

COMPACT CATALYTIC CONVERTER SYSTEM FOR FUTURE DIESEL EMISSIONS STANDARDS

The Euro 6 emissions standard for diesel passenger cars will result in a further rise in the use of NO_x storage catalytic converters or exhaust aftertreatment systems that use selective catalytic reduction. In both cases, this will mean a further increase in the volume and complexity of the exhaust aftertreatment system. BASF has developed a compact integrated catalytic converter that combines the functions of particulate filtration and NO_x reduction in a single unit.



AUTHOR



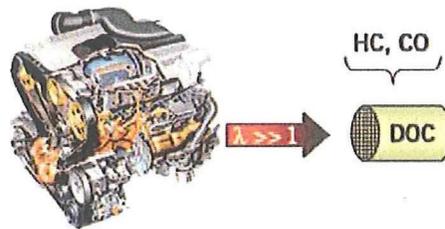
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**INCREASING REQUIREMENTS FOR
THE CATALYTIC CONVERTER SYSTEM**

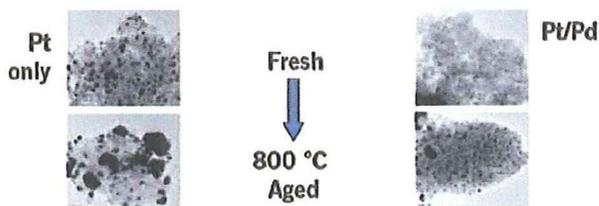
Over the last several decades, advances in environmental catalyst technologies have contributed significantly to reducing tailpipe emissions from combustion engines. At present, a modern catalytic system is capable of converting more than 95 % of the carbon monoxide (CO), hydrocarbons (HC), nitrogen oxides (NO_x) and soot present in the exhaust gas to carbon dioxide, water and nitrogen gas. While future environmental regulations will require further reductions of these harmful emissions, combustion engine development is driven by the need for higher fuel efficiency and less production of carbon dioxide. These trends will demand further continuous performance improvements of the catalytic exhaust gas treatment system. In this article, the development of catalytic systems is explained by the example of diesel passenger cars.

**CATALYTIC COMPONENTS FOR
DIESEL EXHAUST GAS TREATMENT**

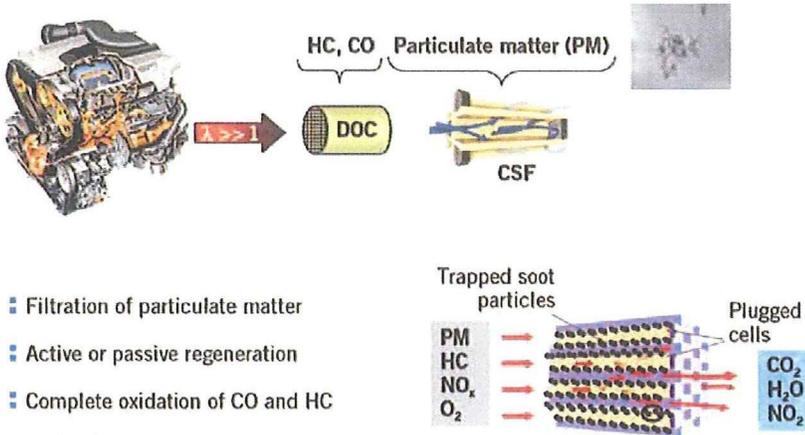
The primary function of the diesel oxidation catalyst (DOC), ①, is to completely oxidize hydrocarbons and carbon monoxide in the exhaust gas to carbon dioxide and water. In specific applications, the DOC is also expected to partially convert nitrogen oxide (NO) to nitrogen dioxide (NO₂). A stable concentration of NO₂ can be used to oxidize soot on a catalytic soot filter (CSF) or to promote NO_x



- Complete oxidation of carbonmonoxide (CO) and hydrocarbons (HC)
- Stable NO₂ formation
- Precious metal particles (Pt or Pt-Pd) with high thermal stability



① Diesel oxidation catalyst (DOC)



- Filtration of particulate matter
- Active or passive regeneration
- Complete oxidation of CO and HC
- Stable NO₂ formation

② System of DOC and CSF

conversion over the selective catalytic reduction (SCR).

