; the absolute values show some variation because of different boundary conditions. The sequence of the mixing efficiency is based on MX/PE>LS/PE>PE/PE>ST/ST (standard smooth channel substrates, radially closed). In practice, the LS/PE substrate offers the best compromise between mixing effect, pressure loss and geometric surface area (GSA) [St06a,b].

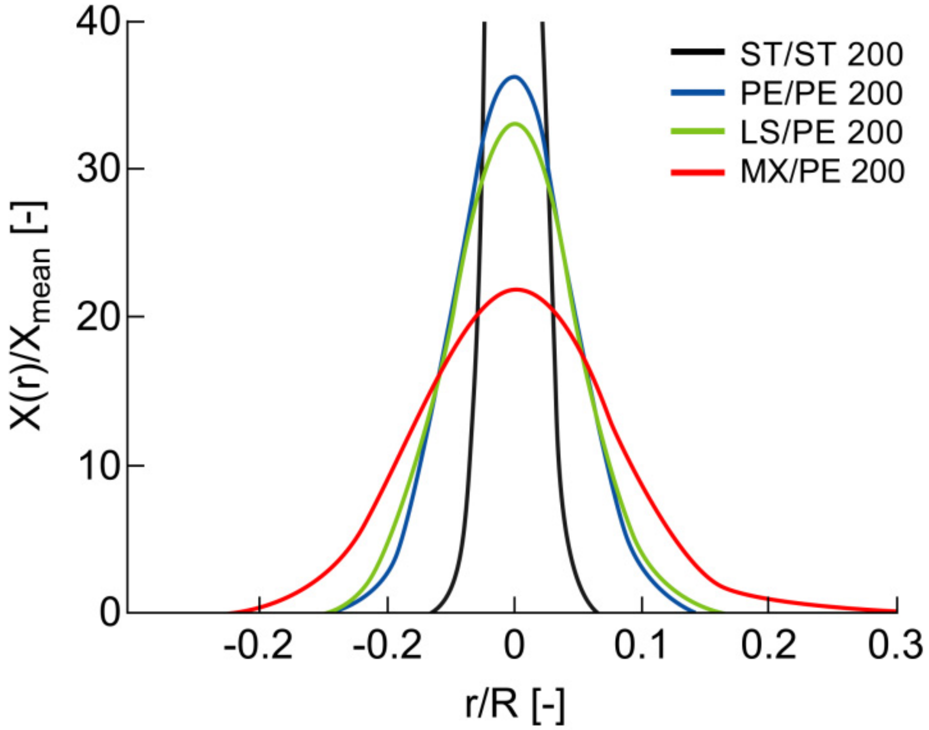

Abb. 5: Mischungsgüte: Dispersion 50 mm nach dem Katalysator bei 100 m³/h, 598 K [St06a]

Fig. 5: Mixing efficiency: Dispersion behind the catalyst at 100 m³/h, 598 K (R=50 mm) [St06a]

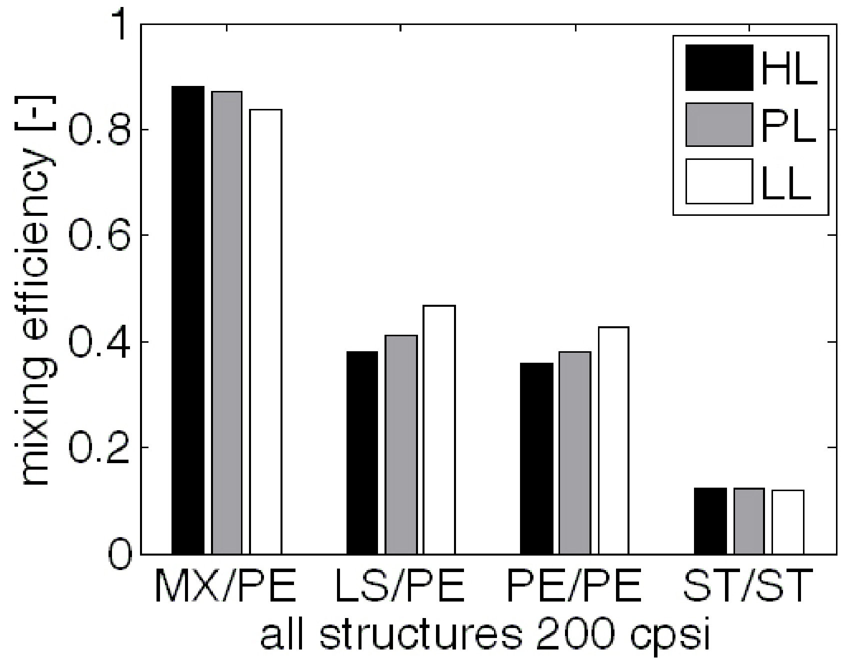

Abb. 6: Berechnete Mischungsgüte (LL: 100 m³/h, 598 K; PL: 200 m³/h, 598 K; HL: 300 m³/h,723 K) [St06b]

Fig. 6: Intermixing between catalyst channels: Calculated mixing efficiency [St06b]

2.2.2 AdBlue® processing: Dispersion, evaporation, mixing and decomposition on H-catalysts

When AdBlue® is sprayed into the hot exhaust gas, the water and urea evaporate. Due to its instability the molecular urea instantly decomposes to form HNCO and ammonia. This process is promoted by the high dispersion rate of the AdBlue® droplets and a longer contact time [Yi04, Bi06, Pi06a]. Therefore a vaporiser/mixer (e.g. H in figure 15) is widely used to produce "scattered" evaporation/decomposition of the AdBlue® droplets to make it much easier to add HNCO and NH_3 to the exhaust gas. The slow decomposition of urea leads to the formation of higher molecular, partially non-volatile solids [Sc04] and must be avoided.

A two-stage, titanium dioxide-coated H-catalyst [Ja06] is a proven design with regard to the high AdBlue® mass flows that have to be broken down in Euro V commercial vehicle applications. Its front part (H-catalyst A) contains a large-cell vaporiser/mixer with an MX/PE structure, which completely "gasifies" the atomised AdBlue® to form H_2O, NH_3 and HNCO [St06a,b]. In a second stage, the highly reactive HNCO is converted to ammonia by catalytic hydrolysis [Ha06, Pi06a,b, St06a,b]. This prevents the formation of non-volatile deposits (e.g. in the form of cyanuric acid produced by the trimerisation of HNCO). The relevant chemical equations are shown in **figure 7**.

Multifunktionsreaktor: Zweistufige Ammoniakbildung

Verdampfung des Wassers

- $[(NH_2)_2CO \cdot 7H_2O]_{fl} \xrightarrow{>135°C} [(NH_2)_2CO]_{fl} + 7H_2O$

Harnstoff-Thermolyse

- $[(NH_2)_2CO]_{fl} \xrightarrow{TiO_2} NH_3 + HNCO$

H-Kat A

Isocyansäure-Hydrolyse

- $HNCO + H_2O \xrightarrow{TiO_2} NH_3 + CO_2$
- **vermeidet Ablagerungsbildung nach:**
  $3\ HNCO \xrightarrow{<350°C} [(HNCO)_3]_S$ **(Cyanursäure)**

H-Kat B

Abb. 7: Harnstoffzersetzung am zweistufigen H-Kat
Fig. 7: Decomposition of urea with a two-stage H-catalyst

The evaporation of water in AdBlue® requires four times more thermal energy than urea thermohydrolysis [Kö02, Ja04a]. As far as the decomposition of the liquid ammonia precursors listed in **table 1** is concerned, precursors with the lowest water content are at an advantage from an energetic aspect.

