Development of a Kinetic Model of Lean-NOx-Trap and Validation through a Reactive CFD Approach

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Our activity is focused on the study of the kinetic of the Pt-Ba/γ-Al$_2$O$_3$ catalyst used in the Lean-NOx-Traps to store NOx as adsorbed nitrites and nitrates, and to reduce them to nitrogen. Kinetically relevant data have been collected by the Laboratoire Catalyse et Spectrochimie (ENSICAEN, France), using a spectroscopic reactor-cell, and on the basis of the collected data, a kinetic model has been developed, using as experimental responses the dynamic evolution of both the gas phase and the adsorbed species. In this work a reactive Computational Fluid-Dynamic (CFD)-based modeling approach is proposed for the first time, in order to keep into account the actual reactor-cell geometry (modeled as ideal PFR for the estimate of the kinetic parameters), and to obtain further information of the space-time evolution of the reactive system. For instance, a sensitivity analysis on the geometry of the system is proposed. Consequently, a new simulation tool, named CATalytic Post Processor, is here presented. CAT-PP is able to acquire the flow/velocity field obtained by the commercial code ANSYS Fluent and to solve the transport equations containing the kinetic scheme.

1. Introduction

Nowadays air pollution regulations from the automotive sector, with special emphasis on diesel NOx emissions, have become more stringent, according to the introduction of new international standards (e.g. Euro 6). Primary techniques could not match these requirements, hence catalytic after-treatment technologies are necessary. The issue of pollutants catalytic abatement from mobile sources, solved in the '80s and in the '90s through the adoption of three-way-catalysts (for the abatement of CO, unburned hydrocarbons and NOx), is today a new matter of research and development activities since when the need to reduce fuel consumption and the corresponding CO2 emissions has led to a shift of the market towards lean-burn engines, such as diesel or direct-injection gasoline engines, which operate in the presence of excess oxygen. Under these conditions, in fact, three-way catalysts, optimized for oxygen-free exhausts, do not ensure required NOx emission levels.

Two main catalytic after-treatment technologies have been studied for lean-burn engines after-treatment applications, which are the Selective-Catalytic-Reduction and the Lean-Nox-Trap. SCR has been the object of many studies, such as the one from (Vega et al., 2011), in which a mathematical model is proposed for the optimization of the SCR operating conditions. In the present work we focus our attention on the Lean-NOx-Trap catalytic system. Since the first Toyota patent (Kato et al., 1993), lean NOx traps (LNT) have been widely studied as potential solution to the NOx issue and today are commercially applied for small engines passengers cars. Such systems are based on the use of supported catalytic materials consisting of an alumina carrier on which alkali- and/or alkali-earth metal compounds (e.g. barium) and noble metals (e.g. platinum) are deposited. These materials, named NOx storage and reduction catalysts (NSR catalysts), operate under cyclic conditions, which conventionally alternate long periods (30-90 s) in the presence of excess oxygen, during which NOx species are

stored on the alkali- and/or alkali-earth metal compounds, with short rich phases (3-5 s), during which the adsorbed NOx species are reduced to nitrogen by means of partial oxidation products from engine exhaust-gases on the noble metal in the absence of oxygen. Nitrites and nitrates have been proposed as the main reaction intermediates involved in this cyclic process (Lietti et al., 2012; Nova et al., 2004). Nitrites, dominant on the catalytic surface during the storage at low temperatures (below 150-200°C), are easy to be reduced, but tends to oxidize to more stable nitrates at higher storage temperatures or after long accumulation period. Nitrates, rapidly formed on the storage sites especially at high temperatures (350°C), are instead more stable and thus more difficult to be removed in the rich phase.

