Influence of Physical and Chemical Parameters on the Conversion Rate of a Catalytic Converter: A Numerical Simulation Study

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ABSTRACT

Monolithic three-way catalysts are applied to reduce the emission of combustion engines. The design of such a catalytic converter is a complex process involving the optimization of different physical and chemical parameters. Simple properties such as length, cell densities or metal coverage of the catalysts influence the catalytic performance of the converter.

Numerical simulation is used as an effective tool for the investigation of the catalytic properties of a catalytic converter and for the prediction of the performance of the catalyst. To attain this goal, a two-dimensional flow field description is coupled with a detailed chemical reaction model.

In this paper, results of the simulation of a monolithic single channel are shown. In a first step, the steady state flow distribution was calculated by a two dimensional simulation model. Subsequently, the reaction mechanism of the chemical species in the exhaust gas was added to the simulation process. The performance of the catalyst was simulated under lean, nearly stoichiometric and rich conditions. For these characteristic conditions, the oxidation of propen and CO and the reduction of NO on a typical Pt/Rh coated three-way catalyst were simulated as a function of temperature. The numerically predicted conversion data are compared with experimentally measured data. The simulation further reveals the coupling between chemical reactions and transport processes within the monolithic channel.

INTRODUCTION

Today three-way catalysts are used extensively to reduce the emissions of combustion engines. The majority of automotive catalytic converters have a monolithic structure, which is coated with an alumina washcoat that supports the noble metal such as platinum, palladium and rhodium. These monoliths can be made of either ceramic or of metal. To achieve a large catalytic surface area, the substrates consist of numerous parallel channels with a diameter of approximately 1 mm. For the design of a catalytic converter, several chemical and physical properties of both the catalyst and the exhaust gas must be considered:

- cell geometry (length and diameter of the channel, wall thickness),
- species of noble metal and noble metal loading,
- species of promoters,
- temperature, velocity and chemical composition of the exhaust gas.

The experimental characterization of the catalytic performance of the converter is time-consuming and requires a large experimental setup. Moreover, multiple experimental measurements should be made to ensure reproducibility. Numerical simulation offers an interesting alternate method for the investigation of the catalytic activity of a converter. This method is also efficient in analyzing the transient flow and thermal phenomena in the catalytic converter and may help to understand the complex interactions between the flow field and the catalytic surface chemistry.

In recent years, several proposals were made for the numerical simulation of catalytic converters /1-6/. In most of these studies, a global model for the chemistry was used. This global model however neglects the various single reactions which occur on the surface. An alternate approach is the description of the chemical reactions by a set of elementary reaction steps. The reaction equations of the elementary steps describe the reactions on a
In this study, we do not only use a more accurate chemical reaction model but also a detailed description of the flow field. One single channel of the monolith is modelled by the two-dimensional Navier-Stokes equations. The flow field simulation is based on the commercially available CFD-code FLUENT /7/. FLUENT was coupled with the chemistry module DETCHEM /8/ in a former study /9/. DETCHEM models chemical reactions in the gas phase and on the surface using elementary step reaction mechanisms. This computational tool was already successfully used to model catalytic partial oxidation processes in monolithic reactors /9/. In the present work, we use this code to study the emission reduction in a single channel of an automotive three-way catalytic converter.

The channel of the monolith is assumed to be a tube reactor. The flow inside this reactor is laminar and the transport coefficients depend on composition and temperature. A detailed multi-step reaction mechanism is used to model the catalytic reactions and to calculate the surface mass fluxes. The surface coverage of the species on the catalytic material is also calculated as a function of the position in the channel. The mechanism includes only surface chemistry, gas phase chemistry can be neglected because of the low pressure and the short residence time of the species inside the catalyst. The conversion calculated for a variety of conditions will be compared with experimental data, measured in laboratory-scale experiments using commercially used three-way catalysts.