There are four processes that can be used to produce ammonia from urea in the exhaust gas (**figure 8**). If the ammonia is generated externally the urea decomposition catalyst (H-catalyst) is located in the auxiliary flow [Ja90, Mü03]. The disadvantage of this approach is the fact that is requires additional heating. If the process takes place inside the exhaust gas the H-catalysts is primarily used in the partial flow in order to increase the contact time for urea decomposition [Ja03,04a/b]. In this case the H-catalyst is not exposed to excessively high NO_2 concentrations, thus preventing the formation of ammonium nitrate deposits in the H-catalyst that would deactivate it [Ja06, Pi06b].

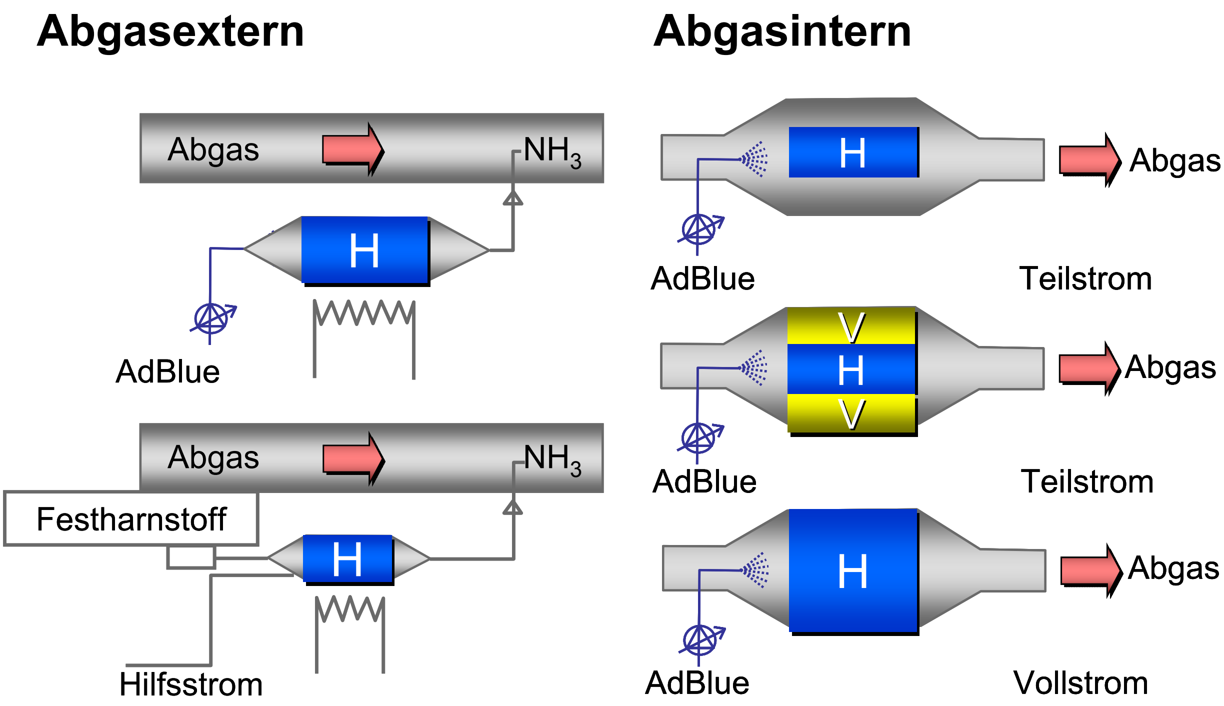

Abb. 8: Externe und interne NH_3-Generatoren

Fig. 8: External and internal generation of ammonia

In commercial vehicle applications the SCR catalyst often also acts as a vaporiser and H-catalyst. As a result the size of the catalyst has to be increased significantly. The NO_x conversion potential and the prevention of impermissible secondary emissions are determined by the high accuracy of AdBlue® dosing and dispersion. Air-assisted atomisation of AdBlue® is a very useful feature [Hü05], but the process could be greatly simplified if it did not require atomising air [Ma06].

In general, AdBlue® vaporisers benefit from being coated with porous, only slightly acidic substances with a great surface area (titanium dioxide, mixed oxides on a titanium dioxide basis) [Ja90,93]. **Figure 9** shows how coating the vaporiser surface has a positive effect on the prevention of the Leidenfrost phenomenon and hence on the rate of evaporation and decomposition of the AdBlue® droplets [St06c]. An oxide or zeolite coating not only accelerates the hydrolysis of HNCO but also catalyses the urea thermolysis [Zh95].

The use of AdBlue® in urea decomposition can be further optimised by "turbulent" catalyst mixers. This approach reliably prevents the formation of solid urea decomposition products in the exhaust gas system.

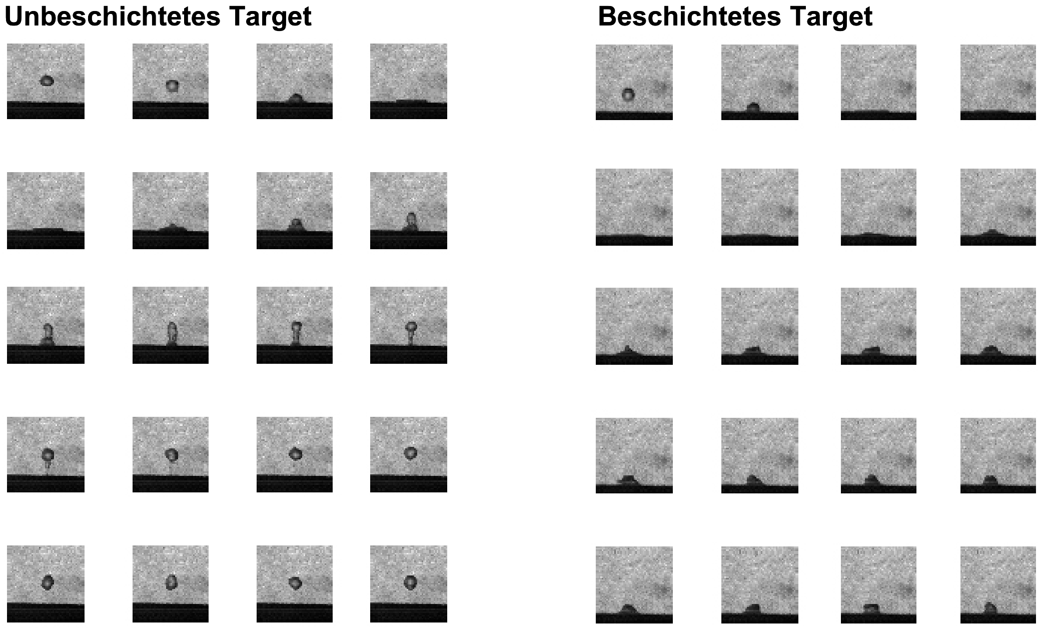

Abb. 9: Einfluss einer Titandioxidbeschichtung auf den Leidenfrost-Effekt bei der Verdampfung von AdBlue®. Bilderserie mit einer Hochgeschwindigkeitskamera bei ~500K [St06c]

Fig. 9: Impact of a titanium dioxide coating on the Leidenfrost effect with AdBlue® vaporisation. Images taken with a high-speed camera at ~500K [St06c]

2.2.3 SCR catalysts (R-catalysts)

2.2.3.1 Summary

Table 2 shows the types of SCR catalysts used in practice with regard to substrate structure, active components and the development stage of mobile applications.

