

Optimisation of a Urea Selective Catalytic Reduction System with a Coated Ceramic Mixing Element

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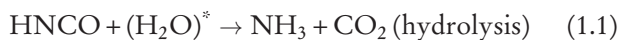
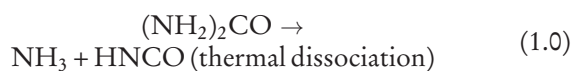
Abstract

The selective catalytic reduction of NO_x emissions to H₂O and N₂ is a major technology in automotive applications for exhaust gas aftertreatment. In this process, the reactant ammonia (NH₃) is produced by injecting AdBlue®. With the help of an SCR catalyst, this NH₃ reduces emitted NO_x to non-toxic nitrogen (N₂) and water (H₂O). For the homogenization and evaporation of the urea solution, usually metallic mixing elements are used. The new approach uses a mixing element based on structured porous ceramic with an enlarged surface and a special catalytic coating. The Solar-Institut Jülich and the German Aerospace Centre have developed a manufacturing process to modify and optimise the structure of basic polyurethane foams to achieve a high NH₃ conversion rate in combination with adjustable backpressure. The optimised flow dynamics of the exhaust gas and the additional special catalytic coating lead to a high-performance mixing element. As a consequence, the size of the conventional SCR catalyst, which is located downstream of the mixer, can be reduced. This leads to cost-efficient and compact exhaust gas aftertreatment. In this paper the experimental results of the performance analysis of this newly designed porous-ceramic-coated mixing element will be presented.

Keywords: Selective catalytic reduction system, selective catalytic reduction catalyst, mixing element, porous ceramic polyurethane foam

I. Introduction

The selective catalytic reduction (SCR) of NO_x emissions to H₂O and N₂ is a major technology in automotive applications for exhaust gas aftertreatment¹. In this process, the reactant ammonia (NH₃) is produced by injecting a liquid water-urea solution (AdBlue®). In a thermal dissociation (Eq. 1.0)² and hydrolysis process (Eq. 1.1)², the required NH₃ is formed.



With the help of an SCR catalyst, this NH₃ reduces emitted NO_x to non-toxic nitrogen (N₂) and water (H₂O) e.g. according to Eq. 1.2²:



The chemical reaction has to be supported by a catalyst in order to accelerate the hydrolysis reaction and to avoid the production of solid polymerization products with high thermal stability from the acid component HNCO^{3,4}. The catalyst for the hydrolysis reaction can be integrated in the SCR catalyst or synthesized as a single component with an additional SCR catalyst.

According to the state of the art, the atomization of the injected urea solution is improved by increasing the pressure of the AdBlue® injection to achieve adequate distri-

bution and rapid formation of NH₃. Such low-cost pulsed pressurised atomizer systems need a static mixing element in front of the SCR catalyst for effective distribution of the reactant concentration in the inflow of the SCR catalyst⁵. For the homogeneous nebulization and complete evaporation of the urea solution, usually metallic mixing elements are used⁶. These systems need a large volume for all their required components, especially the SCR catalyst, and are very expensive. In these applications, the mixing elements act only as a mixer.

An overview of the classic SCR system can be seen in Fig. 1⁷. The new approach presented in this paper uses a mixing element based on structured porous ceramic with an enlarged surface and a special catalytic coating. A structured porous ceramic offers in this way a high specific surface which is needed for the functionality as a catalyst. The catalytic coating is applied to accelerate the hydrolysis reaction (Eq. 1.1) and to achieve a high NH₃ conversion rate. The body material of the mixing element is made of clay-based porous ceramic which is manufactured from blanked polyurethane foam in the Schwartzwalder process. The Solar-Institut Jülich and the German Aerospace Center have developed a manufacturing process to modify and optimise the structure of the basic polyurethane foam to achieve the high NH₃ conversion rate in combination with adjustable backpressure. The optimised flow

