

High Porous SiC for Future SCR-F Solutions

Thomas Wolff,

Dinex GmbH – Dinex Emission Technologies, Bayreuther Str. 9, D-95482 Gefrees, Germany

Abstract: The current concepts for Euro VI exhaust after treatment solutions are combinations of a diesel particle filter (DPF) with a catalyst for selective catalytic reduction (SCR) separated on two different substrates. Reduction of costs and space are the driving factors for the development of combined systems where the SCR functionality is integrated into the DPF, so called SCR-F systems. Off-road applications according to Stage IV are mainly build up without a DPF, but the possible introduction of a maximum allowed particle number (PN) per kWh in future legislation scenarios leads also to developments of SCR-F systems. Beside the main challenges for catalysts for SCR-F solutions like their temperature stability, resistance against hydrocarbons and sulfur and their possible influence on the soot oxidation the most important need is a high porous filter substrate at a porosity level of 60% and even higher, which has a sufficient mechanical strength, a reasonable soot load limit and which fulfills the PN efficiency requirements (at least in combination with the catalyst coating) at a back pressure level equal or lower in comparison to the two brick solutions. The aim of this paper is to present a new high porous filter material on the basis of a silicon carbide as a potential candidate for SCR-F solutions. The potential of this material will be shown by test data of uncoated filters and a SCR-F based on a vanadia coating.

Introduction

Wall flow filter DPFs are the established solutions for particle number (PN) reduction up to 99,99% to meet EURO VI regulations. To meet the NO_x emission levels SCR is the established technology. The current concepts for Euro VI exhaust after treatment solutions are combinations of these two technologies separated on two different substrates. The corresponding legislation for Off-Road applications (Tier 4 in the US and Stage IV in Europe) allows, to operate the diesel engines at higher NO_x output levels to keep the PM output under 20mg/kWh. This leads to SCR only solutions, taking care for the NO_x emissions. However, future legislation levels beyond Tier 4 final and Stage IV will also address maximum allowed PN and therefore it is imperative to introduce the DPF technology also in this application field.

Reduction of overall system costs, reduction of space, and reduction of fuel consumption are the main driving factors for future development. First investigations have shown, that the integration of the SCR-catalyst in the DPF is an effective way to fulfill these requirements. *Naseri et al.*¹ investigated a SCR coated DPF with subsequent flow through SCR and found an improved DeNO_x functionality and an optimized passive regeneration at 400°C at a reduced system packaging. *Tan et al.*² demonstrated the reduction of the total exhaust after treatment catalyst packaging by combination of a DPF with SCR functionality also combined with a SCR catalyst which led to a reduction of the SCR volume by 55%. They found, that an equivalent DPF passive regeneration can be achieved at temperature levels of 20 – 30 °C higher compared to cDPF solutions. In both papers the regeneration strategy is passive regeneration and in both cases, the needed temperature for that is with 380 – 400°C relatively high. The used DPF substrate was a cordierite at 59% and 65%. These systems are very sensitive for regeneration and any overload can cause severe damage. Due to *Tan et al.* the coated cordierite at 65% already reached a peak temperature at a soot load of 5.3 g/l in a drop-to-idle test of more than 1000°C, which caused cracks in the filter. For the 59% cordierite these temperatures are reached at 6,8g/l. However, the used Cu-zeolite SCR catalyst was already damaged at 900°C. This indicates, that SCR-F solutions based on cordierite have a very restricted soot load level. To have a better protection of the catalyst itself, silicon carbide can be chosen for the substrate, which has a higher density and heat capacity than cordierite. Examples are given by *Kawakami et al.*³ and *Nakamura et al.*⁴. They both report on high porous SiC structures with an additional coating on the inlet side. These systems will be used for future passenger car SCR-F solutions, where a robust high porosity DPF is needed. But they are also potential candidates for robust solutions in the HDD and off-road sector.

In the following I will report about a new type of a high porous silicon carbide as one candidate for a substrate for future SCR-F systems. This material is an advanced version of a previously presented reaction formed silicon carbide⁵ (see proceedings of 14th ETH conference 2010). The high porosity levels of 55% - 65% allow high wash coat loadings as needed for SCR-F solutions at a level of the specific weight (thermal mass) which is higher than for cordierite. This leads to higher soot load levels. The characteristic pore structure leads to a reduced back pressure under soot load in comparison to classic sintered systems, i.e. the pore structure itself leads to a membrane like behavior of the cell wall.

¹ SAE 2011-01-1312

² SAE 2011-01-1140

³ SAE 2011-01-0843

⁴ SAE 2011-01-0842

⁵ SAE 2010-01-0539

The high porosity SiC and its comparison to R-SiC

A high porosity SiC material for the design of filters with high wash coat loadings was developed on the basis of a reaction formed β -SiC⁶. Further developments based on this material have led to a new type of high porous α -SiC, which shows an improved back pressure performance at similar PN efficiency levels and an enhanced ability to receive high wash coat amounts at low back pressure impact. The characteristic feature of this new high porous SiC is, that its three dimensional structure is build up only by small plate like hexagonal crystals, which are directly derived from a reaction formed β -SiC structure by a temperature treatment below 2000°C. Figure 1 shows a direct comparison of such a high porous structure to a low porosity structure created by a recrystallization of α -SiC grains. Figure 2 shows an enlarged portion of the high porosity structure of figure 1. It can be seen, that the cell wall is build up by small plate like crystals leading to a high surface area. In contrast to that, the structure of the classic recrystallized SiC is defined by the form of the sintered particles, caused by the grinding process of the original used SiC raw powder.

Table 1: Some characteristic data of the high porous DiSiC_{HP}

	56% DiSiC _{HP}	60% DiSiC _{HP}	65% DiSiC _{HP}	42% DiSiC
*Specific weight, g/l	600	550	510	740
*bending strength, MPa	11	7	5,5	21
CTE (RT – 800°C), K ⁻¹	4,7	4,7	4,7	4,7
therm. heat cond. 400°C, W/mK	4,2	~ 3,5	2,2	11
spec. heat capacity 400°C, J/gK	1,002	< 1	< 1	1,25

*based on a 200cps / 16mil cell design

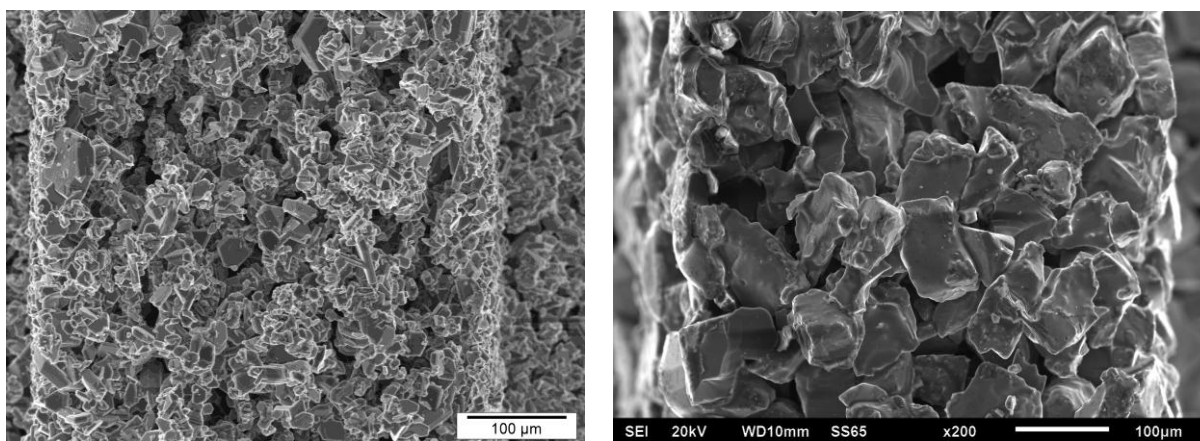


Figure 1: DiSiC_{HP} with 65% porosity (left) and a DiSiC with 42% porosity (right)

In table 1 some characteristic data of the high porous material in comparison to a recrystallized SiC are listed. Of course the increase in porosity leads to a reduction in the mechanical strength, the heat conductivity and heat capacity. But all these parameters will be changed or affected by the subsequent high wash coat loading. The low specific weight at a heat conductivity, which is still 2 - 4 times larger than that of a cordierite at 50% porosity, makes this material also interesting for applications with large filter volumes, where today mainly cordierite is used.

