A semi-empirical method to quantify the impact of mass transfer on lab-scale SCR deNO\textsubscript{x} catalyst activity testing

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Abstract

Industrial denitrification catalyst monoliths are regularly tested in controlled lab-scale conditions to quantify their activity. As mass transfer phenomena occurring inside the channels of the monoliths have an important impact on the global denitrification kinetics, activity measurements must be conducted in well-known conditions in terms of sample geometry and gaseous flow regimes, among others. The lack of accurate mass transfer correlations for the complex flows at stake however prevents any accurate generalisation of the test results. In this paper, we propose a semi-empirical method for the quantification of contribution of mass transfer to the global denitrification kinetics for any given test bench. It is based on the experimental adjustment of mass transfer correlations presenting a suitable form. Mass transfer can therefore be decoupled from the intrinsic kinetics and large ranges of conditions can be covered by conducting a limited number of measurements.

Keywords: catalyst, deNO\textsubscript{x}, activity, mass transfer

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1. Introduction

Selective Catalytic Reduction (SCR) deNO₂ systems are currently the most effective way to significantly reduce Nitrogen oxides (NOₓ) emissions from large scale thermal power plants, as it can reach 90% NOₓ reduction or higher [1]. It is already widely applied for all types of combustion processes and fuels (gas, oil, coal, biomass), and it is expected to further grow in importance in the future, driven by the increasingly stringent NOₓ emission limit values around the world [1].

In SCR systems, nitrogen oxides (essentially nitrogen monoxide) produced during combustion are reduced by reacting with ammonia in the presence of a catalyst. Ammonia or urea is injected in the flue gas upstream of the catalyst. SCR is generally used as a secondary measure, in addition to primary NOₓ production control in the furnace or the combustion chamber, where high temperature peaks and high oxygen concentrations are avoided to limit NOₓ formation. The SCR reaction generally occurs at an optimum operating temperature in the range 300 − 450°C, although this range can be wider depending on the type of catalyst and/or the specific configuration of the process (170 − 510°C) [1]. The heat or thermal effects are negligible in deNO₂ systems such as the ones considered here due to the low concentrations of the reactants (leading to very small adiabatic temperature rise). Thus, the SCR reactors operated at constant load may be considered to be isothermal at the operating temperature. A good mixing between the flue gas and the injected reactant is required to ensure a high efficiency of the process while keeping a low residual ammonia concentration downstream of the flue gas treatment systems. The amount of residual ammonia in the flue gas, the so-called "ammonia slip", is generally limited to a few ppm by the legislation [1, 2].

The catalysts can have various forms and compositions [1, 3]. The honeycomb, plate or corrugate geometries are generally used in large scale applications, see Fig. [1]. They are made of a homogeneous ceramic TiO₂ base material containing catalytically active components like vanadium, tungsten or molyb-
denum \[1, 3\]. The catalysts are generally arranged in several layers in which the flue gas and ammonia mixture flow successively, allowing for a modular management of their remplacement \[2\]. The activity of deNO\(_x\) catalysts indeed decays with time, due to various chemical, thermal and mechanical deactivation mechanisms (e.g. poisoning, fouling, sintering, attrition, ...) \[4, 5\], which requires a regular and careful follow-up of their performances to ensure constant low NH\(_3\) and NO\(_x\) emission values \[2\]. In addition to high intrinsic catalytic activity, good operation and maintenance practices also greatly contribute to the performances of SCR systems \[2\].

Testing the activity of an industrial catalyst monolith can serve two objectives: controlling the quality of a new catalyst after production, or assessing the residual activity of a used catalyst sampled from an industrial process in order to predict the remaining life-time of a catalyst layer \[5\] \[2\]. Such SCR catalyst activity tests must be performed in well-controlled lab-conditions in terms of gas composition, temperature and flow regime. Ideally, all these parameters should be as close as possible to real operation conditions. In a standardisation effort,
the German Technische Vereinigung des Grosskraftwerkbetreiber (VGB) and the American Electric Power Research Institute (EPRI) have published industrial guidelines describing the good practices in terms of sample preparation, test conditions, measurement methods and result reporting for SCR catalyst activity testing [6, 3]. Among others, the EPRI guidelines highlight the influence of the mass transfer phenomena occurring in the channels of the catalysts on the global denitrification kinetics. While the cumulated impact of varying flow conditions and sample lengths on the testing results is briefly discussed, it is finally recommended by EPRI to reproduce the same flue gas velocity as the one observed at full scale (possibly with some adjustment to account for plugged catalyst cells), and to accept only limited reduction of the sample’s length [3]. The purpose is here to ensure that mass transfer plays the same role in lab- and real conditions, so that the measured performances are also valid in full-scale operation. This means that the mass transfer effects and the intrinsic, chemical kinetics cannot be decoupled.

Gu and Balakotaiah [7] identified four reasons for different reactor performances at different scales: (i) different fluid flow patterns, (ii) different heat and mass dispersion effects, (iii) different concentration and temperature ranges, and (iv) different boundary conditions, such as heat exchange with the surroundings. When adiabatic and isothermal reactors are used at smaller scale to test the activity of SCR catalyst in identical concentration and temperature conditions, different fluid flow patterns and different mass transfer effects are thus the main causes of discrepancy to be investigated. Based on their detailed analysis of laminar flows in monolith reactors, they confirmed that different mass Peclet numbers can lead to significant discrepancies.