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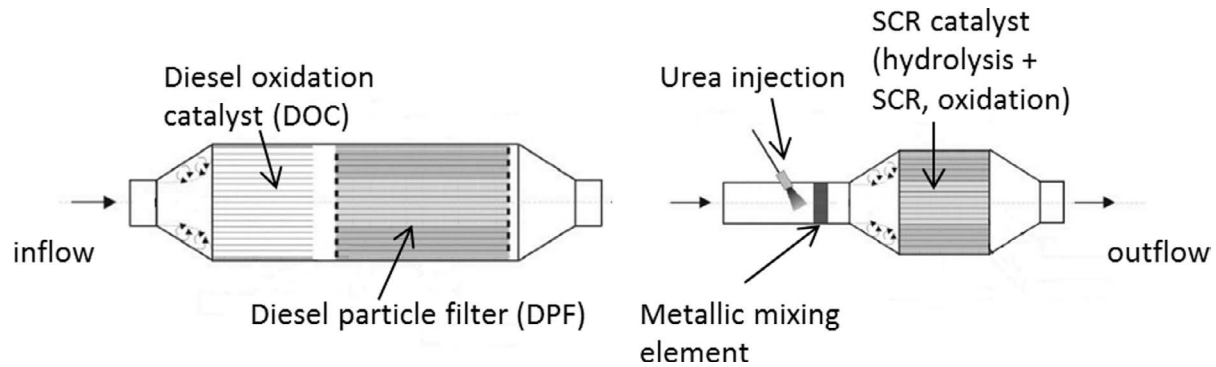


Fig. 1: Classic SCR system with DOC, DPF, urea injection, metallic mixing element and SCR catalyst with hydrolysis-, SCR- and oxidation catalyst.

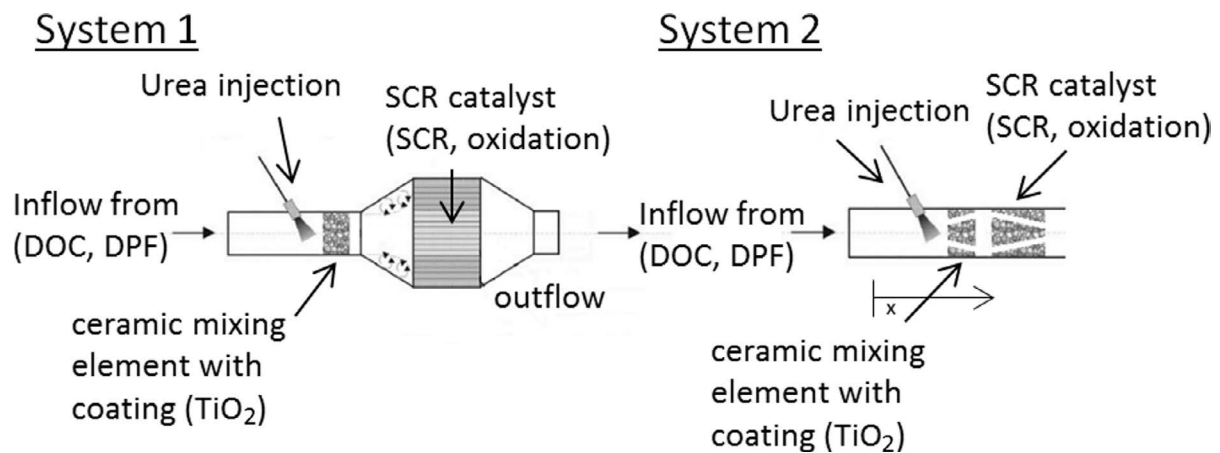


Fig. 2: SCR System with a ceramic mixing element as hydrolysis catalyst (left), SCR system with a ceramic mixing element as hydrolysis catalyst and SCR- and oxidation catalyst (right).

dynamics of the exhaust gas and the additional special catalytic coating lead to a high-performance mixing element. As a consequence, the size of the conventional SCR catalyst or the hydrolysis catalyst, which is located downstream of the mixer, can be reduced (System 1) or replaced (System 2) as shown in Fig. 2^{8,9}. The mixing element becomes part of the SCR catalyst. This leads to cost reduction and more compact exhaust gas aftertreatment. In this paper the experimental results of the performance analysis of this newly designed selectively coated mixing element made from porous ceramics with hydrolysis catalyst are presented.

