115 A Transient Modeling and Simulation Study of Catalytic Decomposition of NO_x over Rhodium

– A H_2-O_2-NO System –

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A Nakatsuji-type rhodium-based catalytic NO_x decomposition/reduction system, which efficiently removes NO_x from automotive exhaust when operated under periodic lean/rich conditions, is investigated. The kinetic behaviour of this system is studied using the recently developed code DETCHEM^{TRANSIENT}. This code treats the non-stationary processes in the chemically reactive flow, and couples detailed surface microkinetic simulations with computational fluid dynamics (CFD). A comparison of experimental and theoretical results, leads to the assumptions that there is significant influence from the short rich period on the NO conversion under the investigated transient conditions. It is discussed how the temperature and lean/rich period ratio affect the efficiency.

***Keywords*: Pollution, Simulation/ Diesel Exhaust Gas Catalysis, Lean Combustion, Aftertreatment, NO_x Decomposition, Transient, Microkinetic Modeling, Rhodium, Nitrogen Oxide**

1. INTRODUCTION

The reduction of NO_x in exhaust emissions from mobile and stationary sources is one of the key environmental problems of our century [1, 2]. Extensive research is focused on the conversion of the nitric oxides into harmless nitrogen. The catalytic reduction/decomposition of NO_x is a very promising solution of this problem.

A central goal is to find a catalyst that efficiently converts NO_x selectively to N_2 under lean-burn conditions, is not deactivated by sulfur, and furthermore does not decrease the fuel efficiency.

Recently, Nakatsuji *et al.* [3, 4] proposed a rhodium-based catalytic NO_x reduction system which, when operated under periodic lean-rich conditions, can reduce NO_x efficiently and endure the exposure to sulfur components. Therefore, this system has a high potential for application in automobiles, yet the detailed surface mechanism is unclear.

In this study, a model exhaust gas consisting of H_2, NO and O_2, in N_2 is used and 6 possible gas phase species, namely H_2, O_2, H_2O, NO, N_2O, and N_2, are taken into account. The surface chemistry is represented by a mechanism consisting of 20 reactions.

The objective of this research is the development of a detailed microkinetic model to simulate and elucidate the transient processes during the catalytic decomposition of NO_x with H_2 as reductant.

A comparison of experimental and theoretical results leads to the assumptions that there is significant influence from the short rich period on the NO conversion under the investigated conditions. The role of the very short lean-rich switching may be mainly the removal of the surface O species.

The periodic removal of surface oxygen atoms by reductants prevents the catalyst from poisoning and consequent deactivation, thus assuring the durability of the catalyst.

2. EXPERIMENTAL

The catalyst used was a rhodium loaded monolithic reactor. The active rhodium surface was determined by CO chemisorption to be 0.80 m^2/g. The ratio of active rhodium surface to geometric surface, i.e. the inner wall surface area of the monolithic catalyst was calculated to be 110. The catalyst's characterization is listed in Table 1.

Table 1. Catalyst parameters used in the numerical simulation of the $DeNO_X$ catalyst [a]

Washcoat loading	8.11 g
Number of channels of the monolith reactor	9
Binding material	4.03 g
Noble metal loading	0.3 mg
Active noble metal surface (determined by CO chemisorption)	0.80 m^2/g
$F_{cat/geo}$ (Catalyst surface/geometric surface)	110
Channel diameter	1 mm
Channel length	30mm
Superficial velocity (STP)	0.926 m/s

[a] Courtesy from hte-Company, Heidelberg.

A series of experiments on NO_x reduction by H_2 under alternating lean/rich conditions in a monolithic reactor was performed.

The oxygen concentration was changed from 14.5% to 0% in order to simulate the lean/rich periods during the experiment. The volume flow rate of the gas mixture in the reactor was 30 l/h at standard conditions (25°C). A uniform superficial velocity of 0.926 m/s corresponds to this volume flow.

