

New German development for NO_x removal from waste gases – Preliminary results and prospects¹⁾

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The process of manufacturing and test results of a new catalyst for the selective catalytic reduction of nitrogen oxides are presented. The catalyst is prepared by a special coating process of a multicomponent sol on top of a porous cordierite honeycomb structure. The catalytically active system is based on a mixture of TiO₂, V₂O₅ and WO₃. Laboratory and industrial tests were carried out.

Neue deutsche Entwicklung zur Entstickung von Rauchgasen – Vorläufige Ergebnisse und Ausblicke

Es werden der Herstellungsprozeß und die Testergebnisse des neuen Katalysators zur selektiven katalytischen Reduktion (SCR-Prozeß) von Stickstoffoxiden vorgestellt. Der Katalysator wird durch einen besonderen Beschichtungsprozeß mit einem Mehrkomponentensol an der Oberfläche eines porösen Cordieritwabenkörpers präpariert. Das katalytisch aktive System basiert auf einer Mischung aus TiO₂, V₂O₅ und WO₃. Labor- und Industrietests wurden durchgeführt.

1. Introduction

The revised 1983 edition of the German directive on air "TA Luft" and its supplement issued in 1986 [1] have made it necessary to develop solutions for reducing the NO_x content of waste gases. The operators of German large-scale electric-power plants have run extensive established decisive tests concerning the plants to be constructed [2]. A survey of the various processes is given in table 1.

The test results [2] achieved can be summarized as follows: Primary means such as controlling the NO_x formation during the combustion process only in a few cases lead to a removal of this pollutant to an acceptable degree. A substantial reduction can only be achieved by secondary means.

According to a market analysis [3], the reduction of the NO_x content in the power plant sector carried out by the Selective Catalytic Reduction (SCR) process plays the most important role. In addition to this, the Selective Non-Catalytic Reduction (SNCR) process (also known as EXXON process, Exxon Research & Engineering Co., Florham Park, NJ (USA)) and the activated coke adsorption process also have been employed in a few applications.

The SCR process [4] is based on a catalytically ceramic body from TiO₂, V₂O₅ and WO₃ as active

oxides. The ceramic body is prepared in form of a honeycomb structure. The catalytic activity depends on the firing temperature and is far below the temperature for obtaining an optimal strength in the TiO₂-V₂O₅-WO₃ system. Therefore, the catalyst is not very abrasion-resistant, and the mechanical strength is rather poor. Moreover, the ceramic body consists of 100 % of rather expensive raw materials which can cause problems because of their toxicity in case of deposition after the catalyst deactivation. Therefore, investigations have been carried out in order to develop a supported catalyst, offering the possibility of an independent optimization of the carrier as well as of the active compound. For the carrier, in the first run, the cordierite system was chosen, mainly due to its low coefficient of thermal expansion and the resulting thermal shock resistance. In order to achieve sufficient activity, the carrier should exhibit a sufficient reactive surface and therefore porosity ≥ 50 vol% was desirable. Due to the high waste gas flow velocity, a structure was necessary having a low flow resistance. Therefore, a honeycomb structure was chosen. The important question is related to the catalytically active phase. The simple concept of impregnating a porous carrier with a solution of the active compounds and then processing it does not work because the active phase generally only works with high surface area supports, e.g. silica or alumina. Since the crystalline cordierite phase with high porosities exhibits low surface areas, another route had to be developed to meet the requirements of sufficient quantities of the active phase and to develop sufficient porosity for high reactivity. Therefore, the sol-gel process seemed to

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Table 1. Survey over nitric oxide reduction technologies

applied processes	reduction of NO _x and SO ₂ /NO _x	type of process	reaction agent	reaction product (deposition by reaction with NH ₃ and Ca(OH) ₂)	reaction conditions	final product	conversion rate in %
dry processes	NO _x	Selective Non Catalytic Reduction (SNCR)	NH ₃	–	900 to 1000 °C	N ₂ , H ₂ O	40 to 50
	NO _x	Selective Catalytic Reduction (SCR)	NH ₃	–	catalyst 300 to 400 °C	N ₂ , H ₂ O	> 80
	SO ₂ /NO _x	Electron Beam Dry Scrubber (EBDS)	radicals O, OH, OH ₂ , N	NH ₃ Ca(OH) ₂ (research-cottrell)	50 to 100 °C 50 to 100 °C	(NH ₄) ₂ SO ₄ / NH ₄ NO ₃ CaSO ₄ / Ca(NO ₃) ₂	90 (SO ₂) 80 (NO _x) 90 (SO ₂) 80 (NO _x)
semi-dry process	SO ₂ /NO _x	adsorption	NH ₃ (mining process)	–	active carbon 120 °C	N ₂ , H ₂ O	90 (SO ₂) 80 (NO _x)
			NaOH	Ca(OH) ₂	filter SO ₂ /NO ₂ > 2/1	CaSO ₃ · ½ H ₂ O CaSO ₄ · H ₂ O	80 (SO ₂) 50 (NO _x)
			(niro atomizer)		80 °C	Na ₂ SO ₃ Ca(NO ₃) ₂	
wet process	SO ₂ /NO _x	oxidation/adsorption	ozone(O ₃)	NH ₃	50 to 60 °C	(NH ₄) ₂ SO ₄ / NH ₄ NO ₃ (SO ₂ , NO _x > 200 mg/m ³)	–