II. Materials and Methods

(1) Production of the mixing elements

The process technology for the mixing elements follows the classical replication technique for ceramic foams with some geometric modifications in the basic material¹⁰. The basic material for the mixing element is polyurethane foam which is modified in a special machine, to add holes with inclination. The holes are designed to reduce the backpressure. The inclination of the holes is intended to improve the mixing efficiency. The polyurethane foam is placed in the machine, where it can be perforated as required. The element is fabricated according to the Schwartzwalder process¹¹ in seven steps, starting from the polyurethane foam, through packing, impregnation with ceramic suspension (SIC), separation of excess suspension, drying, burnout of

the polyurethane foam and finally sintering. A detailed description of the production process of the ceramic mixing element can be found in^{12,13,14,15}. Owing to the different possible combinations of the configuration (numbers of holes, angles and the placement of the holes), a statistical approach for a first small number of mixing elements was chosen. In Fig. 3 the different configurations of the analysed structured-porous ceramic mixing elements are shown. As a reference, a commercial metal mixing element was also tested.

Mixing Element	X1	X2	X3
M1	6	0	60°
M2	6	11	60°
M3	6	11	0°
M4	0	11	0°
M5	6	0	0°
M8	0	0	0°
Referenz mixer	9 blades		60°

The image shows a cross-section of a circular mixing element with a porous structure. It features several holes of different sizes and orientations. Labels X1 and X2 indicate the number of holes in different directions, and X3 indicates the vertical angle of the holes relative to the main flow direction.

Fig. 3: Configurations of the different mixing elements with the counts of drilling for X1 and X2 and their vertical angle in respect of the main flow direction.

(2) Preparation for testing of the coated mixing elements

The set-up for testing the mixing element is shown in Fig. 4. In contrast to standard SCR systems, which are installed close to the engine, in this test track there is a large distance between the engine and the SCR system.

As a consequence, an additional extra heat source had to be used to compensate for heat losses of the pipes and to reach the same temperature conditions at the injection point as in standard SCR systems. The heat is produced by a special gas preparing system called a soot generator and is placed in the measurement section between engine and SCR system as shown in Fig. 4.

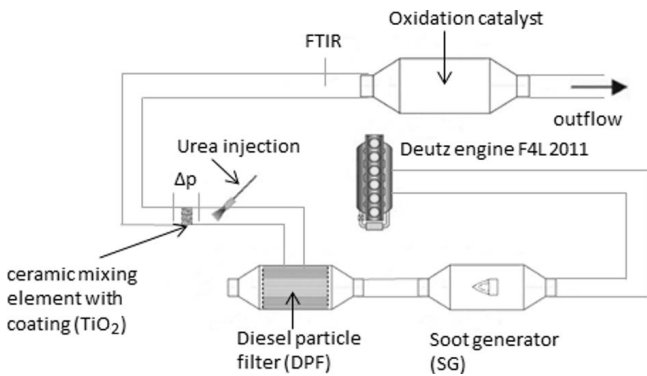


Fig. 4: Test configuration of the ceramic mixing element as hydrolysis catalyst.

The soot generator can be programmed to reach different temperature levels at the injection point. Measurement of the chemical composition is placed far away from the point of injection at a point of fully developed flow area of the exhaust line prior to the muffler. For the gas measurement, Fourier transform infrared spectroscopy (FTIR) is used to measure the NH_3 . The engine was a Deutz F4L2011. Based on the engine map, an operation point with high NO_x emissions was used. All experiments were performed at 1900 rpm and 50 Nm. Before the measurement was started, the engine was driven at operation point “1600 rpm, 25 Nm” to warm up. This process takes about 15 minutes. In the meantime, cooling of the injection nozzle is started. This cooling is realized with an external cooling circuit with an external pump. To get the optimal temperature at the injection point (312 °C), the soot generator is started after reaching the operating point “1900 rpm, 50 Nm”. At 312 °C the FTIR is started and a few minutes later the urea solution can be injected (50 mg/s). For the injection, a De- NO_x system (Bosch) is used.