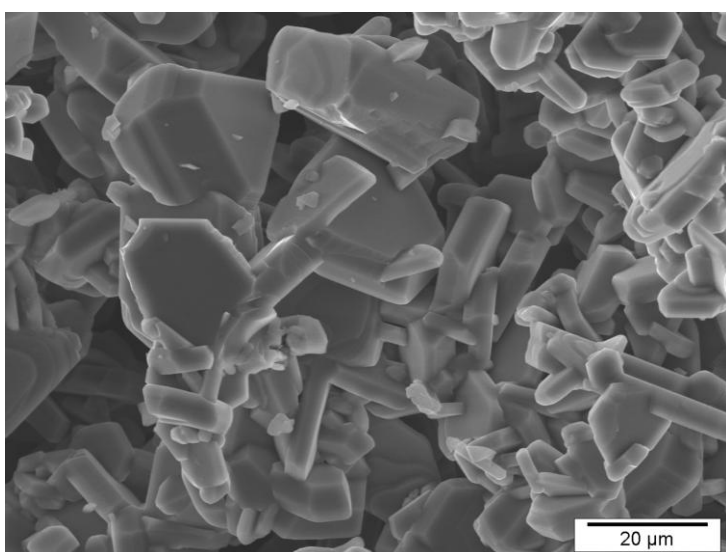


Figure 2: plate like crystals in DiSiC_{HP}

SCR – Coating

The 65% material is currently in use for the adaption of different type of catalyst coatings for DeNO_x functionality. In a first approach the influence of a vanadia based catalyst coating on the performance of this material was investigated. This was done first on single

⁶ EP 1741685 A1, US 7648932 B2, US 7867313 B2, EP 1741687 B1

honey comb elements and subsequently on complete filters. In figure 3 an electron microscope picture is shown of a SiC with 65% porosity coated with an amount of 119g/l of a vanadia based wash coat. The direct comparison to figure 2 shows, that the catalyst is well distributed over the inner surface of the pores and the textured surface is smoothed by the coating. The connecting or transition pores are not blocked. The analysis

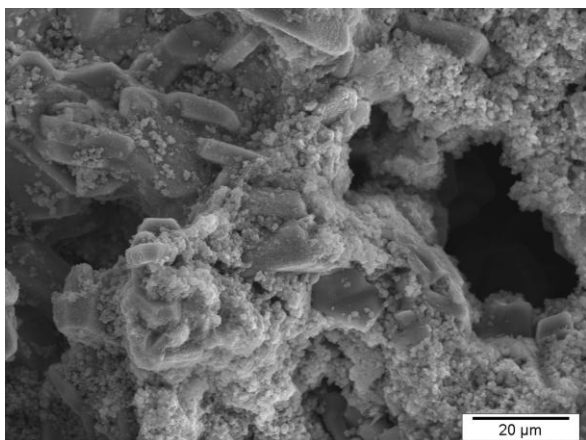


Figure 3: Vanadia based catalyst on a 65% DiSiC_{HP}. The loading level was 119g/l.

with mercury intrusion porosimetry before and after coating shows a reduction from 65% to 49% in porosity and a change from 23μm to 18μm in the mean pore diameter. The corresponding impact on back pressure on a filter with the size of 5,66" in diameter and 8" length is described in the next section.

Investigation of basic performance and SCR efficiency under soot load

To investigate the basic performance of this high porous material a number of filters have been tested. These filters are listed in table 2. Filter #5 is a commercial available cordierite filter. Filter #2 and #3 are coated with a vanadia based wash coat as described in the previous section.

Table 2: Investigated test filters

	cpsi / mil	D x L	porosity	pore diameter	Remark
#1	200 / 16	5,66"x8"	56%	23μm	DiSiC _{HP} uncoated
#2	200 / 16	5,66"x9"	65%	26μm	DiSiC _{HP} uncoated / V2O5 – 117g/l
#3	200 / 16	5,66"x8"	65%	17μm	DiSiC _{HP} uncoated / V2O5 – 100g/l
#4	300 / 12	5,66"x7"	59%	16μm	DiSiC _{HP} uncoated
#5	300 / 12	5,66"x7"	59%	17μm	Cordierite uncoated

In a first test the back pressure was checked on a cold flow test rig (Superflow SF-1020). After that filter #1, #4, and #5 have been tested on an engine test bench with a Mercedes Benz VM R425 engine with a Horiba T250 dynamometer. After a back pressure test of the fresh filters at different loading points they have been loaded under three ESC test cycles to a soot load level of 4g/l while recording the PN with a CPC from TSI. Filter #2 and #3 have been tested using an OM 904 engine from Mercedes Benz, whereas filter #2 was tested in respect to back pressure, soot load and SCR efficiency under soot load and filter #3 only for back pressure unloaded. This filter is thought to be used for further tests. For the SCR efficiency test of filter #2 an airless urea doser from Emitec was used.

The results of the cold flow test have shown an impact of the vanadia coating on the back pressure at 600 std. m³/h of 25% for the 117g/l coating of filter #2 and only of 15% for the 100g/l coating of filter #3. In the direct comparison of the two uncoated filters with 59% porosity, the cordierite filter #5 shows a slightly better performance than filter #4, which can be explained by the reduction of filter surface area by the seaming layers in filter #5.

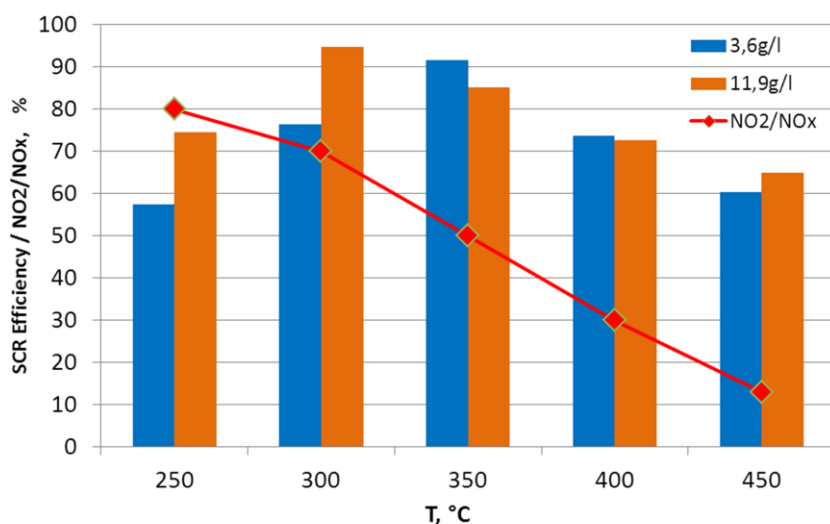


Figure 4: SCR efficiency for filter #2 for two different soot load levels together with the corresponding NO2/NOx ratio.

The results of the engine bench tests of the uncoated fresh filter have shown a PN efficiency of 85% for the filter with large pores (56% and 200cpsi) and more than 90% for the filter with smaller pores (59% and 300cpsi). After two ESC test cycles the 200cpsi filter shows more than 99,9% PN efficiency, the 300cpsi filter ends up at 99,5% which can be explained by the higher porosity level. The direct comparison of the 59% DiSiC_{HP} to the cordierite filter with the same porosity level and cell density shows a similar performance in the PN

efficiency, but a difference in the back pressure under soot load. The slight advantage in back pressure of the cordierite filter disappears already at a very low soot load and at a soot load level of 4g/l the cordierite filter has a more than 50% higher back pressure than the corresponding DiSiC_{HP}. This can be explained by the fact, that the plate-like crystals of the DiSiC_{HP} filter build a more dense structure at the surface of the cell wall in comparison to classic sintered structures, leading in a stronger surface filtration.

The SCR efficiency of filter #3 was tested at different soot loads with and without a DOC in front of the filter. Due to the high soot emissions of the engine a very low soot load was not possible in this test. The test without DOC (standard SCR) shows a maximum conversion at 350 – 400°C up to 69%. With DOC the conversion rate increases up to 95% and the maximum is shifted to lower temperatures. A direct comparison to the conversion rate of a commercial available flow through vanadia based SCR from Haldor Topsoe, which was tested without DOC, shows, that the SCR performance has to be improved especially for low temperatures. It is obvious, that the used DOC produced too much NO₂ at lower temperatures. A plot of the conversion rates together with the NO₂-content versus the temperature is shown in figure 4. The better SCR efficiency at lower temperatures for the high soot load can be explained by the soot oxidation with a part of the NO₂.