From a literature survey, several works focused on the LNT kinetic modeling were found. (Olsson et al., 2005) proposed a kinetic scheme, based on a global approach, which considers only the experimental gas phase information, with a shrinking-core description of the mass transport within the barium particles. First-principles calculations based on density functional theory have been performed by (Broqvist et al., 2002), while thermodynamic calculations for different storage components were performed by (Kobayashi et al., 1997). In a recent work a new spectrokinetic approach, herein recalled, has been developed (Visconti et al., 2013), which uses as experimental responses to estimate the kinetic parameters the information collected from both the gas phase and the adsorbed one. These are innovative kinetic models where adaptive parameters are estimated through the modeling of quantitative information collected under actual process conditions upon using operando spectroscopic reactors. As we have recently shown in a preliminary paper (Visconti et al., 2013), such models, intrinsically consistent with the chemistry of the process, are fundamental in fact both for the understanding of the catalyst structure-activity relationships and for the engineering modeling of the LNT. As reported elsewhere (Na-Ranong et al., 2009), transient operation is indeed an effective method for determining kinetic parameters for such complex systems, according to its intrinsic cyclic and dynamic behavior. Moreover, dynamic FTIR-operando experiments allow to collect unsteady-state information (Lesage et al., 2003) of the active surface coverage during the reaction operation, that in traditional kinetics have to be guessed in order to gain a satisfactory fitting of the time-evolution of the gaseous species. In this regard it is worth noticing that although the potentiality of spectrokinetic approach has been already discussed in the literature (Meunier, 2010b), practical applications to kinetic analysis are not yet available. Severe challenges prevent in fact the development of such knowledge especially due to the difficulty related to a quantitative interpretation and reconciliation of the information coming from different techniques and obtained under ill-defined conditions. Among these, the complex and often unknown fluid-dynamic of the spectroscopic flow reactors has been shown to be a critical aspect (Carias-Henriquez et al., 2013; Meunier, 2010a; Yang et al., 2006).

Accordingly, the detailed spectrokinetic model of the LNT has been extended through the development of a new CFD-based simulation tool (CAT-PP), which can be used either to apply the developed spectrokinetic model to complex (non-ideal) reactor geometries, such as the real after-treatment reactors, or to account for the non-ideality of many commercial operando-reactors. The present modeling approach couples the kinetic and fluid-dynamic aspects as reported in the study of (Shuai and Wang, 2004) about the interactions of fluid-dynamics on a monolithic catalyst. (Kolaczkowski et al., 2007) faced the simulation of an isolated spherical pellet by means of a commercial CFD code, while (Deutschmann, 2001) introduces the Detchem code, and (Kanniche, 2009) the kinetic post-processing of CFD simulations of complex combustion systems.

2. Experimental apparatus

Experimental spectrokinetic data were collected by adopting the AABSPEC #CX spectroscopic reactor-cell (Lietti et al., 2012; Nova et al., 2004). This cell was loaded with a 0.1mm thin 13mm diameter cylindrical-shaped catalytic pellet, which formulation is Pt-Ba/γ-Al$_2$O$_3$ (1-20/100 w/w). Four TRM experiments were performed at 150, 200, 250 and 350°C, feeding the cell with an argon stream, which was enriched of NO + O$_2$ (1,000 ppm + 3%v/v) at zero time. The temporal evolution of both the species adsorbed on the catalyst within the IR-beam region and the gaseous species at the outlet of the cell was measured and recorded. Adspecies were detected with a FT-IR spectrometer, while the gas phase leaving the cell was analyzed with a mass spectrometer and a chemiluminescence detector (Visconti et al., 2013).
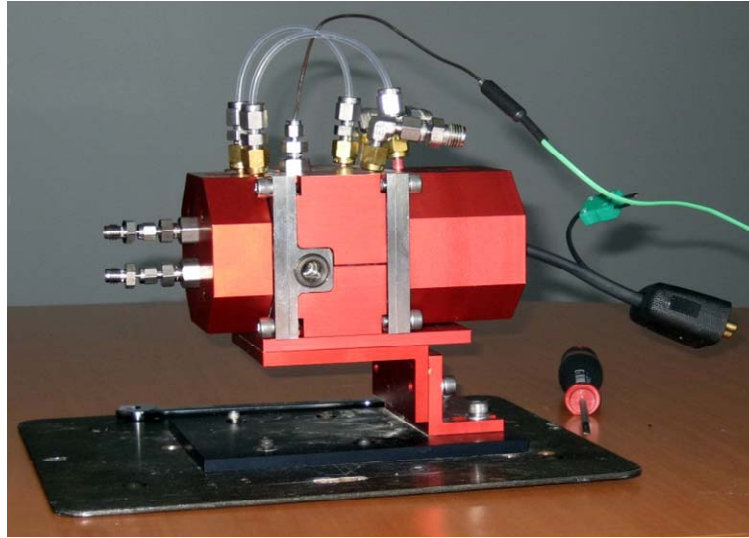
Figure 1: AABSPEC #CX IR-operando spectroscopic reactor-cell