Träger				Entwicklungsstand Aktivkomponenten	
Material	Axialströmung	Radialströmung Durchlässigkeit	Kanalform Zelldichte [cpsi]	VWT	Fe-Zeolith
Metall oder Keramik	"laminar"	geschlossen	glatt 400 oder 600	Serie Nfz (Euro V)	Serie Nfz (JE05) Entw. Pkw
Keramik-Vollextrudat	"laminar"	porös	glatt 300	Serie Nfz (Euro V)	
Metall	"turbulent"	offen	LS/PE 300/600	Entw. Nfz (Euro VI)	Entw. Pkw Entw. Nfz (Euro VI)

Tab. 2: Zusammenstellung verschiedener Typen von SCR-Katalysatoren
Table 2: Configuration of various types of SCR catalysts

Euro V commercial vehicle applications use extruded full catalysts and coated catalysts based on vanadium-impregnated tungsten (“wolfram”)/titanium mixed oxide (VWT type) as the active component. These substrates are usually 230-400 mm long. The maximum operating temperature of the full extrudate is approx. 540°C, whereas VWT-coated catalysts can be stable at temperatures up to 600°C. VWT catalysts are susceptible to poisoning. Additives and contamination in the fuel (incl. the engine oil and AdBlue®) must be minimised, or better still avoided, since their decomposition products have a deactivating effect [Ja01]. Exhaustive model gas tests examining the deactivation of SCR catalysts have identified potassium as a particularly strong catalyst poison [Kr06b]. The most likely source of potassium is first-generation biodiesel. In accordance with European standard EN 14214, biodiesel may contain up to 5 ppm of potassium. If the fuel is of borderline quality the potassium content can reach 150 g or 15 g per 500,000 km depending on whether pure biodiesel or a 10% admixture in conventional diesel is used. This is another reason to speed up the introduction of second-generation, ash-free biofuels.

Catalysts can be shortened by up to 40%, without any adverse effect on conversion efficiency, through the use of “turbulent” LS/PE structures with radial permeability and a VWT coating. The design also optimises flow and concentration equalisation and reduces ammonia slip [Ja06].

A lot of current research focuses on iron-zeolite catalysts in combination with wall-flow DPF to determine their suitability for future developments. The motivation behind this is the iron zeolite’s high activity and selectivity levels at temperatures up to 650°C and their high temperature resistance, which permit operating temperatures of up to 700-850°C depending on the type of structure. They are relatively robust against chemically initiated deactivation.

NO_x emissions from diesel engines typically contain only 2-3% NO_2, the rest is NO. The “standard” SCR reaction

$4\ NH_3 + 4\ NO + O_2 \rightarrow 4\ N_2 + 6\ H_2O$ (equation 1) therefore only takes place on VWT catalysts. By contrast, the catalysis of the “fast” SCR reaction

$2\ NH_3 + NO + NO_2 \rightarrow 2\ N_2 + 3\ H_2O$ (equation 2)

does not only take place on VWT catalysts but also on many vanadium-free, and especially zeolite-based, catalysts at temperatures as low as 200°C.

A detailed summary of the various aspects concerning the development of SCR catalysts for mobile applications is currently being printed [Kr07].

Platinum catalysts are particularly active at low temperatures regarding the reduction of NO_x. However, as shown in **figure 10** their product selectivity with regard to nitrogen is insufficient [Bl92]. The main reaction is based on

$4\ NH_3 + 4\ NO + 3\ O_2 \rightarrow 4\ N_2O + 6\ H_2O$ (equation 3)

and forms unwanted dinitrogen monoxide, a highly effective greenhouse gas. Platinum is therefore not a suitable active component for SCR catalysts.

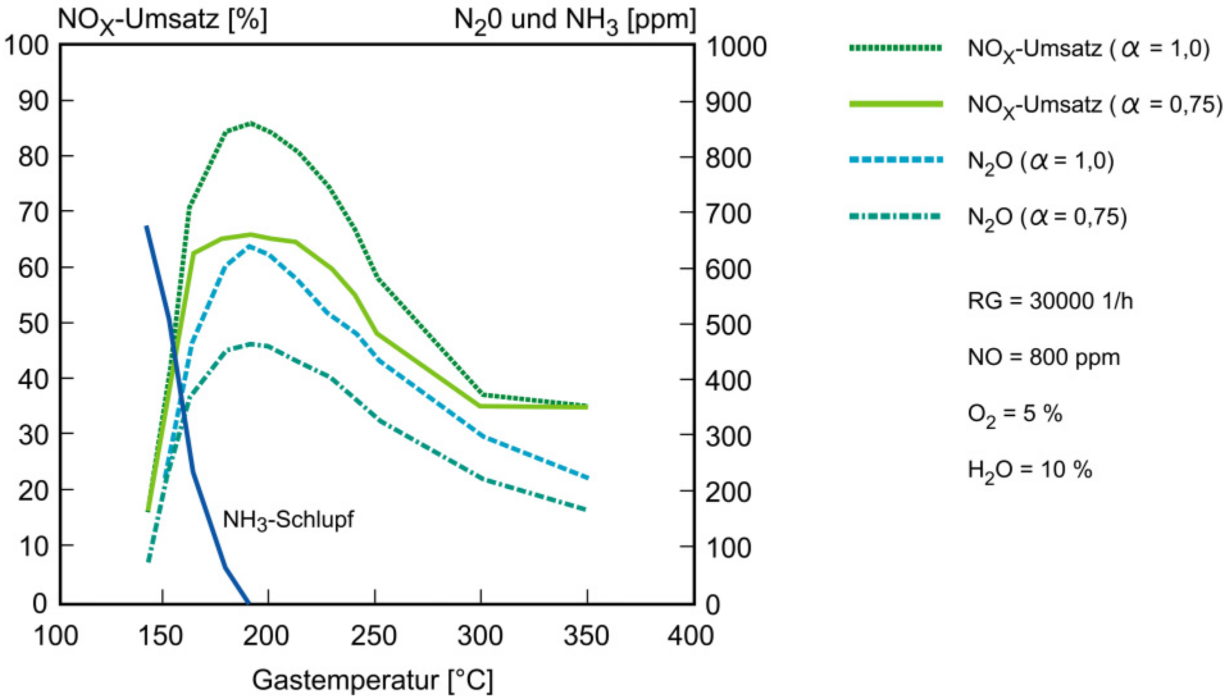

Abb. 10: NO_x-Konversion und N_2O-Bildung an einem Platin-Zeolith-Katalysator [Bl92]

Fig. 10: NO_x conversion and formation of N_2O on a platinum zeolite catalyst [Bl92]

2.2.3.2 “Standard” SCR reaction

A “standard” SCR reaction (equation 1) using VWT catalysts is applied to all Euro V commercial vehicles that are currently in production. Relatively high exhaust gas temperatures between 300 and 450°C often result in conversion rates > 80% [Ja06].

