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Improved emission control due to a new generation of high-void-fraction SCR-DeNO$_x$ catalysts

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Abstract

Successful development of an improved geometry of SCR-DeNO$_x$ catalysts has resulted in significantly increased catalytic selectivity, namely slightly higher DeNO$_x$-activity, but a decrease of 20% of unwanted SO$_2$-conversion and 20% lower pressure drop. Investigation of the kinetics clearly explains the strong influence of the geometry of the monolithic catalyst on both reactions.

Keywords: High-void-fraction SCR-DeNO$_x$ catalysts

1. Introduction

In Europe the first SCR-DeNO$_x$ catalysts for the reduction of nitrogen oxides of exhaust gases of thermal power stations have been produced by Frauenthal in 1986. These catalysts still run to the full satisfaction of the operators.

Due to new applications, e.g., waste incineration plants, as well as the tendency to even lower emission limits Frauenthal being one of the three major European SCR catalyst manufacturers has to find significant improvements to the existing products. Modifications of the chemical composition usually increase the reduction of NO$_x$ but the unwanted side reaction, the conversion rate of sulphur dioxide to sulphur trioxide, rises simultaneously.

SCR-DeNO$_x$ catalysts are monolithic hollow bodies, so-called honeycomb catalysts, the cross section resembling a fine grid. The great advantage of this geometry lies in its optimized combination of a minimum of pressure drop for the passing flue gas with a simultaneously maximum geometric surface for the catalytic detoxification reaction. The key characteristic is the so-called void fraction, defined as percentage of free cross section, which can be increased by manufacturing thinner catalyst walls. However the processing of thinner walls is becoming more and more difficult if the void fraction has to increase at the same time and can only be achieved by means of sophisticated ceramic processing. One example of successful development of high void fraction showing enormous influence on chemical as well as physical properties of the DeNO$_x$ catalysts shall be reported herewith.

2. Experimental

In contrary to various laboratory investigations in Frauenthal which are inevitably carried out at small quantities of catalytic material the presented

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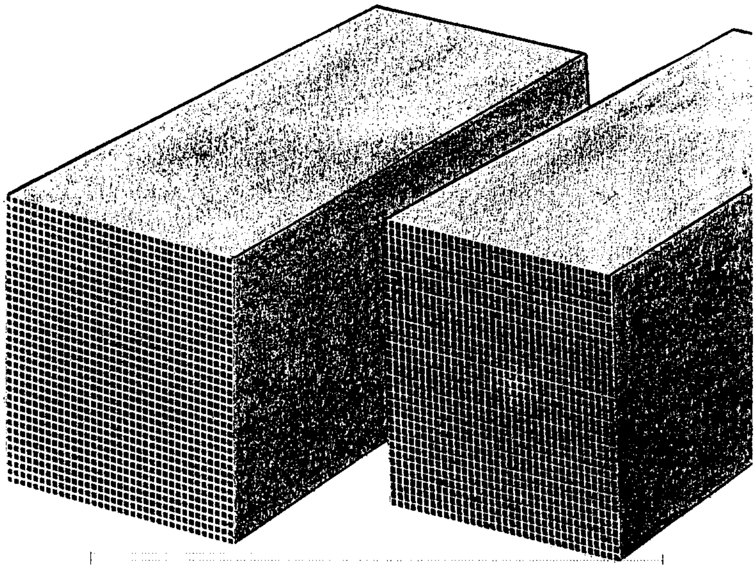

• REDUCTION OF NOx:	5 % more
• OXIDATION OF SOx:	24 % less
• PRESSURE DROP:	19 % less
• GEOMETRIC SURFACE:	5 % more
• CHANNEL DIAMETER:	5 % more
• VOID FRACTION:	11 % more
• WALL THICKNESS:	23 % less

Fig. 1. Comparison of the conventional catalyst with the new type: Overview of the most important changes.

new type of catalyst is a recent result of a large scale production, so hundred tons have already been manufactured and delivered. Fig. 1 gives an overview of the most important changes of the new catalyst type. The data are mean values of several hundred tons of catalysts, the chemical composition remained identical. The so-called '35 by 35' channel type has already been produced ten years ago. As this type is still of commercial importance it has been chosen to illustrate the development. Other $DeNO_x$-types have developed towards different geometries especially to higher numbers of channels, to a maximum of 55 × 55 cells per element.