3. Kinetic modeling

The lean storage phase has been considered in this work. Accordingly, the reactive species involve gas molecules (O_2, NO, NO_2) and adsorbed intermediates such as nitrites and nitrates, interacting with both platinum and barium oxide sites. In line with previous results by some of us, (Lietti et al., 2012; Nova et al., 2004), a kinetic mechanism with NOx accumulation is proposed, involving two different paths: the nitrite route and the nitrate route. The former proceeds with a stepwise oxidation mechanism occurring at Pt-Ba couples and leading to the formation of nitrite adspecies (NO_2^-). The stored nitrites are eventually oxidized to nitrates (NO_3^-) by NO_2. In the latter, NO is oxidized to NO_2 on platinum sites, which is eventually stored as nitrate adspecies. The resulting accumulation mechanism has been formalized as follows:

$$S1 : 2Pt + O_2 \leftrightarrow 2\,Pt-O \tag{1}$$

$$S2 : Pt-O + NO \leftrightarrow Pt + NO_2 \tag{2}$$

$$S3 : Pt-O + O^{2-} + 2NO \rightarrow Pt + 2NO_2 \tag{3}$$

$$S4 : 2NO_2 + O^{2-} \rightarrow NO_2^- + NO_3^- \tag{4}$$

$$S5 : NO_2 + NO_2^- \leftrightarrow NO + NO_3^- \tag{5}$$

The related kinetic rate expressions are here proposed. Further details are available elsewhere (Visconti et al., 2013), as the derivation of the lumped rate expression for the third reaction:

$$r_{S1} = k_{S1d} x_{O2} \theta_{Pt}^2 - k_{S1i} \theta_{Pt-O}^2$$

$$r_{S2} = k_{S2d} x_{NO} \theta_{Pt-O} - k_{S2i} x_{NO2} \theta_{Pt} \tag{6}$$

$$r_{S3} = k_{S3d} x_{NO} \theta_{Pt-O} \theta_{O2-} \tag{7}$$

$$r_{S4} = k_{S4d} x_{NO2}^2 \theta_{O2-} \tag{8}$$

$$r_{S5} = k_{S5d} x_{NO2} \theta_{NO2-} - k_{S5i} x_{NO} \theta_{NO3-} \tag{9}$$

Kinetic parameters have been estimated with a non-linear regression, based on the minimization of the difference between the reactor model simulations and the experimental data both in terms of gas-phase and adsorbed species concentrations. That optimization was performed using the NonLinearRegression class of the BzzMath numerical library (Buzzi-Ferraris and Manenti, 2012).

$$\min \sum_{i=1}^{NS} \left(\sum_{j=1}^{NT} \omega_j \left(y_{i,j}^{\;exp} - y_{i,j}^{\;mod} \left(\vec{b} \right) \right)^2 \right) \tag{10}$$

In Equation (10) b is the vector containing the kinetic parameters.

The reactor-cell was modeled as a series of parallel dynamic isothermal PFR reactors (Figure 2).

$$\varepsilon \frac{\partial C_i}{\partial t} = -\frac{1}{\tau}\frac{\partial C_i}{\partial z^*} + (1-\varepsilon)R_i \Omega_{Pt} \tag{11}$$

I.C.: $C_i(0,z) = C_{i,t0}$ B.C.: $C_i(t,0) = C_{i,z0}$ $C_i(t,0) = C_{i,z0}$ (12)

$$\Omega_{site}\frac{d\theta_j}{dt} = R_j \tag{13}$$

IC: $\theta_j(0,z) = \theta_{j,t0}$ (14)

with i = NO, NO$_2$, O$_2$ and j = NO$_2^-$, NO$_3^-$, Pt-O.