(3) *Thermal shock*

Owing to dynamic changes of the operating point of the engine as well as for operating activities such as diesel particle filter (DPF) regeneration, additional heating of the exhaust line leads to a highly fluctuating thermal load of the material. Therefore, the resistance to thermal shocks or thermal loads is a criterion for the selection of a suitable material. This is particularly important in the case of ceramic materials owing to their low fracture toughness because local stress peaks cannot be compensated by plastic deformation. The experimental set-up used to determine the response of material samples to thermal shocks or thermal loads is an adapted and simplified version of the one described in 16 and shown in Fig. 5. The experiment was set up to identify critical thermal loads of the ceramic material. An adjustable air heater is installed in the air flow path. The fan generates an air flow which can be adjusted with a manual control valve. The foam sample is placed at a distance of 20 mm in front of the opening of the flow path and fixed with heat-resistant materials. The control signal for the air heater (0 – 10 V) is generated by the analog output module of a measurement and control unit which can be operated by a computer via LabVIEW VI. The voltage signal can be switched on and off or can be modulated sine- or ramp-shaped. The test elements were examined under a microscope before and after the thermal stress test.

III. Results and Discussion

(1) *Results for SCR tests*

The quality of the hydrolysis catalyst is based on its NH_3 production rate. For adequate performance of the catalyst, a large specific surface area is needed. This is analyzed analytically with the help of the specific surface of the coating on the ceramic mixing element. To determine the specific surface with the information of the cell density of the ceramic mixing element, an empirical equation from Adler J. 17 is used. To consider the different configurations of the ceramic mixing elements caused by their geometric change, the specific surface of each ceramic mixing element can be calculated 18. For this calculation, the volume of mixing element without holes and the volume of the hole are needed.

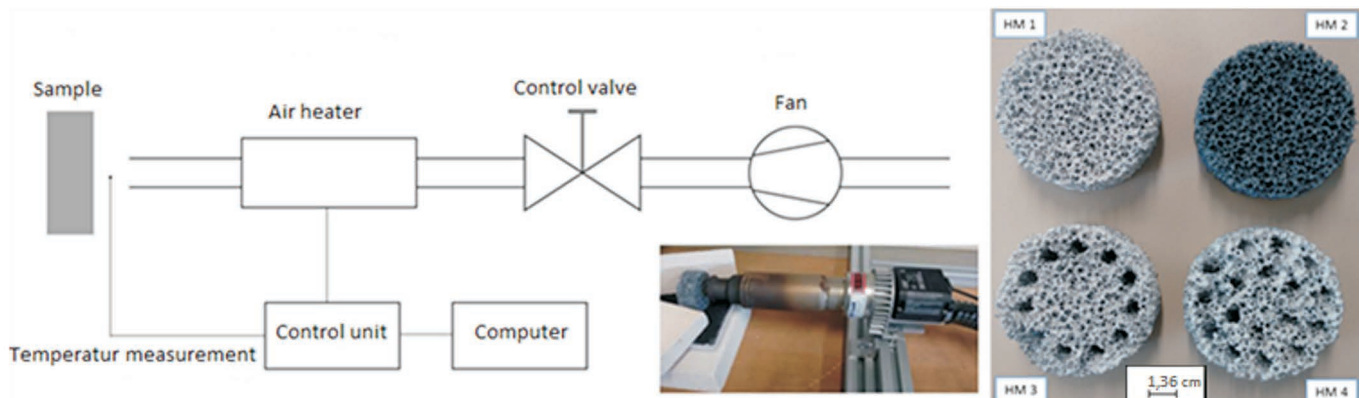


Fig. 5: Experimental set-up for thermal load tests.

