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Modeling of NO oxidation and NO_x storage on $Pt/BaO/Al_2O_3$ NO_x traps

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Abstract

A one-dimensional model of NO oxidation and NO_x storage on $Pt/BaO/Al_2O_3$ monolith catalysts has been developed to predict evolution of the effluent gases as well as surface species during the storage portion of the NO_x trap cycle. The model combines separate descriptions of oxidation and storage. The oxidation portion of the model is based on a kinetic mechanism and quantitative parameters developed in our laboratory for a Pt/Al_2O_3 catalyst. Two NO_x storage models are proposed to account for the multiple time constants that control NO_x storage. A two site in series model was developed to account for diffusion into the bulk of Ba particles, while a two site parallel model was proposed to account for Ba sites close to Pt and those far from Pt. It is shown that both models adequately account for the asymmetric nature of the NO_x breakthrough curves and that current data cannot distinguish between the two models. It is also illustrated that external mass transfer plays a controlling role during early storage times and must be included in any model for the operating conditions used here. When possible, the model parameters were determined via independent experiments, while the remaining parameters were fit to the NO_x uptake data using a nonlinear least squares method.

Keywords: Kinetic modeling; NO_x storage; NO_x trap; NO oxidation

1. Introduction

Due to the ever increasing emissions standards for combustion engines continually better exhaust after-treatment technologies have been developed. An area of particular interest is that of lean burn engines. Lean burn gasoline or diesel engines are more fuel efficient than standard stoichiometric gasoline engines. However, because of the excess oxygen, conventional three-way catalysts cannot reduce NO_x compounds in the exhaust stream. One potential solution is the use of NO_x storage and reduction (NSR) catalysts [1–3]. These catalysts consist of a noble metal for oxidation and reduction of NO_x (e.g. Pt), and an alkaline or alkaline earth metal for storage of NO_x (e.g. Ba). The NSR catalyst is used with a cyclic engine operation, switching between long lean and short rich periods. During the lean period the catalyst oxidizes NO to NO_2 on the noble metal sites and stores the NO_x (NO and NO_2) on the alkaline earth sites. During the rich period, the NO_x is released from the storage sites and reduced to N_2 by the noble metal sites.

Because of the complex, dynamic nature of the NSR system it is highly desirable to have a model of the overall process that could make predictions both during the development of an improved after-treatment system and in an actual engine computer to control operation of the catalyst on stream. During the development stage a good interplay between experiments and modeling is necessary for efficient development of the improved after-treatment system. The model can be used to investigate the behavior of the catalyst under varying operating conditions, make predictions of the performance at these conditions, and to design new experiments for model validation. In addition, a model can provide insight into experimentally difficult to measure phenomena such as surface coverage or catalyst surface temperature. Once the final product is being used on the vehicle, the model could also be used in conjunction with the engine control module to facilitate the most efficient use of the engine and after-treatment system.

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Several different models for the NSR system have been proposed in the literature. Olsson et al. [4–6] have proposed a mean field model of NO_x storage and a global kinetic model for both NO_x storage and catalyst regeneration. The proposed mean field model consists of a reaction network with a large number of reaction rate parameters. The problem was broken into five separate steps in order to simplify the modeling process. The model was fit to experimental data taken from flow reactor experiments, and a least squares fitting procedure was used to obtain the best fit. Their global kinetic model used reaction rates derived from mechanisms proposed in the literature. Diffusion in the washcoat was handled through the use of a shrinking core model on the barium particles. Both these models were solved using the tank in series method and solving the resulting algebraic CSTR equations.

Tuttlies et al. [7] developed a single particle model to study in detail the effects of diffusion and the formation of dense nitrate layers in the barium phase of the catalyst. From this analysis, a reactor channel model was proposed which includes both storage and regeneration. This was accomplished by using the concentration profiles obtained for single particles to model a bed of particles. This model was again solved using a tank in series approach and the parameters were fit to data obtained in an isothermal flat bed reactor which houses a thin slice of catalyst between heating plates. However, this analysis does not capture many of the effects of exothermicity on regeneration. For example, it has been proposed in the literature that the temperature rise could play a very important role in the release of NO_x species from the barium particles [2].