In these expressions, ε is the reactor void fraction, τ the residence time in the reactor, z* the dimensionless axial coordinate of the reactor, θj the degrees of coverage of the adspecies. Ω is instead the NOx adsorption capability [mol/m^3] of barium oxide and platinum sites.
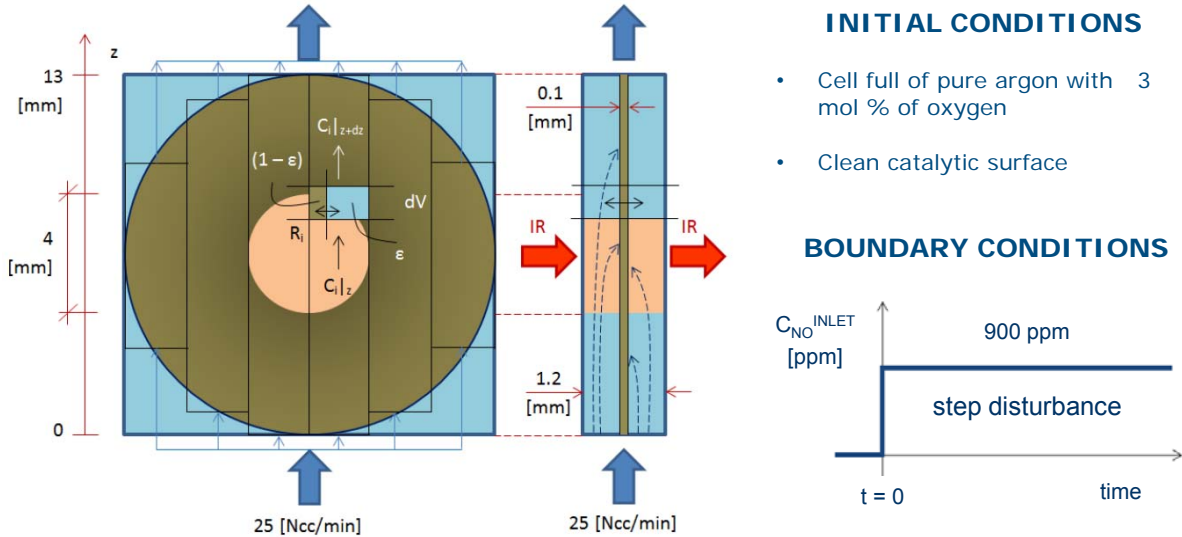

Figure 2: Schematic of the multiple PFR model for the regression of kinetic parameters, with initial and boundary conditions

4. CFD modeling

In order to make possible the application of the developed kinetic model to industrial reactors (NOx traps), due to the non-ideal fluid-dynamic of the latter, a reactive CFD modelling is required. In this paper, such approach has been developed and validated by modelling the flow field within the adopted spectrokinetic reactor. The flow field within the reactor has been obtained with a commercial code (ANSYS Fluent), as reported later on and the chemical evolution of the system has been modelled as follows.

4.1 Gas species transport equations
The gas phase evolution has been obtained by solving the transport equation of each gas species in each control volume of the computational mesh, according with the Finite-Volume-Method.
Particularly, the reactive term is computed only when a control volume have a face adjacent to the catalytic geometrical surface, while it is neglected in all the other elements of the 3D mesh, as it is possible to see in Figure 3, where boundary conditions are provided as well.
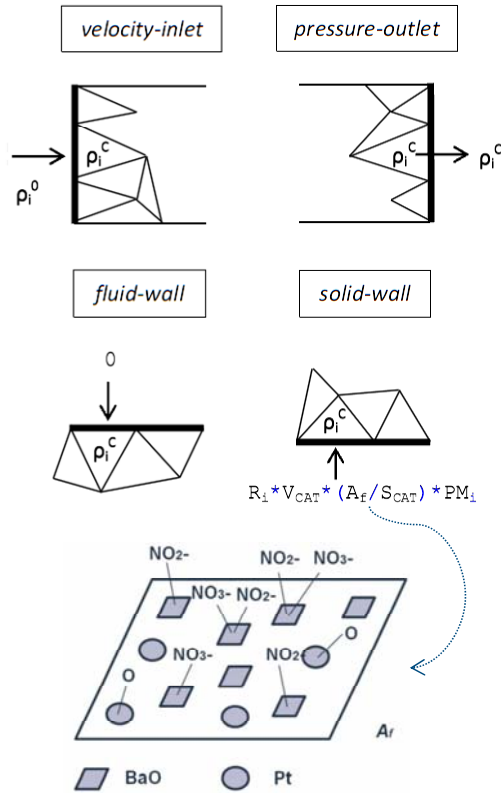
Figure 3: Boundary conditions for the species transport equations

4.2 Adspecies material balances

The evolution of the adsorbed species was obtained solving the following material balances, according with the Mean-Field-Approximation (Deutschmann, 2001).

$$\Omega_{sito}\frac{d\theta_j^{Cs}}{dt} = \sigma_j R_j\left(\overrightarrow{C^{Cs}},\overrightarrow{\theta^{Cs}}\right) \tag{15}$$

$$\text{I.C.: } \theta_j^{Cs}(t=0) = 0 \tag{16}$$

with j = NO_2^-, NO_3^-, Pt-O.

