

# Microkinetic Modeling of Ethanol and other Hydrocarbon (HC)-based Selective Catalytic Reduction (SCR) of NO<sub>x</sub> on Silver-based Catalyst

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## Introduction

SCR is currently considered as one of the most promising methods to reduce NO<sub>x</sub> under an excess of Oxygen. Burch's research group has investigated the SCR mechanism in detail [1]. Power-law and Langmuir-Hinshelwood models have also been developed [2,3]. However, the potential of microkinetic modeling has not yet been explored for this complex chemistry. Microkinetic modeling has various advantages over power-law fits and Langmuir-Hinshelwood analysis and it is valid over a wide range of operating conditions [4]. Since the inception of microkinetic modeling [5], significant advances have been made in this area by applying hierarchical model development strategies [6]. In this work, we employ hierarchical microkinetic modeling to investigate Ethanol-SCR and HC-SCR of NO<sub>x</sub> on Ag-based catalysts.

## Mechanistic Aspects and Parameter Estimation for the Ethanol-SCR Model

Two major pathways are proposed for ethanol consumption on an Ag-based catalyst, as shown in Fig. 1. The first pathway oxidizes ethanol to acetaldehyde [7], forms the isocyanate intermediate, and eventually produces N-containing compounds such as HCN and ammonia. A competitive pathway is dehydration of ethanol to ethylene [7] followed by subsequent oxidation to CO and CO<sub>2</sub>. Both paths are connected to each other via a variety of intermediates.

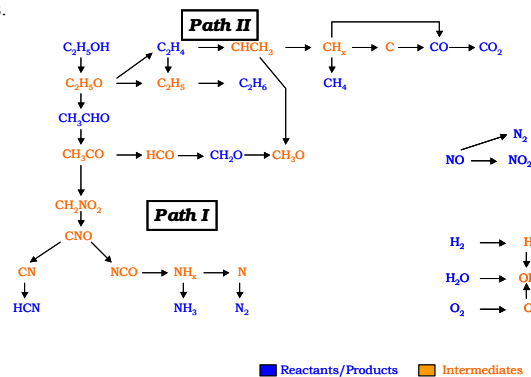


Figure 1. Schematic of the Ethanol-SCR model.

Pre-exponential factors are estimated using the Transition State Theory (TST). A semi-empirical method called Unity Bond Index-Quadratic Exponential Potential (UBIQEP) [8] is used to calculate the heats of adsorption (Q) and activation energies. There is a fair

agreement among the Q values computed using UBIQEP, values extracted from surface science experiments, such as Temperature Programmed Desorption (TPD), and values estimated using quantum mechanical Density Functional Theory (DFT).

## Reduction, Optimization, and Validation of the Ethanol-SCR Model

The initial Ethanol-SCR model of ~400 reactions is simplified based on the following ideas: a) Species that are not observed in the experiments and their corresponding reactions are eliminated from the model. b) Since O/OH are the most abundant catalytic species, reactions of other species with O/OH are considered to be the most important ones. c) Reactions with high activation energies are eliminated while considering competitive paths for a species. Based on these assumptions, the model is simplified to 116 reactions and 36 species.

Commercially available modeling software is used to model the system as a catalytic PFR. A few rate parameters in this model are tuned to capture the experimental data under nominal conditions (experimental data is not shown). The optimized model is then used to understand the axial profiles of various species, as shown in Fig. 2. It is found that the ethanol chemistry primarily happens in the front zone of the catalyst bed. Ethanol is quickly converted to ethylene, acetaldehyde, and formaldehyde over the first few centimeters. Ethylene then oxidizes to CO and CO<sub>2</sub>. Consumption of the aldehydes and NO follows similar slopes, which indicates that the aldehydes are the primary reductants. Major N-containing compounds produced in this system are HCN and ammonia.

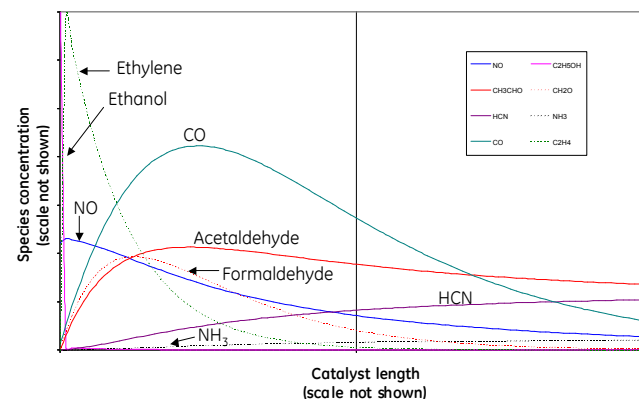


Figure 2. Axial profiles of important species using the Ethanol-SCR model.

