

## Modeling the role of CO and C<sub>3</sub>H<sub>6</sub> in NO<sub>x</sub> reduction over an SCR catalyst

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### Highlights

- Synergy between CO and NH<sub>3</sub> increases NO<sub>x</sub> conversion for slow SCR at low temperatures
- NO formed by C<sub>3</sub>H<sub>6</sub>-NO<sub>2</sub> interaction creates local fast SCR conditions at low temperatures
- Decrease in NO<sub>x</sub> conversion for slow SCR at high temperature is not due to C<sub>3</sub>H<sub>6</sub> adsorption

### 1. Introduction

Hydrocarbon selective catalytic reduction (HC-SCR) technology utilizes the on-board fuel to selectively reduce the diesel NO<sub>x</sub> emissions under oxygen-rich conditions. In addition to NH<sub>3</sub>, species such as CO and C<sub>3</sub>H<sub>6</sub> (representative of unburnt hydrocarbons) that are present in the diesel exhaust have the potential to reduce NO<sub>x</sub> over SCR catalysts. Kim et al. [1] recently reported that the presence of C<sub>3</sub>H<sub>6</sub> along with NH<sub>3</sub> increases the NO<sub>x</sub> conversion under cyclic conditions. Zheng et al. [2] also reported an increase in the NO<sub>x</sub> conversion under standard and slow SCR conditions in the presence of CO and C<sub>3</sub>H<sub>6</sub>. In the current work, global kinetic models are developed for the CO-NO<sub>2</sub> and C<sub>3</sub>H<sub>6</sub>-NO<sub>2</sub> interactions. These models are then combined with the NH<sub>3</sub>-SCR kinetic model to predict the effect of CO and C<sub>3</sub>H<sub>6</sub> on the overall NO<sub>x</sub> conversions under slow and fast SCR reaction conditions over a commercial Cu-chabazite SCR catalyst.

### 2. Methods

A one-dimensional two-phase model is used in the current work. A nitrate based mechanism was used to develop a kinetic model for predicting the NO<sub>2</sub> reduction by CO to form NO. This model was then used to explain the C<sub>3</sub>H<sub>6</sub>-NO<sub>2</sub> interactions through global reactions leading to the formation of N<sub>2</sub>, NO, CO and CO<sub>2</sub>. The CO-NO<sub>2</sub> and C<sub>3</sub>H<sub>6</sub>-NO<sub>2</sub> models were further combined with the NH<sub>3</sub>-SCR model to elucidate the effect of the reductant species such as CO and C<sub>3</sub>H<sub>6</sub> on slow and fast SCR reactions at different temperatures. The kinetic models were validated by using the experimental data reported by Zheng et al. [2] under different operating conditions.

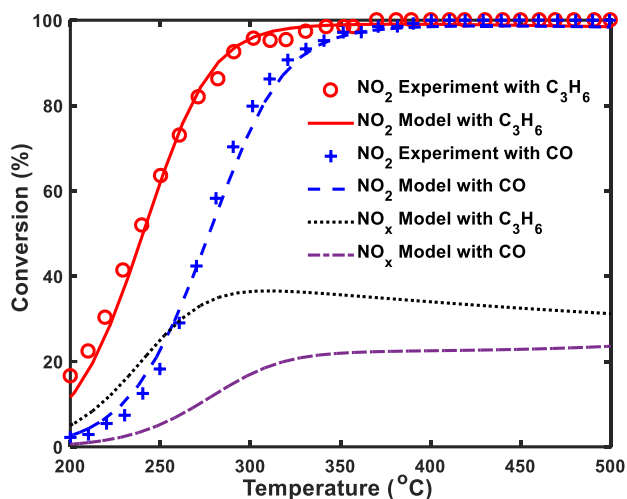
### 3. Results and discussion

A comparison of our model predictions with the experimental data reported by Zheng et al. [2] on NO<sub>2</sub> reduction by CO and C<sub>3</sub>H<sub>6</sub> is shown in Figure 1. The CO-NO<sub>2</sub> interaction is explained by the formation of surface nitrates and nitrites through a disproportionation reaction (R1). In agreement with the experimental data, the model predicts that NO is the major product formed during the NO<sub>2</sub> reduction by CO. CO is found to react with the nitrates to form nitrites (R2), which favor the reduction of NO<sub>2</sub> to NO through its reaction with the nitrites (R3).

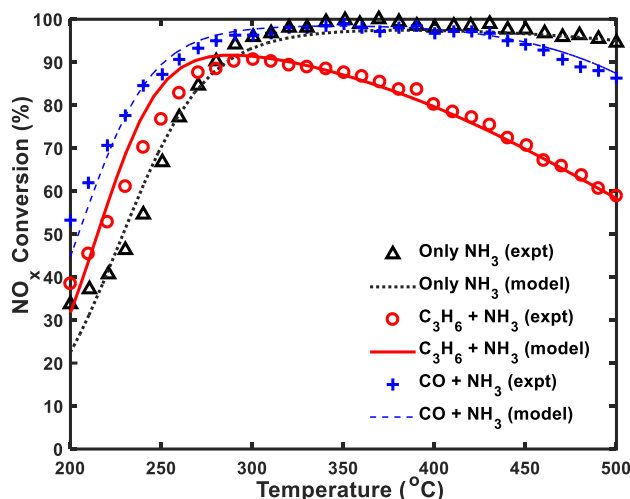


Kim et al. [1] reported the formation of CO during NO<sub>2</sub> reduction by C<sub>3</sub>H<sub>6</sub>. Thus, the interaction of C<sub>3</sub>H<sub>6</sub> and NO<sub>2</sub> is explained in our model by global reactions leading to the formation of NO, N<sub>2</sub> and CO. Similar to the case of CO, NO is formed as the major product during the reduction of NO<sub>2</sub> with propene. On comparing the overall NO<sub>x</sub> conversions for the two reductants, it is observed that the model can predict that C<sub>3</sub>H<sub>6</sub> is a better reductant than CO for all the temperatures. It is also observed that for temperatures lower than 350 °C, NO<sub>2</sub> conversion is higher with C<sub>3</sub>H<sub>6</sub> as the reductant, whereas close to complete NO<sub>2</sub> conversion is obtained with both the reductants for temperatures higher than 350 °C.