MATHEMATICAL AND NUMERICAL MODEL

The numerical simulation is based on the CFD code FLUENT /7/. The code is well established and can easily be used to set up fluid flow problems and to solve them. However, modeling of detailed chemistry in current versions is limited because of a maximum number of reactions and because of the difficulties with handling complex chemistry which yield a stiff differential equation set. Furthermore, FLUENT’s surface reaction model does not take the surface coverage into account. Therefore, the FLUENT code was coupled to external subroutines that model surface chemistry using FLUENT’s interface of user-defined subroutines. The reader is referred to /9/ for a more detailed description of the coupling procedure.

CONSERVATION EQUATIONS

The basic conservation equations for laminar flow fields, as used in FLUENT /7/, are summarized in this section. Due to the axial symmetry of the problem, cylindrical coordinates are used, resulting in the following equations:

continuity equation:

$$\frac{\partial \rho u}{\partial z} + \frac{1}{r} \frac{\partial (r \rho v)}{\partial r} = 0 \quad (1)$$

axial momentum:

$$\rho u \frac{\partial u}{\partial z} + \rho v \frac{\partial u}{\partial r} =$$

$$- \frac{\partial p}{\partial z} + \frac{\partial}{\partial z} \left[ \mu \left( \frac{\partial u}{\partial z} + \frac{1}{3} \frac{\partial (\rho u v)}{\partial r} \right) \right] + \frac{1}{r} \frac{\partial}{\partial r} \left[ \mu r \left( \frac{\partial u}{\partial z} + \frac{1}{3} \frac{\partial (\rho u v)}{\partial r} \right) \right] \quad (2)$$

radial momentum:

$$\rho u \frac{\partial v}{\partial z} + \rho v \frac{\partial v}{\partial r} =$$

$$- \frac{\partial p}{\partial r} + \frac{\partial}{\partial z} \left[ \mu \left( \frac{\partial v}{\partial z} + \frac{1}{3} \frac{\partial (\rho u v)}{\partial r} \right) \right] + \frac{1}{r} \frac{\partial}{\partial r} \left[ \mu r + \frac{2}{3} \frac{\partial (\rho u v)}{\partial r} \right]$$

$$+ \frac{2 \mu}{r} \left( \frac{\partial v}{\partial r} - \frac{v}{r} \right) \quad (3)$$

species conservation equation:

$$\rho \frac{\partial Y_i}{\partial z} + \rho v \frac{\partial Y_i}{\partial r} = \left( \frac{\partial j_{i,1}}{\partial z} + \frac{1}{r} \frac{\partial (r j_{i,1})}{\partial r} \right) + R_i \quad (i = 1, N_s) \quad (4)$$

with diffusion mass flux:

$$j_{i,1} = - \rho D_{i,m} \frac{\partial Y_i}{\partial r} \quad (5)$$

thermal energy:

$$\rho c_p \left( \frac{\partial T}{\partial z} + v \frac{\partial T}{\partial r} \right) =$$

$$\left( \frac{\partial p}{\partial z} + v \frac{\partial p}{\partial r} \right) + \frac{\partial}{\partial z} \left[ \Lambda \frac{\partial T}{\partial z} + \frac{1}{r} \frac{\partial}{\partial r} \left( r \Lambda \frac{\partial T}{\partial r} \right) \right]$$

$$- \sum_{i=1}^{N_s} c_m \left( j_{i,1} \frac{\partial T}{\partial z} + j_{i,1} \frac{\partial T}{\partial r} \right) - \sum_{i=1}^{N_s} h_i R_i \quad (6)$$

Here are \( \rho \) = density, \( t \) = time, \( r \) = radial spatial coordinate, \( z \) = axial spatial coordinate, \( u \) = axial velocity, \( v \) = radial velocity, \( p \) = static pressure, \( Y_i \) = mass fraction of species \( i \), \( R_i \) = net rate of production of species \( i \) due to chemical reactions, \( D_{i,m} \) = diffusion coefficient of species \( i \) in the mixture, \( T \) = temperature, \( h_i \) = enthalpy of species \( i \), \( N_s \) = number of gas phase species.
The density is computed via the ideal gas law. The viscosity $\mu$ and the thermal conductivity $\Lambda$ of the mixture as well as the diffusion coefficient of species $i$ in the mixture $D_{i,\text{mix}}$ depend on the local composition and on the temperature and they are calculated via kinetic theory. The specific heat $c_{p,i}$ at constant pressure of species $i$ is modeled as a polynomial function of temperature.