The PN filtration efficiency of the SCR-F was checked only at one operating point at a soot load in the range of 3g/l and it was found to be higher than 99,95%. Due to the high soot emissions of the engine, a passive regeneration was only possible when the urea dosing was switched off.

Conclusions and discussion

A high porous SiC as a potential substrate material for SCR-F solutions was presented. Without any coating this material shows an improved soot load characteristic in comparison to conventional sintered ceramics like cordierite. The high porosity level up to 65% allows SCR coatings in the range of 100 – 120g/l at reasonable back pressure increase.

The used engine in the test of the SCR performance had high soot emissions leading into a fast loading of the SCR-F. Under these conditions it was possible to investigate the SCR efficiency under high soot load, but a parallel passive regeneration was not possible. The usage of a DOC with a high NO₂ production rate demonstrated the importance of an accurate control of the NO₂ content for the functionality of the SCR-F. Based on these first results the following conclusions can be drawn in respect to the design and regeneration of future SCR-F systems:

- The NO₂/NO_x ratio has to be adjusted accurately to realize passive regeneration parallel to a maximum SCR efficiency
- High soot emissions do not allow passive regeneration of a SCR-F
- The soot load on the SCR-F does not affect the functionality of the catalyst. The change in the conversion rate is caused by the NO₂ consumption by soot oxidation.
- vanadia based catalyst loadings in the range of 120g/l together with an optimized DOC can lead to conversion rates of 95% and more. This indicates, that with the current technology most of the SCR functionality can be integrated into the DPF.
- Further optimizations of the coating process (distribution in the cell wall), the catalyst morphology (grain size distribution) and the adaption of both to the pore structure will lead to catalyst loading levels up to 150g/l. This is the potential for the full integration of SCR functionality into the DPF.

Discussion of the further development:

DOC - SCR-F - SCR - CUC: In this system, the major part of the SCR functionality is integrated into the DPF and the remaining NO_x will be converted in a subsequent SCR. At best the regeneration strategy will be passive, but if a passive-only regeneration is not possible (due to the emissions of the engine or the duty cycle of the vehicle), it has to be supported by active sequences. As we have seen, an overloading can cause changes of the NO₂ level at the SCR on the SCR-F and therefore affect the SCR efficiency. A continued overload can cause a stop due to high back pressure or severe damage to the SCR-F.

A complete integration of the SCR functionality into the DPF in the setup **DOC - SCR-F - CUC** makes active regeneration necessary. This would lead to the most cost effective solution and the biggest reduction in space. But to integrate enough wash coat in the filter, a porosity level on the high end side of 65% and even higher is needed, which leads to restricted soot mass limits. And high temperature stable catalysts are needed. Right now, only SiC in combination with Cu-zeolithes ZSM-5 are potential candidates.

High Porous SiC for Future SCR-F Solutions

16th ETH conference
June 24 - 27, 2012



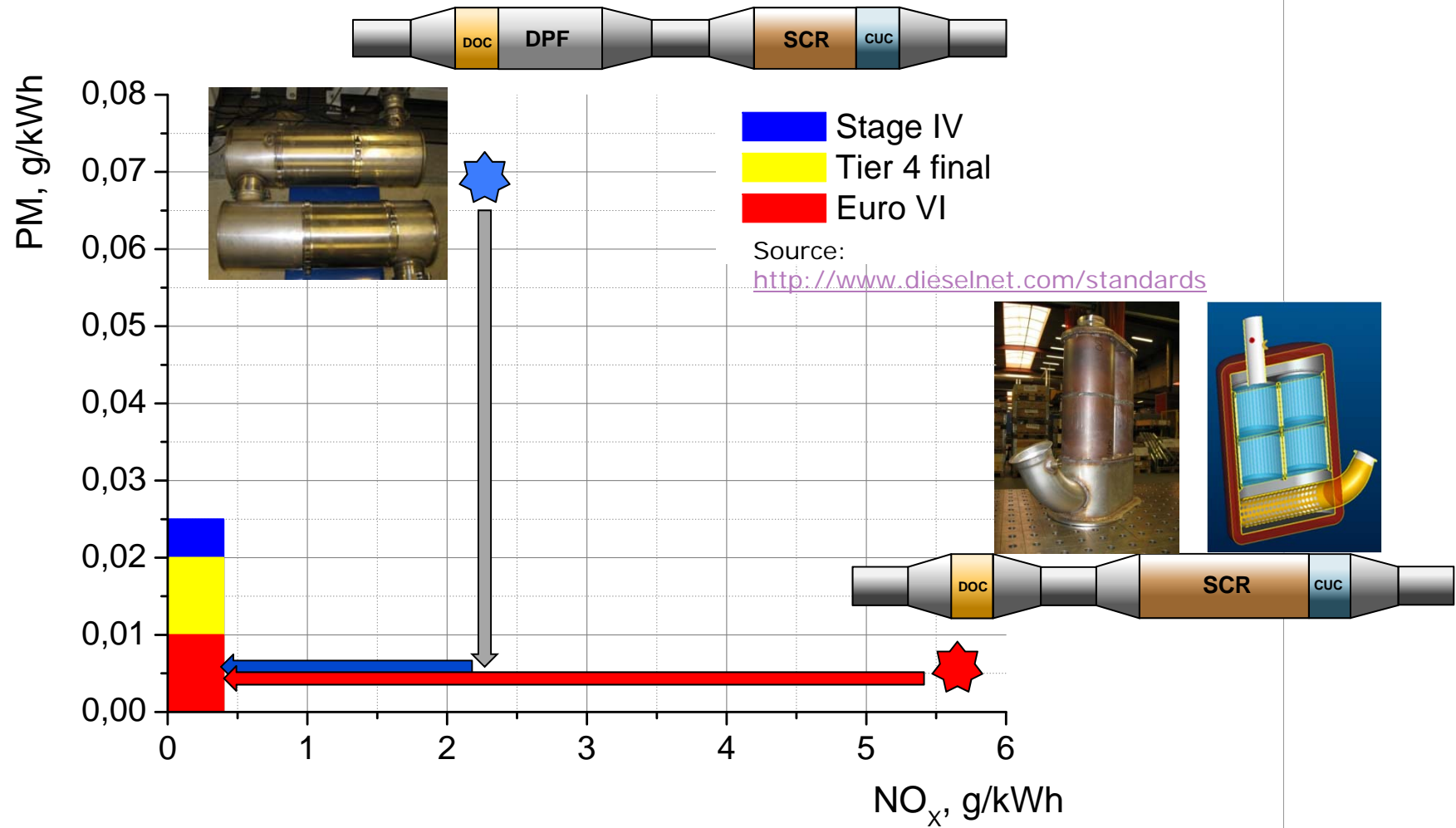
going the extra mile

Outlook

- Market situation & development trend
- High porous material based on reaction formed SiC
- Vanadia based SCR coating
- First test results
- Summary & Discussion



Current Concepts



Ongoing development

- ▶ Space reduction / packaging
- ▶ Reduction of costs
- ▶ Future legislation beyond Tier4F and Stage IV

SAE 2011-01-1312 Naseri et al.
SAE 2011-01-1140 Tan et al.



