Detailed kinetic modeling of NO$_x$ storage and reduction with hydrogen as the reducing agent

Anna Lindholm[1], Neal W. Currier[2], Junhui Li[2], Aleksey Yezerets[2] and Louise Olsson[1*]
[1]*Competence Centre for Catalysis, Chalmers University of Technology, SE-412 96 Göteborg, Sweden,*
[2]*Cummins Inc., 1900 McKinley Ave, MC 50183, Columbus IN 47201, USA.*
*louise.olsson@chalmers.se

Introduction

The NO$_x$ storage and reduction technology (NSR), is a promising method to reduce NO$_x$ in lean exhausts from diesel and lean burn gasoline engines [1,2,4]. The catalyst operates in a cyclic manner; NO$_x$ is stored in the catalyst under lean periods (oxygen excess) and under the subsequent fuel rich periods NO$_x$ is released and reduced. A detailed kinetic model of NO$_x$ storage and reduction, in the presence of H$_2$O and CO$_2$, with H$_2$ as the reducing agent was developed and validated in this study [2]. In addition, ammonia formation is included in the modeling of the rich period.

Materials and Methods

The mechanism for NO$_x$ storage and reduction was derived from flow reactor experiments conducted at 200 – 400 °C over a Pt/Ba/Al monolith sample. The detailed kinetic model is divided into four sub-models: (i) NO oxidation over Pt, (ii) NO$_x$ storage, (iii) NO$_x$ reduction over Pt, and (iv) NO$_x$ regeneration. The kinetic parameters are derived from kinetic gas theory, transition state theory, statistical thermodynamics, thermodynamic constraints, the literature, experiments, or fitted in this work using the least square method. The fitted parameters are given with the 95 % linearised confidence intervals.

Results and Discussion

The NO oxidation mechanism (i) developed by Olsson et al. over Pt/Al$_2$O$_3$ [1] was used in this work to model NO oxidation. The sub-model for NO$_x$ storage (ii) is based on our earlier work [1] and is further developed in this study to include high concentrations of CO$_2$ and H$_2$O in the feed and also storage of NO$_x$ at low temperatures. Nitrogen oxides are allowed to be stored on two different types of storage sites: BaCO$_3$ and a second storage site denoted S$_3$, which can be interpreted as alumina covered to some extent by hydroxyl groups or as a second type of barium sites. The NO$_x$ reduction sub-model (iii) used here was developed earlier over Pt/Si [3]. Additional to the reduction of NO$_x$ into N$_2$, it describes the formation of NH$_3$ over Pt. In the sub-model describing the regeneration of NO$_x$ (iv), adsorbed NO$_x$ species react with hydrogen adsorbed on Pt sites. Ammonia oxidation over Pt and reactions between surface species of barium and NH$_3$ according to ammonia selective catalytic reduction (SCR) chemistry are also incorporated in the regeneration sub-model. The SCR steps between stored NO$_x$ and NH$_3$ is crucial in order to describe the delay of the ammonia and also the height of the NH$_3$ peak, simultaneously with the high steady state level of ammonia in the end of the rich period. Figure 1 shows the experimental and simulated results from a NO$_x$ storage and reduction cycle conducted at 400 °C. The model can describe the complete uptake of NO$_x$ in the beginning of the lean period, the NO$_x$ breakthrough, and the slow NO$_x$ storage in the end of the lean period very well as well as the following release and reduction. Furthermore, the

ammonia formation predicted by the model fits well with experimental data. In addition, the model can predict the gradual decrease in the storage capacity occurring in lean (210 s)/rich(15s) cycling experiments conducted at 200 - 400 °C. Experiments that were not included in the development of the model were conducted to validate the model. The validation experiments were constituted by short lean (60s) and rich (15s) cycles. The model predicted these experiments well for all temperatures investigated (200, 300 and 400 °C)
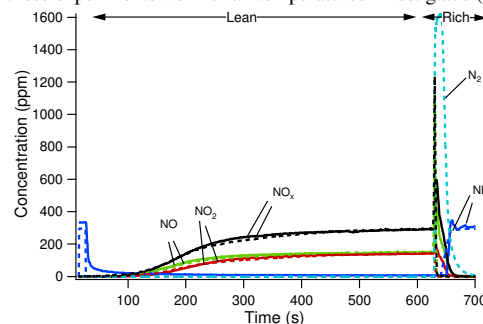

Figure 1. Measured (solid) and calculated (dashed) outlet concentrations of NO, NO$_2$, N$_2$ and NH$_3$. The catalyst was exposed to 300 ppm NO, 8 % O$_2$, 3 % H$_2$O and 3 % CO$_2$ during the lean period (10 min) and to 300 ppm NO, 8000 ppm H$_2$, 3 % H$_2$O and 3 % CO$_2$ during the rich period (5 min) at 400 °C. Ar was used as inert balance.

Significance

Several mechanistic studies of the NSR process under various conditions have been published and detailed descriptions, particularly of the storage period, have been proposed [4]. However, very few of the mechanisms presented in the literature have been examined and verified by detailed kinetic models. Before this study [2] there were no detailed kinetic models that describe the storage and regeneration with H$_2$, including ammonia formation. In addition, no detailed models were available that considered experiments with high concentrations of CO$_2$ and H$_2$O, which is the case in real applications.

References
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