

## Development of a Kinetic Model of Lean-NO<sub>x</sub>-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<sub>2</sub>O<sub>3</sub> catalyst used in the Lean-NO<sub>x</sub>-Traps to store NO<sub>x</sub> 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 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. 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 NO<sub>x</sub> emissions, has become more stringent, according to the introduction of new international standards (e.g. Euro 6). Primary techniques could not match these requirements and so catalytic after-treatment technologies, such as SCR and LNT are necessary. Selective-Catalytic-Reduction has many literature references, such as the work of (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-NO<sub>x</sub>-Trap catalytic system. This technology allows to accumulate NO<sub>x</sub> as nitrites and nitrates on alkaline-earth metals active sites (e.g. barium), during a lean phase for a few minutes. Then the catalyst is regenerated during a rich phase that lasts a few seconds, in which the adsorbed NO<sub>x</sub> are reduced to nitrogen by means of partial oxidation products from engine exhaust-gases on noble metals active sites (e.g. platinum). From a literature survey, several types of LNT kinetic modeling were found. Olsson et al. (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. (Broqvist et al., 2002), while thermodynamic calculations for different storage components were performed by Kobayashi et al. (Kobayashi et al., 1997). In a recent work a new spectrokinetic approach, herein recalled, has been developed (Visconti et al., 2012), which uses as experimental responses to estimate the kinetic parameters the information collected from both the gas phase and the adsorbed one. As reported elsewhere (Na-Ranong et al., 2009), transient operation is indeed an effective method for determining kinetic parameters for such complicated systems, according to its intrinsic cyclic behavior. Moreover, dynamic FTIR-Operando experiments allow to obtain 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 the following the detailed spectrokinetic model of the LNT has been extended through the

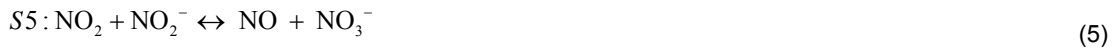
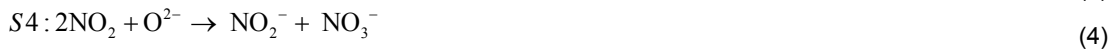
development of a new CFD-based simulation tool, which can be used both to apply the developed spectrokinetic model to complex (non-ideal) reactor geometries (such as the real after-treatment reactors) or to account for the non-ideality of many commercial operando-reactors (Meunier, 2010). It is thus necessary to couple the kinetic and fluid-dynamic aspects as reported in the scientific literature facing the analysis of the interactions of fluid-dynamics on a monolithic catalyst, the simulation of an isolated spherical pellet by means of a commercial CFD code, and the kinetic post-processing of CFD simulations of complex combustion systems (Deutschmann, 2001; Kanniche, 2009; Kolaczkowski et al., 2007; Shuai and Wang, 2004).

## 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/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (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<sub>2</sub> (1000ppm + 3%v/v) at zero time. The temporal evolution of both the species adsorbed on the catalyst and the gaseous species was monitored. 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., 2012).

## 3. Kinetic modeling

The lean storage phase has been considered in this work. Accordingly, the reactive species involve gas molecules (O<sub>2</sub>, NO, NO<sub>2</sub>) 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 NO<sub>x</sub> 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<sub>2</sub><sup>-</sup>). The stored nitrites are eventually oxidized to nitrates (NO<sub>3</sub><sup>-</sup>) by NO<sub>2</sub>. In the latter, NO is oxidized to NO<sub>2</sub> on platinum sites, which is eventually stored as nitrate adspecies. The resulting accumulation mechanism has been formalized as follows:



The related kinetic rate expressions are here proposed. Further details are available elsewhere (Visconti et al., 2012), as the derivation of the lumped rate expression for the third reaction:

$$r_{S1} = k_{S1d} x_{O_2} \theta_{Pt}^2 - k_{S1i} \theta_{Pt-O}^2 \quad (6)$$

$$r_{S2} = k_{S2d} x_{NO} \theta_{Pt-O} - k_{S2i} x_{NO_2} \theta_{Pt} \quad (7)$$

$$r_{S3} = k_{S3d} x_{NO} \theta_{Pt-O} \theta_{O_2-} \quad (8)$$

$$r_{S4} = k_{S4d} x_{NO_2}^2 \theta_{O_2-} \quad (9)$$

$$r_{S5} = k_{S5d} x_{NO_2} \theta_{NO_2-} - k_{S5i} x_{NO} \theta_{NO_3-} \quad (10)$$

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. The reactor-cell was modeled as a dynamic PFR.