The active components of a DOC coating are small precious metal particles of Pt and Pd supported on high surface area inorganic oxides (e.g. alumina). The DOC washcoat may also contain components like zeolites to better manage the conversion of hydrocarbons during cold start.

In addition to the architecture of the washcoat, the size, composition and matrix of the precious metal particles play a crucial role in reliable DOC performance under real driving conditions. Utilizing the broad experience in catalysis and material science, BASF has developed a broad portfolio of high performance DOCs for different applications. These DOCs can be further tailored to specific customer applications.

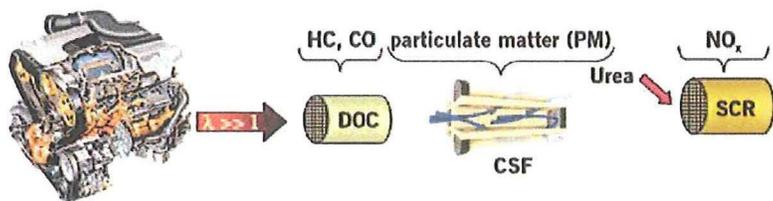
Early emission regulations for light duty diesel vehicles could be met with a single DOC plus engine control adjust-

ments. At that time, the volume of the DOC was comparable to the engine displacement volume. Recently, filter elements (CSF) have been added to diesel vehicles to prevent soot-particles from getting to the atmosphere, ②. In contrast to flow-through substrates of conventional vehicle catalysts, the channels of a filter substrate are blocked at alternating ends. This forces the exhaust gas to flow through the porous wall of the monolith. Soot particles are retained and accumulated in the filter until a critical pressure drop across the filter element triggers an active regeneration. Regeneration occurs when extra fuel is combusted over the DOC and the resultant heat ignites of soot in the filter. This extra fuel is injected either into the combustion chamber or directly into the exhaust gas upstream of the DOC.

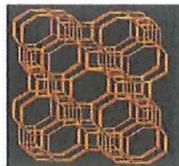
In addition to this active regeneration principle, passive regeneration systems

can currently be found in heavy duty diesel vehicles. The soot retained in passive systems undergoes continuous oxidation by the NO₂ produced by the upstream DOC. In addition, the filter itself may contain catalytic components. Common coatings comprise precious metals, which – in analogy to DOC – ensure complete oxidation of CO and HC as well as a stable formation of NO₂.

The two leading technologies for controlling NO_x emissions are lean NO_x traps (LNT) or selective catalytic reduction catalysts (SCR), ③. Each uses a reducing agent for the conversion of NO_x to nitrogen gas. The LNT uses partially combusted diesel fuel and the SCR uses ammonia as the reducing agent. Ammonia is usually produced by the decomposition of urea on board the vehicle. Incorporation of these NO_x abatement components into the exhaust gas treatment system adds significant volume and com-

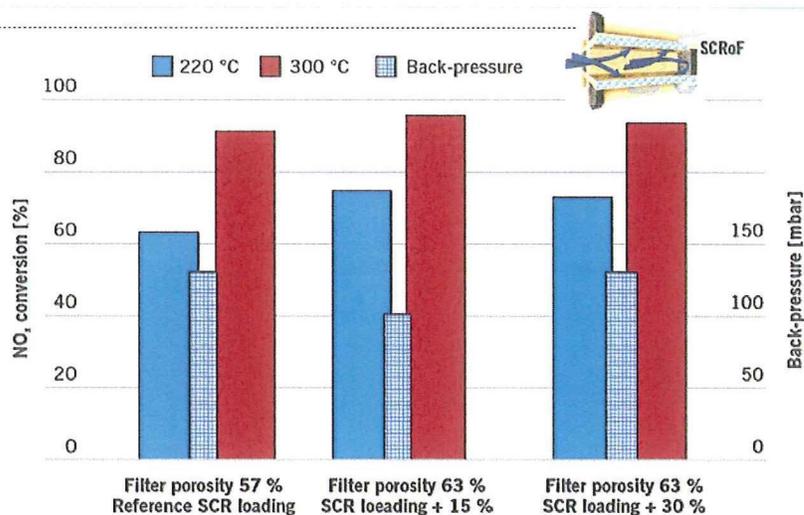


- Reduction of NO_x by ammonia (NH₃):
 $NO + NO_2 + 2NH_3 \rightarrow 2N_2 + 3H_2O$
- Ammonia produced by on-board hydrolysis of urea
- Metal-zeolites (e.g. Cu-chabazite) with high activity and stability



③ System of DOC, CSF and SCR

④ DeNO_x performance and dependence of backpressure on filter-porosity and SCR material loading



plexity to the emission control system.