Though easy in theory the solution to produce improved catalysts by making thinner walls is difficult to put into practice especially in combination with higher void fraction as honeycomb extrusion is a high-tech ceramic process and sophisticated in detail. Fig. 2 demonstrates the composite structure of a $DeNO_x$ catalyst wall. Due to the totally different chemical nature compared with traditional ceramics these catalysts need reinforcing fibers evenly dispersed throughout the walls. The porous $DeNO_x$ catalysts consist homogeneously throughout the wall of the catalytic active material, that is mainly TiO_2. In contrast to cordierite or mullite which obtain by firing at high temperatures its mechanical strength, SCR-$DeNO_x$ catalysts must not be fired but only calcined at moderate temperatures otherwise they loose activity. Therefore the strengthening fibers are indispensable but complicate significantly the production process. By means of electron micros-

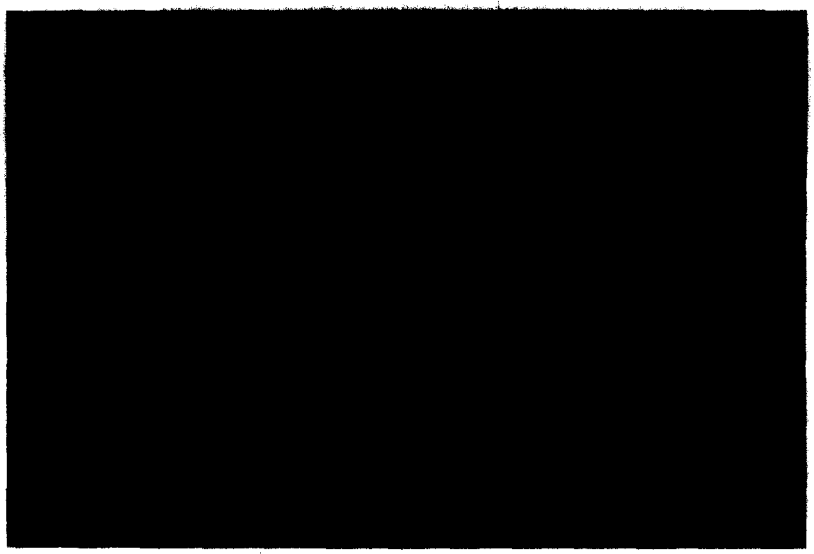

Fig. 2. Wall of DeNO$_x$-Catalyst by means of electron microscopy (enlargement 100 ×).

copy Fig. 2 reveals that the fibers are aligned with the longitudinal axis due to strong lateral pressure during processing. The diameters are only a few micrometers, but as the catalyst wall thickness is only thrice the length of the fibers, lack of homogenization can cause critical plugging of the shaping tool and consequently lead to reject. So detailed control of processing parameters, perfect

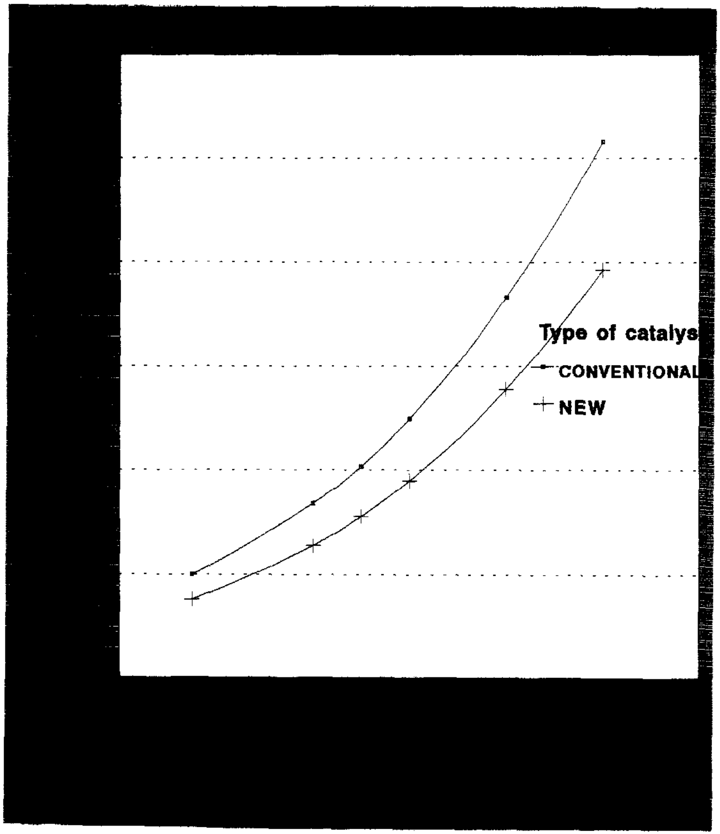

Fig. 3. Oxidation of SO$_2$ as a function of temperature: Improvement of new catalyst type compared with the conventional one (Flow: 1.2 Nm^3/h; 500 ppm SO$_2$; 2% O$_2$; 10% H$_2$O; rest N$_2$).

homogenization as well as appropriate lengths of the fibers had to be worked out for new high void fraction catalysts.