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

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

$$\Omega_{site} \frac{d\theta_j}{dt} = R_j \quad (13)$$

$$\text{I.C.: } \theta_j(0, z) = \theta_{j,t0} \quad (14)$$

with  $i = \text{NO}, \text{NO}_2, \text{O}_2$  and  $j = \text{NO}_2^-, \text{NO}_3^-, \text{Pt-O}$

In these expressions,  $\varepsilon$  is the reactor void fraction,  $\tau$  the residence time in the reactor,  $z^*$  the dimensionless axial coordinate of the reactor,  $\theta_j$  the degrees of coverage of the adspecies.  $\Omega$  are instead the NO<sub>x</sub> adsorption loads [mol/m<sup>3</sup>] of barium oxide and platinum sites.

#### 4. CFD modeling

In order to make possible the application of the developed kinetic model to industrial reactors (NO<sub>x</sub> 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.

##### 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).

$$\Omega_{site} \frac{d\theta_j^{Cs}}{dt} = \sigma_j R_j \left( \overline{C}^{Cs}, \overline{\theta}^{Cs} \right) \quad (15)$$

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

with  $j = \text{NO}_2^-, \text{NO}_3^-, \text{Pt-O}$ .

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

$$\theta_{Pt}^{Cs} = 1 - \theta_{Pt-O}^{Cs} \quad (17)$$

$$\theta_{BaO}^{Cs} = 1 - \theta_{Nitrite}^{Cs} - \theta_{Nitrate}^{Cs} \quad (18)$$

##### 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. 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, monocomponent 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 multivalued family.

## 5. Results and discussion

### 5.1 Kinetic simulation

In Figure 1 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<sub>2</sub> 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<sub>2</sub> is totally absent from the outlet stream at 150°C, while increasing the temperature, the production of NO<sub>2</sub> 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<sub>2</sub>, 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.

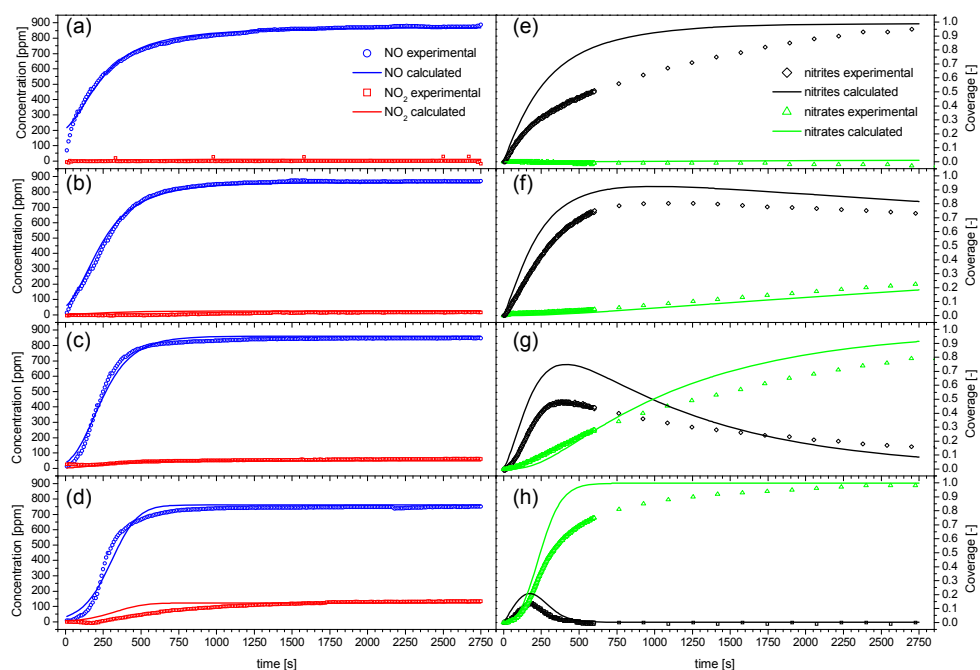


Figure 1 - Experimental and calculated time evolution of the concentration of the gas species (left column) and of the coverage of the ad-species (right column) at different temperatures. (a,e) 150°C; (b,f) 200°C; (c,g) 250°C; (d,h) 350°C.