If the contribution of mass transfer to the overall kinetics could be quantified during activity testing, the constraint of identical mass transfer effects could however be relaxed, with a double advantage: test conditions could differ from the real conditions in terms of flow regime and sample length, and access to the intrinsic kinetics would be gained, which would in turn allow for extrapolation to other mass transfer regimes. In their discussions, EPRI provides an
attempt to quantify the intensity of mass transfer in a specific case, through the calculation of an average Sherwood number using the correlation proposed by Hawthorn [8, 9]. However, this correlation is not valid in usual industrial catalyst testing conditions and cannot be generally applied in a test procedure. More recent works by Gupta et al. [10], Balakotaiah et al. [11] and West et al. [12] provide more in-depth discussions of the impact of various flow regimes (including developing flows) and channel shapes on mass transfer in catalyst monoliths, combining theoretical developments and experimental validations.

The objective of this paper is to take advantage of these developments to propose a semi-empirical method to quantify the impact of flow regimes in SCR catalyst activity testing, in order to decouple the mass transfer phenomena and the intrinsic, chemical kinetics. Such a method will relax the testing constraints, make the conclusions of such tests more general through an access to the intrinsic kinetics, and decrease the overall costs of SCR catalyst production and management, for instance by reducing the amount of flue gas needed to perform a test.

Section 2 recalls the basic equations generally used in practical applications to assess the performances of SCR catalysts, as well as the related assumptions. In Section 3, the impact of the flow regime and the sample length on the average mass transfer coefficient is discussed in more details, based on the current state-of-the-art knowledge. In Section 4, we propose a semi-empirical method to quantify the contribution of mass transfer during industrial activity testing. It is based on the experimental adjustment of mass transfer correlations presenting a suitable form. In Section 5, the proposed method is applied to experimental data from the literature.

2. Catalytic NO\textsubscript{x} reduction and catalyst activity

In this Section, a simplified approach is used to derive the basic equations generally used in practical applications to assess the performances of SCR catalysts. It is mainly based on the industrial and scientific references [3] and [9].
A recent, more rigorous development of a one-dimensional model of a straight channeled, washcoated catalytic monolith can be found in [13].

Selective Catalytic Reduction (SCR) of NO\(_x\) (essentially NO) by NH\(_3\) can be described by the following lump reaction [9]:

\[
4 \text{NO} + 4 \text{NH}_3 + \text{O}_2 \rightarrow 4 \text{N}_2 + 6 \text{H}_2\text{O}
\]  

(1)

The overall kinetics of this process are essentially first-order in NO and zero-order in NH\(_3\) concentrations in typical industrial conditions [9, 3]. In other words, the NO concentration is the limiting factor for the reaction. In order to react, NO must first migrate from the bulk gas to the surface of the catalyst and then diffuse into the pores to reach active sites. The transfer of NO\(_x\) molecules from the bulk gas to the surface is ruled by the mass transfer coefficient \(h_m\), that is a function of the flow regime and the properties of the gas phase. The driving force for this mass transfer is of course the difference in NO\(_x\) concentration between the gas phase and the catalyst surface, as expressed in the following equation:

\[
\dot{n}_{NO_x} = h_m ([NO_x]_B - [NO_x]_S)
\]  

(2)

where \(\dot{n}_{NO_x}\) is the molecular flux of NO\(_x\) from the bulk gas to the surface of the catalyst (per unit of surface), \([NO_x]_B\) is the bulk concentration of NO\(_x\) and \([NO_x]_S\) is the concentration of NO\(_x\) at the surface of the catalyst. Considering a first-order reaction in NO\(_x\), the subsequent consumption of NO\(_x\) in the pores of the catalyst can be expressed as [9, 3]:

\[
\dot{\omega} = -k_c [NO_x]_S
\]  

(3)

where the kinetic constant \(k_c\) also accounts for pore diffusion [3]. In steady state conditions, the chemical rate of consumption \(\dot{\omega}\) is equal to the flux to the catalyst surface, and the following relation between \([NO_x]_B\) and \([NO_x]_S\) can
Therefore be derived:

\[ [NO_x]_S = \frac{1}{1 + \frac{k_c}{h_m}} [NO_x]_B \]  

(4)

where the ratio between the kinetic constant \( k_c \) and the mass transfer coefficient \( h_m \) appears. These coefficients are functions of the temperature, but they can be considered as constant as long as the SCR system is operated at a constant temperature, which is the case during constant load operation of the power plant.

In order to obtain the evolution of the bulk NO\(_x\) concentration along the channels of the catalyst, we state that the rate of decrease of \([NO_x]_B\) in the longitudinal direction is equal to the rate of consumption of NO\(_x\) in steady-state conditions, which can now be expressed both as a function of \([NO_x]_S\) or \([NO_x]_B\):

\[
d(\bar{u}S[NO_x]_B) = -k_c[NO_x]_S dA = -k_c \frac{1}{1 + \frac{k_c}{h_m}} [NO_x]_B dA
\]

(5)

where \( S \) is the section of the channel, \( \bar{u} \) is the average gas velocity in the channel, and \( A \) is the available surface of catalyst in the channel. In isothermal conditions and for a negligible pressure drop, the product \( (\bar{u}S) \) is constant, and this gives the following differential equation ruling the evolution of \([NO_x]_B\) along the catalyst channels:

\[
\frac{d[NO_x]_B}{dz} = -\frac{a}{\bar{u}S} \frac{1}{\frac{k_c}{h_m}} [NO_x]_B
\]

(6)

where \( z \) is the longitudinal position along the channel, and \( a \) is the available catalyst surface per unit length, such that \( dA = a \, dz \).