3. Results and discussion

Fig. 1 compares the traditional type of catalyst with 64–65% void fraction with the new type which is improved by 11%. As the chemical composition is the same, the new catalytic performance is merely due to the change of geometry. The mean values of numerous measurements are demonstrated in detail in Fig. 3, Fig. 4 and Fig. 5. The catalytic activity has been examined in microreactors at standard test conditions (Flow: 1.2 Nm^3/h; 500 ppm SO_2; 2% O_2; 10% H_2O; rest N_2)

The catalytic main reaction, the reduction of NO, is only slightly improved, namely 3–5%, but the efficiency of any catalyst is also defined by its selectivity, that is the relation of main reaction to unwanted side products. Over the whole range of operation temperature the new catalyst type exhibits lower SO_2-conversion by 20–24% (Fig. 3). This decrease represents an enormous improvement in practice as even few ppm SO_3 within one million of cubic meters of waste gas of a medium sized power station might sum up to tons of ammonium bisulfate or sulfuric acid.

The reason why the reduction of NO_x is accelerated but the oxidation of SO_2 is decelerated with increasing void fraction is given by examination of the kinetics. Due to Japanese as well as numerous European literature [1] the NO-reduction

$$NO + NH_3 + 1/2O_2 \rightarrow N_2 + 3/2H_2O \qquad (1)$$

follows a first order mechanism. By substitution of the conversion

$$x = (NO_{(out)} - NO_{(in)})/NO_{(in)} \qquad (2)$$

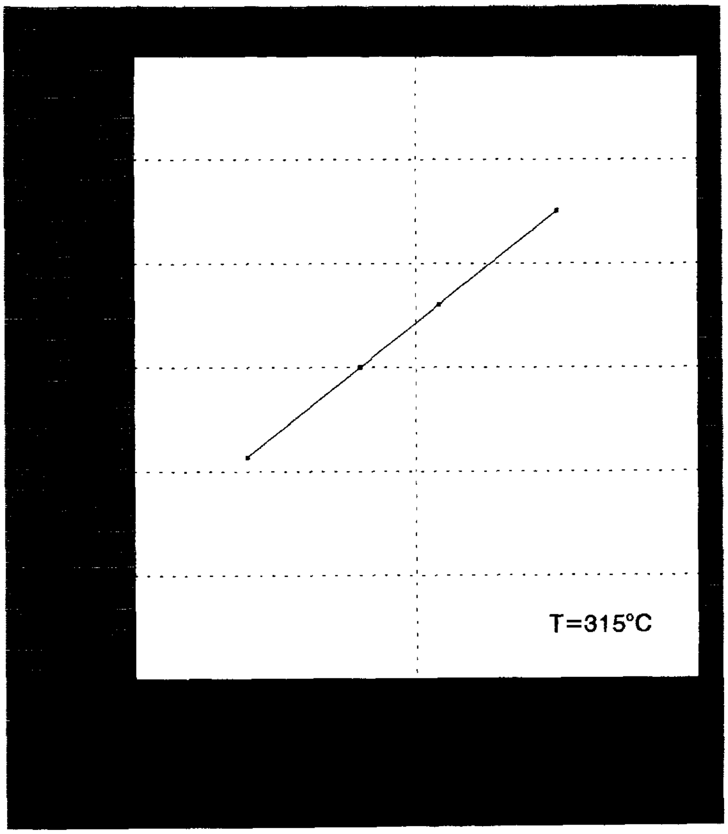

Fig. 4. Oxidation of SO_2 as a function of the void fraction: Dependance on void fraction at 315°C (Flow: 1.2 Nm^3/h; 500 ppm SO_2; 2% O_2; 10% H_2O; rest N_2).