### 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 2). 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.

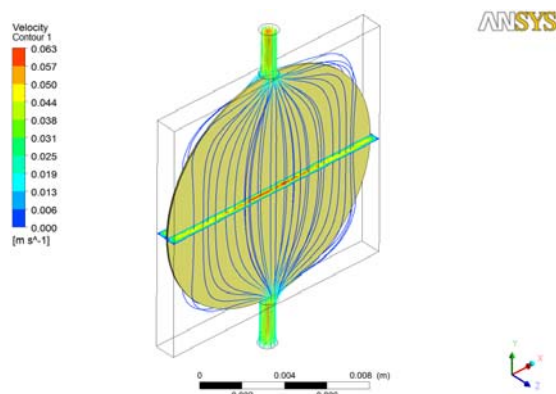


Figure 2 - CFD simulation of the sample-holder

### 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 500s, 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 3 at 600s. The production of NO<sub>2</sub> 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.

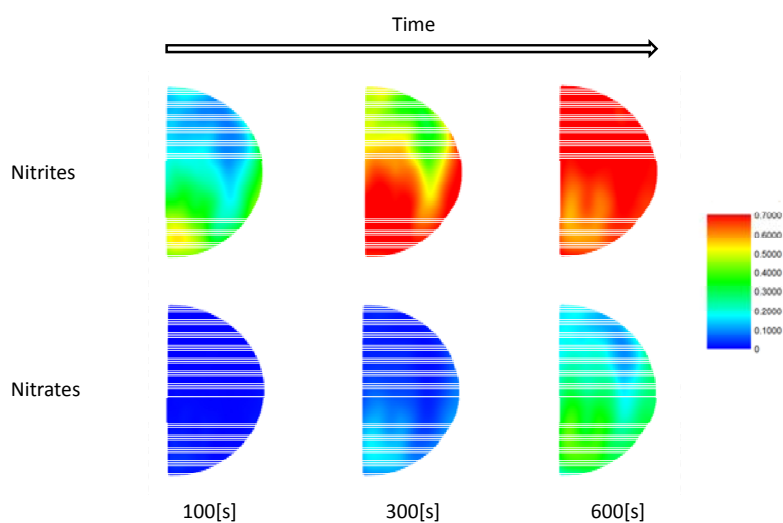


Figure 3 - Space-time evolution of the surface coverage of nitrites and nitrates @  $T = 250^{\circ}\text{C}$

## 6. Conclusions

In this study a kinetic model for the NO<sub>x</sub> 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

Marco Daturi, who is responsible for the experimental spectrokinetic data discussed in this paper, is gratefully acknowledged for his valuable contribution and his fundamental help.

## Nomenclature

Symbol	Dimension	Description
$x_i$	[-]	Molar fraction of the i-th gaseous species.
$\theta_j$	[-]	Surface coverage of the j-th adspecies.
$E_{att}$	[kJ/mol]	Activation energy.
$A$	[-]	Temperature dependence parameter.
$T$	[K]	Reaction temperature.
$T_{ref}$	[K]	Reference temperature.
$\rho_i$	[kg/m <sup>3</sup> ]	Massive concentration of i-th gaseous species.
$\Delta V_{cell}$	[m <sup>3</sup> ]	Computational cell volume.
$v_f$	[m/s]	Cell face velocity.
$A_f$	[m <sup>2</sup> ]	Control volume face f area.
$R_i$	[mol/m <sup>3</sup> /s]	Reaction source term.
$PM_i$	[g/mol]	Molar weight.
$V_{cat}$	[m <sup>3</sup> ]	Catalyst overall volume.
$A_{cat}$	[m <sup>2</sup> ]	Catalyst geometrical external area.
$\Omega_{site}$	[mol/m <sup>3</sup> ]	Active site concentration.
$\sigma_j$	[-]	Coordination number of j-th adspecies.
$T$	[s]	Time.