Assuming that \( k_c \) and \( h_m \) also remain constant along the channel, the integration of this differential equation gives:

\[
[NO_x]_{out} = [NO_x]_{in} \exp \left( -\frac{A}{\bar{u}S} \frac{1}{\frac{k_c}{h_m}} \right)
\]

(7)
showing that the bulk concentration of NO$_x$ decreases exponentially with the available catalyst surface. By defining the efficiency of the system $\eta_{NO_x}$, the area velocity $A_V$ and the activity of the catalyst $K$ as follows:

$$\eta_{NO_x} = \frac{[NO_x]_{in} - [NO_x]_{out}}{[NO_x]_{in}}$$

$$A_V \equiv \bar{u}S \frac{A}{\bar{A}}$$

$$k \equiv \frac{1}{k_c + 1/h_m}$$

one gets the well-known expression for the efficiency of a catalyst as a function of $A_V$ and $k$ [3, 9]:

$$\eta_{NO_x} = 1 - \exp\left(-\frac{k}{A_V}\right)$$

The activity $k$ of a given catalyst can therefore be obtained from the efficiency $\eta_{NO_x}$ that is measured for a known area velocity $A_V$:

$$k = -A_V \ln (1 - \eta_{NO_x})$$

which is the purpose of activity testing.

Eq. [10] shows that the catalyst activity $k$ is a function of the intrinsic chemical constant $k_c$ and the mass transfer coefficient $h_m$, under the form of two conductivities put in series. If one of those two constants was significantly higher than the other one, it could be neglected: $k$ is equal to $k_c$ if mass transfer occurs very quickly compared to the intrinsic kinetics (kinetically controlled process) and $k$ is equal to $h_m$ if the reaction occurs much faster than mass transfer (mass transfer controlled process). None of these two constants can actually be neglected: the SCR process is neither purely kinetically nor purely mass transfer controlled [3].

Although the activities derived from catalyst testing are obtained using Eq. [12] it should be noted that this equation is only valid under the strong assumption that $k_c$ and $h_m$ are constant along the catalyst channel. This is certainly
not the case for \( h_m \), as both the gas velocity and the NO\(_x\) concentration profiles need to develop at the inlet of the channel. This is why it is recommended that the length of a tested sample remain as close as possible to the actual length of the catalyst, in addition to the gas velocity in the channel: the relative length of the entry zone can have a significant impact on the derived activity [12, 3, 14]. This will be discussed in Section 3.

Most probably, \( k_c \) also varies along the channels of a used catalyst, as the various deactivation mechanisms at stake do not necessarily occur in a homogeneous way through the whole catalyst [15]. It can however be considered constant for a new catalyst.

Strictly speaking, Eq. 6 can therefore not be integrated in such a straightforward manner to obtain Eqs. 7 and 11. \( k_c \) and \( h_m \) should be expressed as a function of \( z \) before integration. Alternatively, equivalent parameters \( k_{c,eq} \) and \( h_{m,eq} \) can be defined such that Eq. 7 becomes:

\[
[NO_x]_{out} = [NO_x]_{in} \exp \left( -\frac{A}{uS} \frac{1}{k_{c,eq}} + \frac{1}{h_{m,eq}} \right) \tag{13}
\]

This leads to a new definition of the derived activity \( k \):

\[
k \equiv \frac{1}{\frac{1}{k_{c,eq}} + \frac{1}{h_{m,eq}}} \tag{14}
\]

that is the actual result of activity testing. It should be noted that, unlike what is suggested in [3], \( k_{c,eq} \) and \( h_{m,eq} \) are not equal to the average values of \( k_c \) and \( h_m \) along the channel (\( \bar{k}_c \) and \( \bar{h}_m \)), because \( k \) is not a linear function of those two parameters. They are the equivalent, constant parameters to be taken into account such that Eq. 13 holds.

3. Variable mass transfer coefficients in developing flows

In order to investigate the possible relaxation of the restrictive assumption of constant mass transfer coefficient, we will discuss here the evolution of mass transfer along the catalyst channels.
The state-of-the-art knowledge on mass transfer phenomena in catalytic monoliths is not specific to SCR systems used in thermal power plants: such catalysts are also used for pollution reduction in automobiles, or catalytic oxidation of volatile organic compounds (VOCs), among others [11]. The flow in the channels of such catalysts, once fully established, is generally laminar (with Reynolds numbers in the range $0 - 2300$) [11, 12], which is the case for the considered SCR systems [9].