VWT catalysts contain 1-2% vanadium oxide as a minor constituent. At these low concentrations vanadium oxide occurs in a chemical compound with tungsten oxide and titanium oxide and is thus immobilised. This prevents it from sublimating from these mixed oxides at high temperatures. Crystalline divanadium pentoxide is toxicologically classified and is not used in VWT catalysts.

The SCR activity of hydrothermally stable zeolite catalysts, such as Fe-ZSM5, is not sufficient at exhaust gas temperatures < 400°C. However, the activity and selectivity of this type is surprisingly high at temperatures up to 650°C [Kr06a]. Copper zeolites are more active at low temperatures but they are less effective with regard to product selectivity for nitrogen than iron zeolites and are hydrothermally less stable [Kr07].

2.2.3.3 “Fast” SCR reaction

VWT catalysts are highly suitable for the catalysis of “fast” SCR reactions (equation 2) [Ja98, Kö02, Ch06, Ci06]. Among the metal-exchanged zeolites, iron zeolites with an MFI structure (e.g. ZSM5) or BEA (Beta) are particularly suitable.

Compared to the VWT catalyst, the Fe-zeolite provides a wider temperature range for the “fast” SCR reaction based on equation 2. The level of activity of an Fe-zeolite is also higher than that of a VWT catalyst at higher NO_2 shares [De06].

2.2.3.4 NO_2 SCR reactions

At an NO_2 content > 50% of NO_x the “fast” SCR reaction (equation 2) is accompanied by the following reaction on the SCR catalyst:

$6\ NO_2 + 8\ NH_3 \rightarrow 7\ N_2 + 12\ H_2O$ (equation 4)

This reaction consumes 25% more reducing agent than the SCR reactions based on equations 1 and 2. It is slower on the VWT catalyst than the “fast” reaction and slower than even the “standard” SCR reaction (equation 1) [Ko01]. Only a minor reduction of the reaction rate was observed on the Fe-zeolite [Kr07].

The formation of ammonium nitrate during the reaction between NO_2 and NH_3 on catalyst surfaces at temperatures < 200°C based on

$2\ NO_2 + 2\ NH_3 \rightarrow [NH_4NO_3] + N_2 + H_2O$ (equation 5)

is of particular interest. This reaction was observed at a very early stage [Kö92], but only Koebel’s research [Kö01] was able to explain this reaction in every detail. At temperatures > 200°C ammonium nitrate on the VWT catalyst surface is broken down by NO:

$[NH_4NO_3] + NO \rightarrow N_2 + NO_2 + 2\ H_2O$ (equation 6)

When combining the reactions based on equations 5 and 6 that take place separately one arrives at the “fast” SCR reaction based on equation 2. The latest research [Ch06, Ci06] confirms Koebel’s work (for a summary see [Kr07]). In order to minimise the ammonium nitrate deposits on the catalyst surface, formed on the basis of equation 5, the operating temperatures of SCR catalysts should be regularly raised above 200°C. Any ammonium nitrate that forms despite this is decomposed according to equation 6.

2.2.4 Oxidation catalysts

2.2.4.1 Pre-oxidation catalysts (V-catalysts)

V-catalysts contain only platinum as the active component. Thanks to their NO oxidation activity they increase the NO_2 content of NO_x. This is what makes the “fast” SCR reaction (equation 2) and the practical application of iron zeolite catalysts possible in the first place.

NO oxidation activity is limited by mass transfer (diffusion through the stagnant thin film of gas) and in “laminar” catalyst substrates increases with the exhaust gas speed in the channels. This means that cigar-shaped catalysts are more active than disc catalysts with the same volume. However, the “cigars” suffer from an accordingly higher level of pressure loss. “Turbulent” substrates, e.g. LS/PE, offer an elegant solution to improving mass transfer since any increase in pressure can be offset by shortening the substrate.

The light-off behaviour of NO oxidation catalysts also depends on the NO concentration in the exhaust gas. At a temperature of 200°C a model catalyst, for example, is able to achieve a conversion rate of approx. 45% at 100 ppm of NO, at 1,000 ppm this figure is only 10% under otherwise identical conditions [De04].

At higher sulphur concentrations the sulphation of the washcoat inhibits the NO oxidation activity of V-catalysts. Therefore V-catalysts must be used with sulphur-free diesel (S<10ppm). Area-wide availability in the EU will be guaranteed by law from 2009. The start of production of SCR systems with V-catalysts should be set to coincide.

The long-term stability of the NO oxidation activity in V-catalysts presents a particular problem and stands in contrast to the excellent long-term stability of HC and CO oxidation catalysts. The catalyst industry is currently busy working on improvements. An average concentration of 50% NO_2 in NO_x with long-term stability should be obtained through the use of Fe-zeolites.

2.2.4.2 Ammonia oxidation catalysts (O-catalysts)

An online dosing algorithm may lead to excessive quantities of reducing agent being dispensed over a short period. In this case O-catalysts are used to prevent ammonia emissions while permitting high NO_x conversion rates even at load changes during a few cycles of the engine. Ammonia can be subjected to relatively selective oxidation to form nitrogen on platinum catalysts in pulse mode and in the absence of NO_x. At temperatures < 420°C, N_2O is formed on the basis of equation 3 in the presence of NO_x. Selectivity is supported by the catalyst's disc-shaped geometry. The impregnation of the outlet side of the VWT-type SCR catalyst with approx. 0.2% platinum over a length of 10-15 mm is an elegant and cost-effective way of producing O-catalysts. The volume of the O-catalyst should not exceed 7-8% of the volume of the R-catalyst. The design of O-catalysts must also take account of the fact that direct NO_2 emissions caused by an increase in the NO_2 content of the remaining NO_x must be prevented.

Product selectivity for nitrogen at a level of 35-55% was specified for another type of O-catalyst [Hü06].

2.3 Systems for commercial vehicles

2.3.1 Engine-internal measures

It is possible to meet NO_x emission limits up to 2 g/kWh with state-of-the-art technology by using every available engine-based measure. The current minimum level is 1 g/kWh of NO_x, which can be achieved in future engines by a combination of high EGR, two-stage turbocharging and high injection pressures if fuel consumption is to remain competitive [Lä06]. Since the sum of all NO_x emissions from mobile applications is not appreciably affected by the introduction of emission limits below 1 g/kWh by 2020, the only acceptable reason for the implementation of this technology would be air quality [Ja05a]. On the other hand, the emission limits for Euro VI that are currently being discussed [Hö04] will have to be aligned with EPA 2010 limits and be around 0.3 g/kWh and 15 mg/kWh PM. This will make a combination of high EGR and SCR inevitable. The advantage of such a low limit lies in the great opportunity to put an end to further reductions in emission limits and to promote global harmonisation of emission reduction technology.