Whereas the evolution of the free active sites was obtained by the following stoichiometric relations:

$$\theta_{Pt}^{Cs} = 1 - \theta_{Pt-O}^{Cs} \tag{17}$$

$$\theta_{BaO}^{Cs} = 1 - \theta_{Nitrite}^{Cs} - \theta_{Nitrate}^{Cs} \tag{18}$$

4.3 Numerical methodology

A completely new methodology is proposed and, accordingly, a novel numerical approach is developed, implemented, and executed to simulate the system with a CFD approach (Corbetta et al., 2014). The main hypothesis underlying the following procedure is related to the possibility to decouple the CFD and the kinetics, mainly due to the strong dilution of the inlet stream. Accordingly, a non-reactive CFD simulation is first performed with inert gas (argon) only as inlet flow. Next, the flow field is exported from the commercial CFD software, and used to solve the chemical species transport equations. Starting from the geometry, the adopted spectrokinetic reactor has been modeled in the ANSYS environment with a parallelepiped 1.2mm wide and with a square base of 13mm length, as well as the cylindrical pellet diameter. Therefore after the simulation of the laminar, isothermal, single-component case, the flow field obtained from the ANSYS Fluent commercial code was exported by means of a User-Defined-Function, and the collected data were introduced in a C++ code, which characterizes the chemical evolution of the system. The C++ code solves a stiff, diagonally dominant, sparse Jacobian, ODE system with 27594 equations. Three large blocks on the main diagonal refer to the accumulation and convective terms of the three gas phase species, whereas other three diagonal blocks refer to the adspecies.

Non-diagonal blocks are related to reaction terms. BzzOdeSparseStiff class belonging to BzzMath numerical library (Buzzi-Ferraris and Manenti, 2012; Manenti et al., 2009) is adopted to solve the resulting system. Numerical methods implemented are based on the Gear multivalue family.

5. Results and discussion

5.1 Kinetic simulation

In Figure 4 adspecies and gas phase evolution of the concentration are reported. It is clear that gas phase NO is stored as nitrites and nitrates and, eventually, NO_2 are released in the gas phase. The system behaviour strongly varies upon varying the catalyst temperature. For example, it is possible to observe that NO_2 is totally absent from the outlet stream at 150°C, while increasing the temperature, the production of NO_2 is observed. Moreover the delay time of the outflowing NO increases with temperature too. These phenomena can be ascribed to the presence of the nitrate mechanism, which is dominant at higher temperatures, and to the increased storage ability of the catalyst at high temperatures, respectively. Also nitrites and nitrates abundance shows a strong correlation with temperature. In fact at lower temperature, 150°C, only nitrite adspecies is measured by FT-IR spectrometer. Increasing the temperature nitrite adspecies are progressively converted to nitrates, reacting with NO_2, and the predominant mechanism is the nitrate route. Nevertheless also at 350°C it is possible to see in the initial stage the accumulation of nitrite adspecies.
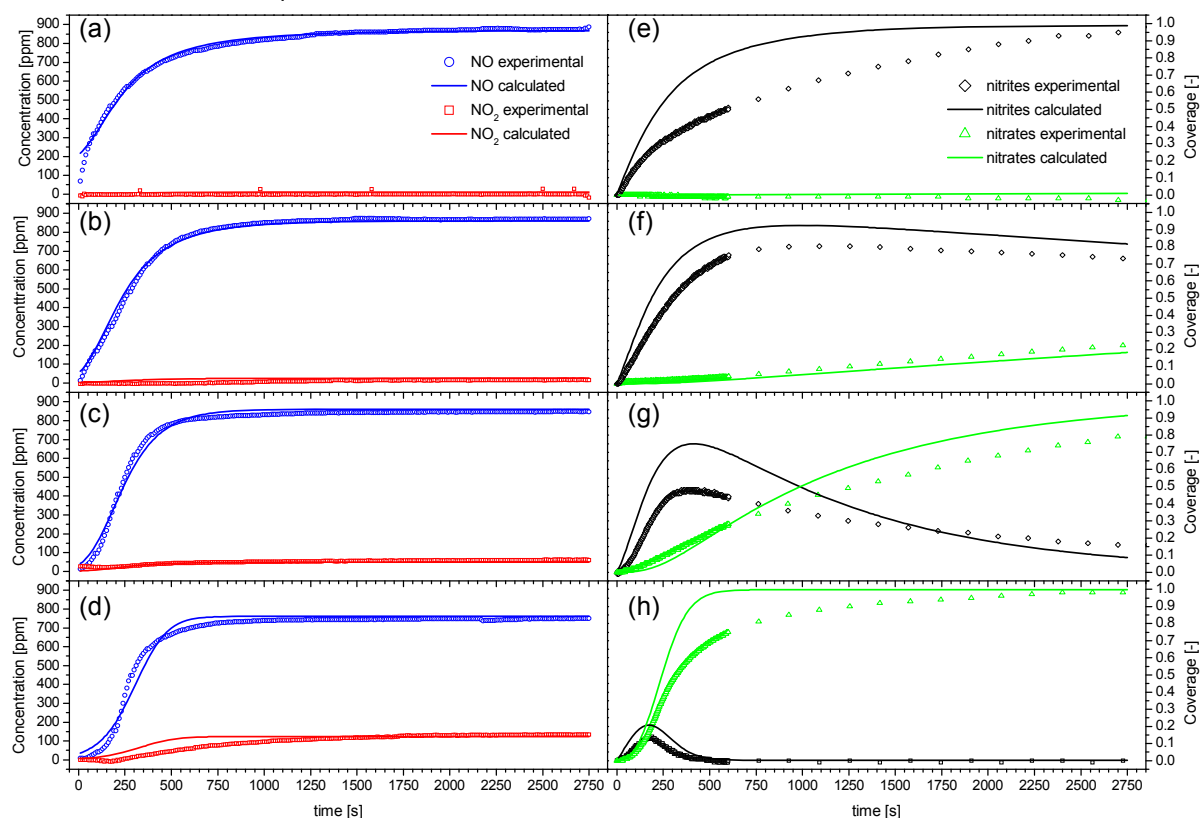