The experimental conditions were as follows:

Lean: 2.0% H_2, 500 ppm NO, 14.5% O_2 in nitrogen.

Rich: 2.0% H_2, 500 ppm NO in nitrogen.

Lean/rich period: 60s/5s or 6s/1s.

Investigated temperature: 165~425°C.

3. MODELING AND SIMULATION

Modeling and simulation of the transient behavior of reacting fluids inside an automotive catalytic converter is a significant challenge. While considerable progress has been made with steady-state models, which contributed to the development and understanding of catalysts [5], it is necessary to develop models and computer code implementations for the dynamic behavior of the converter in a relatively simple and efficient way [5]. A computer code DETCHEM^{TRANSIENT}, a module of DETCHEM [6] (see 3.1) was developed in our group to simulate the transient performance of the catalytic converter.

The kinetic behavior of the rhodium system was studied using DETCHEM^{TRANSIENT} [6]. This code treats the non-stationary processes in the chemically reactive flow, and couples time-dependent microkinetic simulations of surface reactions with the instationary flow field.

3.1 DETCHEM Package

Deutschmann and co-workers developed a library of FORTRAN routines to simulate the kinetics of complex chemically reacting surface systems using detailed chemistry (DETCHEM) [6]. Detailed chemistry refers to the detailed description of a chemical reacting system using elementary-step reaction mechanisms.

Tischer developed a CFD module for the DETCHEM package – DETCHEM^{CHANNEL}. DETCHEM^{CHANNEL} simulates annular flows such as the flow inside tubular reactor, *e.g.*, the channels in a honeycomb monolith [8]. In the presented work, DETCHEM^{TRANSIENT} utilizes DETCHEM^{CHANNEL} to simulate the transient behavior of a catalyst operated under altering fuel lean/rich conditions. In automotive catalytic converters, only reactions on precious metal surfaces are of importance and therefore only the implementation of surface chemistry in DETCHEM is discussed here.

3.2 DETCHEM^{TRANSIENT} Module Structure

Even though transient processes in heterogeneous catalysis can be simulated by commercially available Navier-Stokes based codes like FLUENT [9], fully coupled models based on detailed surface chemistry are generally not applicable owing to the stiffness of the mathematical description and the consequently high CPU costs [10]. Based on the idea of time scale decoupling according to a hierarchical approach [11], the transient inlet gas composition (time scale of seconds) can be regarded as decoupled from the flow, since the residence time of the gas inside the reactor is much shorter (time scale of milliseconds). Furthermore, the flow field in the catalyst can be assumed stationary during the time step necessary for the accurate resolution of the surface chemistry.

4. RESULTS AND DISCUSSION

In this section, the results of simulations are compared to experimental observations and discussed. The H_2-O_2-NO system was simulated with DETCHEM^{TRANSIENT}: two different lean/rich periods, 60s/5s and 6s/1s, were studied. The temperature dependence of NO conversion and the influence of different lean/rich period ratios are discussed.

4.1 Temperature dependence of the transient NO conversion behavior

The average mole fraction of NO in the outlet gas versus temperature in the (lean: 60 s, rich: 5s) system is simulated with DETCHEM^{TRANSIENT} and the results are compared with experimental results, as shown in Fig. 1. The simulation conditions are provided in the legend of the figures. Both investigations - theoretical and experimental - clearly show that, the NO concentration here decreases to a minimum concentration at around 200°C, and increases again subsequently (maximum NO conversion of 57 %).

NO is mainly converted to N_2, only very little N_2O is produced (data not shown). Thus, the system has a high N_2 selectivity, which is quite advantageous compared to other catalytic systems, e.g. on Pt or on Pd. This supports the suggestion that such after-treatment system is well-suited for automotive application. From Fig. 1, it can be seen that the trend and the nu-

merical values of experimental data are reproduced well. However, in the low temperature region around 165°C the difference between calculated and measured data is larger.