To understand the effect of the reductants such as CO and C<sub>3</sub>H<sub>6</sub> on NH<sub>3</sub>-SCR, the experimental trends reported by Zheng et al. [2] were modeled based on the global reactions proposed by Metkar et al. [3]. Figure 2 shows the effect of CO and C<sub>3</sub>H<sub>6</sub> on NH<sub>3</sub>-SCR reactions under slow SCR conditions. The model predictions are obtained by combining the NH<sub>3</sub>-SCR model with the CO-NO<sub>2</sub> and C<sub>3</sub>H<sub>6</sub>-NO<sub>2</sub> kinetic models. It is shown that at low temperatures, the NO<sub>x</sub> conversion is higher when CO and C<sub>3</sub>H<sub>6</sub> are used along with NH<sub>3</sub> as compared to the case when only NH<sub>3</sub> is used. In contrast, the NO<sub>x</sub> conversions are lower with CO and C<sub>3</sub>H<sub>6</sub> at high temperatures. The presence of C<sub>3</sub>H<sub>6</sub> reduces the NO<sub>x</sub> conversion significantly at high temperatures, whereas the inhibitive effect of CO is relatively low. The promotional effect of CO at low temperatures is explained by the synergistic effect of CO and NH<sub>3</sub> in enhancing the consumption of NO<sub>2</sub> through the disproportionation reaction (R1). The enhancement in NO<sub>x</sub> conversion at low temperatures in the presence of C<sub>3</sub>H<sub>6</sub> is explained by the formation of NO, which creates local fast SCR conditions [2]. The reduced NO<sub>x</sub> conversion in the presence of CO and C<sub>3</sub>H<sub>6</sub> is explained by the selective reduction of NO<sub>2</sub> to NO by CO and C<sub>3</sub>H<sub>6</sub> instead of its reduction by NH<sub>3</sub> through SCR reactions. It is also reasoned that the inhibiting effect is not due to the competitive adsorption between NH<sub>3</sub> and the reductants since the inhibiting effect was found to increase with temperature.



**Figure 1.** Comparison of NO<sub>2</sub> and NO<sub>x</sub> conversion during NO<sub>2</sub> reduction with CO and C<sub>3</sub>H<sub>6</sub> at various temperatures. Reaction Conditions: 500 ppm NO<sub>2</sub>, 1% CO (if present), 500 ppm C<sub>3</sub>H<sub>6</sub> (if present) and 2.5% H<sub>2</sub>O.



**Figure 2.** Effect of CO and C<sub>3</sub>H<sub>6</sub> on NH<sub>3</sub>-SCR under slow SCR conditions. Reaction Conditions: 500 ppm NO<sub>2</sub>, 500 ppm NH<sub>3</sub>, 1% CO (if present), 500 ppm C<sub>3</sub>H<sub>6</sub> (if present) and 2.5% H<sub>2</sub>O.

#### 4. Conclusions

Kinetic models are developed to predict the effect of CO and C<sub>3</sub>H<sub>6</sub> on NH<sub>3</sub>-SCR under slow SCR conditions. The kinetic models are able to explain the experimental data reported by Zheng et al. [2]. NO is predicted to be the major product formed during the reduction of NO<sub>2</sub> by CO and C<sub>3</sub>H<sub>6</sub>. The CO-NO<sub>2</sub> and C<sub>3</sub>H<sub>6</sub>-NO<sub>2</sub> models when combined with the NH<sub>3</sub>-SCR model are able to capture the promotional effect of CO and C<sub>3</sub>H<sub>6</sub> on NO<sub>x</sub> conversion at low temperatures and the inhibiting effect at high temperatures under slow SCR conditions. The increase in NO<sub>x</sub> conversion in the presence of C<sub>3</sub>H<sub>6</sub> at low temperatures is because of the local fast SCR conditions created due to NO formation whereas the inhibiting effect at high temperatures is explained by the selective reduction of NO<sub>2</sub> to NO by C<sub>3</sub>H<sub>6</sub>. The effect of CO and C<sub>3</sub>H<sub>6</sub> on NH<sub>3</sub>-SCR under fast SCR conditions were also analyzed and the results will be presented in the full manuscript.

#### References

- [1] M. Y. Kim, H.Y. Choi, M. Crocker, Catal. Today 231 (2014) 90-98.
- [2] Y. Zheng, M. P. Harold, D. Luss, Catal. Today 264 (2015) 44-54.
- [3] P. S. Metkar, M. P. Harold, V. Balakotaiah, Chem. Eng. Sci. 87 (2013) 223-230.

#### Keywords

Hydrocarbon Selective Catalytic Reduction (HC-SCR); NH<sub>3</sub>-SCR; Cu-chabazite; global kinetics.