Reduced SCR size
Passive regen. at 400°C
PN and SCR efficiency meet legislation



used cordierite in SCR-F sensitive to
high temperatures / soot overloading



High porous SiC DPFs in development
SAE 2012-01-0843, SAE 2012-01-0842

Design of a high porous Substrate for SCR integration

- ▶ High porosity level ($> 60\%$)
- ▶ High spec. surface area

- ▶ Good mechanical strength
- ▶ Reasonable soot load limit ($> 5\text{g/l}$)
- ▶ Specific weight not too low
sufficient heat capacity

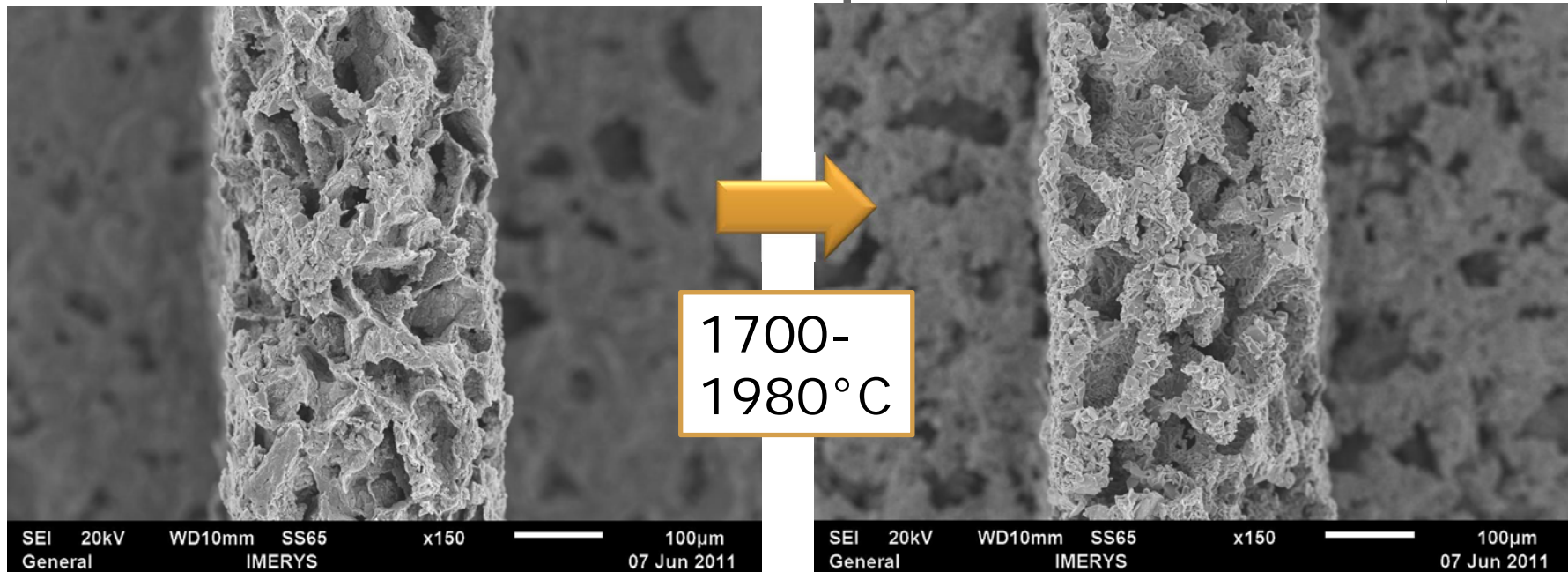
- ▶ High filtration efficiency

High wash coat
for high NO_x
conversion

Robustness and
protection of
catalyst

PN efficiency
requirements

High porous SiC based on reaction formed preform



β -SiC structure

EP 1741685 A1, US 7648932 B2
US 7867313 B2, EP 1741687 B1

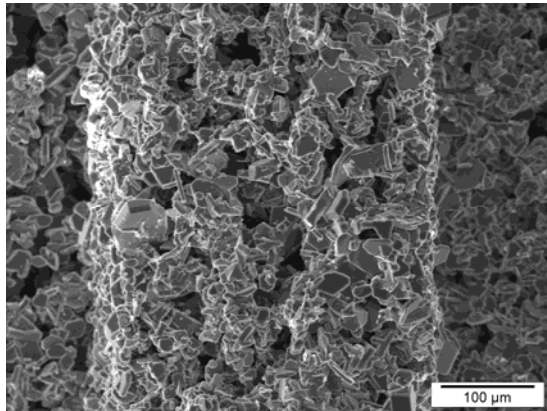
end in α -SiC

patent pending

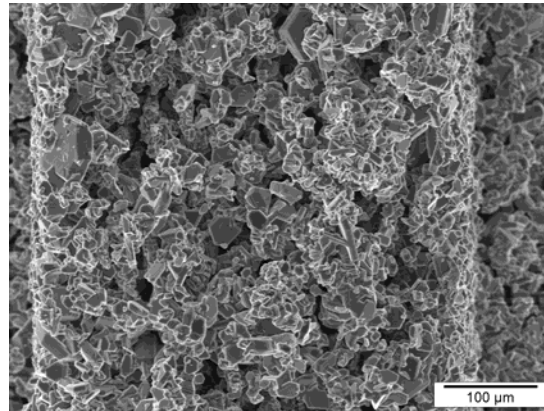


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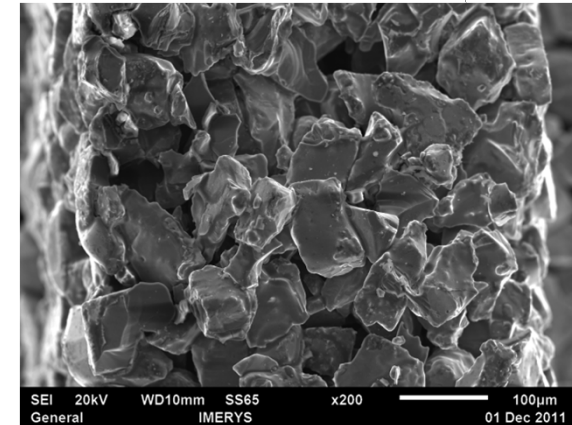
Comparison of Microstructure