For light duty diesel applications the SCR catalyst consists of a Cu or Fe containing zeolite. Typical zeolites are Fe-beta and Cu-chabazite. Cu-chabazite exhibits an excellent low temperature activity, a broad temperature window of activity and superior high temperature stability. In addition, an ammonia oxidation catalyst may be used downstream of the SCR to prevent ammonia slip. Systems of this type are already in use for heavy duty applications. They require sophisticated control of timing of CSF regeneration cycles and an active urea dosing strategy. For light duty applications, systems with smaller volume requirements and less complexity are highly desired.

INTEGRATED CATALYST

The increasing complexity of catalytic systems for vehicles with diesel engines is a driving force to develop smart and less complex systems for the future. Here, the trade-off between complexity and cost reduction on one side and the requirements to meet current and future emission regulations on the other side must be balanced.

A possible approach to simplification is to integrate CSF and SCR function in one component and place the active mass of the SCR catalyst on the filter substrate of the CSF. This integrated catalyst is in the following called SCR on Filter or just SCRoF. For such an SCRoF component there are complex requirements. To achieve on the one hand a high NO_x conversion level, particularly

in the aged state, SCR-active materials with very high intrinsic activity are required. At the same time it is desirable to accommodate the highest possible amount of these active compositions in the pores of the filter substrate. However, here limits are set by the maximum pressure loss, a filter component may have. On the other hand, filters with low porosity are preferred for the safe control of all particulate matter emissions and the compliance of small so-called soot mass limits.

Therefore SCRoF applications require filter substrates with tailor-made porosities which overcome this conflict. In addition to the filter porosity, the catalytic material and the coating process are of critical importance. For use as an integrated system, such as a close coupled position, the dosage and the thermolysis of urea and the regeneration concept must also be addressed.

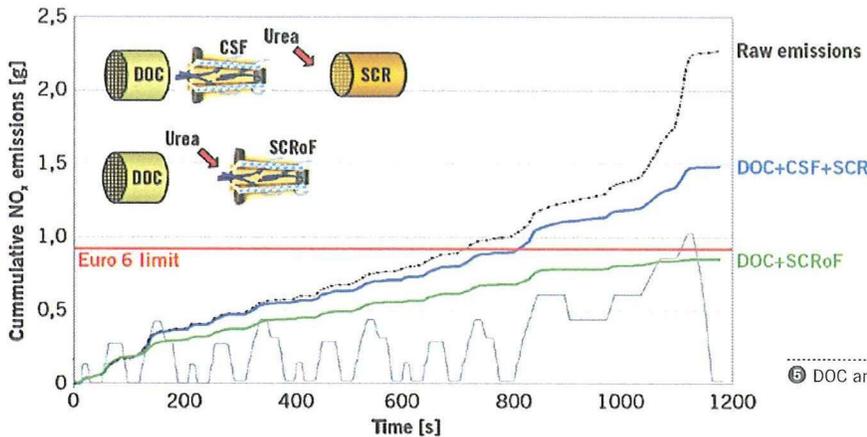
④ shows the possibilities that open up the use of filters with optimized porosity. Shown are the measured NO_x conversion levels in stationary engine tests for catalysts with different porosity and active mass loading. This evaluation was carried out at BASF's engine laboratory in Hanover. A filter substrate with a medium porosity of 57 % and a standard SCR catalyst loading served as reference. The use of filters with higher porosity (63 %) leads to a lower initial back-pressure and enables to increase the SCR loading by 15 %. This results in an increase of at least 10 % points versus the reference. A further increase of SCR catalyst mass on the high porosity filter does not lead to an addi-

tional increase in NO_x conversion under the chosen stationary conditions.