Figure 4: Experimental and calculated time evolution of the concentration of the gas species (left column) and of the area-averaged coverage of the ad-species within the IR-beam region (right column) at different temperatures. (a,e) 150°C; (b,f) 200°C; (c,g) 250°C; (d,h) 350°C.

5.2 CFD simulation

5.2.1. Hydrodynamics

Simulation results show the presence of a gas stream flowing on the pellet surface and licking it along the axial direction, within the gap between the pellet and the sample holder, as occurring in conventional automotive honeycomb-based catalytic converters (

Figure 5). The gas flux at the feeding capillary embraces the catalytic pellet redistributing along the radial direction. After the inlet zone, the gas flow goes on with a uniform front in the axial direction, until it reaches the outlet zone. The system is thus rather ideal in the central portion of the cell (PFR like behaviour), nevertheless there are some dead volumes at the corner of the sample-holder.
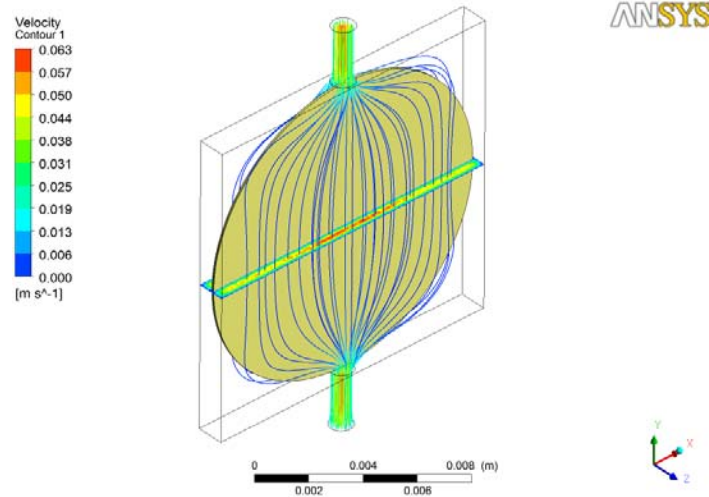