FLUENT solves the conservation equations using a control volume based finite difference method. A non-staggered system is applied for storage of discrete velocities and pressure. The resulting equations are solved using SIMPLE-like algorithms with an iterative line-by-line matrix solver and multigrid acceleration.

SURFACE CHEMISTRY MODEL

Chemical reactions on the catalytic reactor wall lead to the following boundary conditions:

$$\eta F \dot{s}_i M_i = (j_{i\tau} + \rho Y_i v_{at}) \quad (i = i, N_g)$$

(7)

where $\dot{s}_i$ is the creation or depletion rate of species $i$ by adsorption and desorption processes, $j_{i\tau}$ the diffusive flux and $Y_i$ the mass fraction of species $i$ in the gas phase adjacent to the surface, $v_{at}$ the Stefan velocity and $F$ the ratio between catalytic active surface area and geometric area. The active catalytic surface was experimentally determined. $\eta$ is the effectiveness factor to account for pore diffusion within the washcoat. In this work, the effectiveness factor is related to the diffusion of the species CO (lean and stoichiometric mixtures) or $O_2$ (rich mixtures) within the pores of the washcoat, because CO and $O_2$, respectively, are the most crucial species in the surface kinetics. The effectiveness factor depends on the porosity, the gas-phase species concentration at the wash coat, the surface reaction rates and diffusion coefficients using the Thiele module approach /10/.

The state of the catalytic surface is described by its temperature and the coverages of adsorbed species which vary in the flow direction. External subroutines calculate the surface coverages $\Theta_i$ (the fraction of surface sites covered by species $i$) at each computational cell at the tube wall. The same apply for the calculation surface mass fluxes (left term of Eq. 7). The surface chemistry is modeled by elementary reactions. The chemical source terms $\dot{s}_i$ of gas phase species due to adsorption/desorption and surface species (i.e. adsorbed species) are given by:

$$\dot{s}_i = \sum_{k=1}^{K_s} \nu_{ik} k_{ik} \prod_{j=1}^{N_g+N_s} [X_j]^{\nu_{ij}^*} \quad (i = 1, N_g + N_s)$$

(8)

where $K_s$ is the number of elementary surface reactions (including adsorption and desorption), $\nu_{ik}$ (right side minus left side of reaction equation) and $\nu_{ij}^*$ (left side of reaction equation) are the stoichiometric coefficients and $N_s$ is the number of species adsorbed. The concentration $[X_j]$ of an adsorbed species is given in mol/m$^2$ and equals the surface coverage ($\Theta_i$) multiplied by the surface site density ($\Gamma$).

The temperature dependence of the rate coefficients is described by a modified Arrhenius expression:

$$k_{ik} = A_k T^{\beta_k} \exp \left[ -\frac{E_{aik}}{RT} \right] \prod_{i=1}^{N_s} \Theta_i^{\mu_{ik}} \exp \left[ \frac{E_{rik} \Theta_i}{RT} \right]$$

(9)

This expression takes an additional coverage dependence into account using the parameters $\mu_{ik}$ and $\varepsilon_{rik}$.

The rate coefficient for adsorption processes is calculated from the initial sticking coefficient $S_i^0$, that is the sticking probability at vanishing coverage:

$$k_{ik}^{ads} = S_i^0 \frac{1}{\Gamma} \sqrt{\frac{RT}{2\pi M_i}}$$

(10)

where $\tau$ is the number of occupied adsorption sites of species $i$.

