**NOx reduction with hydrogen.**

A kinetic study.

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Introduction

The NOx storage and reduction technology (NSR), also referred to as lean NOx traps (LNT), is a promising method to reduce NOx 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 NOx over Pt/SiO2 model catalysts [3]. Earlier studies have shown that hydrogen is very effective at regenerating NSR catalysts from stored NOx and therefore has hydrogen been used as reducing agent. The purpose of the modeling of NOx reduction on Pt/SiO2 is to isolate the reduction on Pt without interference of the released NOx 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 NOx storage/reduction model with hydrogen as reducing agent.

Materials and Methods

The experimental study of NOx reduction was conducted over a Pt/SiO2 monolith catalyst by means of flow reactor experiments at different temperatures. Experiments were performed with different compositions of the gas feed, NO or NO2 as NOx source and different concentrations of H2. The dispersion of platinum was determined by N2O dissociation experiments [4].

In the kinetic model the monolith is described as a series of continuously stirred tank reactors. NO oxidation and NOx reduction cycles were modeled in order to capture the transient behavior of NOx reduction on Pt in lean NOx traps. The NO oxidation mechanism developed by Olsson et al. over Pt/Al2O3 [1] was used in this work to model NO oxidation and NO2 dissociation over Pt/SiO2. The reduction mechanism is described by a number of reactions containing the gas phase species NO, H2, N2, NH3, and H2O and the surface coverage of NO, H, N, O, NH2, and H2O. 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 NOx reduction efficiency. The outlet NOx concentration is zero under rich conditions, which means that all NOx is reduced. With the hydrogen concentration used in these experiments a significant quantity of ammonia is formed. At higher temperatures almost all NO, that is fed into the system is converted into ammonia when 8000 ppm H2 is used. The selectivity towards NH3 is lower at 100 °C and at this temperature also N2O is formed (not shown here). The experimental results are the basis for the proposed reduction mechanism in the model. In the mechanism NOx 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 NOx and NH3 for NO oxidation and NOx reduction cycles with 8000 ppm H2 (left) and 2000 ppm H2 (right). The inflow concentrations are 300 ppm NO and 8 % O2 during lean and 300 ppm NO and 2000 or 8000 ppm H2 during rich.

Significance

The NOx storage and reduction technology is an important method for the automotive industry, since it is a way to reduce NOx 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 NOx traps.

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References