Figure 5: CFD simulation of the sample-holder

5.2.2. CFD-kinetics

Gas phase fields, not reported for sake of conciseness, show that the concentration of NO is gradually reduced along the axial direction, due to the accumulation in form of adspecies (nitrites and nitrates). At 250°C, for example, nitrite adspecies are rapidly accumulated on the pellet, reaching a maximum, at about 500 s, when the whole surface is homogeneously covered. These intermediate adspecies are then converted to nitrate, starting from the front of the pellet, as it is possible to observe in Figure 6 at 600 s. The production of NO2 is also observed: it is mainly concentrated in the thin circular layer above the catalytic pellet. Nitrogen dioxide is then progressively transported through the cell outlet.
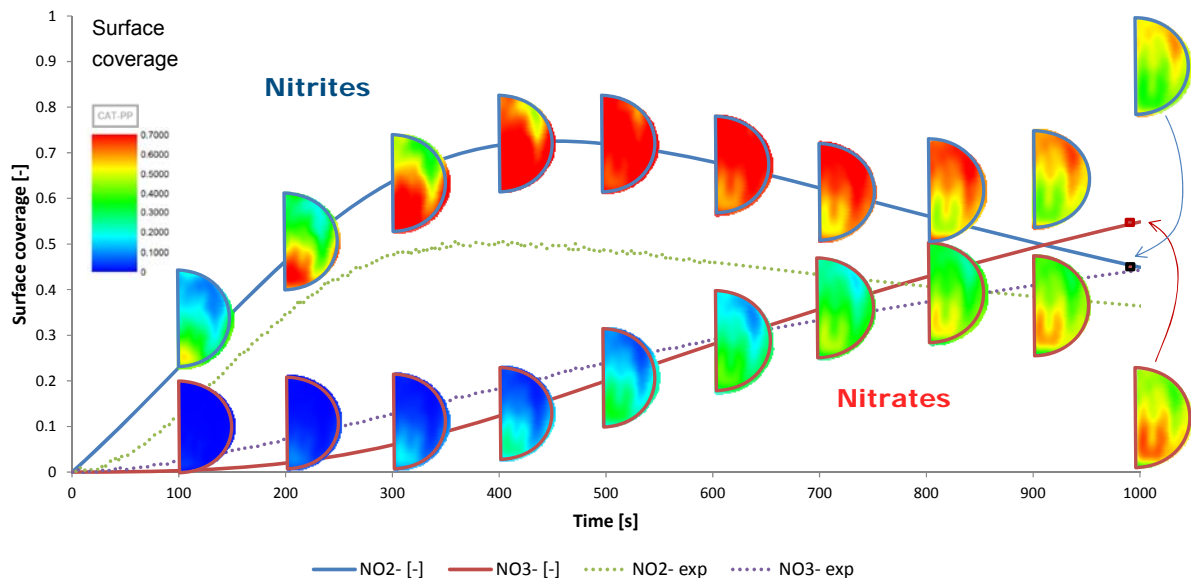

Figure 6: Space-time evolution of the surface coverage of nitrites and nitrates @ T = 250°C

5.2.3. Sensitivity analysis on geometry

The CAT-PP code was then applied to the study of different reactor configurations. For instance, the effect of a possible displacement of the catalytic pellet inside the sample-holder is here assessed.