The steady state solution is the point of interest. Hence, the time variation of the surface coverage ($\Theta_i$) is zero:

$$\frac{\partial \Theta_i}{\partial \tau} = \frac{\dot{s}_i}{\Gamma} = 0 \quad (i = N_g + 1, N_g + N_s)$$

(11)

In DETCHEM, this equation system is solved to obtain surface coverages and surface mass fluxes. Here, FLUENT provides the concentration of the gas phase species and the temperature at each computational cell with a catalytic wall as boundary. In the DETCHEM module, coverages and surface mass fluxes are calculated for each “global” iteration, keeping the local species concentrations and temperature constant. The algebraic equation system (Eq. 11) is solved by a time integration of the corresponding ODE system until a steady state is reached. An implicit method based on LIMEX /11/ is used for the time integration. DETCHEM provides an analytical Jacobian, which is automatically generated from the surface reaction mechanism. The coverage data of the former iteration are used as initial conditions for the next step. Under-relaxation of the variation of the surface mass fluxes may be necessary, e.g. if a species which is largely produced on the surface has a high sticking coefficient such as CO in our examples.

GEOMETRY AND BOUNDARY CONDITIONS

A tube reactor serves as a model for a single channel of the monolithic catalyst. The tube has cylindrical geometry with the axial direction $z$ and the radial direction $r$. The equations are solved in radial direction between $r = 0$ and $r = d/2$ with $d$ as channel (tube)
diameter. At the tube centerline \((r = 0)\), a symmetry boundary condition is applied.

The flow enters the computational domain with a known velocity, gas composition and temperature. A flat profile of the axial velocity \(u\) and a vanishing radial velocity \(v\) are used in the simulation at the inlet boundary. At the reactor exit, an outlet boundary is applied at which values for all variables are extrapolated from the interior cells adjacent to the outlet.

A structured grid is used for the simulation. The grid has to be very fine around the catalyst entrance and the catalytic wall to resolve the flow field and also to determine the variations in the species concentration due to the chemical reactions at the catalytic wall. The total number of computational cells used for each channel were 20 cells in radial direction and 72 cells in axial direction.

**EXPERIMENTAL**

The catalyst used in this study is a commercially available tree-way catalyst. The catalyst contains 50 g/ft\(^3\) of metal (Pt/Rh = 5:1) impregnated on a ceria stabilized \(\gamma\)-alumina washcoat. The washcoat was supported by a cordierite monolith with a cell density of 62 cells per cm\(^2\) (400 cpsi) and a wall thickness of 0.165 mm (6.5 mil).

The experimental determination of the conversion rate and therefore the performance of the three-way catalyst was done in a laboratory-scale tube reactor. For this application, a sample of 22 mm in diameter and 29 mm in length was taken from the catalyst. Before the investigation the sample was treated for one hour at a temperature of 650°C for conditioning. Table 1 shows the composition and the concentration of the species in the exhaust gas used for the conditioning process.

**TABLE 1**

Composition and concentration of the species used for the conditioning process (1h at 650°C).

<table>
<thead>
<tr>
<th>Species</th>
<th>Concentration [Vol.%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{C}_3\text{H}_6)</td>
<td>0.0450</td>
</tr>
<tr>
<td>(\text{C}_3\text{H}_8)</td>
<td>0.0450</td>
</tr>
<tr>
<td>CO</td>
<td>1.4200</td>
</tr>
<tr>
<td>NO</td>
<td>0.1000</td>
</tr>
<tr>
<td>(\text{O}_2)</td>
<td>1.0875</td>
</tr>
<tr>
<td>(\text{H}_2\text{O})</td>
<td>13.1000</td>
</tr>
<tr>
<td>(\text{N}_2)</td>
<td>balance</td>
</tr>
</tbody>
</table>