2.3.2 Engine-external measures

Figure 11 shows the NO_x/PM trade-off of emissions from a common rail test engine with two-stage turbocharging, a high EGR and high injection pressure. The necessary NO_x conversion rate for SCR aftertreatment is given for an NO_x limit of 0.3 g/kWh depending on NO_x emissions from the engine. The graph clearly shows that an NO_x reduction of 80% corresponds to engine PM emissions of 35-40 mg/kWh. A PM-METALIT® partial flow filter whose efficiency has been improved to 75-80% is able to reduce emissions to below a PM limit of 15 mg/kWh. A reduction in the average catalyst load of 6-8 g/kWh of NO_x (Euro V) to a maximum of 2 g/kWh and a reduction in the exhaust gas flow through EGR can help to achieve these high conversion rates with long-term stability. Map-controlled thermal management ensures that the optimum temperature range for exhaust gas aftertreatment (250-450°C) is reached in high-EGR engines. The consumption of reducing agent is reduced by a factor of 3-4 while the range of the vehicle can be increased by the same factor.

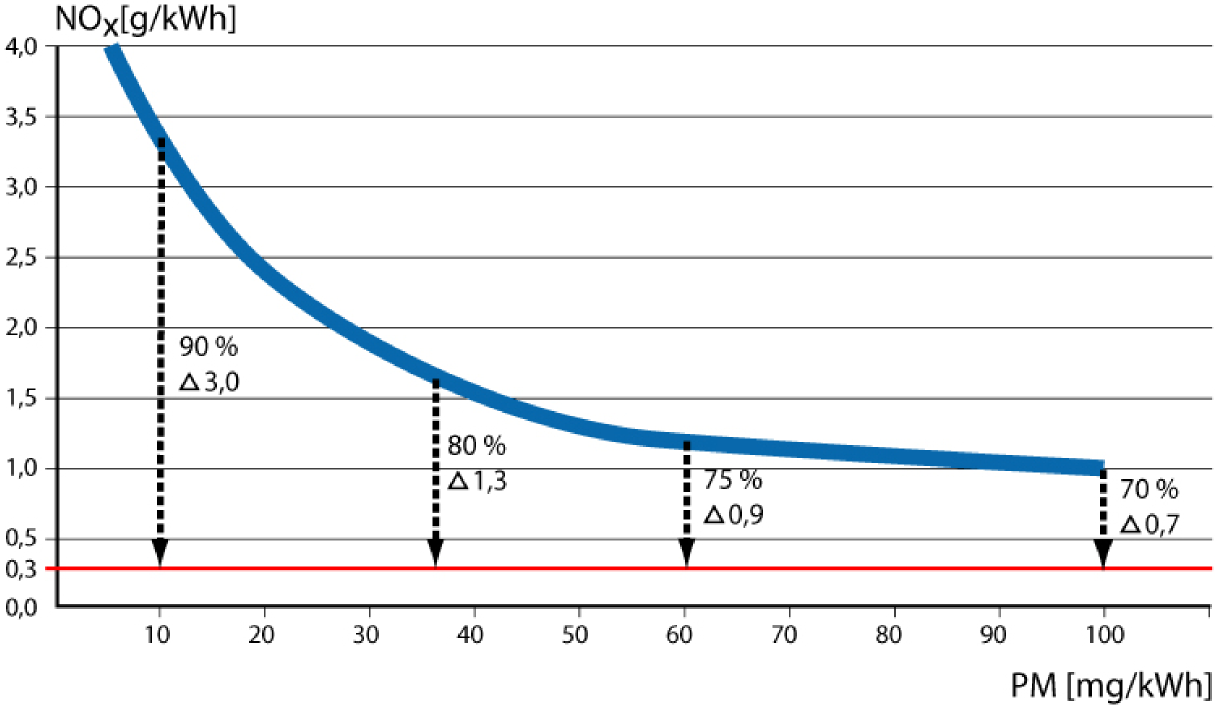

Abb. 11: NO_x-Konvertierungsgrad für eine NO_x-Emission von 0,3 g/kWh als Funktion der Motorabgasrohemissionen

Fig. 11: NO_x conversion rate for NO_x emissions of 0.3 g/kWh as a function of exhaust gas raw emissions

Figure 12 shows a setup of a simple combination of SCR and PM filter systems that complies with Euro VI limits. Here, the setup of the PM filter differs fundamentally from previous setups (e.g. see [Hü05, Lä06, Mu06]). A V-catalyst increases the NO_2 content of NO_x to a maximum of 50% in a close-coupled pre-reactor with parallel catalysts, while on the H-catalyst the injected AdBlue® is decomposed to form ammonia in the exhaust gas partial flow, which amounts to approx. 20% of the main flow. In the main silencer an uncoated, continuously operating PM METALIT® filter is located upstream from the SCR catalyst. Because of its chemisorbed ammonia content the soot deposited on the PM filter is oxidised more quickly by NO_2 and O_2 compared to pure soot. NO_2 and ammonia are able to coexist at higher temperatures in a diluted state without catalyst contact. **Figure 13** shows the chemical reactions taking place in this V/H-PR system. More precise measurements on this system are currently being carried out using the test bench and measurement setup shown in **figure 14**.