be an adequate tool, if the preparation of a sol suitable for a coating process for honeycomb structures and its transformation into porous gel with sufficient catalytical activity were possible. For technical use, a technical process for the production of porous cordierite honeycomb structures and the catalytic material as well as a coating technique were necessary.

2. Experimental

The honeycomb structures are produced by extrusion of a plastic ceramic mass, drying and firing at defined conditions. Figure 1 shows a flow chart of the production process. Combining different raw materials yields different ceramics, e.g. cordierite or mullite. The addition of substances which can burn out entirely generates porosity adjusted between 20 and 60 vol%. Products with good mechanical and physical qualities are obtainable. Honeycombs with a free cross section of more than 80 vol% can be produced.

The catalyst preparation in general is described elsewhere [5]. For the catalyst used for the large-scale production titanium and vanadium alkoxides are mixed homogeneously, WCl₆ is dissolved in the mixture and then methanol added. After the addition

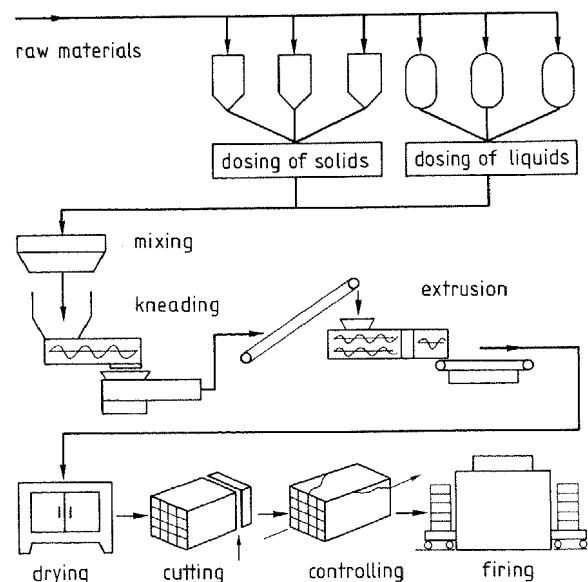


Figure 1. Flow chart of the carrier production process.

of the water, the colloidal suspension is used for a special dipcoating process. The gelation occurs during the drying step at 120 °C for 1 h (see figure 2).

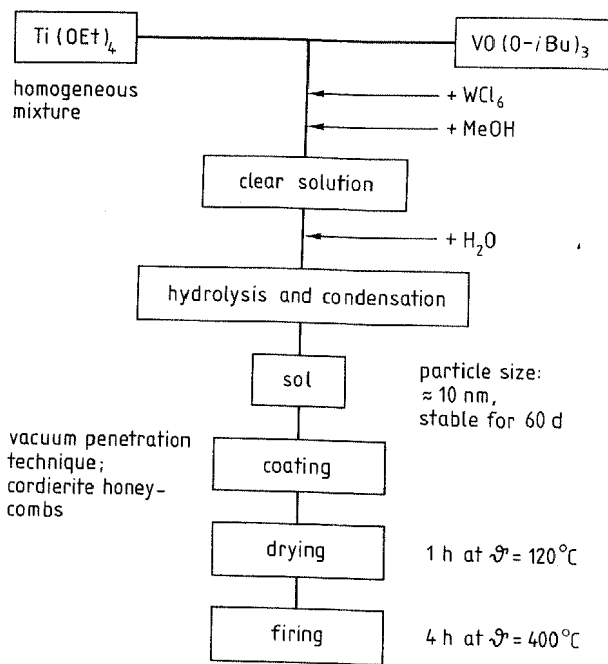


Figure 2. Path of the large-scale catalyst production.