After conditioning the sample was treated with different gas mixtures in a temperature range of 150-600°C. Table 2 summarizes the composition and the species concentrations of the simulated exhaust gas. The oxygen concentration was varied in order to simulate a stoichiometric, a rich and a lean exhaust gas mixture. The \(\lambda_{\text{ox}}\)-values are defined as the inverse of the redox ratio \(/1,5/:\)

\[
\lambda_{\text{ox}} = \frac{X_{\text{NO}} + 2X_{\text{O}_2}}{X_{\text{CO}} + 9X_{\text{C}_3\text{H}_8}}
\]

With this definition \(\lambda_{\text{ox}} = 1\) represents a stoichiometric, \(\lambda_{\text{ox}} > 1\) a lean and \(\lambda_{\text{ox}} < 1\) a rich mixture. The volume flow of the simulated exhaust gas into the sample was 15 l/min at standard conditions (25°C). A uniform axial inlet velocity of 1.35 m/s corresponds to this volume flow. The reactor was heated with a tubular oven with a heat rate of 100°C/h. The oven leads to an isothermal sample temperature. The concentration of the different species and therefore the conversion rate was measured in 20°C-steps, the steady state of the system was granted.

**TABLE 2**

Composition of the simulated exhaust gas and concentration of the gas species used for the simulation studies.

<table>
<thead>
<tr>
<th>Species</th>
<th>Concentration [Vol.%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>1.4200</td>
</tr>
<tr>
<td>(\text{O}_2)</td>
<td>0.7700</td>
</tr>
<tr>
<td>(\text{C}_3\text{H}_8)</td>
<td>0.0450</td>
</tr>
<tr>
<td>NO</td>
<td>0.0450</td>
</tr>
<tr>
<td>(\text{N}_2)</td>
<td>balance</td>
</tr>
</tbody>
</table>

The \(\text{CO}_2\) concentration in the inlet exhaust gas mixture was zero due to experimental reasons. Tests have shown that there was no difference in the conversion rate of CO, HC and NO between measurements with and without \(\text{CO}_2\) in the inlet gas.

After the experimental studies of the temperature-dependent conversion rate the sample was investigated with \(\text{H}_2\) chemisorption in order to obtain the properties of the active metal phase. The active metal surface of the catalyst was determined to 28 m\(^2\)/g, the dispersion of the conditioned catalyst was 33\%. Calculation of the ratio of active metal surface area and geometrical surface area \((F\text{ in Eq. 7})\) of the catalyst leads to a value of 70. The ratio of the platinum to rhodium surface was taken from the literature as 3:1 for a catalyst with a noble metal composition of Pt/Rh with 5:1 which corresponds to the catalyst we used for our investigations /12/.

**CHEMICAL REACTION SYSTEM**

The conversion reactions of the harmful exhaust gases into harmless components inside a monolithic three-way catalyst can globally be written as

- \(\text{CO} + 1/2 \text{O}_2 \rightarrow \text{CO}_2\)
- \(\text{C}_n\text{H}_m + (n + m/4) \text{O}_2 \rightarrow n \text{CO}_2 + m/2 \text{H}_2\text{O}\)
- \(\text{CO} + \text{NO} \rightarrow \text{CO}_2 + 1/2 \text{N}_2\)
This kind of global chemistry has been used in most of the studies described in the literature. The surface reaction mechanism however consists of numerous elementary reaction steps. In this study, we apply a more detailed approach to model the surface chemistry. The sample mixture used here consists of C₃H₆, CO, NO and O₂ (see Table 2). The reaction scheme consists of 56 elementary reaction steps and 31 chemical species, e.g. dissociative oxygen adsorption, nondissociative adsorption of C₃H₆, CO and NO, the formation steps of carbon dioxide (CO₂), water (H₂O) and nitrogen (N₂) and desorption of all species. Some activation energies (e.g. oxygen desorption) are coverage-dependent due to interactions between adsorbed species. It is assumed that all species are adsorbed competitively. The model also considers the different adsorption places (platinum or rhodium) on the metallic catalyst surface. However, on rhodium only surface reactions between NO, CO, O₂ are considered /14,15/. The kinetic data of the mechanism was taken either from the literature or from fits to experiments. In a forthcoming paper, the mechanism will be presented in detail.