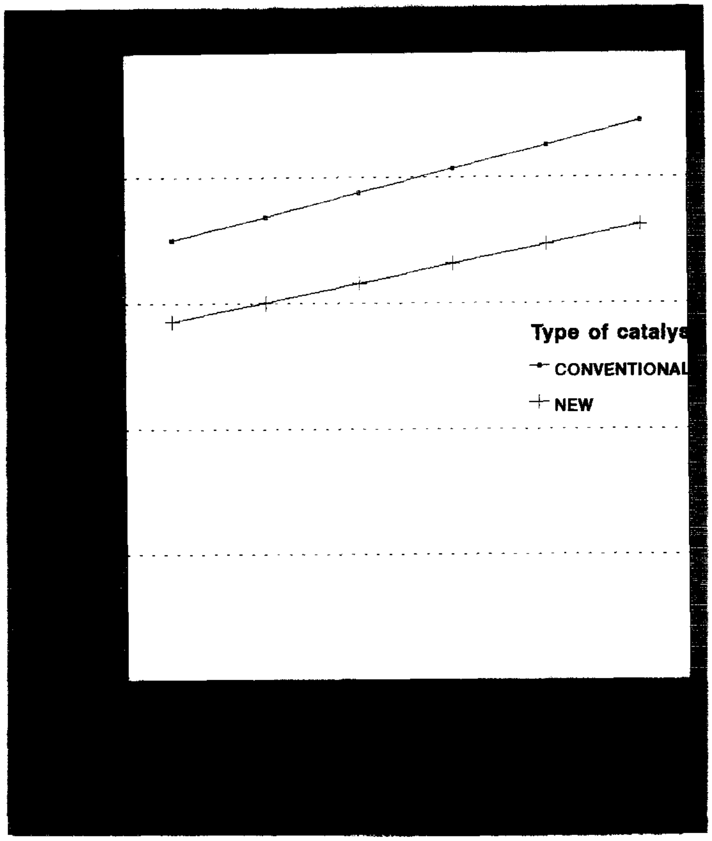

Fig. 5. Pressure drop as a function of temperature: Improvement of the new catalyst type compared with the conventional one.

and replacing the mean residence time τ by the reciprocal space velocity $1/SV$ with SV being the quotient of gas flow and catalyst volume the time law

$$x = 1 - \exp(-k/SV) \qquad (3)$$

is found. The SV related rate constant k of the reduction of NO on $DeNO_x$ catalysts is directly proportional to the geometric catalyst surface standardized to the catalyst unit of volume (A_p)

$$k = KA_p \qquad (4)$$

and consequently

$$x = 1 - \exp(-KA_p/SV) \qquad (5)$$

follows. In terms of physical mechanisms the first order rate constant indicates diffusion control within the catalyst channels which is due to the very specific situation of monolithic honeycomb catalysts because of the laminar gas flow. The NO kinetics has already been analyzed in detail elsewhere [1,2]. In contrast to the chemical reaction rate of NO which depends directly and linear on the geometric surface of the catalyst the oxidation of SO_2 is a slow chemical reaction:

$$SO_2 + 1/2\ O_2 \rightarrow SO_3 \qquad (6)$$

Examination of the kinetic control leads to a first order rate constant like Eq. (3) as well but it is directly proportional to the mass of the catalyst

$$k_{(SO_2)} = K_{(SO_2)}(1 - \epsilon) \qquad (7)$$

with the void fraction ϵ of the catalyst defined as percentage of free cross section of the monolithic honeycomb, $(1 - \epsilon)$ representing the part of the catalyst walls. Fig. 4 illustrates this dependance by examination of several catalyst geometries. The oxidation of SO_2 can be calculated as follows

$$x_{(SO_2)} = 1 - \exp(-K_{(SO_2)}(1 - \epsilon)/SV) \qquad (8)$$

As higher void fraction always enlarges the geometric surface

$$\epsilon = A_p d/4 \qquad (9)$$

the NO-reduction is improved whereas the oxidation of SO_2 is decreased significantly at the same time. Chemical modifications usually increase both reactions at the same time.

In addition the physical properties change in a favorable way as indicated in Fig. 5. The pressure drop is about 20% less, which is of vital importance for the operators as it saves operation costs of the fan. As the void fraction is proportional to the square of the catalyst channel diameter, d^2, it directly determines the pressure loss, which consequently depends on the fourth power of the channel d.

For this reason the precise measurement of *d* as well as an accurate calculation formula for the pressure drop are indispensable. A detailed investigation of the pressure drop of all types has been carried out including mathematical modelling for all catalyst geometries and flow regimes. This has laid the basis for a more precise engineering of catalysts under operating conditions. This model however shall be presented elsewhere.

4. Conclusion

The presented development of a $DeNO_x$ catalyst by geometric modification, at the price of a more complex ceramic processing, is able to combine the favorable characteristics of a catalyst. The improved properties namely are better reduction of nitrogen oxide but a lower conversion rate of sulphur dioxide to sulphur trioxide. In addition favorable physical properties like lower pressure drop of the waste gas can be realized.

The presented example of high void fraction catalysts outlines the importance of a dynamic development of ceramic processing of the honeycomb structure in addition to chemical modifications. In pilot scale even higher void fractions have already been produced in order to develop better catalysts for environmental emission control.

5. List of symbols

k: reaction rate constant $[h^{-1}]$
SV: space velocity $[h^{-1}]$
τ: mean residence time $[h]$
ϵ: void fraction or free cross section
A_p: standardized geometric catalyst surface $[m^2/m^3]$
d: diameter of one catalyst channel $[m]$

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[2] I. Binder-Begsteiger, G.W. Herzog, E. Megla and M. Tomann-Rosos, Chem. Ing. Tech., 62(1) (1990) 60.