The new case was simulated considering one half of the system (due to the occurrence of just one symmetry axis) and the catalytic pellet in oblique position. This led to a strong modification of the flow-field. In fact, in the previous configuration, the gas had a uniform front, which liked the catalyst pellet from just one side. In other words, the gas stream entering the reactor-cell was split in two identical parts and each of them was in contact with just one side of the catalytic pellet. Differently, in the new case, the flow is forced to cross the catalyst pellet due to the constriction of the cross-sectional area along the main flow direction. This introduces some small dead volumes in proximity of the contact region between the pellet and the sample-holder internal wall, as it could be possible to see from Figure 7. In fact, in the oblique result, there is a region near the outlet where the gap between pellet and wall is thin and the concentration of NO_2 is close to zero. Moreover, the oblique pellet case forces the mixing between the upper and the lower sides of the catalyst, leading to a more uniform spatial distribution of the gas in proximity of the outlet region.
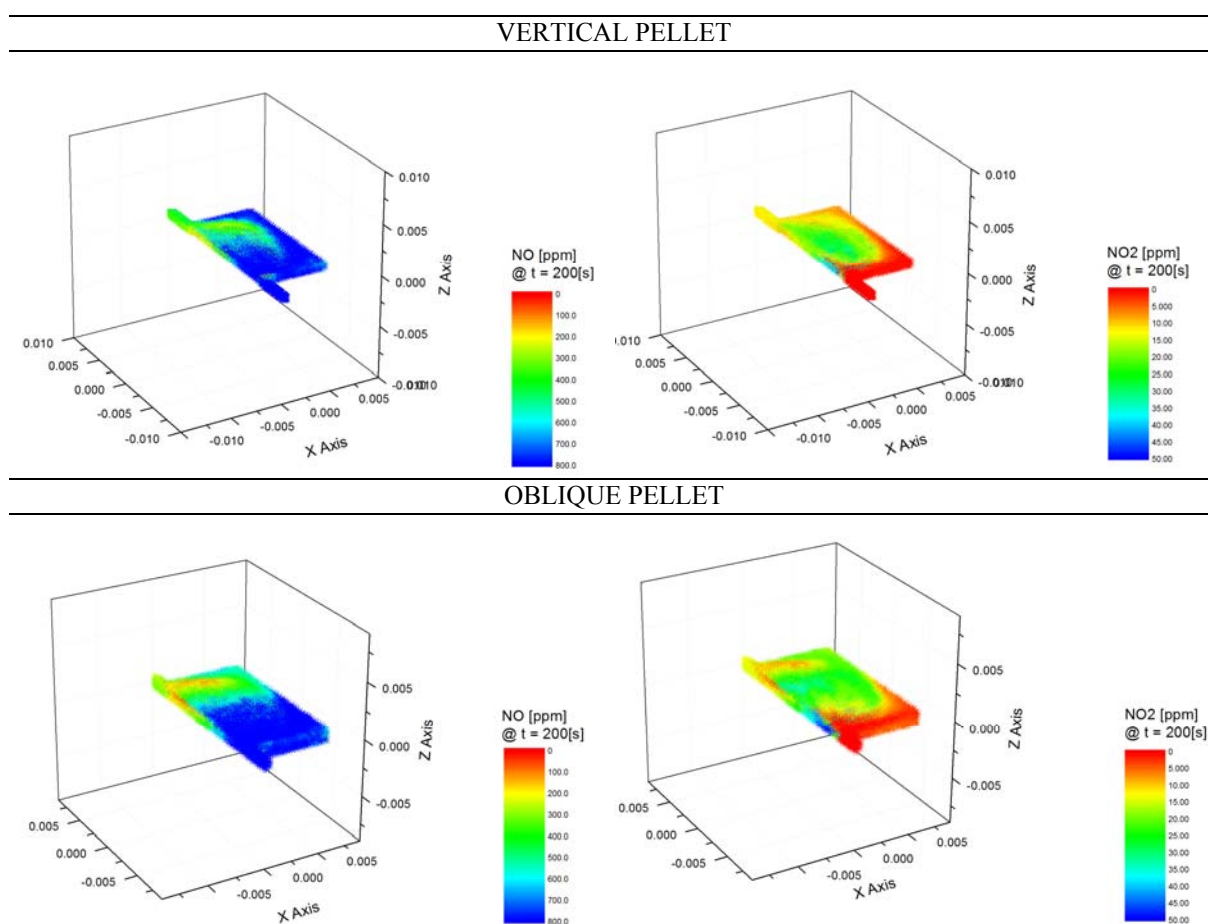
VERTICAL PELLET

OBLIQUE PELLET

Figure 7: Space evolution of NO and NO2 @ (250 °C, 200 sec) in case of vertical pellet (line above) and oblique (line below)

6. Conclusions

In this study a kinetic model for the NOx storage over a LNT catalyst has been developed, following a new spectroscopic approach, which uses conjointly adspecies and gas phase concentration measurements as experimental responses to estimate the kinetic parameters. A numerical tool was then implemented, able to simulate non ideal LNT reactors with a CFD approach, and to integrate the storage kinetics in the simulation. This

new reactive CFD approach is thus able to simulate non-ideal reactor geometries, as occurring in commercial configurations, using a physically consistent kinetic model and taking into account the hydrodynamic non idealities.

Acknowledgment

Nomenclature

Symbol	Dimension	Description
x_i	[-]	Molar fraction of the i-th gaseous species
θ_j	[-]	Surface coverage of the j-th adspecies
E_{att}	[kJ/mol]	Activation energy
T	[K]	Reaction temperature
T_{ref}	[K]	Reference temperature
C_i	[mol/m^3]	Molar concentration of i-th gaseous species
R_i	[mol/m^3/s]	Reaction source term
PM_i	[g/mol]	Molar weight
V_{cat}	[m^3]	Catalyst overall volume
A_{cat}	[m^2]	Catalyst geometrical external area
Ω_{site}	[mol/m^3]	Active site concentration
σ_j	[-]	Coordination number of j-th adspecies
T	[s]	Time

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