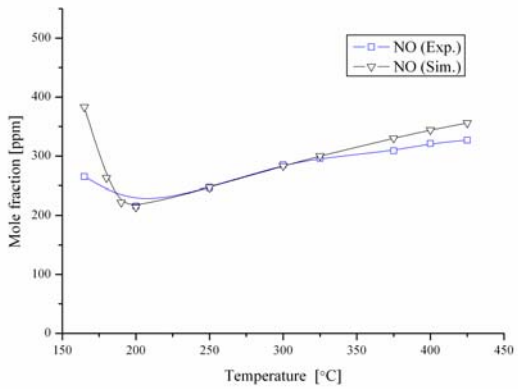

Fig. 1: Temperature dependent conversion of NO.
Conditions: Lean/rich: 60s/5s, Lean: H_2=2%, O_2=14.5%, NO=500ppm, Fill N_2; Rich: H_2=2%, NO=500ppm, Fill N_2.

This discrepancy between the simulations and experimental results may possibly be attributed to omitting diffusion effects in the surface chemistry model [12], an insufficient description of the surface mechanism, and other reasons, which need to be assayed in detail in subsequent studies.

The results for the mole fractions of NO and produced N_2 at 300°C are plotted as a function of time in Fig. 2.

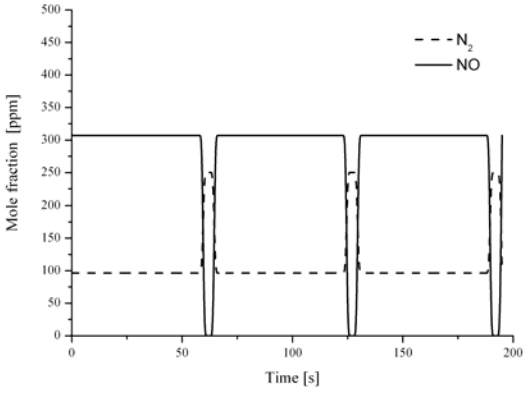

Fig. 2: Mean NO and N_2 concentrations in the outlet gas as a function of time at 300 ºC.
Conditions: Lean/rich: 60s/5s, Lean: H_2=2%, O_2=14.5%, NO=500ppm, Fill N_2; Rich: H_2=2%, NO=500ppm, Fill N_2.

4.2 Predicted Surface Coverage of Different Species

The predicted surface species coverages at 300°C on rhodium are plotted as a function of time in Fig. 3. It can be concluded that during the lean phase, the surface is mainly covered with oxygen species (θ_O = 0.70), while 29% of the surface remains uncovered. Hence, the metal overlayer mainly consists of oxygen. It is furthermore interesting to note that during each lean/rich interval, the coverage of Rh(s) increases to a higher value, while the coverage of O(s) changes in a reverse way.

A comparison of the calculated surface overlayer with the calculated nitrogen formation shows that the transient behavior of vacant surface rhodium sites (Rh(s)) at 300°C (see Fig. 3) reflects in the formation of nitrogen (Fig. 2). The nitrogen formation peaks during the rich period, simultaneously with the uncovered rhodium sites on the surface. Furthermore, the catalyst is activated for further NO decomposition, because subsequent to the reduction of the surface (O(s) decreasing with Rh(s) increasing), more NO can adsorb. This activation is related to the nitrogen formation during the oxygen-rich (lean) phase.

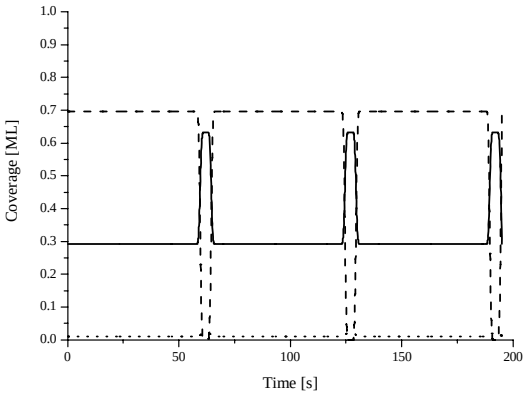

Figure 3: Predicted species surface coverage over time at 300ºC (Simulation results). Solid line Rh(s), dash line O(s) and dotted line N(s).
Simulation conditions: Lean/rich: 60s/5s, Lean: H_2=2%, NO=500ppm, O_2=14.5%, Fill N_2; Rich: H_2=2%, NO=500ppm, Fill N_2.