Table 1 shows that the reduction of the specific surface of the mixing elements owing to the holes is minimal. The maximum reduction of specific surface of 6.64 % is shown by mixing element M3 (18 holes). Hence, the effect of the holes on the specific surface can be neglected.

Table 1: Specific surface and data for the different mixing elements.

	X1	X2	V_M[m ³]	A_M (1/m)	V_LV [%]
M8	0	0	0.000151	1106.06	0.00
M5	6	0	0.000151	1080.14	2.34
M4	0	11	0.000151	1058.53	4.30
M3	6	11	0.000151	1032.61	6.64

For the metallic mixing element, which was investigated for comparison, an average equilibrium of 43.98 ppm NH₃ in the exhaust gas was measured. The standard deviation for this measurement was ±0.921 ppm.

The results of the experiments show that with different configuration of the geometry of the mixing element different NH₃ concentrations can be achieved in the exhaust gas (Fig. 6.). The highest concentration of NH₃ (155 ppm) was detected for mixing element 8, (without a hole configuration). With regard to the metallic element as a reference probe without coating, the increase in NH₃ for mixing element 8 is evidence of a hydrolysis reaction at the element’s surface. With mixing element 8, 250 % more NH₃ could be measured in the exhaust gas with the same amount of injection compared to the reference component. The lowest concentration of NH₃ (127 ppm) was detected for mixing element 1 (M1, six holes in the inner ring with an angle of 60°).

A second key aspect is the backpressure for the different mixing elements. A low backpressure of each exhaust gas component supports the overall performance of the engine. With an increasing number of holes, the backpressure could be reduced to the lowest level for mixing element 3 with 9.7 mbar compared to 19 mbar for the pure foam without any modification, which showed the highest backpressure. It has been established that the influence of the hole angle on the backpressure is not significant. Consequently, the NH₃ conversion and backpressure can be optimized without consideration of the inclination angle. Fig. 7 shows the NH₃ conversion as a function of the back-

pressure of mixing elements with straight holes. As seen together with Table, modification of the geometry with the addition of holes leads to a lower NH₃ conversion with a strong effect on the backpressure. The optimal performance of low backpressure and improved hydrolysis has to be found.

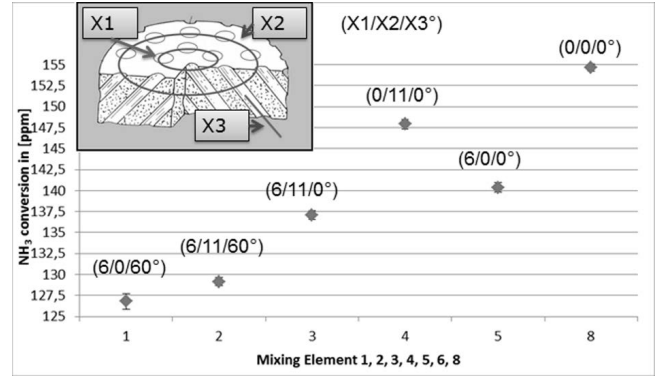


Fig. 6: NH₃ conversion for different ceramic mixing elements.

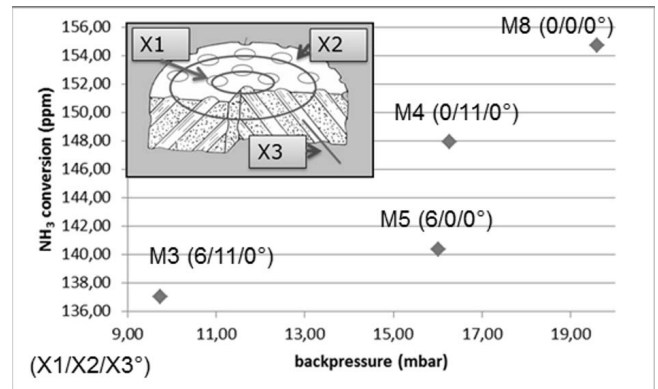


Fig. 7: Backpressure for different mixing elements with their specific NH₃ conversion.