Mass transfer phenomena are generally described in terms of evolution of the non-dimensional Sherwood number:

$$Sh \equiv \frac{h_m d}{D}$$  \hspace{1cm} (15)

where $d$ is the hydraulic diameter of the channels and $D$ is the molecular diffusion coefficient of NO molecules in the flue gas. The evolution of $h_m$ along a specific channel in a specific fluid can therefore be easily derived from a general correlation for the local Sherwood number. It is generally admitted that the local $Sh$ in the channel of a catalyst monolith is a function of the non-dimensional longitudinal variable $z^*$ [9]:

$$z^* \equiv \frac{z}{d} \frac{1}{Re \cdot Sc} = \frac{zD}{d^2 \bar{u}}$$ \hspace{1cm} (16)

where $Re$ and $Sc$ are the Reynolds and the Schmidt numbers, respectively. The Reynolds number compares the inertia of the fluid to its kinematic viscosity $\nu$,

while the Schmidt number compares the fluid viscosity to its molecular diffusivity $D$:

$$Re \equiv \frac{\bar{u} d}{\nu}$$ \hspace{1cm} (17)

$$Sc \equiv \frac{\nu}{D}$$ \hspace{1cm} (18)

Other authors use the transverse Peclet number $Pe_t$ as a variable [10, 11, 12], which is actually equal to $1/(16 \cdot z^*)$. When $z^* \to \infty$ (or $Pe_t \to 0$), i.e. when
a laminar flow is fully established in the channel, the Sherwood number tends
towards the asymptotic value $Sh_\infty$, which is only a function of the shape of the
channel and can be analytically determined [11, 12]. Figure 2 shows values of
$Sh_\infty$ for common channel geometries.

\begin{align*}
Sh_\infty &= 2.977 \\
Sh_\infty &= 3.656 \\
Sh_\infty &= 7.541 \\
Sh_\infty &= 2.496 \\
Sh_\infty &= 3.392 \\
Sh_\infty &= 2.966
\end{align*}

Figure 2: Values of the asymptotic Sherwood number $Sh_\infty$ reached in a developing laminar
flow for common channel geometries [12].

Many previous studies describe experimental, theoretical and simulation re-
sults for the evolution of $Sh$ towards $Sh_\infty$ as a function of $z^*$. Tronconi et al. [9],
Gupta et al. [10], Balakotaiah et al. [11] and West et al. [12] provide literature
reviews of the proposed correlations. The most common ones actually describe
the evolution of the average Sherwood number $\overline{Sh}$ as a function of the length of
the channel and the asymptotic value $Sh_\infty$. The most widely used correlation,
proposed by Hawthorn [8], has the following form [9, 12, 3]:

$$\overline{Sh} = Sh_\infty \left[ 1 + \frac{C}{z^*} \right]^n$$  \hspace{1cm} (19)

where $C$ and $n$ are adjustable parameters. Hawthorn [8] proposes $C = 0.095$
and $n = 0.45$ [9, 3]. Based on experimental data, Uberoi et al. [16] propose
C = 0.139 and n = 0.81, with a modified value of $Sh_\infty$ for a square channel compared to the analytic value ($Sh_\infty = 2.696$ instead of 2.977) \cite{9}. Holmgren et al. propose another form of correlation for a square channel \cite{12}:

$$Sh = Sh_\infty \exp(0.03/z^*)$$

(20)

with an asymptotic Sherwood number $Sh_\infty$ equal to 3.53, which is significantly higher than the values of Hawthorn \cite{8} and Uberoi et al. \cite{16}. Their correlation however applies to square channel with rounded corners. Figure 3 illustrates the evolution of $\overline{Sh}$ following Hawthorn \cite{8}, Uberoi et al. \cite{16} and Holmgren et al. \cite{17} for the case of a square channel (honeycomb monolith). In all three cases, the effect of an entry region is seen for $z^* < 0.2$ – 0.4, where the mass transfer coefficient is significantly higher than its asymptotic value (notice the logarithmic scale). This effect is due to the development of the concentration profile in the first part of the channel, that is considered as flat for $z^* = 0$ (homogeneous NO\textsubscript{X} concentration). In order to limit the impact of the entry zone on the overall mass transfer process, large values of $z^*$ should therefore be favoured. In typical SCR catalyst test conditions, i.e. sample lengths in the range 0.3 – 1 m, channel hydraulic diameters in the range 3 – 10 mm and flue gas velocities in the range 1 – 10 m/s \cite{3}, $z^*$ is the range 0.005 – 2. This means that the influence of the entry zone can be very high when short samples are tested at high velocities, while the combination of long samples and reduced velocities results in fully established laminar flows, with a limited contribution of the entry zone to the overall mass transfer. In \cite{3}, although full scale sample lengths and flue gas velocities are generally advised, it is also concluded that, in order to limit the impact of varying mass transfer regimes, short samples should be tested at low velocities, while there is more latitude with longer samples \cite{3}, which is to say that $z^*$ should be as high as possible, such that the average Sherwood number is as close as possible to its asymptotic value. From this discussion, it is also interesting to conclude that same values of $z^*$ should result in the same $\overline{Sh}$, which means that a reduction of the sample length can be
compensated by a proportional decrease of the flue gas velocity to obtained the same test results, as confirmed by the calculations performed by EPRI in [3].

Based on an analogy with heat transfer in developing laminar flows in ducts (the Graetz problem), and by curve-fitting the experimental results of Shah and London [18], Tronconi et al. proposed the following correlation for the local Sherwood number and used it in steady and dynamic simulations of honeycomb SCR systems [19]:

\[
Sh = Sh_\infty + 8.827(1000z^*)^{-0.545} \exp(-48.2z^*)
\]  

(21)

where the original value of the asymptotic Sherwood number was adapted to square channels [19].