Other groups have also contributed to the NSR modeling literature. Koci et al. [8,9] and Crocoll et al. [10] have both developed 1D monolith models with complex mechanisms, ranging from 15 to 18 different reaction steps and at least that many rate parameters in an attempt to obtain an accurate description of the overall chemistry of the NSR system. Also, Daw et al. [11] proposed a storage model based on Freundlich isotherms, which were third order polynomial fits of adsorption data. The purpose of this model was to incorporate phenomena that can be measured experimentally with relatively simple experiments, while at the same time to be able to make predictions about storage in an actual lean NO_x trap. Also, Laurent et al. [12] and Sharma et al. [13] have made significant contributions to the modeling literature.

The present paper analyzes NO oxidation and NO_x storage in NSR catalysts using a one-dimensional model of a monolith reactor and is compared to in house experimental results obtained from model $Pt/BaO/Al_2O_3$ monolith catalysts. The model includes both gas phase and adsorbed species and accounts for surface reactions and boundary layer mass transport. A two layer approximation is utilized in order to account for diffusion effects within the washcoat. This assumption is shown to capture the experimental data quite well. The focus of the model development is to keep the model as simple as possible while capturing the important chemistry and physical phenomena of the real system. For the purpose of developing the model using a building up approach, we have chosen to omit any complications associated with the product molecules CO_2 and H_2O. These important effects are being studied and will be reported in a future paper.

2. Experimental methods

2.1. Reactor studies

Both NO oxidation and NO_x storage were studied. The detailed experimental setup for the oxidation studies is described elsewhere [14,15]. Oxidation experiments for this work were performed on the same setup used for the NO_x storage experiments, but with a Pt/Al_2O_3 catalyst. The catalyst used for NO_x storage was a $Pt/BaO/Al_2O_3$ (46 g/ft^3, 20%) washcoat deposited on a cordierite monolith consisting of 200 channels per square inch. The washcoat loading was 2.22 g/in.^{3} of the monolith. If the distribution of Pt and Ba is assumed to be uniform throughout the monolith, the weight loadings are 1.2% Pt, and 17.9% Ba within the washcoat. The experimental setup consists of a vertical bench-top, plug-flow stainless steel reactor. High-temperature Zetex insulation was wrapped around the catalyst (monolith) sample, and the assembly was placed in the reactor tube. The insulation material blocks the space between the monolith and the wall of the reactor, minimizing the gas flow bypassing the catalyst. Glass beads were placed upstream of the catalyst sample to ensure mixing and uniformity of the gas flow and the reactor was placed inside a clam shell temperature-controlled furnace. To minimize temperature gradients, the inlet gas was preheated before entering the reactor. Thermocouples were placed 6 mm before and after the catalyst sample to verify inlet and outlet gas temperatures. A reactor bypass loop after the pre-heater, and thus at the reactor conditions, was used for measurement of the inlet concentrations of the feed gases. All the gas lines were heated to 120–150 °C. Exit gases were analyzed using an FT-IR gas analyzer (Thermo Electron Corporation, Nicolet Antaris IGS). The FT-IR was set to measure a data point every second at a resolution of 0.5 cm^{-1}. The FT-IR is capable of monitoring NO, NO_2, N_2O, CO, CO_2, and H_2O gas concentrations, and the data was analyzed using the Nicolet TQ analysis software. The system is automated to control gas flows through mass flow controllers, switch valves between lean/rich cycles, and monitor the temperature output from the thermocouples using National Instruments LabVIEW software and FieldPoint units.

Preliminary work on the $Pt/BaO/Al_2O_3$-NSR catalyst consisted of long lean/rich cycles up to the point of saturation of the catalyst. That is, the lean period extended to the point where the NO_x slip through the catalyst is equivalent to the feed concentration. Here we chose to first understand the storage of NO_2 in the presence of O_2, N_2, and NO only. Commonly found exhaust gases such as CO_2 and H_2O which have been shown to compete for sites, and hence have a significant effect on storage [16], have not been considered in these initial experiments. The inlet O_2 concentration was held constant at 10% while the inlet NO_2 concentration was varied between 90 ppm and 390 ppm (balance N_2) and the temperature was held constant at 300 °C. The regeneration was done using 0.5% H_2 in N_2 for 300 s. This time period was sufficient to regenerate the catalyst completely