Parts of the surface reaction mechanism were already used for numerical modeling of catalytic ignition /13/, simulation of total and partial oxidation of light hydrocarbons on platinum /14/ and modeling the CO-O₂ and NO-CO reactions on rhodium /15,16/.

RESULTS AND DISCUSSION

In this section, the results of the simulations are discussed. First, the predicted conversion rates of the pollutants C₃H₆, CO and NO as function of temperature for three different gas mixtures (see Table 2) will be shown and compared with experimentally measured data. Then, the interaction of transport and chemistry within a single channel is described as revealed by the two-dimensional simulation.

CONVERSION RATE VS TEMPERATURE

In the simulation, the conditions used experimentally and described above are applied. Table 3 summarizes the input data for the simulation, the concentrations of the incoming exhaust gas are already given in Table 2. The gas flows at a uniform inlet velocity into the cylindrical tube. Due to isothermal sample temperature, the channel wall is assumed to be isothermal.

In Fig. 1, the conversion rates of CO, C₃H₆ and NO are shown as function of temperature. The composition of the inlet gas mixture is lean. The conversion of CO, C₃H₆ and NO starts at 300°C and increases up to 100% for CO and C₃H₆ at 500°C and 400°C, respectively. The NO conversion shows a maximum at 360°C and decreases at higher temperatures. The predicted conversion rates of all three species agree well with the experimentally measured data. Especially the temperature behavior of the NO conversion and the slow increase of the C₃H₆ conversion in the temperature range above 360°C. The simulation shows some CO conversion at temperatures lower than 300°C probably due to the fact that in the reaction mechanism reactions for hydrocarbons on rhodium are not included. Therefore C₃H₆ is not able to block the CO oxidation on Rh in contrast to the CO oxidation on Pt.

<table>
<thead>
<tr>
<th>Noble metal composition</th>
<th>Pt/Rh, 5:1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Noble metal loading</td>
<td>50 g/ft³</td>
</tr>
<tr>
<td>Active metal surface</td>
<td>28 m²/g</td>
</tr>
<tr>
<td>Surface ratio Pt/Rh₈</td>
<td>3:1</td>
</tr>
<tr>
<td>Metal dispersion</td>
<td>33%</td>
</tr>
<tr>
<td>Ratio active metal surface/ geometrical surface</td>
<td>70</td>
</tr>
<tr>
<td>Channel diameter</td>
<td>1.0 mm</td>
</tr>
<tr>
<td>Channel length</td>
<td>29 mm</td>
</tr>
<tr>
<td>Temperature range</td>
<td>100-600°C</td>
</tr>
<tr>
<td>Velocity/temperature dependent</td>
<td>1.35 m/s at 25°C</td>
</tr>
</tbody>
</table>

The conversion rates as a function of the temperature for the nearly stoichiometric mixture are shown in Fig. 2. Again, the conversion of CO, C₃H₆ and NO starts at 300°C, but increases more slowly with temperature compared to the lean mixture. Because of the insufficient amount of O₂ in the mixture, CO conversion is not complete. The conversion of C₃H₆ is complete at 500°C, which indicates that C₃H₆ can compete with CO for O₂. Also, for temperatures higher than 450°C, NO reduction is complete. Concerning the conversion rates of CO and NO and the competition between CO and C₃H₆ for O₂, the simulation results agree well with the experimental data. Only the C₃H₆ conversion rate shows deviations between 340°C and 460°C. Compared to the experimental data the predicted conversion rate is too high.