The filtration efficiency was also evaluated. Because of the close-coupled design of the system, there was no significant adverse effect observed with the SCRoF. Even with the higher porosity of the filter, the soot-mass regulation (4.5 mg/km in the Euro cycle) and the limit for the soot particle number ($6 \cdot 10^{11}$ /km in the Euro cycle) could be met.

An important method for evaluation of catalyst systems remains the transient evaluation on the vehicle. Several transient cycles were studied for SCRoF. The performance in the European Driving Cycle (NEDC), the U.S. light duty cycle (FTP72 and US06), and other cycles (e.g. WLTP) was evaluated. It turns out that the exact system design is an important element for performance optimization. It is important that a high-performance DOC has a very fast light-off and ensures complete oxidation of CO and HC as well as stable oxidation of NO. In addition, because of the extremely close-coupled location of the DOC, it has to be thermally stable. The DOC developed by BASF met the limit for CO (500 mg/km in the Euro cycle) after aging for 16 h at 800 °C. A significant improvement was achieved for the NO oxidation behavior as well. The deterioration of the NO oxidation could be significantly reduced.

The Euro 6 limit values for NO_x (80 mg/km in the Euro driving cycle) can be met with a SCRoF system on a vehicle even under difficult testing conditions, ⑤. In this example, the average NO to NO₂ ratio was 25 % (as opposed to



⑤ DOC and SCRoF system can meet Euro 6 NO_x limit

the optimum of about 50 %). This constraint was deliberately chosen to push the boundaries of the system and also to differentiate the ability of next generation DOC to work with SCRoF catalysts. Only an optimized DOC and an optimized SCRoF were able to meet these limits. With this optimized system, a significant improvement was observed compared to the classical system composed of DOC, CSF and SCR.

The new generation DOC and SCRoF catalyst system was also evaluated on the U.S. cycle. The NO_x conversion observed was >85 % and the requirements of Tier2 Bin5 were met. Additional performance improvement can be achieved when a small SCR catalytic converter is used under the floor (downstream of the SCRoF). The catalyst volume of this SCR part was 50 % of the SCRoF component.

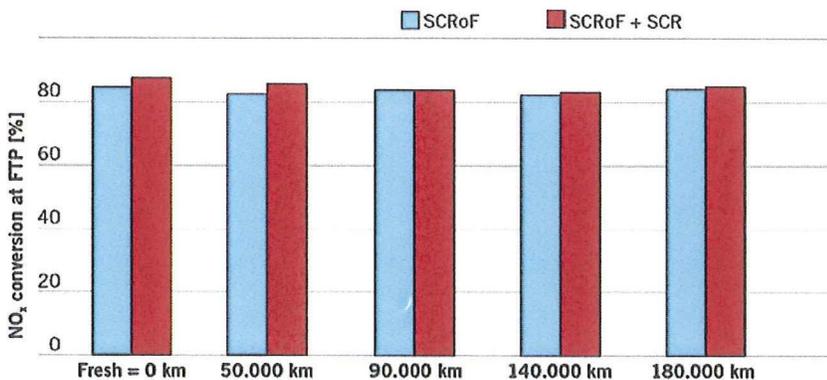
This additional SCR increased NO_x conversion to more than 90 %.

DURABILITY

An important and crucial development goal for SCRoF catalyst systems is the durability, ⑥. The U.S. test cycle (FTP72) was chosen. Similar results were obtained under steady state and in other transient cycles (e.g. NEDC). In this test, the components were loaded with soot and regenerated under engine conditions. This process was repeated more than 220 times to mimic realistic end-of-life conditions for the catalysts. Over an equivalent mileage of 180,000 km, no significant deterioration of the NO_x conversion was observed. This result clearly underlines the robustness of the SCRoF system developed by BASF.

CONCLUSION

BASF has developed a new smart catalyst technology based on the broad know-how in catalysis and materials research. This new compact system comprising an SCRoF is able to meet stringent emission requirements.



⑥ Cycle aging were conducted on engine bench with full system (soot loading on filter and soot filter regeneration every 800 km)
 Evaluation in Hannover engine lab after described mileage with full system
 DeNO_x activity is very stable over long term durability

⑥ DOC and SCRoF thermal durability