It is however very important to notice that, as highlighted by West et al. [12], a correlation with the form of Eqs. [19, 20] or [21] does not distinguish between fully developed and developing flows in terms of velocity profile. Indeed, they do not explicitly contain the Schmidt number Sc. Therefore, such correlations
do not account for an entry region in terms of velocity, but only in terms of concentration, as if the velocity profile was immediately established at the inlet of the channel. This would correspond to the case of a fully developed flow for \( z^* = 0 \), i.e. a flow in which the viscous effects are infinitely rapid compared to molecular diffusion (\( \text{Sc} = \infty \)) \[12\]. The limit case where \( \text{Sc} = 0 \) would correspond to a flat velocity profile \[12\].

There is sometimes a confusion in the literature between the developments of the concentration profile and the velocity profile, and correlations with the form of Eq. \[19\] are used to described the effect of entry regions attributed to the transition from a turbulent flow to a laminar flow along the channel, which is indeed expected in industrial applications \[3, 14\]. In full rigour, accounting for a flow transition in the first part of the channel cannot be done without considering a finite Schmidt number.

West et al. \[12\] studied in details the influence of the Schmidt number and derived expressions for the Sherwood number in developing laminar flows. They showed that \( \text{Sh} \) must approach that corresponding to the fully developed case (\( \text{Sc} = \infty \)) for \( Pe_t \to 0 \) (or \( z^* \to \infty \)) while in the entry region it is independent of the duct geometry, but of course varies with the Schmidt number \[12\]. As a first approximation, they propose to combine those two asymptotes in a single correlation \[12\]:

\[
\begin{align*}
\text{Sh} &= 1.4 \, Pe_t^{1/2} \, Sc^{-1/6} \quad \text{for} \, Pe_t > 0.5 \, \text{Sh}_{\infty}^2 \, Sc^{1/3} \\
&= \text{Sh}_{\infty} \quad \text{for} \, Pe_t < 0.5 \, \text{Sh}_{\infty}^2 \, Sc^{1/3}
\end{align*}
\]  

(22)

(23)

In order to reduce the error in the transition zone, they also propose the following expression \[12\]:

\[
\text{Sh} = \text{Sh}_{\infty} + 2.565 \, Sc^{-\frac{1}{6}} \frac{z^*^{-2}}{10^4 + 9.125 \, z^*^{-\frac{5}{2}}} \quad \text{for} \, Pe_t < 0.5 \, \text{Sh}_{\infty}^2 \, Sc^{1/3}
\]  

(24)

where \( \text{Sh}_{\infty} \) accounts for the shape of the channel. When \( \text{Sc} \) or \( z^* \to \infty \), \( \text{Sh} \to \text{Sh}_{\infty} \). They found that the use of this correlation with the proposed parameters results in a maximum error of 3 % when compared to numerical simulations.
of the Navier-Stokes equations for developing laminar flows. Their correlation is also validated against experimental results, although where the effect of turbulence at the inlet of the channel was minimised, i.e. for laminar flows only.

When a turbulent flow enters narrow deNO\textsubscript{x} catalyst channels, it transitions to a laminar flow. This process is called laminarization, or reverse transition. As explained by Holmgren and Anderson [17], turbulence in the entry zone of the channels can actually have several causes: the turbulent nature of the flow entering the monolith, the turbulence generated by the wall of the catalyst at the entrance, and the surface roughness of the channels. In practical applications, the flow upstream of the catalyst is generally turbulent. From their experimental and numerical studies of CO oxidation in monolith catalysts, they concluded that the higher mass transfer that they observed and simulated at moderate but increasing inlet Reynolds numbers are due to the turbulence generated at the inlet of the catalyst. Tronconi and Beretta [9] also suggested that the correlation of Uberoi and Pereira [16] predicts higher Sherwood numbers because of turbulent effects [20]. The impact of turbulence in the cited works is also suggested and discussed by West et al. [12] to argue that their own experiments are conducted in the absence of such effects. More recently, Ström et al. [21, 20] used Large-Eddy Simulations (LES) to study the impact of the turbulence in the entry zone of automotive monolithic reactors. No significant time-averaged effects on mass transfer due to the inlet turbulence was found for the investigated system. Temporal fluctuations of the conversion at the outlet were however observed. Tanno et al. [15, 22] used Laser-Doppler Velocimetry (LDV) in a wind tunnel and Direct Numerical Simulation (DNS) to study the impact of the turbulent-laminar flow transition on the degradation and on the efficiency of deNO\textsubscript{x} catalysts used in thermal power plants. The studied catalysts presented larger channels than those modelled by Ström et al. for automotive applications, which made the system more sensitive to the impact of inflow turbulence [20]. The authors also suggest that turbulent-to-laminar transitions might not be accurately captured by LES [22]. Based on their experimental and numerical studies, they characterised the flow transition
and concluded that higher intensities of inflow turbulence results in higher mass transfer in the channels. Interestingly, they also point out from the DNS results that, although turbulent eddies promote mass transfer mainly in the entry region, remaining cross-sectional fluid motions still contribute to a higher activity further in the channel, before vanishing as the flow becomes completely laminar. Based on the latter experimental and DNS results [15, 22], we will here consider that turbulence can have a non-negligible impact on mass transfer in the entry zone of deNO\textsubscript{x} catalysts used in power plants, and should be considered when assessing the role of mass transfer in the overall activity of a catalyst sample.

