NO_x reduction with hydrogen.
A kinetic study.

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Introduction

The NO_x storage and reduction technology (NSR), also referred to as lean NO_x traps (LNT), is a promising method to reduce NO_x in lean exhaust [1-2]. The catalyst operates in a cyclic manner where nitrogen oxides are stored in the catalyst under lean periods (oxygen excess) and are released and reduced under fuel rich periods.

Flow reactor experiments and kinetic modeling have been used to study the reduction of NO_x over Pt/SiO_2 model catalysts [3]. Earlier studies have shown that hydrogen is very effective at regenerating NSR catalysts from stored NO_x and therefore has hydrogen been used as reducing agent. The purpose of the modeling of NO_x reduction on Pt/SiO_2 is to isolate the reduction on Pt without interference of the released NO_x from storage materials, such as barium, and support materials that are not inert, such as alumina. This model is a first step towards a complete NO_x storage/reduction model with hydrogen as reducing agent.

Materials and Methods

The experimental study of NO_x reduction was conducted over a Pt/SiO_2 monolith catalyst by means of flow reactor experiments at different temperatures. Experiments were performed with different compositions of the gas feed, NO or NO_2 as NO_x source and different concentrations of H_2. The dispersion of platinum was determined by N_2O dissociation experiments [4].

In the kinetic model the monolith is described as a series of continuously stirred tank reactors. NO oxidation and NO_x reduction cycles were modeled in order to capture the transient behavior of NO_x reduction on Pt in lean NO_x traps. The NO oxidation mechanism developed by Olsson et al. over Pt/Al_2O_3 [1] was used in this work to model NO oxidation and NO_2 dissociation over Pt/SiO_2. The reduction mechanism is described by a number of reactions containing the gas phase species NO, H_2, N_2, NH_3, and H_2O and the surface coverage of NO, H, N, O, NH_3, and H_2O. Collision theory and sticking probability was used to calculate pre-exponential factors for adsorption and some parameters are taken from the literature. The purpose was to decrease the number of free parameters in the model.

Results and Discussion

Results from experiments and simulations of NO oxidation and reduction cycles with different hydrogen concentrations are presented in Figure 1. The experimental results show that hydrogen has a high NO_x reduction efficiency. The outlet NO_x concentration is zero under rich conditions, which means that all NO_x is reduced. With the hydrogen concentration used in these experiments a significant quantity of ammonia is formed. At higher temperatures almost all NO_x that is fed into the system is converted into ammonia when 8000 ppm H_2 is used. The selectivity towards NH_3 is lower at 100 °C and at this temperature also N_2O is formed (not shown here). The experimental results are the basis for the proposed reduction mechanism in the model. In the mechanism NO_x is reduced to nitrogen which further can be reduced to ammonia. Production of nitrous oxide is described as formation from a NO dimer species. From Figure 1 it can also be seen that the transient part of the experiments are well described by the model. Furthermore, the ammonia and nitrous oxide formation at different conditions are also well described by the model.

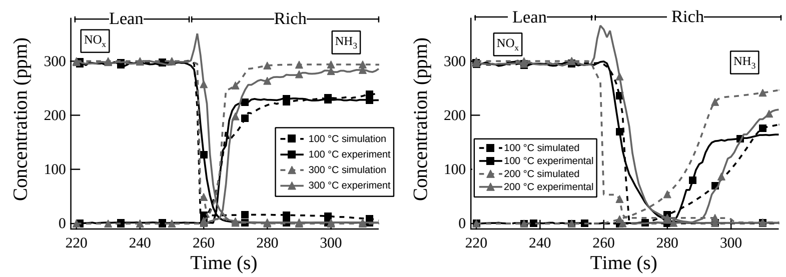

Figure 1. Measured (solid) and calculated (dashed) outlet concentrations of NO_x and NH_3 for NO oxidation and NO_x reduction cycles with 8000 ppm H_2 (left) and 2000 ppm H_2 (right). The inflow concentrations are 300 ppm NO and 8 % O_2 during lean and 300 ppm NO and 2000 or 8000 ppm H_2 during rich.

Significance

The NO_x storage and reduction technology is an important method for the automotive industry, since it is a way to reduce NO_x emissions under mixed lean operations. It is important to have a model that can describe this process. Kinetic models have been constructed earlier [1-2]. However, most studies have focused on details of the storage period. Since the reactions occurring under the reduction phase has not yet been fully resolved, more knowledge about the reduction is needed to describe the whole process of lean NO_x traps.

Acknowledgements

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