

Experimental and Kinetic Investigations of NO Oxidation on Model Pt Catalysts

Divesh Bhatia¹, Michael P. Harold¹, Vemuri Balakotaiah¹ and Robert W. McCabe^{2*}

¹Department of Chemical & Biomolecular Engineering, University of Houston, Houston, TX (USA)

²Research and Innovation Center, Ford Motor Company, Dearborn, MI, 48124 (USA)

*rmccabe@ford.com

Introduction

Due to the rising fuel costs recently, lean burn gasoline and diesel engines have been in focus because of their better fuel mileage. However, the presence of excess O₂ in the exhaust requires a special aftertreatment for reducing NO_x emissions. Several NO_x reduction technologies are under development, including selective catalytic reduction (SCR) with NH₃, urea or hydrocarbons, and NO_x storage and reduction (NSR). The focus of the current work is NSR, which consists of two cyclic steps: NO_x storage during the lean cycle and reduction during the rich cycle. Since the operation of a NSR catalyst is a complex process involving NO oxidation, storage and reduction, we limit our attention to the lean cycle in this work.

Since NO₂ stores readily on a lean NO_x trap (LNT) catalyst as compared to NO [1], NO has to be oxidized to NO₂ for NO_x storage. Elucidating the kinetics of the NO oxidation reaction on Pt/Al₂O₃ has been a topic of active research [2]. However, the study of NO oxidation on Pt/BaO/Al₂O₃ is challenging because of its coupling with NO_x storage. Moreover, a transient decrease in NO oxidation rates has been reported in the literature [3], which results in the non-achievement of a steady state for a certain range of temperature (200°C-300°C). Nevertheless, steady-state rate expressions have been proposed in the literature [2]. In this work, we point out the limitations of steady-state models and the importance of transient models in the fundamental understanding of NO oxidation reaction. Since the reverse reaction, i.e. NO₂ decomposition, is neglected in many modeling studies, we conduct experiments to show the contribution of NO₂ storage and decomposition in the formation of NO, thus highlighting the need of incorporating the effect of NO₂ in the proposed models. Olsson and Fridell [3] attributed the transient decrease in NO oxidation activity to the formation of Pt oxides. We present results of pretreatment experiments with O₂ and NO₂ that demonstrate poisoning, which is consistent with the formation of Pt oxides. Also, transient NO oxidation experiments for various NO₂ concentrations are done to highlight the inhibitive role of NO₂.

Materials and Methods

Pt/Al₂O₃ and Pt/BaO/Al₂O₃ samples used in this study were provided in monolithic form by BASF Catalysts LLC. The flow rates of various gases (NO, O₂, NO₂, N₂) were controlled by mass flow controllers. The catalyst sample was placed in a heated quartz tube, and both catalyst and inlet gas temperatures were measured. The effluent from the flow reactor was analyzed using a FT-IR spectrometer. Pretreatment experiments were performed by flowing the desired gas (5% O₂ or 524 ppm NO₂) over the pre-reduced Pt/Al₂O₃ catalyst. NO oxidation kinetics were then measured as a function of time at a constant temperature. A one-dimensional two-phase model was used to predict the NO conversion for various catalyst temperatures using the arc-length method.

Results and discussion

The transient NO conversion profiles after various pretreatments are plotted in Figure 1. After one hour, NO conversion is the highest for reductive pretreatment with H₂, whereas the lowest NO conversion is found with NO₂ pretreatment. This shows that both O₂ and NO₂ pretreatments deactivate the catalyst – more so with NO₂, which is consistent with the stronger oxidizing potential and Pt surface oxygen coverage reported for NO₂ [4]. The transient NO conversion profiles following the pretreatment show that NO conversion decreases with time

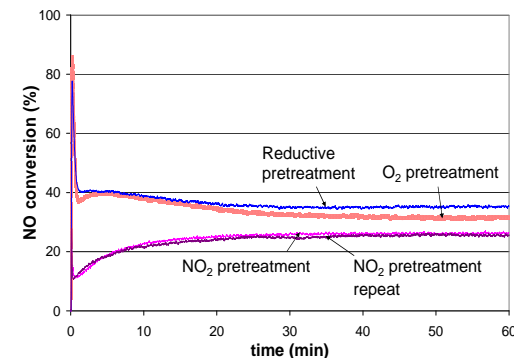


Figure 1. Comparison of transient NO conversion for various pretreatments on Pt/Al₂O₃ catalyst (Inlet NO=500 ppm, O₂=5%; Inlet temperature=192°C)

for reductive and O₂ pretreatments, whereas the conversion increases with time following NO₂ pretreatment. The transient increase can be explained by reaction of NO with surface oxygen deposited during the NO₂ pretreatment. However, after 60 minutes, the NO conversion after NO₂ pretreatment is less than that after either reductive or O₂ pretreatment, and the difference indicates the formation of irreversible Pt oxides. The intermediate level of NO conversion observed after 60 minutes with the O₂ pretreatment is consistent with an amount of irreversible oxide formation which is between that of the pre-reduced and NO₂ pretreated Pt surfaces.

Modeling efforts are underway to propose a global rate expression, which predicts the inhibiting effect of NO₂ on NO oxidation and the reverse reaction, i.e., NO₂ decomposition.

Significance

The present work focuses on the lean cycle of NSR process, a key technology for reducing NO_x emissions. The study points out the limitations of steady state NO oxidation kinetic models arising from slow changes in the nature of the catalyst surface. In addition to NO oxidation, NO₂ decomposition and storage is studied for various conditions, and the importance of including both reactions explicitly in the models of NSR catalysts is noted.

References

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