Although reliable correlations were obtained for the average Sherwood number in developing laminar flows (including in terms of velocity profile, i.e. as a function of the Schmidt number), no correlation is available for the cases where a transition from a turbulent to a laminar flow occurs in the entry zone of the catalyst. The effect of turbulence can however not be avoided in practical applications, both in full-scale and lab-scale conditions [12, 3, 15, 21, 14], and this effect is expected to be more pronounced for catalyst samples presenting a low non-dimensional length $L^* \left( \frac{L}{D_d \bar{u}} \right)$, i.e. for reduced lengths and/or high velocities.

It should also be noted that, even if an average Sherwood number could be computed using adequate correlations, it would still differ from the equivalent Sherwood number needed to decouple the intrinsic kinetics from mass transfer in Eq. 14, as in general $h_{m,eq} \neq \bar{h}_m$.

4. Semi-empirical assessment of mass transfer contribution in entry zones

In this paper, we want to address the need for a quantification of mass transfer phenomena (i.e. the role of Sh, or $h_m$) during industrial catalyst activity testing in which turbulence can impact the mass transfer in the entry zone, in order to decouple their contribution to the overall denitrification kinetics from that of the intrinsic kinetics (i.e. $k_c$). In order to reach this objectives, it is therefore needed to:
1. Derive a general expression of the overall catalyst activity $k$ as a function of a variable Sherwood number along the catalyst channels (i.e. relax the assumption of a constant $h_m$);

2. Combine this expression with a correlation for the Sherwood number along the catalyst channel during industrial testing.

The first point is addressed in Sec. 4.1. As far as the second point is concerned, the purpose of this study is not the derivation of a general correlation valid for all possible cases of transition from a turbulent entry zone to an established laminar flow. The development or the decay of turbulence indeed depends on many influencing factors, like the nature of the inlet stream, the shape of the entrance of the channel, the manner in which the fluid flows towards the channel entrance, the roughness of the channel wall, and the disturbances in the velocity of the flow [23], which makes the contribution of the turbulent entry zone to the overall mass transfer very much case-dependent.

Instead, we propose a semi-empirical approach taking advantage of a limited number of experimental test results performed on a given sample for various flue gas velocities and/or catalyst lengths (i.e. for various $z^*$) to calibrate a correlation presenting a suitable form. We will show in Sec. 4.3 that 2 activity tests at various $z^*$ are in principle sufficient to characterise the contribution of mass transfer to the overall kinetics and to derive the value of the equivalent, intrinsic parameter $k_{c,eq}$.

### 4.1. Generalised expression for the catalyst activity

In order to generalise Eq. 14 to the case of a varying mass transfer coefficient, we need to come back to the differential form of Eq. 6 and express $k_c$ and $h_m$ as a function of $z$:

$$\frac{d [NO_x]_B}{[NO_x]_B} = -\frac{a}{\bar{u}S} \frac{1}{k_c(z)} + \frac{1}{h_m(z)} dz$$

(25)

The non-dimensional Sherwood number $Sh$ and longitudinal position $z^*$ can
here be introduced, which gives:

\[
\frac{d [NO_x]_B}{[NO_x]_B} = -\frac{a d}{S} \frac{1}{D \frac{1}{d} k_c(z^*) + \frac{1}{Sh(z^*)}} dz^*
\] (26)

Integration leads to the following expression:

\[
[NO_x]_{out} = [NO_x]_{in} \exp \left( -\frac{a d}{S} \int_0^{L^*} \frac{1}{D \frac{1}{d} k_c(z^*) + \frac{1}{Sh(z^*)}} dz^* \right)
\] (27)

which reduces to Eq. 13 when \(k_c\) and \(Sh\) are constant along the channel. Once the evolution of the NO\(_x\) concentration along the channel is known, expressions can be easily be derived for the efficiency and the activity of the catalyst:

\[
\eta_{NO_x} = 1 - \exp \left( -\frac{a d}{S} \int_0^{L^*} \frac{1}{D \frac{1}{d} k_c(z^*) + \frac{1}{Sh(z^*)}} dz^* \right)
\] (28)

\[
k(L^*) = \frac{D}{d} \frac{1}{L^*} \int_0^{L^*} \frac{1}{D \frac{1}{d} k_c(z^*) + \frac{1}{Sh(z^*)}} dz^*
\] (29)

For a new catalyst, the reaction rate \(k_c(z^*)\) can be considered as constant. It is however not the case for a used catalyst, in which deactivation mechanisms do not occur homogeneously along the catalyst length. As it is not possible to have access to the spatial distribution of \(k_c\) in the latter case, the notation \(k_{c,eq}\) will be used for this parameter, in order to highlight that it may correspond to a restrictive assumption. Eq. therefore becomes:

\[
k(L^*) = \frac{D}{d} \frac{1}{L^*} \int_0^{L^*} \frac{1}{D \frac{1}{d} k_{c,eq} + \frac{1}{Sh(z^*)}} dz^*
\] (30)

which is the general equation we were seeking. Eq. 30 of course reduces to Eq. 14 when \(Sh\) is also constant along the channel. It should also be noted that, if \(Sh(\to 0) = \infty\) and \(Sh(\to \infty) = Sh_\infty\), i.e. the limit cases considered in all the presented correlations, then

\[
k(\to 0) = k_{c,eq}
\] (31)
and

\[
k(\to \infty) = \frac{1}{k_{c,eq} + \frac{d}{D} \frac{1}{Sh_\infty}} \tag{32}
\]

4.2. Mass transfer correlation for entry zones

As already stated, we aim here at proposing a suitable form of semi-empirical correlation for the local Sherwood number \(Sh(z^*)\) when a turbulent-laminar transition occurs, to be calibrated on a limited number of catalyst activity tests and to be used in Eq. \[30\] in order to decouple the contribution of \(Sh\) from the contribution of the intrinsic, chemical kinetic parameter \(k_{c,eq}\). Assuming that mass transfer is also ruled by the transverse Peclet number \(Pe_t\) (or \(z^*\)) in a turbulent-laminar transition zone, we start from an analogy with heat transfer in turbulent entry zones, as previously done by Tronconi et al. to derive their correlation for laminar flows [19].

