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# Experimental and modeling study of the impact of interphase and intraphase diffusional limitations on the DeNOx efficiency of a V-based extruded catalyst for $NH_3$–SCR of Diesel exhausts

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## HIGHLIGHTS

- ▶ Mass transfer in extruded SCR monolith assessed by comparison with powdered catalyst.
- ▶ Importance of mass transfer phenomena depends on temperature and $NO_2/NO_x$ feed ratio.
- ▶ 1D + 1D model provides good account of intra and interphase diffusional resistances.
- ▶ Role of intra- and interphase limitations discriminated by model simulations.

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## ABSTRACT

The influence of inter- and intra-phase diffusional limitations on the DeNOx activity of an extruded $V_2O_5$–$WO_3/TiO_2$ SCR monolith catalyst was studied by both experimental and modeling tools over a wide temperature window and over the full range of $NO_2/NO_x$ feed ratios. The comparison of the DeNOx activity of monolith and powdered catalyst enabled a direct evaluation of the mass transfer resistances. These were found to affect $NH_3$ and $NO_x$ conversions to an extent depending on temperature and on $NO_2$ feed content, and were satisfactorily predicted by a 1D + 1D mathematical model of SCR monolith converters.

## 1. Introduction

In order to control the $NO_x$ emissions from Diesel and other lean burn engines, the well-known DeNOx technology based on Selective Catalytic Reduction of $NO_x$ by ammonia/urea has been adapted in recent years to Heavy Duty (HD) and Light Duty (LD) Diesel vehicles with excellent results [1,2]. In this context, numerical simulations have been found a valuable and effective tool to support SCR development for practical applications. It is nowadays widely recognized, in fact, that the use of mathematical models for design and optimization of on-board SCR systems can help in reducing time and costs associated with the development of the technology.

In particular, modeling of SCR converters should take into account the presence of mass transfer resistances, whose importance has been emphasized in the literature [3–7]. Recent studies [7,8] focused their attention especially on the mass transfer limitations within the washcoat layer of Cu- or Fe-zeolite wash-coated monolith catalysts. Although metal promoted zeolites are promising formulations for the abatement of $NO_x$ due to their activity and stability at high temperature, extruded SCR monoliths made of $V_2O_5$–$WO_3/TiO_2$ catalysts with improved thermal stability are largely applied in commercial vehicles, especially in heavy duty applications. Since these are extruded bulk catalysts, we can expect in principle a more significant role of intraporous diffusional limitations as compared to washcoated monolith catalysts. Indeed, the important impact of intraporous diffusion in extruded V-based SCR monolith catalysts for stationary applications is well known [9]. Nevertheless, there are no dedicated studies in the literature to our knowledge addressing specifically the role of mass transfer limitations in V-based SCR catalysts for automotive applications.

In the present work we investigate the impact of mass transport on the performance of vanadium-based bulk catalysts both experimentally and by mathematical modeling. For these purposes we adopt a multi-scale approach wherein first intrinsic SCR kinetic data, addressing the effects of temperature and $NO_2/NO_x$ feed content, are collected over a catalyst in the form of powder, and such data are used to estimate the rate parameters of the reactions included in an existing SCR kinetic model [10]. Intrinsic rate equations are then incorporated into a 1D + 1D dynamic mathematical

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model of SCR monolithic converters which accounts for both gas/solid and intra-porous mass-transfer resistances, [8,11], and model simulations are compared to experimental data collected on a small core catalyst monolith sample for different feed conditions and reaction temperatures. The comparison between data collected over the powdered catalyst operating in a kinetic regime and over a lab scale monolith catalyst points out directly the impact of mass transfer phenomena on the activity of V-based SCR catalytic converters. Moreover, the numerical simulations of the monolith channel model not only provide an overall quantitative evaluation of such effects, but also enable to decouple the effects of intra- and inter-phase mass transfer resistances.

## 2. Experimental

### 2.1. Kinetic runs over the powdered catalyst

For the micro-reactor runs a commercial V-based catalyst, originally supplied in the form of an extruded monolith by an unnamed provider, was crushed and sieved to 140–200 mesh, resulting in an average particle size of 90 μm. Diagnostic criteria [10] confirmed that this size, corresponding to an internal diffusion length of 15 μm, was suitable to guarantee a kinetic regime in our tests. 80 mg of catalyst were then diluted with 80 mg of cordierite, and the powder was loaded in the micro-reactor, consisting of a quartz tube of 6 mm internal resulting in a catalyst bed length of about 10 mm. The reactor was then placed into an electric furnace and the reaction temperature was measured and controlled by a K-type thermocouple directly immersed in the catalyst bed. The main typical SCR reacting systems ($NH_3$, $NH_3$–NO, $NH_3$–$NO_2$, $NH_3$–NO–$NO_2$) were investigated in the 150–550 °C temperature range, using total volumetric flow rates corresponding to GHSV = 30000–70000 $h^{-1}$ calculated on an equivalent volume of monolithic catalyst with a feed content of 8% of water, 2–8% of oxygen, and balance Helium as carrier gas. Concentrations of 0–500 ppm of $NH_3$, NO and $NO_2$ were fed to the reactor. The temporal evolutions of NO, $NO_2$ and $NH_3$ at the reactor outlet were continuously monitored both by a UV analyzer (ABB LIMAS 11HW) and by a quadrupole mass spectrometer (Balzers QMS 200) which could, in addition, measure the concentrations of reaction products such as $N_2$ and $N_2O$. A more detailed description of the experimental equipment is provided elsewhere [11–14].