(2) Results of thermal shock tests

The microscopic examinations of a test element before the thermal stress test showed a typical picture for such SiC quality. Caused by an inhomogeneous wetting, the material shows heterogeneous web beads (Fig. 8, left). Previous damage in the form of cracks can be found (Fig. 8, centre and right).

Fig. 9 shows an examination of a specific crack before and after the thermal shock test. No change of the initial crack could be detected. It can be concluded that no additional damage is caused by the thermal stress test.

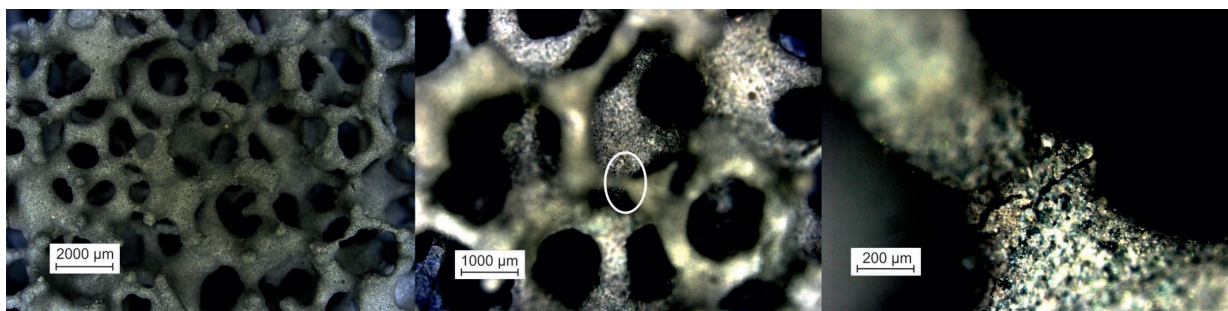


Fig. 8: Image of the test body before the stress tests.

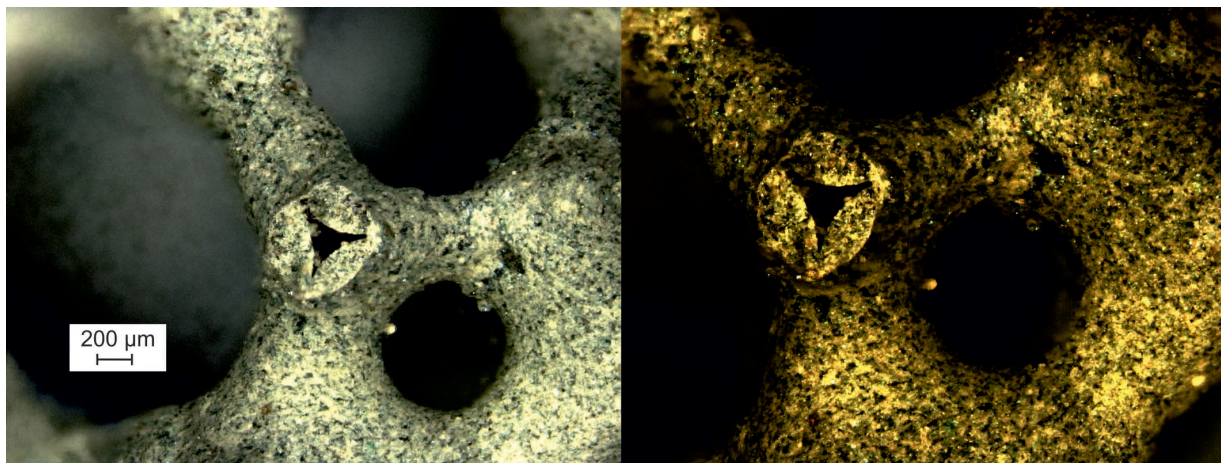


Fig. 9: Images of a detail section before (left) and after the thermal shock tests (right).

IV. Conclusions

A new mixing element to be used in an SCR system is presented in this paper. The mixing element combines the function of the mixing element with the features of a hydrolysis catalyst.