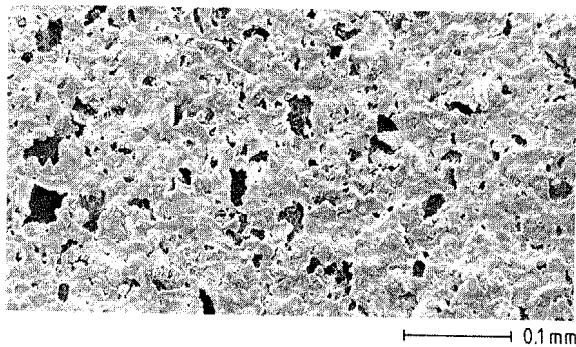


Figure 3. Surface of a cordierite honeycomb with open pores.

3. Results

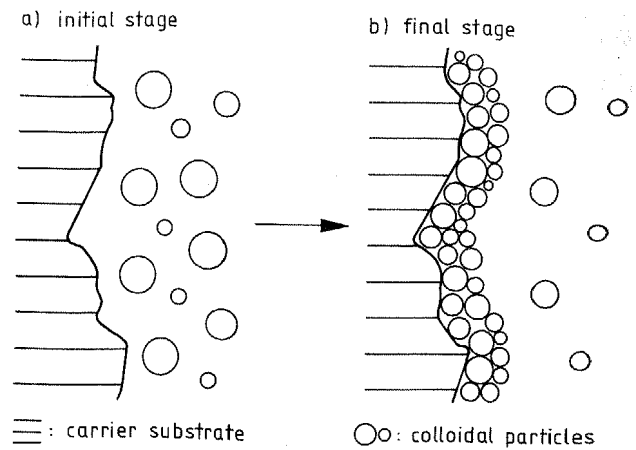
3.1. Porous honeycomb structures

A large surface area is very important on carriers for catalytic active materials. Honeycombs make this available by their geometry, but porosity in the ceramic itself raises the surface area much more. Figure 3 shows a honeycomb surface with many open pores. For the preparation and the use as catalysts a porosity of about 40 to 55 vol% is favourable.

Pore size distribution is also important. There have to be sufficient large pores for the transport of gases and sufficient small pores which maintain the surface for the adhesion of the catalytic active material. The surface area produced by porosity is about 60 times greater than that produced by geometry.

3.2. Sol-gel coating

The coating solution shows a stable viscosity of about 2 mPa s over 60 days, if stored at room temperature and moisture is excluded. After this, a sharp increase of viscosity followed by gelation is observed. For



Figures 4a and b. Schematic of colloidal particle coating process of the carrier; a) initial stage before coating, b) final stage after coating.

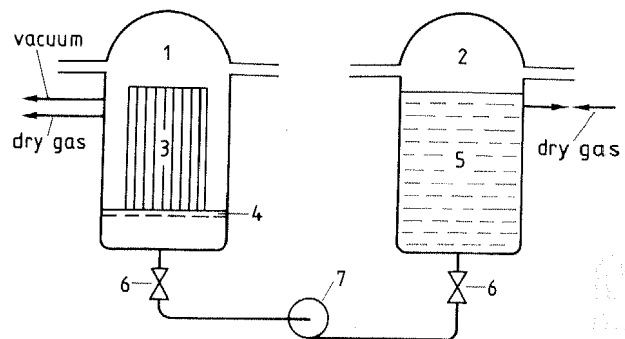


Figure 5. Schematic of the vacuum loading system for pore filling. 1: coating processing container, 2: sol reservoir, 3: honeycomb, 4: grid, 5: sol, 6: valves, 7: pump.

penetration of the suspension into the pores of the cordierite honeycomb the particle size should be very small to avoid filtration effects and pore clogging. The particle size of the sol averages to about 10 nm, a size which should be suitable for pore sizes down to 1 μm . The coating of the cordierite ceramic surfaces and pore walls occurs by adsorption of the colloidal particles to the surface (figures 4a and b). The major advantage of this technique compared to the coating by a salt solution is the fact that the particles, once fixed to the surface, are not transported outside the pores with the solvent during the drying step. On the other hand, by this technique only relative thin layers can be obtained in a one-step process and, in order to infiltrate about 10 to 15 wt% of catalytically active material (which is necessary to achieve sufficient activity) a multistep coating has to be applied. As experiments showed simply dipping the cordierite into the sol does not lead to a sufficient filling of the pores with the coating liquid due to the gas within the pores. Therefore, a vacuum process was developed leading to a perfect pore filling (figure 5). Chamber 1 is evacuated and then the sol is led into the chamber. It penetrates the cordierite, and is then pumped back into chamber 2.