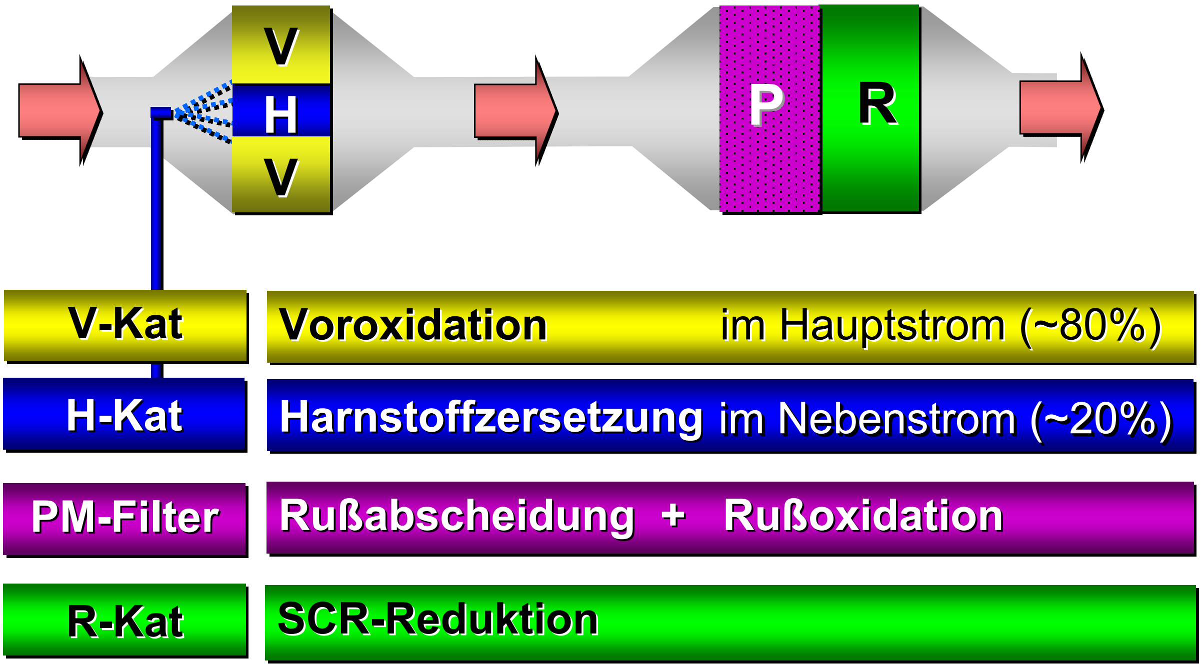

Abb. 12: Aufbau und Reaktionen: V/H-PR-System

Fig. 12: Setup and types of reaction: V/H-PR system

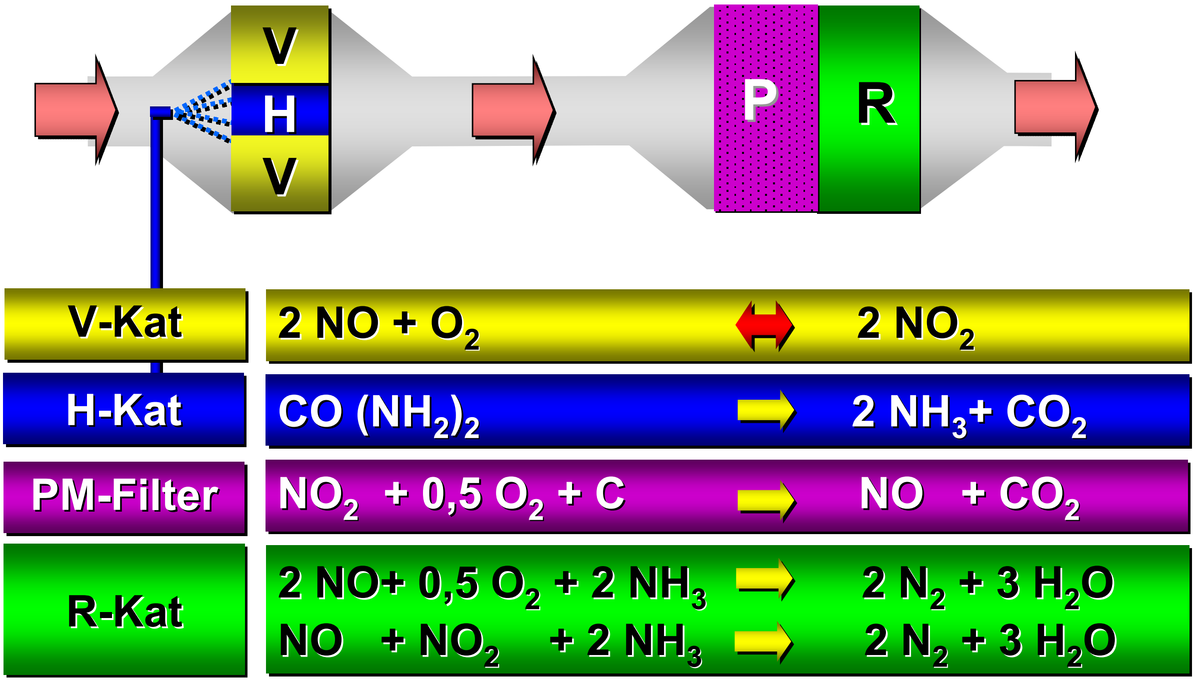

Abb. 13: Chemische Reaktionen im V/H-PR-System
Fig. 13: V/H-PR system: Chemical reactions

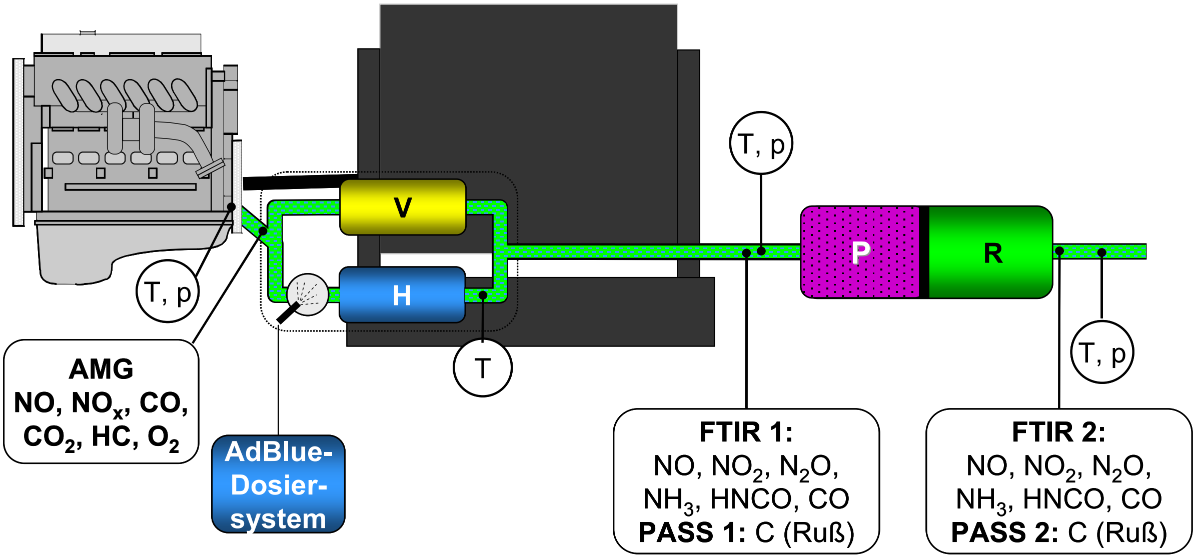

Abb. 14: Prüfstandsaufbau und Messtechnik
Fig. 14: Test bench setup and exhaust gas analyser techniques

Figure 15 shows a vehicle version of this of modular V/H-PR system that can be used in US 2010 and EuroVI applications.