## References

- Broqvist, P., Panas, I., Fridell, E., Persson, H., 2002. NO<sub>x</sub> storage on BaO(100) surface from first principles: a two channel scenario. *Journal of Physical Chemistry B* 106, 137-145.
- Buzzi-Ferraris, G., Manenti, F., 2012. BzzMath: Library Overview and Recent Advances in Numerical Methods. *Computer Aided Chemical Engineering* 30, 1312-1316.
- Deutschmann, O., 2001. Interactions between transport and chemistry in catalytic reactors.
- Kanniche, M., 2009. Modelling natural gas combustion in gas turbine: Coupling 3D combustion simulations with Chemical Reactor Network for advanced NO<sub>x</sub> prediction. *Chemical Engineering Transactions*, 18(1-2), 135-140.
- Kobayashi, T., Yamada, T., Kayano, K., 1997. Study of NO<sub>x</sub> trap reaction by thermodynamic calculation. *SAE Tech. Pap. Ser.*
- Kolaczowski, S.T., Chao, R., Awdry, S., Smith, A., 2007. Application of a CFD code (FLUENT) to formulate models of catalytic gas phase reactions in porous catalyst pellets. *Chemical Engineering Research & Design* 85, 1539-1552.
- Lesage, T., Verrier, C., Bazin, P., Saussey, J., Daturi, M., 2003. Studying the NO<sub>x</sub>-trap mechanism over a Pt-Rh/Ba/Al<sub>2</sub>O<sub>3</sub> catalyst by operando FT-IR spectroscopy. *Phys. Chem. Chem. Phys.* 5, 4435-4440.
- Lietti, L., Daturi, M., Blasin-Aube, V., Ghiotti, G., Prinetto, F., Forzatti, P., 2012. Relevance of the Nitrite Route in the NO<sub>x</sub> Adsorption Mechanism over Pt-Ba/Al<sub>2</sub>O<sub>3</sub> NO<sub>x</sub> Storage Reduction Catalysts Investigated by using Operando FTIR Spectroscopy. *Chemcatchem* 4, 55-58.
- Manenti, F., Dones, I., Buzzi-Ferraris, G., Preisig, H.A., 2009. Efficient Numerical Solver for Partially Structured Differential and Algebraic Equation Systems. *Industrial & Engineering Chemistry Research* 48, 9979-9984.
- Meunier, F.C., 2010. The design and testing of kinetically-appropriate operando spectroscopic cells for investigating heterogeneous catalytic reactions. *Chemical Society Reviews* 39, 4602-4614.
- Na-Ranong, D., Yuangsawad, R., Kitchaiya, P., Aida, T., 2009. Application of periodic operation to kinetic study of NO-CO reaction over Rh/Al<sub>2</sub>O<sub>3</sub>. *Chemical Engineering Journal* 146, 275-286.
- Nova, I., Castoldi, L., Lietti, L., Tronconi, E., Forzatti, P., Prinetto, F., Ghiotti, G., 2004. NO<sub>x</sub> adsorption study over Pt-Ba/alumina catalysts: FT-IR and pulse experiments. *Journal of Catalysis* 222, 377-388.
- Olsson, L., Blint, R.J., Fridell, E., 2005. Global kinetic model for lean NO<sub>x</sub> traps. *Industrial & Engineering Chemistry Research* 44, 3021-3032.
- Shuai, S.J., Wang, J.X., 2004. Unsteady temperature fields of monoliths in catalytic converters. *Chemical Engineering Journal* 100, 95-107.
- Vega, E.M., Garcia, S.O., Sanz, F.V.D., 2011. Ammonia Selective Catalytic Reduction of NO in a Monolithic Reverse Flow Reactor. *Chemical Engineering Transactions*, 24(1-3), 79-84.
- Visconti, C.G., Lietti, L., Manenti, F., Daturi, M., Corbetta, M., Pierucci, S., Forzatti, P., 2013. Spectrokinetic Analysis of the NO<sub>x</sub> Storage Over a Pt-Ba/Al<sub>2</sub>O<sub>3</sub> Lean NO<sub>x</sub> Trap Catalyst, *Topics in Catalysis*, doi: 10.1007/s11244-013-9972-x.