The rich mixture, shown in Fig. 3, contains 0.4 Vol.% O₂, which leads to only a maximum of CO conversion of approx. 33%. The conversion of NO reaches 100% for temperatures higher than 570°C. In comparison with the results of the two other mixtures, the increase of the conversions of CO, C₃H₆ and NO with the temperature is more slow, in particular the C₃H₆ conversion rate. Regarding the CO and NO conversion, the simulations agree with the experimental values. However, large deviations exist between the predicted C₃H₆ conversion and the experimental data. This deviations can be explained by the fact that in the rich regime a wider variety of surface species, e.g. partial oxidation products of C₃H₆, resides on the catalytic surface, which can reduce the oxygen coverage and lead to different reaction paths. In the reaction mechanism used in this study only a limited number of possible surface species are included. Therefore further reactions and surface species have to be included in order to improve the prediction of the C₃H₆ conversion at richer mixtures.
Figure 1. Conversion of CO, C$_3$H$_6$ and NO at lean conditions with increasing temperature; comparison of experimental and calculated data.

Figure 2. Conversion of CO, C$_3$H$_6$ and NO at nearly stoichiometric conditions with increasing temperature; comparison of experimental and calculated data.
TRANSPORT AND CHEMISTRY WITHIN A SINGLE CHANNEL

In Fig. 4, the mass fractions of C$_3$H$_6$, CO, CO$_2$ and NO for the lean mixture (see Table 2) at 407°C within the channel are shown. The input data are the same as in Table 3. The mass fraction profiles show that most of the C$_3$H$_6$ is converted within the first centimeter. In this axial range CO is nearly completely converted. The NO conversion is limited to the first centimeter and vanishes behind.

This behavior can be explained by means of the surface coverages. The calculated coverages of the most relevant surface species on platinum and rhodium are shown as a function of the axial position along the channel in Fig. 5 and 6, respectively. The coverages are defined in respect of the whole catalytic area, consisting of rhodium and platinum.

In Fig. 5 it is revealed that at the axial distance of 1.1 cm the surface coverage state varies strongly, because of the decreasing CO concentration in the gas phase, from a mainly CO(s) covered state to an O(s) covered state. This variation is initiated from the decreasing CO/O$_2$ ratio in the gas phase. During this transition the number of free platinum sites, Pt(s), increases, which allows more NO to be adsorbed and dissociated. When the surface reaches the O(s) covered state the number of free platinum sites is decreased and the equilibrium of NO dissociation is shifted to NO(s), resulting in a vanishing NO conversion.

The rhodium surface goes from a N(s) covered state to an O(s) covered state. This transition phenomenon can be seen in Fig. 6. The O(s) covered surface state on rhodium prevents also NO conversion. Below 1 cm the surface is mainly covered with N(s) and active for NO conversion.

With increasing reaction temperature the transition point moves toward the channel entrance, which reduces the area that is active for NO conversion. In Fig. 3 the resulting decrease of NO conversion with increasing temperature can be seen.
Figure 4. Flow fields of the mass fraction of the species C_2H_6, CO, CO_2 and NO at 407°C. Different scales are used in axial and radial direction for visual clarity; lean mixture.

Figure 5. Surface coverage at 407°C on Pt as a function of the axial position; lean mixture, (s) denotes surface species.

Figure 6. Surface coverage at 407°C on Rh as a function of the axial position; lean mixture, (s) denotes surface species.
A typical feature of the three-way converter is the \( \lambda \)-window behavior, that means, \( \text{C}_3\text{H}_6 \), CO and NO are simultaneously converted with high efficiency in a narrow range around the stoichiometric air/fuel ratio. Fig. 7 presents the predicted conversions for the catalytic converter at 500°C for different gas mixtures. This chosen temperature is a typical catalyst inlet temperature for partial load /17/. The experimental data were already presented in the Fig. 1, 2 and 3. Our simulation well predicts the \( \lambda \)-window in the lean region. For the rich regime, as already shown in Fig. 3, the CO conversion is also well predicted, while there are major deficiencies for \( \text{C}_3\text{H}_6 \) conversion, as discussed above.

