Kinetic Measurements and Modeling of NOx Storage/Reduction Catalysts

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Introduction

The use of internal combustion engines in a lean burn operation offers higher fuel efficiency when compared to a stoichiometric burn operation. Current three-way catalysts do not effectively reduce NOx under lean burn exhaust conditions so one method proposed to reduce the emission of NOx is through a cyclic operation of the engine between lean and rich periods and the use of a NOx Storage/Reduction (NSR) catalyst. The entire cycle can be broken down into three main steps: oxidation of NO to NO_2 and NOx storage on the sorber component during the lean phase followed by regeneration of the catalyst during the rich phase transforming the NOx to N_2.

Materials and Methods

A 2.13wt% Pt/20wt% Ba/Al_2O_3 monolith catalyst was used for NSR cycles with a space velocity of 32,000 h^{-1} in a stainless steel plug flow reactor. The exit gases were analyzed using an FT-IR analyzer (Thermo Electron Corporation, Nicolet Antaris IGS). The diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) spectra were collected on a Nicolet Magna 550 FTIR with a Spectra-Tech Collector II accessory fixed with the optional high temperature/pressure chamber at a resolution of 4 cm^{-1} and averaged over 32 scans. The NOx breakthrough curves were modeled using a transient, 1-dimensional, two phase approximation with mass transfer across the boundary layer to the washcoat. The resulting differential equations were solved by the finite element method using COMSOL®. Model predictions of the outlet gas concentrations were fit to experimental data by coupling the COMSOL® model with a nonlinear least-squares optimization function in MATLAB®.

Results and Discussion

The first step is the oxidation of NO with O_2 to form NO_2 on Pt. The NO oxidation reaction was found to have a first order dependence with respect to both the reactants NO and O_2 and a negative first order dependence with respect to the product NO_2, over the concentration range studied, indicating that the product NO_2 is an inhibitor of this reaction. A reaction mechanism that is consistent with the observed reaction orders has been proposed [1]. The reaction was found to be sensitive to the structure of the catalyst with higher turnover rates (TOR) seen for larger Pt clusters.

The 1-D model developed to describe NOx breakthrough curves includes the NO oxidation model described above coupled with NOx adsorption on the barium component of the NOx trap. The model indicates that NOx adsorption is controlled by multiple time constants required to give the asymmetric breakthrough curves seen experimentally. Figure 1 shows that both the "two BaO sites in parallel" and "two BaO sites in series" models are capable of capturing the asymmetric nature of NOx breakthrough curves during capture with only NO_2. Models were further validated by predicting NOx breakthrough at two other different NO_2 inlet concentrations. Time-dependent DRIFTS spectra were collected on the monolith with a reactant stream of 376 ppm NO_2 and 12% O_2 at 300°C, and it was found that NOx is mainly stored in the form of ionic (bulk) barium nitrates with barium nitrites present during the first three minutes. Furthermore, the effects of H_2O and CO_2 were monitored since both gases are always present in lean burn exhaust. The addition of 5% H_2O forms hydroxyl groups which lower the amount of nitrates stored on the barium component. The addition of 5% CO_2 forms bidentate, monodentate, and non-coordinated carbonates. During storage, the formation of ionic barium nitrates is observed with a decrease in the amount of bidentate carbonates. The result of addition of both H_2O and CO_2 resembles that for the CO_2 only case, but with a larger decrease in the amount of bidentate carbonates. Changes in storage capacity observed from breakthrough curves are fully consistent with changes monitored by IR during the lean phase.

The final step is the regeneration of the NSR catalyst. Regeneration was found to involve a localized reaction front of the reductant traveling through the catalyst bed with complete regeneration of the trapping sites. The process is consistent with the release of NOx from the trapping material, followed by its reduction over Pt, and the reactions are seen to be fast enough to make the process mass transfer limited. The results also indicate that the catalyst regeneration using H_2 as the reductant occurs with NH_3 serving as a carrier of the hydrogen atoms [2]. Regeneration using NH_3 is equivalent and equally effective to using H_2. This presentation will emphasize how the details of these phenomena can be represented in a quantitative, predictive model.
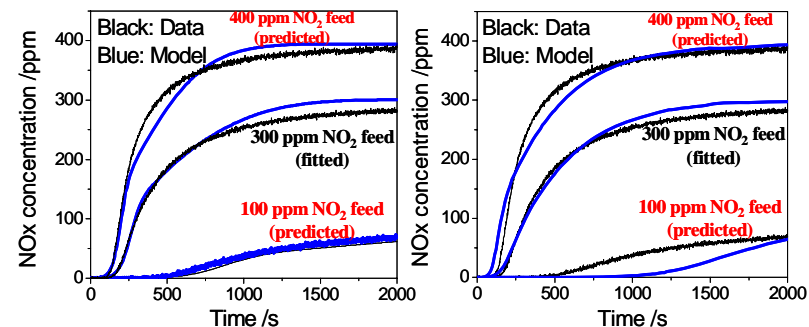
Figure 1. Modeling of NOx breakthrough at 300°C using two sites in parallel (left) and two sites in series (right) model.

References

1. Mulla, S.S., Chen, N., Delgass, W.N., Epling, W.S., and Ribeiro, F.H. *Catal. Lett.* 100, 267 (2005).
2. Cumaranatunge, L., Mulla, S.S., Yezerets, A., Currier, N.W., Delgass, W.N., and Ribeiro, F.H. *J. Catal. (2006)* doi:10.1016/j.jcat.2006.11.008.