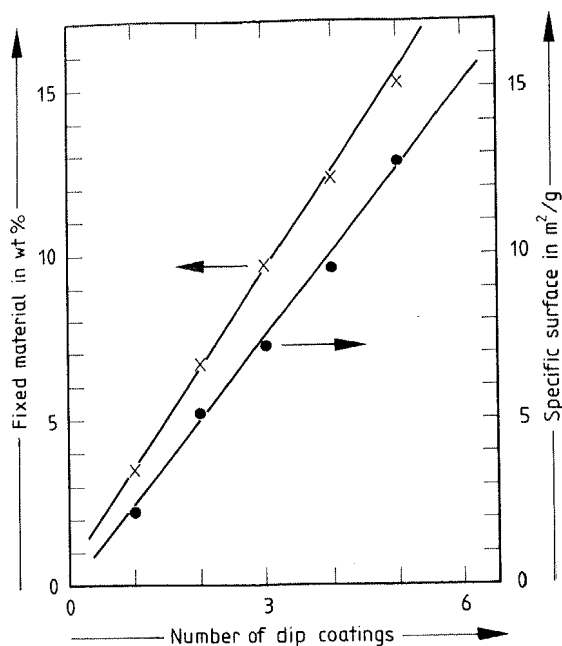


Figure 6. Weight increase by multiple loading (composition of the catalytic component in wt%: 70.9 TiO₂, 8.4 V₂O₅, 20.9 WO₃).

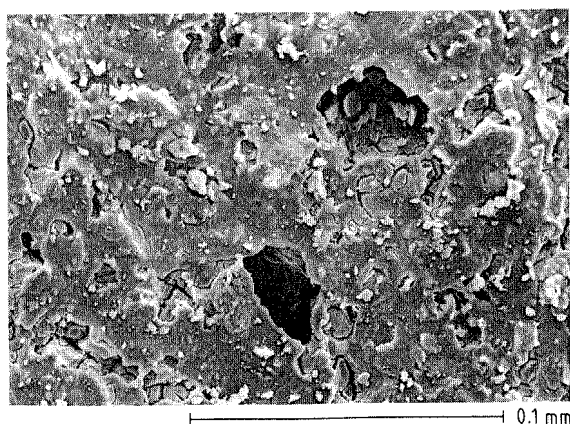


Figure 8. SEM micrograph of a coated catalyst surface.

The dipcoating process as well as the catalyst production process are scaled up for a 1 m³/d unit size. During the drying process which must be carried out in a closed system the waste gases are recovered by condensing the HCl-containing methanol.

3.3. Catalytic performance

The wet honeycomb is dried for 1 h at 120 °C and the process repeated for several times. Figure 6 shows the weight increase of the catalytically active component as a function of the loading steps. Figure 7 shows the activity coefficient *K* as a function of the load after firing at 400 °C. The data show that about 15 wt% are a suitable load for conversion rates.

3.4. Microstructures

In figure 8 the microstructures of the surface of a supported catalyst is shown and figure 9 illustrates the

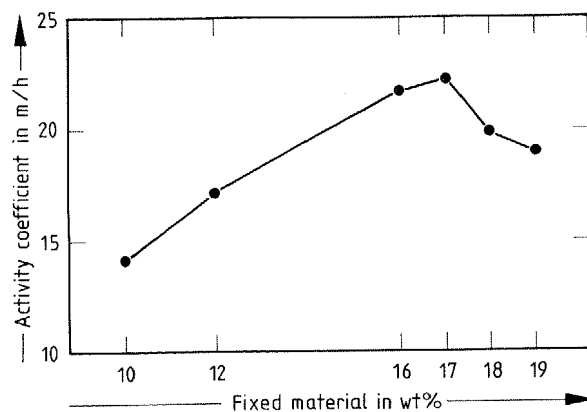


Figure 7. Dependence of catalytic activity on load (after firing at 400 °C).