The Nusselt number is the equivalent of the Sherwood number for heat transfer. It compares the heat transfer coefficient \(h\) to the thermal conductivity of the fluid \(\lambda\):

\[
Nu = \frac{hd}{\lambda} \tag{33}
\]

In a turbulent entry zone, it is generally admitted that \(Nu\) decreases towards its asymptotic values as function of the longitudinal length to the power \(-\frac{2}{3}\), although various coefficients and asymptotic values are proposed [24] [25] [23].

By analogy, we will consider here that the decrease of the Sherwood number towards its asymptotic value in a turbulent entry zone is proportional to \(z^*^{-\frac{2}{3}}\) and use the form of correlation proposed for the local Nusselt number in [23] to write:

\[
Sh_T(z^*) - Sh_\infty \propto \frac{1}{3} I_t Sc^{-\frac{1}{6}} z^*^{-\frac{2}{3}} \tag{34}
\]

where \(I_t\) is the turbulence intensity of the inflow. We accounted for the dependence on the \(Sc\) number to the power \(-\frac{1}{6}\) for the development of the velocity
profile, as used by West et al. [12] (see Eqs. 22 and 24). ShT is considered here as the upper limit for the mass transfer in an entry zone where a transition from a turbulent to a laminar flow occurs. The lower limit is the Sherwood number ShL proposed by West et al. [12] for a developing laminar flow in the absence of a turbulent entry zone, see Eq. 24:

\[ Sh_L(z^*) = Sh_{\infty} + \frac{2.565 \cdot 10^4 \cdot z^* - 2}{1 + 9.125 \cdot z^* - 2} \]  \hspace{1cm} (35)

As both ShT and ShL converge towards Sh\(\infty\) (but at different rates), we propose here to characterise the mass transfer in a catalyst channel as a linear combination of the defined upper and lower limits, depending on a single adjustable parameter \(\varepsilon\) accounting for the relative influence of turbulence in the entry zone:

\[ Sh(z^*) = Sh_{\infty} + (1 - \varepsilon) (Sh_L(z^*) - Sh_{\infty}) + \varepsilon \frac{1}{3} Sc^{-\frac{1}{6}} z^{*-\frac{2}{3}} \]  \hspace{1cm} (36)

4.3. Semi-empirical method

Based on the previous developments, we propose to use the following methodology to quantify the contribution of mass transfer and intrinsic kinetics to the overall denitrification kinetics for a given catalyst monolith sample tested in a given bench:

1. Perform at least 2 activity tests at various \(z^*\), in order to obtain different values of the overall activity \(k\);
2. Combine the correlation of Eq. 36 in the general expression obtained for \(k\) (Eq. 30):
3. Through numerical integration, seek the values of \(k_{c,eq}\) and \(\varepsilon\) that minimise the least-square error between the computed activities and the experimental results.

Although 2 activity tests are sufficient in principle to determine the value of \(k_{c,eq}\) and \(\varepsilon\), the efficiency of such a method will of course increase with a larger number of experimental data for various flue gas velocities and/or sample
length (i.e. various \(z^*\)). The selected values should adequately cover the zones of interest, e.g. a sufficient amount of low \(z^*\) values if a large influence of the entry zone is suspected. Once \(k_{c,eq}\) and \(\varepsilon\) are determined, the overall activity \(k\) can be derived for any value of \(z^*\). The average \((\overline{h}_m)\) and the equivalent \((h_{eq})\) mass transfer coefficients can also be retrieved.

5. Case study

The proposed semi-empirical method is here applied to experimental data from the literature. Detailed catalyst activity results obtained for various flue gas velocities and sample lengths are not easy to find, especially for low values of \(z^*\). In order to validate their mathematical model of a SCR reactor, Tronconi et al. \[19\] however published the results of 24 tests performed on the same honeycomb catalyst for various area velocities, and for 3 different sample lengths. Those results are illustrated in Fig. 4 (left). The tests were performed at 380\(^\circ\)C. The hydraulic diameter of the channels \(d\) is equal to 6 mm. The related uncertainties are unfortunately not available.

The activity \(k\) of the catalyst can be computed for each of these test results based on Eq. 12, and plotted vs. the non-dimensional length of the sample \(L^*\) (for \(d = 6\) mm \[19\] and \(D = 2.32 \times 10^{-5}\) m\(^2\)/s \[26\]). Figure 4 (right) shows that the resulting activity of the catalyst is not constant, but exhibits a sharp increase for \(L^* < 0.04\), while it seems to tend towards an asymptotic value for \(L^* > 0.2\). This is consistent with an increased influence of an entry zone for low values of \(z^*\), where mass transfer is significantly higher than in the established flow. Notice that the lengths of the samples are short compared to what is recommended for industrial activity testing \[3\]. These results however highlight the role of the entry zone for low values of \(L^*\), which is of great interest in the frame of this study.