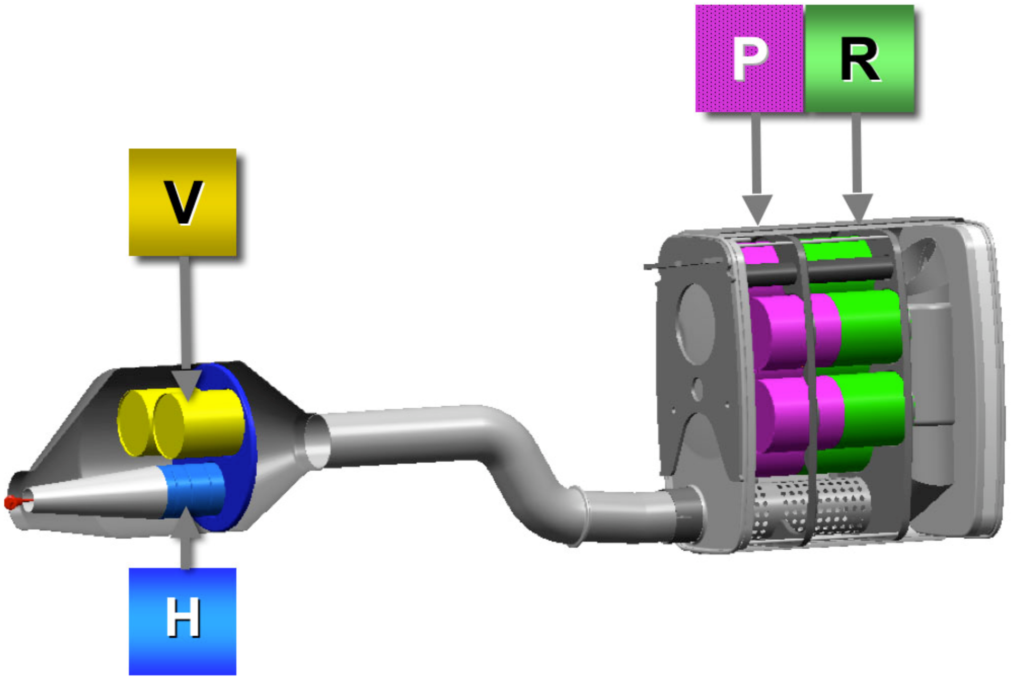

Abb. 15: V/H-PR-System in Fahrzeugausführung (Fa. RTA)
Fig. 15: V/H-PR system for use in commercial vehicles (Fa. RTA)

This system can also consist of individual substrates rather than modular systems. Depending on flow conditions the mixing effect of the individual substrate can be applied more efficiently than that of a modular system to the homogenisation of the exhaust gas and reducing agent.

When comparing several small catalysts (e.g. 4 x ∅ 150 mm) to a correspondingly large individual catalyst (∅ 356 mm) with the same end face, a modular system is more expensive with regard to substrate production, handling and coating [Al06].

A Euro VI SCR system does not necessarily require a downstream ammonia slip catalyst (O-catalyst) since the ammonia feed concentrations are 50% lower than those in a Euro 5 system. By choosing the correct activity and size of the R-catalyst it is possible to ensure that NO_x reduction takes place only on the R-catalyst. This prevents the formation of N_2O on the O-catalyst, which occurs under a permanent ammonia load. For example, the use of an 8.5-litre zeolite catalyst and a 5.7-litre O-catalyst in a 13-litre commercial vehicle engine [Hi05] is extremely likely to lead to significant N_2O formation on the O-catalyst.

2.4 Systems for cars

In Europe engine-based measures are used to ensure that car diesel engines meet Euro 4 limits. A future Euro 5 limit of 200 or 180 mg NO_x/km already presents a great technical challenge to engine developers. It is currently impossible to achieve any further reductions in Europe since SCR systems for cars will not be widely available before 2010. The first systems are expected to be launched in 2008 [Vd06]. Engine-based measures and SCR exhaust gas aftertreatment will have to be combined in order to meet the so far strictest NO_x limits of 50 mg/mile in the US while maintaining acceptable consumption levels (tier II bin 5). The widespread application of diesel particulate filters in cars eliminates the traditional conflict of objectives between NO_x and PM, however, this is replaced by a conflict between NO_x and fuel consumption. The use of an SCR process to reduce NO_x is a solution that can preserve the fuel consumption advantages of diesel engines.

Engine-based measures to reduce NO_x (preferably a combination of low-pressure EGR and alternative combustion processes in a low-load range) should be sufficiently effective to ensure that a realistically achievable SCR exhaust gas aftertreatment conversion rate of 70-80% is adequate to meet tier 2, bin 5 limits [Bü06].

Together with a reduction in engine size the combination of DPF and SCR technology maintains acceptable fuel consumption levels while complying with very low NO_x emission limits (80 mg/km). **Figure 15** shows a combined DPF/SCR system developed by FEV. The exhaust gas passes through the DPF system, which consists of oxidation catalyst V and particulate filter P, then through the AdBlue® vaporiser and mixer H and subsequently through SCR catalyst R. The axial arrangement between the AdBlue® nozzle and the inlet tube of the R-catalyst, which facilitates the homogenisation of AdBlue®, is a notable feature [Kö06]. DaimlerChrysler's Bluetec® system, which is currently being developed, has a similar setup [En06, Sc06, We06]. Both systems dispense with an ammonia slip catalyst (O-catalyst).

By contrast, an SCR system proposed by Ford uses an inverse arrangement with the DPF system located behind a VR catalyst assembly [Te04]. The disadvantages of this system include an additional pre-oxidation catalyst V and the potential formation of N_2O if the R-catalyst in the DPF system is too small or aged, since the DPF system also functions as an extremely active, but not nitrogen-selective, O-catalyst.