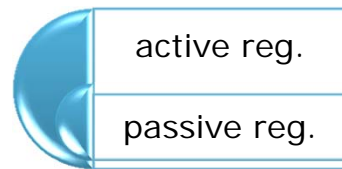
DiSiC_{HP} 55%



DiSiC_{HP} 65%

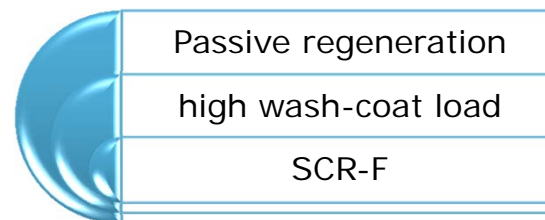


DiSiC - 42%



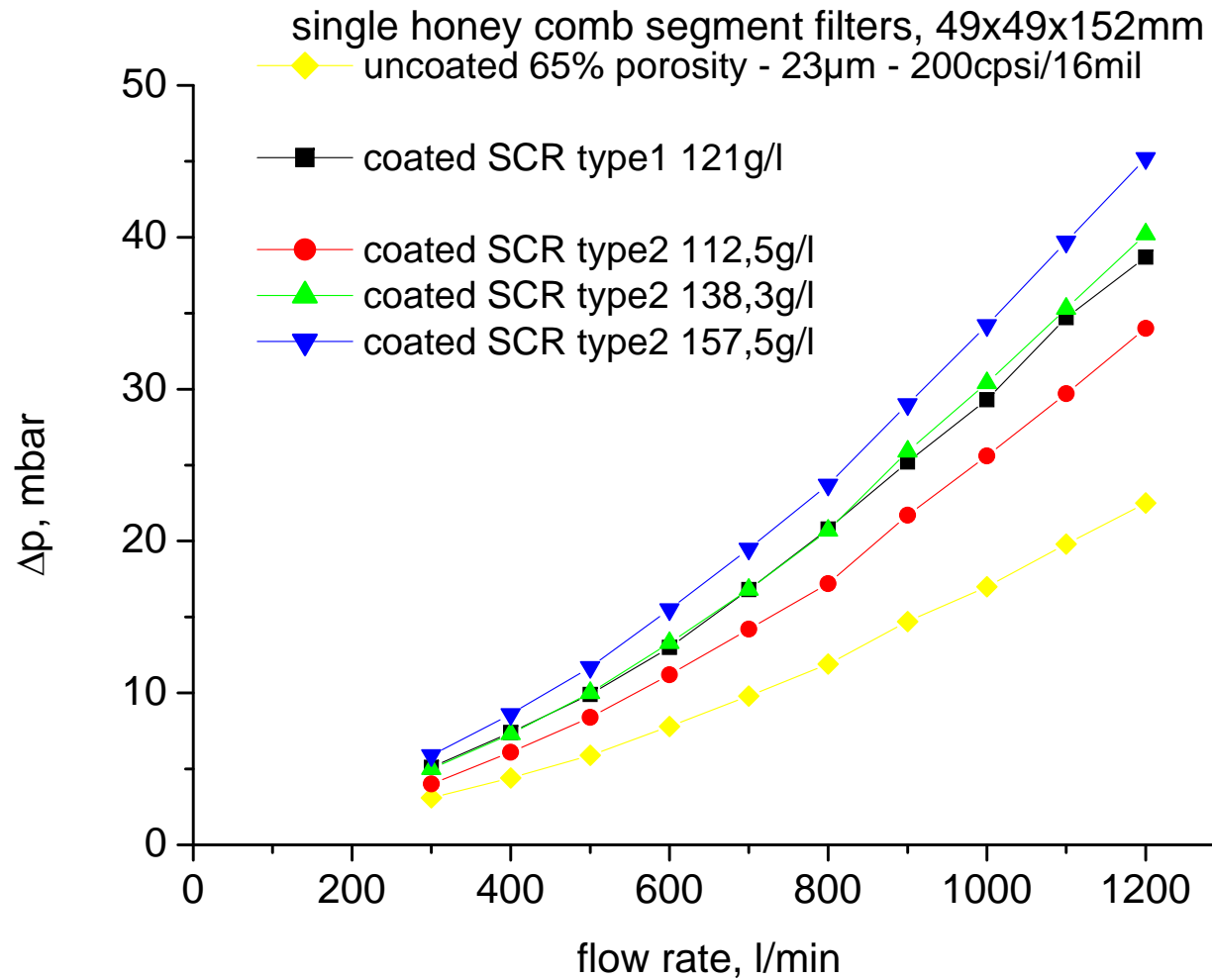
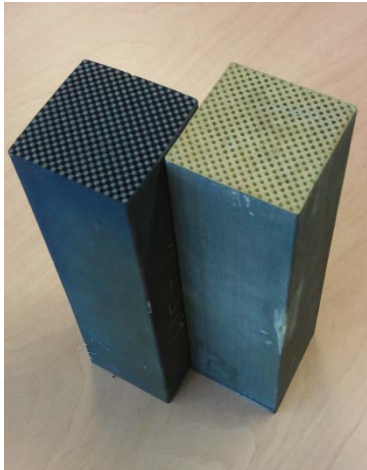
	55% DiSiC HP	60% DiSiC HP	65% DiSiC HP	42% DiSiC
*Specific weight, g/l	600	550	510	740
*bending strength, MPa	11	7	5,5	21
CTE (RT – 800°C), K ⁻¹	4,7	4,7	4,7	4,7
therm. Heat cond. 400°C, W/mK	4,2	~ 3,5	2,2	11
spec. heat capacity 400°C, J/gK	1,002	< 1	< 1	1,25