The Ethanol-SCR model is rigorously validated against the effect of different process variables, such as space velocity, temperature, inlet Ethanol:NO<sub>x</sub> ratio, etc. (data is not shown).

## Similarities between Ethanol-SCR and HC-SCR Models

a) Reaction pathways in HC-SCR are similar to those in Ethanol-SCR. In fact, hydrocarbons are known to convert into oxygenates, which drive the NO<sub>x</sub> SCR reaction [1,9]. In the proposed HC-SCR mechanism, we have utilized this information by considering

pathways of hydrocarbon oxidation to alkoxy species and breakdown into Ethoxy/Acetaldehyde. b) Reactor modeling of the HC-SCR data and the Ethanol-SCR data is quite similar. c) Finally, the main catalytic component in both systems is the same, an Ag-based catalyst. Therefore, the HC-SCR mechanism is developed with the Ethanol-SCR mechanism as a good starting point.

### Mechanistic Aspects and Parameter Estimation for the HC-SCR Model

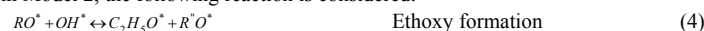
Two different models (Model 1 and Model 2) are proposed for the HC-SCR case. In both models, the following reactions are common:



In Model 1, the following reaction is assumed to take place:



However, in Model 2, the following reaction is considered:



The crucial difference between Model 1 and Model 2 is that acetaldehyde can be mainly consumed via the  $NO_x$  reduction pathway, whereas ethoxy can be consumed via the  $NO_x$  reduction pathway and the combustion pathway. Even though the backbone chemistry of Ethanol-SCR is complex (116 reactions), each additional HC results in a total of only 6 reactions. The total number of reactions after including all 11 HC reductants is only 152. This approach of adding only a few reactions to capture the chemistry of an entirely different species is based on the hierarchical microkinetic modeling concept.

TST and UBIQEP are used for parameter estimation. For alkane HC species, experimental information of heats of adsorption is used. For some cases, where reliable experimental data for heats of adsorption are not available, interpolation is used to compute these values.

### Optimization and Validation of the HC-SCR Model

The development of the microkinetic model is carried out from bottom to top, i.e., from lowest to the highest HC. For each HC, a rate-determining step is identified and its activation energy is tuned to capture the  $NO_x$  conversion data at different temperatures. Each time the data for a HC is captured; all simulations are repeated for lower HCs to ensure the validity of a single mechanism for all HCs. The RDS in both Model 1 and Model 2 is the alkoxy formation step.

It is found that the Model 1 captures the experimental data and trends at low-mid temperatures fairly well. However, at higher temperatures, it significantly overpredicts the  $NO_x$  conversion. This could be due to the inability of Model 1 (and its intermediate acetaldehyde) to proceed via the combustion pathway. In comparison, Model 2 considers the ethoxy species as an intermediate, which can be consumed to form acetaldehyde as well as ethylene.

Figure 3 shows the difference in  $NO_x$  conversion predictions of Model 2 from the experimental data for all 11 HCs. The Model 2 captures the experimental data fairly well. We have also explored the effect of other process variables, such as flow rate and HC: $NO_x$  ratio, using Model 2. The model shows the expected trends with respect to these variables. The effect of temperature increase over the catalyst bed is also studied. It is especially important for higher alkanes.

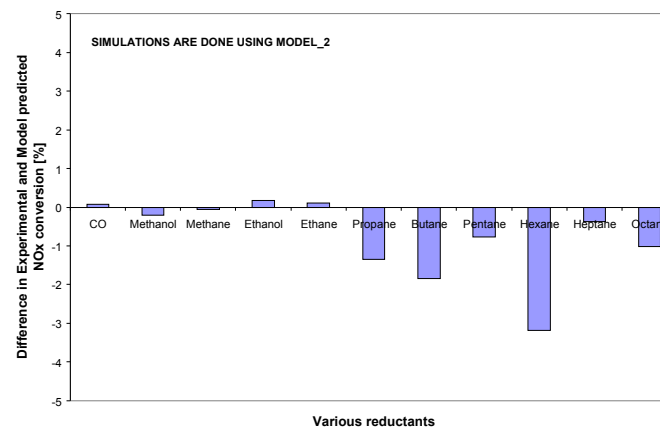


Figure 3. Performance of the HC-SCR Model 2.

### Significance

Detailed elementary microkinetic models are developed for the Ethanol-SCR and other HC-SCR systems. Rate parameters are estimated from semi-empirical calculations as well as extracted from literature experiments. The models are optimized and validated to capture  $NO_x$  conversion data for multiple HC reductants. These models can provide a unique capability of capturing the complicated catalytic behavior of the SCR catalyst and play a critical role in overall system integration.

### References

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