

## Modeling and Experimental Studies of HNCO as a Reactant for NO<sub>x</sub> Control

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### Introduction

The selective catalytic reduction with NH<sub>3</sub> is widely used to reduce the NO<sub>x</sub> emissions from both stationary and mobile sources. In mobile sources such as diesel vehicles, NH<sub>3</sub> is replaced by aqueous urea solution for safety reasons<sup>1</sup>. Unfortunately, during low temperature engine operating conditions, urea droplets might not evaporate and thermolyze to form NH<sub>3</sub>, and isocyanic acid (HNCO) might not hydrolyze to form another molecule of NH<sub>3</sub> required to reduce NO<sub>x</sub> in diesel exhaust. To address this shortcoming, there is a need to investigate alternate reactants such as NH<sub>3</sub> and HNCO for NO<sub>x</sub> control.

HNCO formed from urea undergoes a series of condensation reactions leading to a variety of secondary compounds such as biurets and other high molecular weight melamine compounds<sup>2</sup>. These compounds can plug the monolith channels thus impacting the NO<sub>x</sub> conversion and urea penalty in the aftertreatment system. Therefore, it is essential to understand the kinetics and surface chemistry of various HNCO reactions on the catalyst surface to enhance NO<sub>x</sub> conversion. This paper presents the experimental procedure to generate HNCO and discusses possible reaction pathways involving NO, NO<sub>2</sub>, NH<sub>3</sub> and HNCO species on the catalyst, along with a brief modeling exercise.

### HNCO Synthesis

HNCO is generated by de-polymerizing cyanuric acid, following the procedure presented by Lercher and Zhan<sup>3</sup>. A heated tubular reactor is divided into two temperature zones. Half of the first zone is filled with quartz beads to pre-heat the carrier gas stream. The second half of the first zone contains solid cyanuric acid. The first zone is maintained at a temperature of 320°-330°C. The second zone contains Al<sub>2</sub>O<sub>3</sub> catalyst particles to lower the de-polymerization temperature of cyanuric acid to 370°C. HNCO is collected in two serial cold traps placed downstream of the tubular reactor. During start-up, hydrolysis on surface OH groups of the catalyst occurs. As suggested<sup>4</sup>, it is essential to by-pass HNCO stream from the cold traps to avoid condensation of NH<sub>3</sub> and CO<sub>2</sub> into the product.

### Reactor Set-up

The set-up for HNCO tests is shown in Figure 1. HNCO is introduced into the reactor via an N<sub>2</sub> stream and a saturator at -30°C as shown. Based on a HNCO saturated vapor pressure curve as a function of temperature, the desired HNCO test concentrations can be prepared. For the reactor tests, a stream of 350 ppm of NO<sub>x</sub>, 350 ppm of HNCO, 4.5% H<sub>2</sub>O, 4.5% CO<sub>2</sub>, 14% O<sub>2</sub> and balance N<sub>2</sub> is used. To investigate the HNCO/NO<sub>x</sub> effect on NO<sub>x</sub> conversion, the concentrations are varied based on reaction stoichiometry.

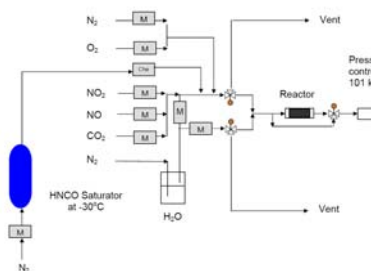


Figure 1: HNCO Reactor Set-up

### Results and Discussion

A comparison is made between a validated Cu-zeolite NH<sub>3</sub>-SCR steady state model and an uncalibrated HNCO-SCR model as shown in Figure 2. The figure shows that HNCO hydrolysis to NH<sub>3</sub> is fast and complete at T > 150°C and the downstream concentrations of NO, NO<sub>2</sub>, NH<sub>3</sub> and N<sub>2</sub>O are within 5 ppm for the two models at all 200°C < T < 450°C.

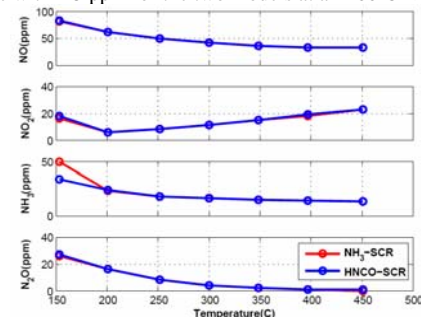


Figure 2: Comparison between Validated NH<sub>3</sub>-SCR and Uncalibrated HNCO-SCR Models

### Significance

This work helps understand the mechanistic aspects of HNCO hydrolysis on the SCR catalyst while investigating the possible reaction pathways leading to formation of secondary compounds.

### References

1. Piazzesi, G., Devadas, M., Krocher, O., and Elsener, M., *Catalysis Communications*, Vol. 7, 600-603, 2006.
2. Hauck, P., Jentys, A., and Lercher, J.A., *Applied Catalysis B: Environmental*, Vol. 70, 91-99, 2007.
3. Lercher, J.A., and Zhan, Z., *European Patent Application 94,113,599*, 1995.
4. Zhan, P., *Ph.D. Dissertation*, University of Twente, 1995.