*based on a 200cpsi

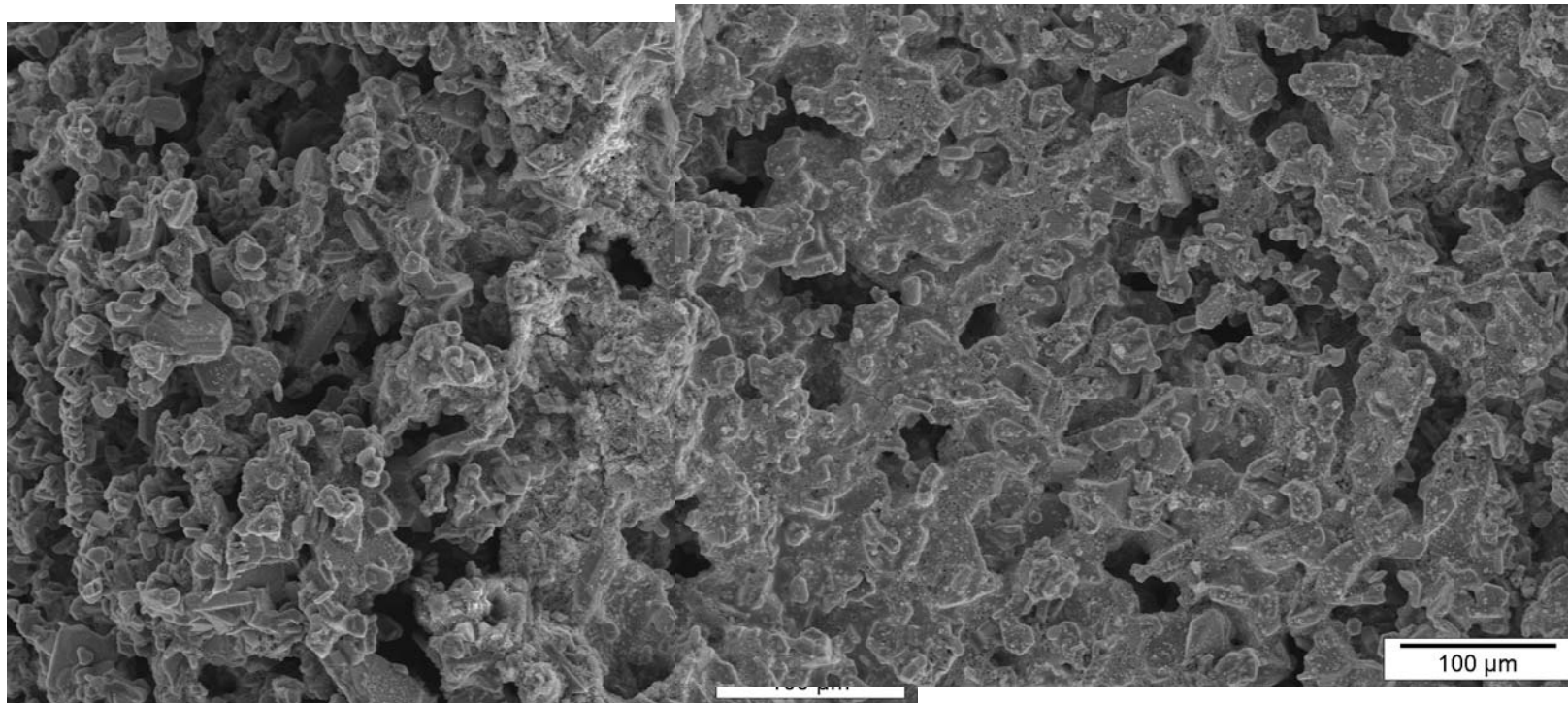


going the extra mile

Vanadia based SCR coating



Vanadia based coating



Cell wall fracture

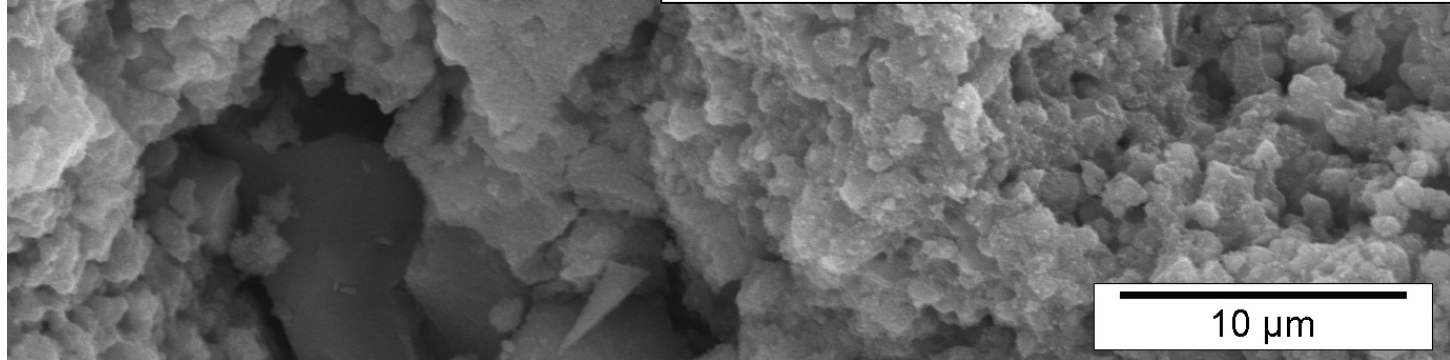
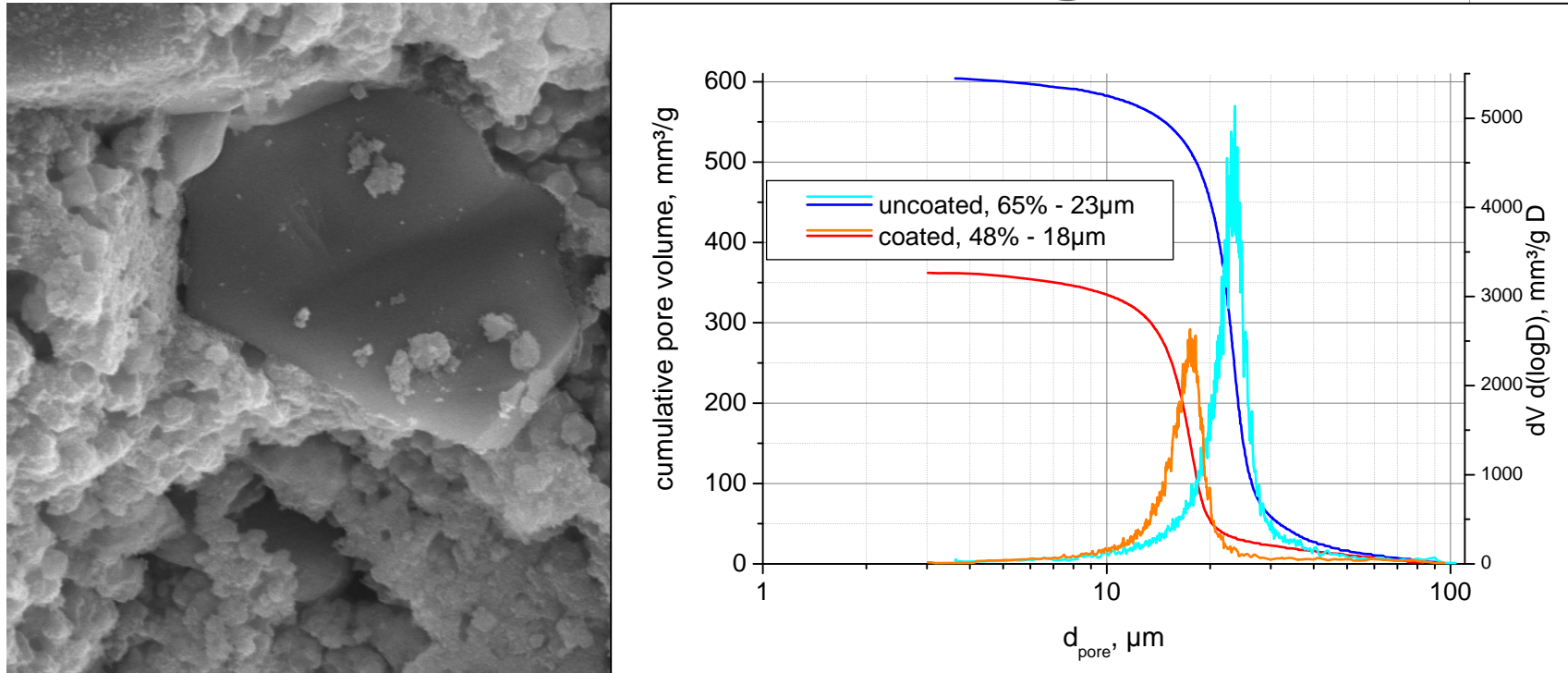


Cell wall surface



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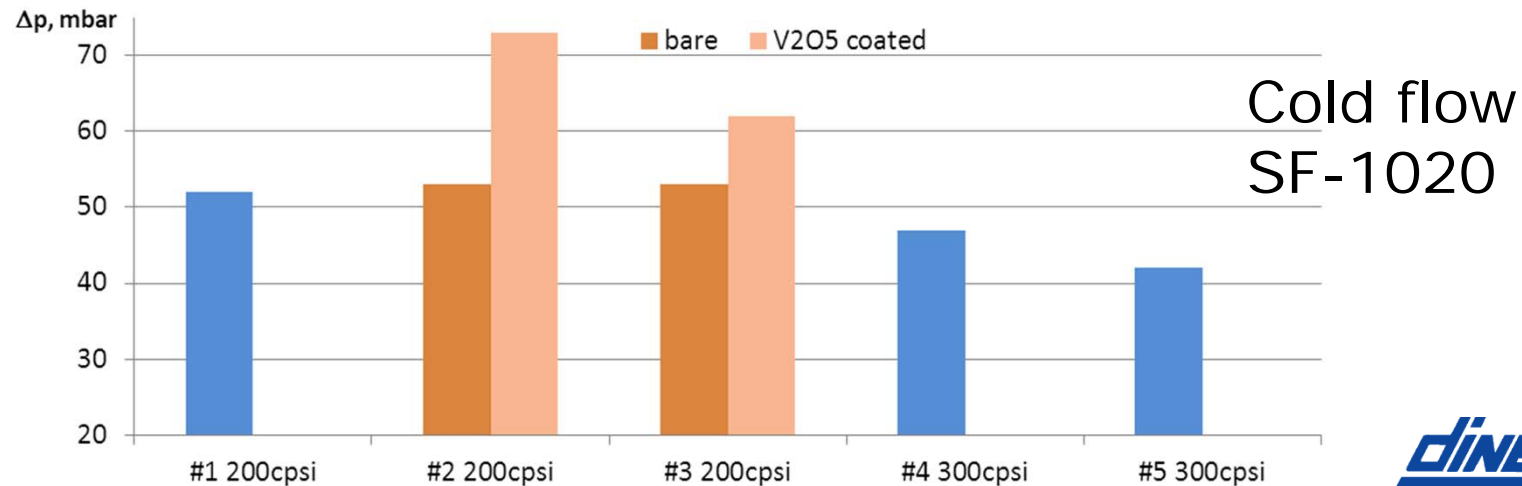
Vanadia based coating



going the extra mile

Performance tests

	cpsi / mil	D x L	porosity	pore diameter	Remark
#1	200 / 16	5,66"x8"	56%	23 μ m	DiSiC _{HP} uncoated
#2	200 / 16	5,66"x9"	65%	26 μ m	DiSiC _{HP} uncoated / V2O5 – 117g/l
#3	200 / 16	5,66"x8"	65%	17 μ m	DiSiC _{HP} uncoated / V2O5 – 100g/l
#4	300 / 12	5,66"x7"	59%	16 μ m	DiSiC _{HP} uncoated
#5	300 / 12	5,66"x7"	59%	17 μ m	Cordierite uncoated