### 2.2. Validation runs over the monolith catalyst

Another set of experiments was carried out over the same V-based catalysts, now in its original shape of a 300 cpsi monolith with square channels and a wall thickness of 0.32 mm. A core sample with volume of about 5 $cm^3$ was used in these runs. Since the aim of the study was to quantify the effect of diffusional limitations in bulk catalysts, the tests at the monolith scale were performed using the same experimental conditions of the kinetic runs over the powdered catalyst to enable a direct comparison of the results. 0–500 ppm of $NH_3$, NO, $NO_2$ were fed in a total volumetric feed flow corresponding to GHSV of 30000–70000 $h^{-1}$ referred to the monolith volume, with a feed content of 8% of water and 2–8% of oxygen. The higher oxygen concentration, closer to realistic concentrations in the engine exhausts, was used in the Standard SCR experiments both on the powdered and on the monolith catalyst. In the case of the powder experiments the $O_2$ feed content was kept at 2% in all the other runs to prevent damages to the mass spectrometer filament. Based on previous work over similar V-based catalysts [14], the kinetic effect of $O_2$ is expected to be negligible in the presence of significant amounts of $NO_2$. To enable a direct comparison, runs with $NO_2/NO_x > 0$ were performed with a 2% oxygen feed concentration also at the monolith scale.

$N_2$ was used as a carrier gas in the monolith runs; a UV analyzer (ABB LIMAS 11HW) continuously measured the NO, $NO_2$ and $NH_3$ outlet concentrations, while the $N_2O$ concentration was measured by a Non Dispersive IR analyzer (ABB URAS-14). Further information about the experimental configuration used for monolith catalyst testing is provided in [8,15].

Notably, most of the runs were carried out at a GHSV of 70000 $h^{-1}$: it was expected in fact that at such a relatively high space velocity potential mass transfer limitations could be more evident than at a lower GHSV.

### 2.3. Mathematical models

A kinetic model of $NH_3$–SCR over V-based catalysts, developed and reported in [10,14] (see Table 1), has been used for the estimation of the rate parameters by multiresponse non-linear regression of data collected in the micro-reactor runs, based on a dynamic one-dimensional isothermal isobaric heterogeneous plug flow model of the test micro-reactor. The adopted kinetic scheme includes global steps for $NH_3$ adsorption and desorption, $NH_3$ oxidation and $NH_3$–NO–$NO_2$ reactivity [10].

After determining the intrinsic kinetics, the rate equations, together with the geometrical (CPSI, wall thickness) and the morphological data (porosity, pore size distribution, etc.) of the V-based extruded monolith catalyst, have been incorporated in a 1D + 1D heterogeneous dynamic model of SCR monolith converters, which accounts for both internal and external mass transfer limitations. The 1D + 1D model is more extensively described in [8,11,13], and is only schematically summarized in the following. Briefly, it relies on the assumptions of identical conditions within each channel of the monolith catalyst and of negligible axial dispersion and pressure drop. It provides a one-dimensional representation of the gas-phase C- and T-gradients along the monolith channels, accounting for inter-phase (gas–solid) mass and heat transfer via semi-theoretical transport coefficients derived from the analogy with the Graetz–Nusselt problem [16]. Furthermore, at each axial location intraporous concentration gradients are determined by solving reaction–diffusion equations across the porous walls of the extruded honeycomb catalyst, for which a slab geometry is assumed. The effective diffusivities are estimated from the measured catalyst pore size distribution according to a modified Wakao–Smith approach [17,18]. Notably, a dedicated study [17] reported good agreement between effective diffusivities measured in V-based extruded SCR monolith catalysts and diffusivities predicted from the catalyst morphology according to Wakao–Smith. The same approach was also successfully applied in the past to simulation of both extruded and washcoated SCR monolith converters [11,8].

Based on the porosity and pore size distribution of the tested catalyst and on gas-phase diffusivities computed as binary diffusivities in $N_2$ according to the Fuller–Schettler–Giddings correlation, the estimates for the effective diffusivities of NO, $NO_2$ and $NH_3$ at 200 °C were $4.2 \times 10^{-6}$, $3.6 \times 10^{-6}$ and $2.9 \times 10^{-6}$ $m^2/s$, respectively.

## 3. Results and discussion

### 3.1. Intrinsic SCR kinetic study over powdered catalyst

The fit for estimation of the intrinsic rate parameters was organized according to a strategy of growing complexity: first, $NH_3$ adsorption and desorption was analyzed, then ammonia interaction with oxygen and the $NO_x$ species, with varying $NO_2/NO_x$ ratios,