4.3 Effect of different lean/rich periods

To study the effect of different lean/rich periods, an analogue system with a lean period of 6s and a rich period of 1s is studied experimentally and theoretically. The results are shown in Fig. 4. Compared to the 60s/5s system the 6s/1s system gives very high NO conversion (above 90% versus 40% on average) within the temperature range investigated. In the low temperature region around 165°C, the activity of the catalytic system is underestimated by the simulation, while at high temperature, the model overestimates the conversion of NO. In general, the simulations resemble experimental observations well. Yet, considering that the 6s/1s system needs much more fuel to reduce/decompose the NO, it is unrealistic to be adopted in a real vehicle compared to the 60s/5s system. Nevertheless, the study shows that the lean/rich ratio affects the NO conversion considerably and may be a central practical matter.

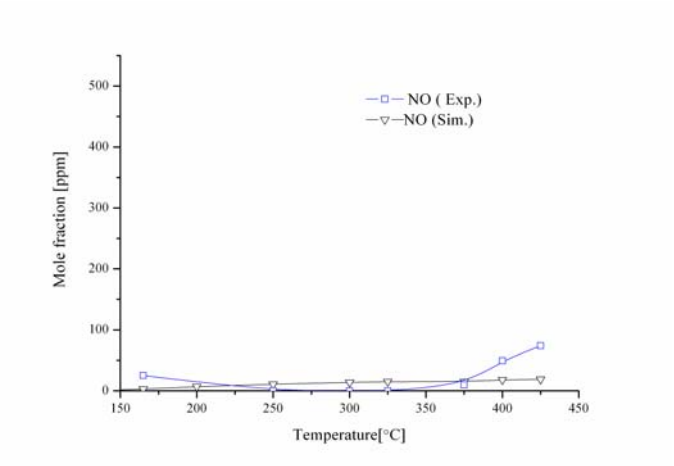

Fig. 4: Temperature dependent conversion of NO. Conditions: Lean/rich: 6s/1s, Lean: H_2=2%, O_2=14.5%, NO=500ppm, Fill N_2; Rich: H_2=2%, NO=500ppm, Fill N_2.

4.4 Analysis and discussion of the NO decomposition

A comparison of experimental and theoretical results supports the following view (based on the mechanism proposed by Nakatsuji [3, 4]):

(1) NO decomposition and subsequent N_2 (or N_2O) desorption;
(2) The left oxygen from the above step accumulates on the metal surface and blocks the Rh surface by oxidation;
(3) Surface oxygen removal by reductant leaves a reduced, clean Rh surface.

The rapid switching from lean to rich enables the removal of the surface O species so that the poisoning and deactivation by the surface O is avoided. The proposed mechanism of this Nakatsuji-type transient lean/rich NO decomposition/reduction system is completely different from that of NO_x Storage and Reduction (NSR) system. Therefore, it is anticipated that the former has good lasting conversion [3, 4, 13, 14]. Especially in presence of SO_x, this advantage is presumably more pronounced.

5. CONCLUSIONS

In this paper, a transient NO_x decomposition system is studied with the newly developed computer code DETCHEM-TRANSIENT. From the comparison of the theoretical and experimental results, we can draw the conclusion that this code, in combination with an accurate detailed surface reaction mechanism, can well describe the transient behaviour of the NO_x reduction/decomposition catalyst. We could support results published by Nakatsuji and co-workers which show that by alternating the inlet gas composition periodically between lean and rich NO_x can be efficiently decomposed with high selectivity towards N_2.

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