going the extra mile

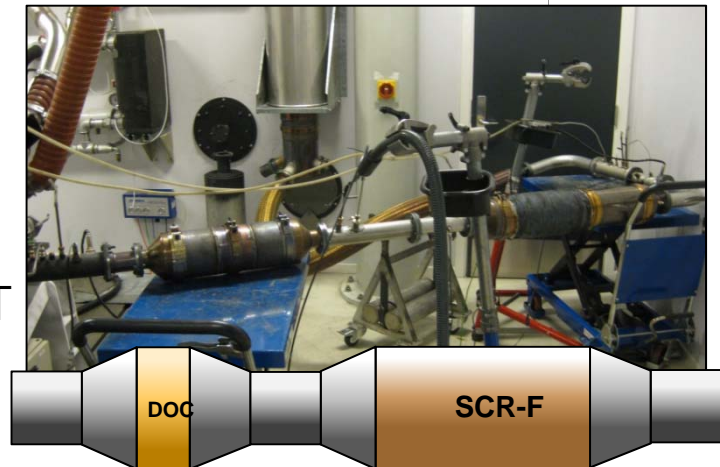
Engine bench tests

Filter #1, #4, #5

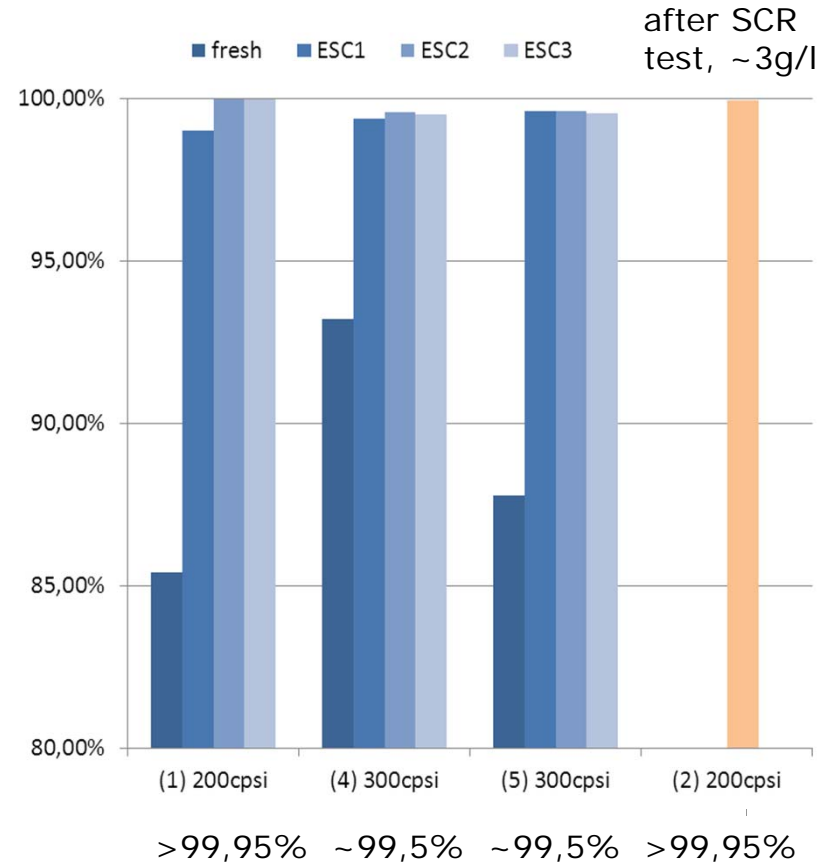
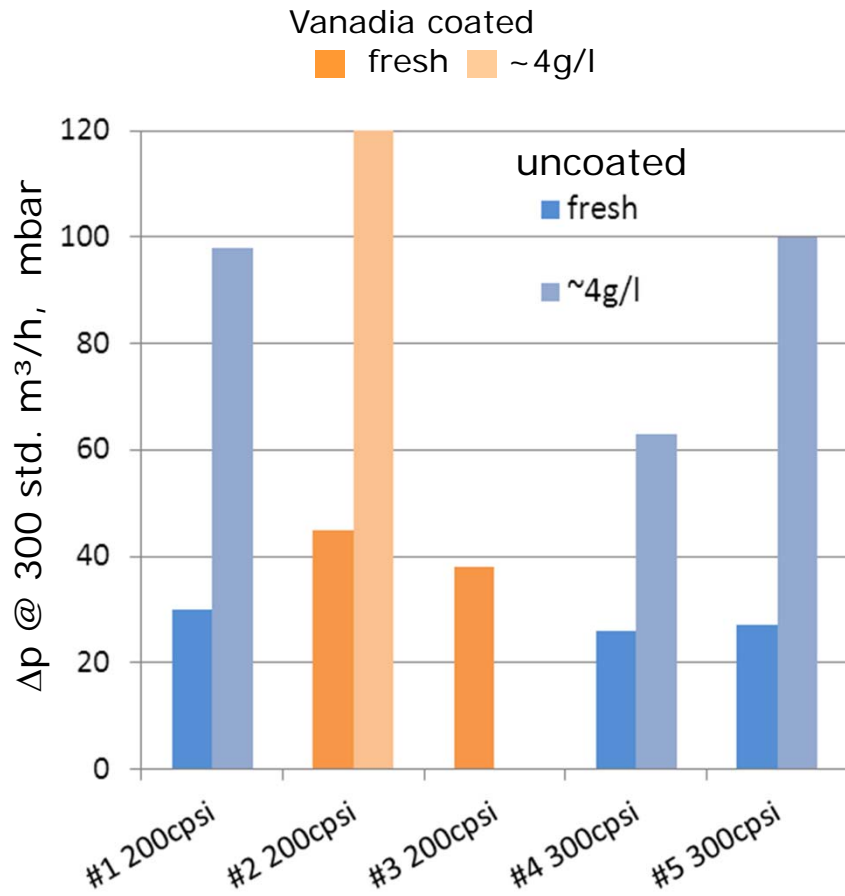
- ▶ **Engine:** VM Motori R425 2.5 liter
- ▶ **Dynamometer:** Horiba T250
- ▶ **Gas analyzer:** Horiba MEXA6000-FT
- ▶ **PN analyzer:** CPC from TSI

Filter #2, #3

- ▶ **Engine:** Mercedes Benz OM904
- ▶ **Dynamometer:** Horiba T250
- ▶ **Gas analyzer:** Horiba MEXA6000-FT
- ▶ **PN analyzer:** CPC from TSI
- ▶ **Urea doser:** Emitec Air Assisted
- ▶ **DOC:** two 5.66" x 3" 100 g/ft³ Pt