Figure 7. \( \lambda \)-window at 500°C; comparison of experimental and calculated data.

CONCLUSION

A two dimensional flow field description, including a detailed reaction mechanism for the conversion of CO, \( \text{C}_3\text{H}_6 \), \( \text{O}_2 \) and NO has been used to simulate the exhaust gas treatment in a platinum/rhodium coated single channel of a typical three-way catalytic converter. The simulation is based on the CFD code FLUENT and the chemistry module DETCHEM, which were coupled for the simulations performed.

The computational tool was used to predict conversion rates at lean, nearly stoichiometric and rich conditions as function of temperature. The calculated data are compared with experimentally measured data and a good agreement could be achieved. Only for rich conditions the prediction of \( \text{C}_3\text{H}_6 \) conversion is too high. Furthermore, the interaction of transport and kinetics within a single channel were revealed by the simulation.

Numerical simulation of the emission reduction inside a monolithic three-way catalyst offers an efficient method to investigate converter performance. As a first step on the way to a complete model, a reliable multi-step reaction mechanism has to be developed. This mechanism will finally allow simulations to predict emissions over a broad range of conditions. In this work, a surface reaction mechanism consisting of 56 reactions among 31 species was used and validated by a comparison with experimental data.

OUTLOOK

The simulation presented in this paper is carried out for a single channel in a monolithic catalytic converter. In the ongoing research, several extensions will be made for a more accurate model for the real catalytic converter. The next step in using numerical simulation is to expand the model from a single channel model to the total monolith. A simulation of the total monolith using FLUENT requires too much computer time and memory. Therefore, a boundary layer model will be used as an alternate method to simulate the behaviour of the single channel. This future work will also take the thermal conductivity of the catalyst into account for the calculation of the heat distribution of the whole monolithic converter. The final goal is the simulation of the behaviour of an automotive catalytic converter during a whole test cycle using models that are based on the real physical and chemical processes. The test cycle simulation will include the light-off behaviour of the converter.

In order to improve the prediction quality for rich mixtures, further reactions have to be included in the reaction mechanism.

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REFERENCES


Citation and notation:


**NOTATION**

- $c_{p,i}$ specific heat at constant pressure of species $i$
- $d$ channel (tube) diameter
- $D_{i,m}$ diffusion coefficient of species $i$ in the mixture,
- $F$ ratio between catalytic active surface area and geometric surface area
- $h_i$ enthalpy of species $i$
- $K_s$ number of elementary surface reactions (including adsorption and desorption)
- $M_i$ molar mass of the species $i$
- $N_g$ number of gas phase species
- $N_a$ number of adsorbed species
- $p$ static pressure
- $R_i$ net rate of production of species $i$ due to chemical reactions
- $r$ radial spatial coordinate
- $S^0$ initial sticking coefficient
- $\dot{\gamma}_i$ creation or depletion rate of species $i$ by adsorption and desorption processes/ chemical source term
- $\dot{\gamma}_iM_i$ surface mass fluxes
- $T$ temperature
- $t$ time
- $u$ axial velocity
- $v$ radial velocity
- $Y_i$ mass fraction of species $i$
- $z$ axial spatial coordinate
- $j_{i,x}$ diffusive flux
- $v_{st}$ Stefan velocity
- $\Gamma$ surface site density
- $\epsilon_{ik}$ parameter for coverage dependent activation energy
- $\Theta_i$ surface coverages (fraction of surface sites covered by species $i$)
- $\lambda_{ax}$ lambda value
- $\Lambda$ thermal conductivity of the mixture
- $\mu$ viscosity
- $\mu_{ik}$ parameter for coverage dependent reaction order
- $V_{ik}, V_{jk}$ stoichiometric coefficients
- $\rho$ density
- $X_i$ concentration of an adsorbed species
- $\tau$ number of occupied adsorption sites of species $i$