The methodology proposed in Section 4.3 is applied to the data of Fig. 4 for each data point, numerical integrations of Eq. 30 are performed, using Eq. 36 for the expression of \(Sh(z^*)\) (with \(Sc = 0.7\) \[12\]). The values of the
parameters $k_{c,eq}$ and $\varepsilon$ resulting in the best possible fit with the experimental data were determined using the least-squares regression method. In order to avoid overweighting the first part of the curve of Fig. 4, clusters of points were reduced to a single representative point. As the objective of the proposed method is to limit the number of necessary activity tests, such a reduction of the data set will however not be needed in practical cases.

The optimum values in this case were found to be: $k_{c,eq} = 244 \text{ m/h}$ and $\varepsilon = 0.61$. Figure 5 illustrates the excellent agreement between the resulting evolution of $k$ with the non-dimensional sample length $L^*$ and the experimental data. It should however be noted that these results do not constitute a formal validation, nor a formal quantification, of the role of turbulence in the entry
zone. Other correlations could lead to the same (or better) results, especially if one considers the simple approach that was followed to derive the basic equations of Section 2. Advanced correlations derived for developing laminar flows with various boundary conditions are obvious candidates [13]. Notwithstanding the discussion of Section 3 on the role of turbulence in the entry zone, the proposed semi-empirical method could indeed be applied to adjust other types of correlations.

\[ K_{c, eq} = 244 \text{ m/h} \]

\[ \varepsilon = 0.61 \]

Figure 5: Catalyst activity \( k \) vs. non-dimensional sample length \( L^* \): agreement between the proposed correlation and the experimental results from [19]. L = 30 cm (circles), 15 cm (triangles) and 10 cm (squares).

Figure 6 compares the evolution of the local Sherwood number \( Sh(z^*) \) for the studied case with the laminar correlation \( Sh_L(z^*) \) of Eq. 35. The evolution of the local mass transfer coefficient \( h_m \) can be deduced from \( Sh \), and therefore also its average value as a function of the non-dimensional sample length \( L^* \). Using Eq. 14, the equivalent mass transfer coefficient \( h_m, eq \) can also be deduced from the values of the global activity \( k \) that were computed (see Fig. 5). These three functions are compared in Fig. 7. As the mass transfer coefficient decreases
along the catalyst channels, both the average and the equivalent coefficients ($\bar{h}_m(L^*)$ and $h_{m,eq}(L^*)$) are higher than the local value at the outlet of the sample ($h_m(L^*)$). As the global activity $k$ is not a linear function of $h_m$, but presents an asymptote for high values of $h_m$ (i.e. $k_{c,eq}$), the equivalent mass transfer coefficient is lower than its average value along the channel. It should be noticed that $k_{c,eq}$, $h_{m,eq}$, and therefore $k$, are of the same order of magnitude, which confirms that this problem is neither purely kinetically controlled, nor purely mass transfer controlled.

![Figure 6: Evolution of the local Sherwood number $Sh(z^*)$ for $\varepsilon = 0.61$, compared to the upper and lower limits ($Sh_T(z^*)$ and $Sh_L(z^*)$, respectively).](image)

6. Conclusions

In this paper, we proposed a semi-empirical method to quantify the role of mass transfer in industrial lab-scale activity tests performed on SCR deNO$_x$ catalyst samples. The proposed method is based on the experimental adjustment of a mass transfer correlation presenting a suitable form for channel flows where a transition from a turbulent to a laminar regime occurs, which is the
Figure 7: Local, average and equivalent mass transfer coefficients vs. non-dimensional length of the catalyst sample.

case for industrial applications. Two activity tests at various sample lengths and/or gas velocities are sufficient to derive the evolution of the mass transfer coefficient along the catalyst channel as well as the intrinsic chemical reaction rates.

The proposed method was applied to a series of 24 tests performed at various sample lengths and gas velocities. The test conditions are such that the effect of low non-dimensional sample lengths is highlighted. The agreement between the adjusted correlation and the experimental results is excellent. The intrinsic chemical reaction rate and the evolution of the mass transfer coefficient were deduced. Their values confirm that the denitrification process in SCR systems is neither purely kinetically controlled, nor purely mass transfer controlled, which justifies the development of a method to decouple their impacts. The derived evolution of the mass transfer coefficient was compared to its average value and to the equivalent parameter to be taken into account in a lump expression of the catalyst activity. Our results show that the equivalent mass transfer coefficient
is lower than the average coefficient, which is consistent with the non-linear relation between the mass transfer rate and the overall catalyst activity.

These results are however not sufficient to validate, nor quantify, the role of turbulence in the entry zone of monolithic catalysts. Considering the simplified approach that was followed here, advanced correlations derived for developing laminar flows could give similar or better results. Notwithstanding the discussion on the role of turbulence in the entry zone, the proposed semi-empirical method could indeed be applied to adjust other types of correlations.

The proposed method allows for the relaxation of some constraints expressed in industrial activity testing standards. As the contribution of mass transfer to the global kinetics can now be quantified, lab-test flow conditions such as the length of the sample and/or the flue gas velocity can differ from the full scale application. The test results can also be extrapolated to various flow conditions. This can lead to a reduction of the overall industrial cost of deNO<sub>x</sub> catalyst production and management.

References


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