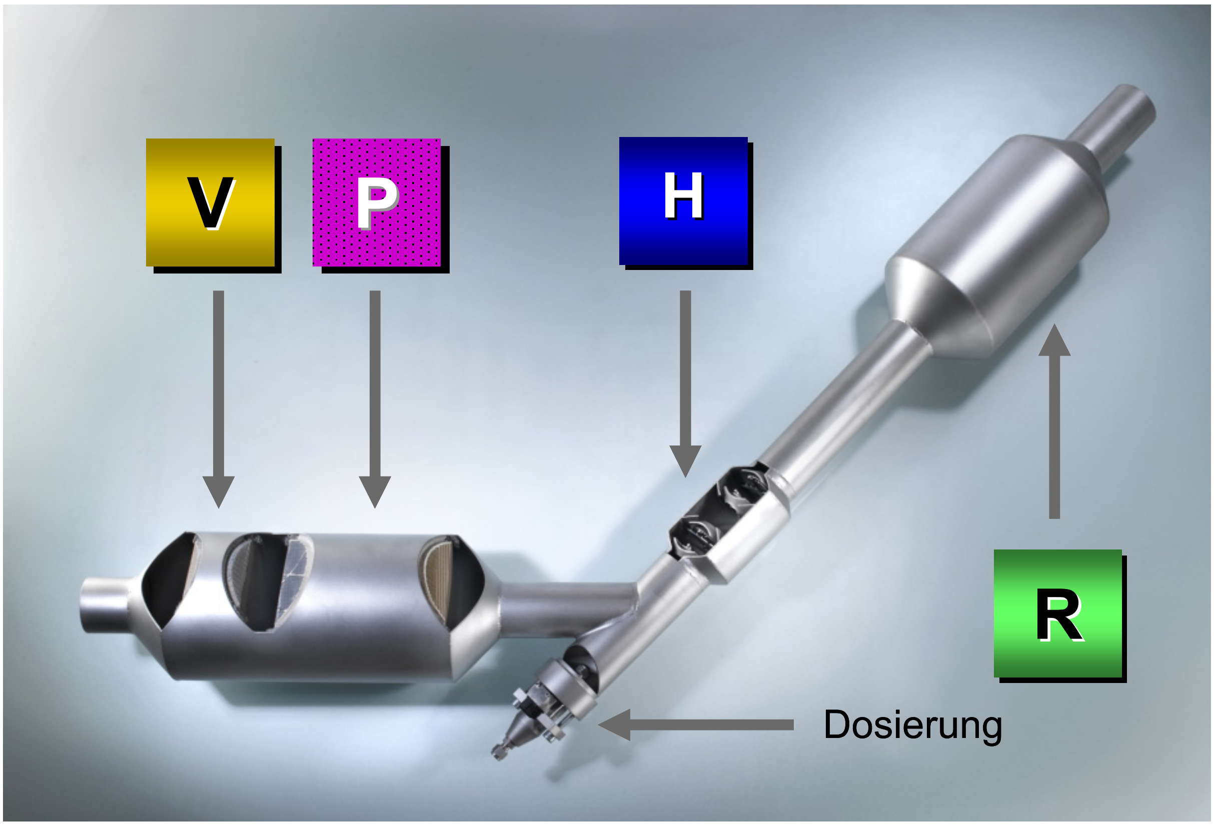

Abb. 16: VPHR-System (Kombination von DPF und SCR) für die Anwendung beim Pkw-Dieselmotor [Kö06]

Fig. 16: VPHR system (combination of DPF and SCR) for diesel engine application [Kö06]

Cold start efficiency presents a particular challenge to SCR processes in cars. Heating the V-catalyst is an important factor in achieving the light-off temperature of the V-catalyst (approx. 200°C) as quickly as possible in order to increase the NO_2 content of the NO_x to an optimum of 50% and ensure the evaporation/decomposition of AdBlue®. This makes it possible to reach an NO_x conversion rate of over 80% at a temperature of 200°C. Guaranteeing the system's high cold start efficiency over its entire life is another great challenge. At this point it is worth thinking about engine-based measures.

The potential of SCR exhaust gas aftertreatment for DI petrol engines with spray-guided fuel mixture generation at the spark plug and lean combustion is the subject of current research.

2.5 A comparison between commercial vehicle and passenger car systems

Future technology will be based on a dramatic reduction of NO_x formation in the engine and so significantly lower the specific catalyst load with NO_x and urea. This will enable the systems to comply with the very low NO_x limits in future. The introduction of engine-internal NO_x reduction through high-EGR will bring SCR technology for commercial vehicles in line with that for passenger cars. **Figure 17** shows a comparison between catalyst loads of commercial vehicles and cars with regard to NO_x conversion in SCR systems. The catalyst load is based on the number of engine-internal EGR measures to reduce NO_x and the limit value stages and corresponds to AdBlue® consumption. AdBlue® consumption of EuroV commercial vehicles with non-EGR engines is expected to be 5-6% of fuel consumption, which will be reduced to 1-2% in EuroVI vehicles, which is the figure for passenger cars.

Another positive effect of reducing catalyst loads is a higher NO_x conversion potential [Kr07] and a lower risk of ammonia slip.

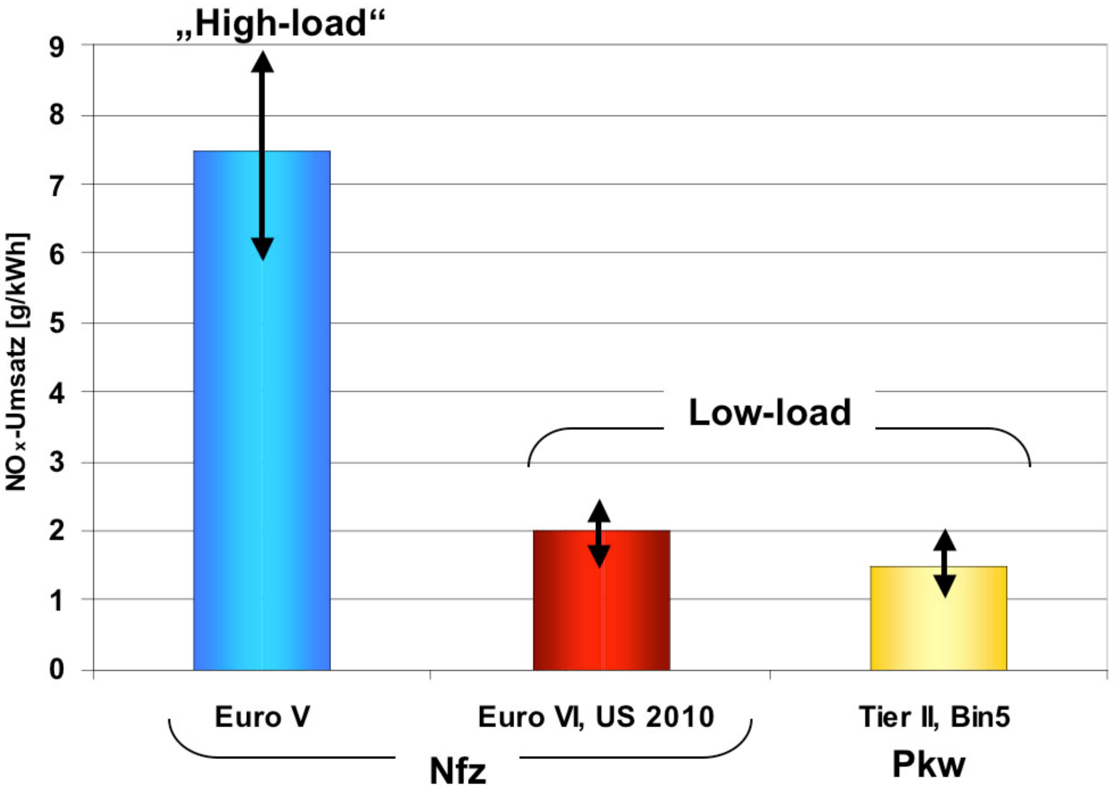

Abb. 17: Vergleich der SCR-Katalysatorbelastung bei Nfz und Pkw in Abhängigkeit vom Einsatz der AGR und der Grenzwertstufe

Fig.17: High and low load SCR at CV and cars

3 Conclusion and future prospects

Innovative combustion processes involving engine-internal NO_x and PM reduction will become as important in commercial vehicle engines as in lean-running car engines in order to limit the complexity of aftertreatment systems by reducing exhaust gas, NO_x and PM emissions. On the other hand, the performance of exhaust gas aftertreatment systems has to be increased to meet the growing requirements of European and international legislation. The answer lies in both a conflict-free functional coordination of the integrated solutions, consisting of engine-internal and post-engine measures, and an improvement in fuel quality. The prevention of discontinuous processes in exhaust gas aftertreatment should be one long-term aim to reduce complexity, fuel consumption and costs.

The potential orientation of Euro VI limits for commercial vehicles towards EPA US 2010 limits opens up opportunities for the promotion and worldwide harmonisation of new technologies and an end to further reductions in emission limits. With respect to SCR technology this is associated with a significant fall in reducing agent consumption, an increase in the conversion rate due to a reduced catalyst load and harmonisation with car exhaust gas aftertreatments.

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