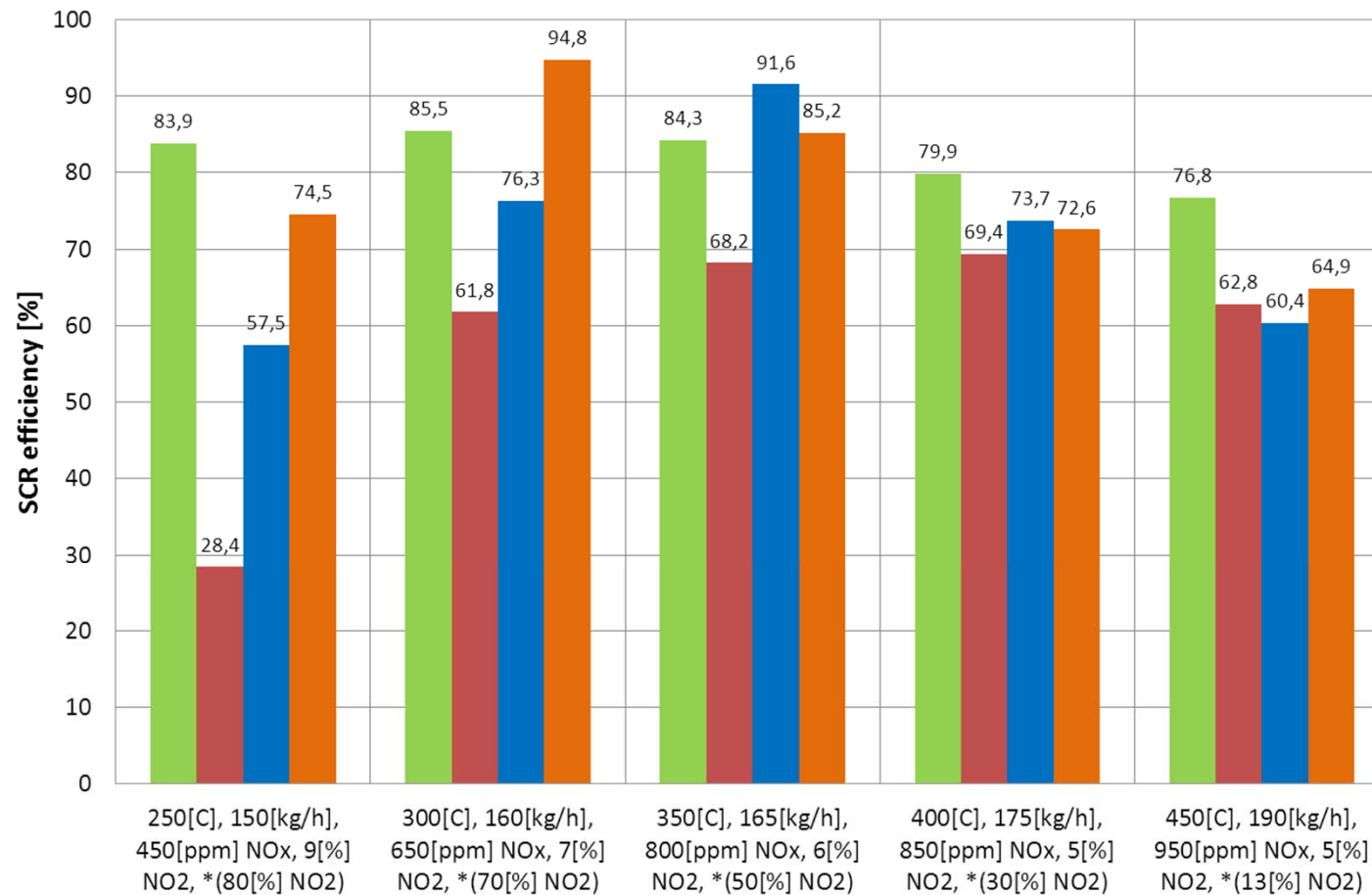
Back pressure & PN efficiency



going the extra mile

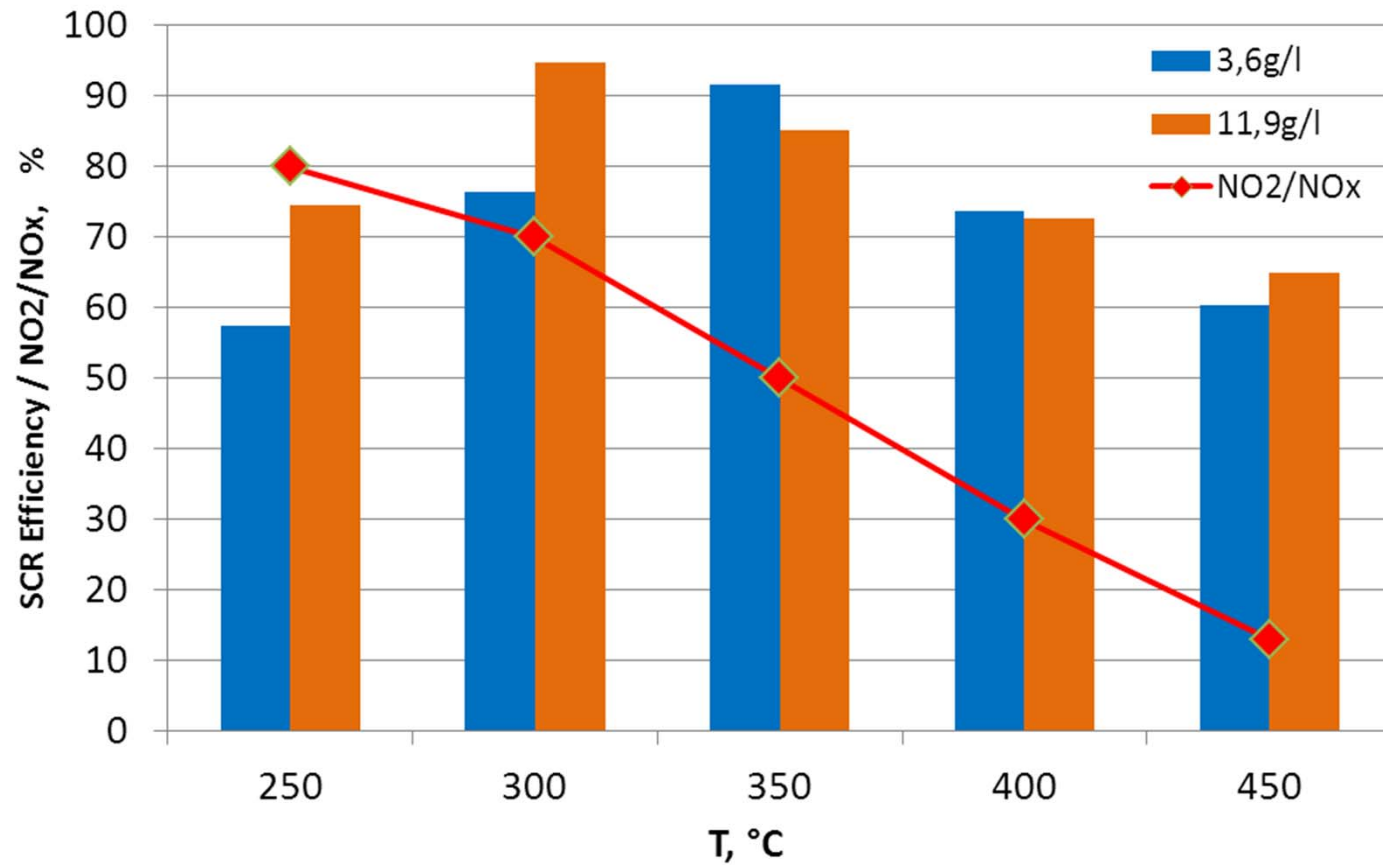
SCR efficiency steady state with 25ppm NH3 slip

■ Haldor Topsoe 5,66"x9,5" Vanadium SCR ■ Dinex 5.66" x 9" SCRf (5.9 g/l)
■ DOC + Dinex 5.66" x 9" SCRf (3.6 g/l) ■ DOC + Dinex 5.66" x 9" SCRf (11.9 g/l)



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Conversion rate / NO₂ content

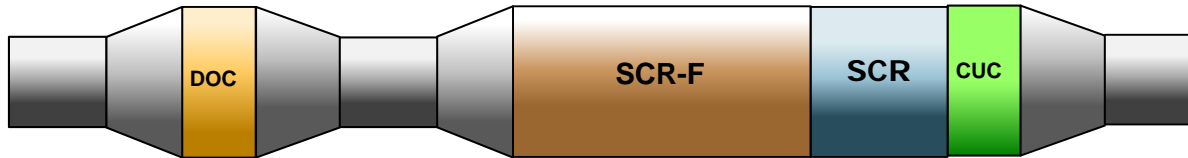


Summary

- A high porous SiC substrate for SCR-F solutions is available at porosity level up to 65%
- Improved soot load characteristics
- A first test with a Vanadia based SCR coating has shown NO_x conversion rates up to 95%
- To reach the performance of a conventional SCR, optimizations will be done in respect to
 - the coating process (distrib. in cell wall)
 - catalyst morphology (grain size distrib.)
 - adaption to the pore structure
 - temperature stability of the catalyst



Discussion

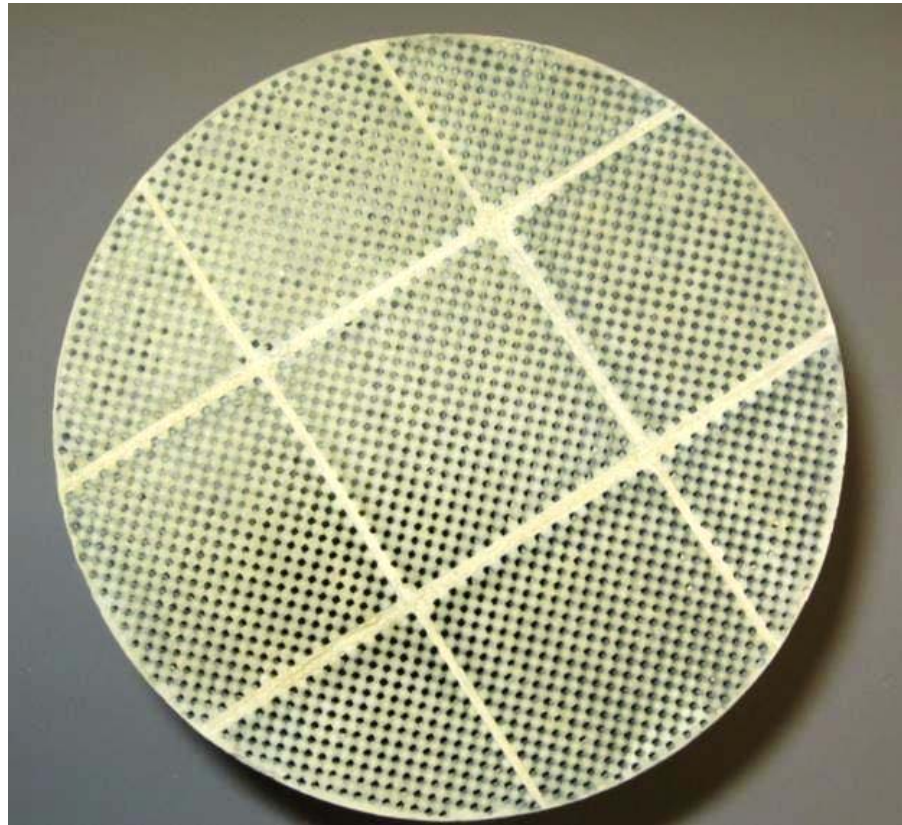


- Major part of SCR functionality integrated in DPF
- Best case: only passive regeneration
 - if necessary: active sequences
- Adjustment SCR – NO₂/NO_x can change with soot load
- Reduction of total packaging

full SCR integration?

- Porosity level DPF → 65%
- Temperature stable catalysts
- active / combined regeneration

Thank You for your Attention!



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