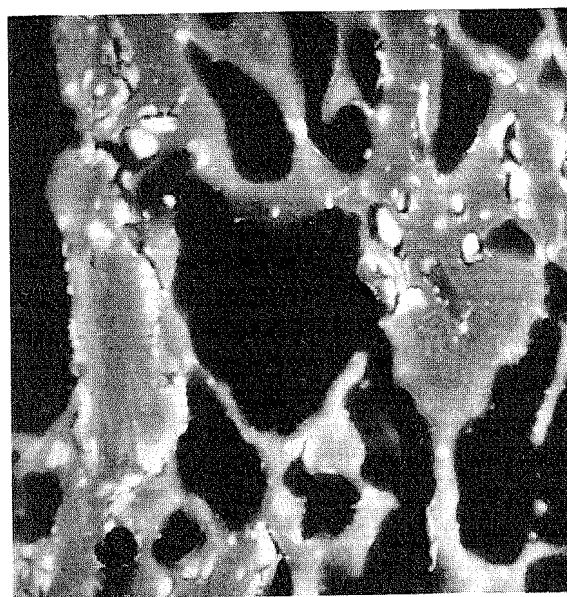
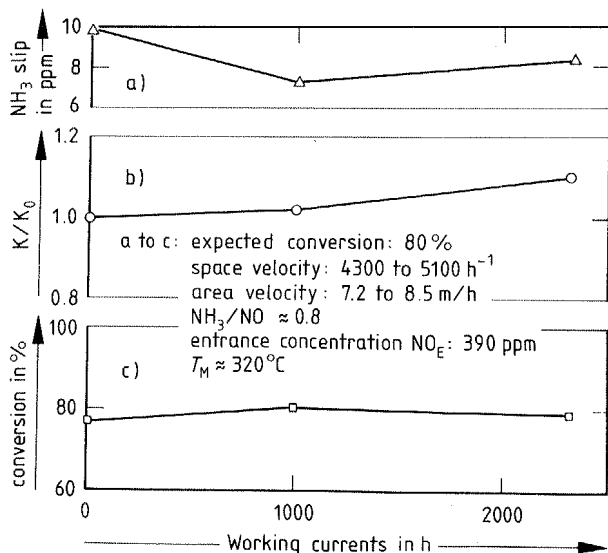


Figure 9. Cross section of a loaded cordierite catalyst.

cross section of the catalyst. A relatively good coverage of the pore walls with titanium and tungsten could be determined. Due to the high specific surface area of the active coating (100 m²/g) the overall specific area of the catalyst reaches 15 m²/g. It is clearly shown by X-ray diffraction measurements that the catalytically active phase is amorphous. Firing to temperatures above 450 °C leads to a sharp decrease in activity and crystallisation takes place, leading to various crystalline phases (anatas, rutil, WO₃). This is an important difference to the TiO₂-V₂O₅-WO₃ ceramic which is in a crystalline state [4].

3.5. Catalytic field tests

Laboratory and field tests were carried out to check the catalyst performance. Figures 10a to c represent the results in the Voerde electrical power plant which are representative for the results from other tests.



Figures 10a to c. Catalyst performance in the Voerde electrical power plant; a) NH₃ slip, b) K/K₀ ratio, c) conversion.

They show that after more than 3000 h the catalyst does not decay in its catalytic activity.

4. Discussion

The investigations show that by the sol-gel process it is possible to prepare a high-performance SCR-supported catalyst which offers some specific advantages:

- a low consumption of heavy metals in the course of production,
- good adaptability of the individual operating conditions,
- minimum flow resistance in the waste gas flues due to the large free cross-sectional area of the carrier material,
- high mechanical strength of the carrier body compared with known SCR catalysts,
- excellent resistance to thermal shock due to the specific material properties of the carrier,
- no disposal problems since the material can be recycled by means of ceramic methods as a result of the small amount of catalytic material applied to the carrier.

5. Outlook on the glass industry

Among the advantages listed above mention was made of the good adaptability of this catalyst system. This feature makes the present catalyst type useful for a wide range of applications, inter alia for use in the glass industry. It is to be assumed that in the course of

updating the German directive on air "TA Luft" [1] limits for the admissible NO_x emissions will be established.

Unlike feasible application possibilities in industrial furnace installations it is presently assumed that in the glass industry SCR catalysts can only be used downstream of hot dedusting plants. To comply with already established limits of dust and sulphur dioxide emissions invoked by the German directive on air "TA Luft" [1] a number of retrofits were made during recent years which have to be supplemented with NO_x removal systems. In all these cases individual solutions have to be developed. Here emphasis must be on how such NO_x systems can be combined with design concepts employing heat recovery methods via batch preheating. In this case the question whether NO_x can be separated from the waste gases will among other factors be decisive for the success of such concepts in future.

It can already be foreseen now that ways have to be tried out by which the catalytic removal of NO_x can as well be realized in temperature ranges below 300°C. First approaches have already been made in extensive laboratory investigations which must now be put to the test in the field.

The concept introduced in this paper is to be regarded as a first step. Further variants which will considerably broaden the existing basis are already in sight. However, forthcoming pilot plant testing will have to clarify to which extent sulphur contaminations will react with the reduction agents employed and thus affect the proper functioning of the catalyst. Moreover, the issue of possible catalyst poison in the temperature ranges mentioned has to be investigated.

6. References

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