It could be shown that the ceramic mixing component presented in this paper, which has been proposed for a combined mixer/hydrolysis catalyst, is a promising candidate for application. Performance tests demonstrated that the overall performance is significantly improved compared to a standard commercial component. The NH_3 conversion rate can be increased significantly with the new mixing element. Furthermore, although the geometry modifications in form of additional holes do not have a marked influence on the reaction surface and do not significantly influence the effect of the catalyst, they do reduce the backpressure of the component. In the end, it is necessary to weigh up whether a slightly improved hydrolysis performance or a low backpressure is of importance for the overall operation of the engine. For this optimization, further experiments have to be done.

References

- Jean, E., Michelin, J.: Improvement of the Compact Mixing Systems for Optimum SCR-Filter Integration on Passenger Cars, 23rd Aachen Colloquium Automobile and Engine Technology, Aachen, (2014).
- Gehrlein, J., Lang, A., Palmer, G.: Optimization of SCR systems by integration of mixture elements, *MTZ*, [03], (2009).
- De Rudder, K.: Tier 4 high efficiency SCR for agricultural applications, SAE 2012-01-1087, (2012).
- Koebel, M., Elsner, Kleemann, M.: Urea-SCR: a promising technique to reduce NO_x emissions from automotive diesel engines, *Catal. Today*, 59, [3-4], 335-345, (2000).
- Zheng, G., Palmer, G., Salanta G., Kotrba, A.: Mixer development for urea SCR application, SAE, 2009-01-2879, (2009).
- Zuoco, S.C., Halbei, J., Neumann, F., Oesterle, J.J., Rudelt, J.: Urea SCR system in focus - new challenges in the development of exhaust systems, *MTZ*, [09], (2007).
- Bunar, F., Schirmer, S., Hansen, K.F., Hartland, J.: High performance diesel NO_x -aftertreatment concept for future worldwide requirements, 23rd Aachen Colloquium Automobile and Engine Technology, Aachen, (2014).
- Dimopoulos, P., Bach, C., Vogt, U., Herrmann, K.: Ceramic foams as catalyst substrate: Pre-catalyst application homogenizing the exhaust flow upstream of aftertreatment devices, SAE Paper, 2007-24-0097, (2007).
- Zygorakis, K.: Transient operation of monolithic catalytic converters: A two-dimensional reactor model and the effects of radially nonuniform flow distribution, *Chem. Eng. Sci.*, 44, [9], 2075-2086, (1989).
- Binner, J.: Ceramic Foams, in: Scheffler, M. and Colombo, P. (Eds.): Cellular ceramics: structure, manufacturing, properties and applications, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, (2005).
- Schwartzwalder, K., Somers, A.V.: Method of Making Porous Ceramic Articles. U.S Patent Application, US 3090094 (1963).
- Becker, M., Hoffschmidt, B., Meurer, J.: Gas exhaust system. World Intellectual Property Organization Patent Application, WO PCT/EP98/05022 (2001).
- Becker, M., Hoffschmidt, B., Meurer, J.: Exhaust gas system. German Patent Application, DE19814585A1, (1999).
- Hoffschmidt, B.: Porous member with penetrating channels for fluid flow there through and a method of producing the member. World Intellectual Property Organization Patent Application, WO PCT/EP98/05024 (2002).
- Hoffschmidt, B., Vaessen, C., Holzheid, F., Gonsior, D.: Efficient SCR system using an innovative static mixer, TIBKAT, (2009).
- Vedula, V.R., Green, D.J., Hellman, J.R.: Thermal shock resistance in ceramic foams, *J. Am. Ceram. Soc.*, 82, [3], 649-656, (2005).
- Fend, T., Pitz-Paal, R., Reutter, O.: Convective heat transfer investigations in porous materials, International Conference Porous Ceramic Materials, Brügge, (2005).
- Fend, T.: Unpublished data from the Institute of Solar Research, German Aerospace Center (DLR), Germany, (2014).

