# Global kinetic modeling of hydrothermal aging of $NH_3$-SCR over Cu zeolites

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## Introduction

Ammonia based selective catalytic reduction (SCR) is an important technology for reducing the $NO_x$ emissions from lean burn diesel vehicles. Copper zeolites have been studied extensively for this reaction, due to their high activity. In our previous work, we have examined the hydrothermal deactivation of Cu-BEA, regarding both activity and selectivity [1], as well characterizing the material properties [2, 3]. However, there are to our knowledge no kinetic models presented that describes aging of copper zeolites used for ammonia SCR.

The objective of this work was to develop a kinetic model for $NH_3$ SCR of copper zeolites upon hydrothermal aging, using a broad range of conditions and temperatures.

## Materials and Methods

Cu/BEA was prepared through ion-exchange of BEA zeolite (Zeolyst international) [1]. The same Cu/BEA monolith was hydrothermally aged at 600, 700, 800 and 900°C and the activity for the following reaction were studied: Ammonia TPD, NO oxidation, $NH_3$ oxidation and SCR with $NO_2/NO_x$ ratio of 0, 0.5 and 0.75 [1]. The catalyst material was characterized after hydrothermal aging using XRD, UV-vis, XPS, BET, $H_2$ TPR and micro calorimetry [1-3].

The simulations were done using AVL BOOST, with user defined kinetics written in FORTRAN. The model contains one channel, which was discretized into 15 grid points.

## Results and Discussion

Micro-calorimetry was used for estimation of heat of adsorption of ammonia after different aging steps. This information was used for modeling ammonia adsorption and desorption during $NH_3$ TPD experiments. Further, aging experiments of ammonia and NO oxidation were used as a base for the model development. The parameters for these reactions were used when simulating the aging of the SCR reactions. Different $NO_2/NO_x$ ratios were used in the model development (0, 0.5 and 0.75%). Fig. 1 shows the NO, $NO_2$, $NH_3$ and $N_2O$ concentration after aging at 800°C. First, the pre-exponential factor for standard SCR was re-tuned, which was a successful approach after 700°C aging. However, it was not possible to describe the standard SCR after 800°C aging with only this change. Thereafter, we instead retuned both the pre-exponential factor and activation barrier and the results are depicted in Fig 1a. There is good agreement at low temperature, however, the agreement is poor at high temperature. If the activation barrier is changed to get a good fit at high temperature, it results in poor agreement at low temperature. The UV-vis characterization showed that copper was in the form of copper hydroxides after aging at low temperature, but after aging at high temperature CuO was observed [2]. We therefore suggest that after 800°C aging the catalyst contains both copper hydroxides and CuO, resulting in SCR reaction on both sites, but with different rates. We therefore added a second SCR reaction to the model in order to describe SCR on the CuO and the results are seen in Fig 1b. The model is now able to predict the experimental findings adequately.

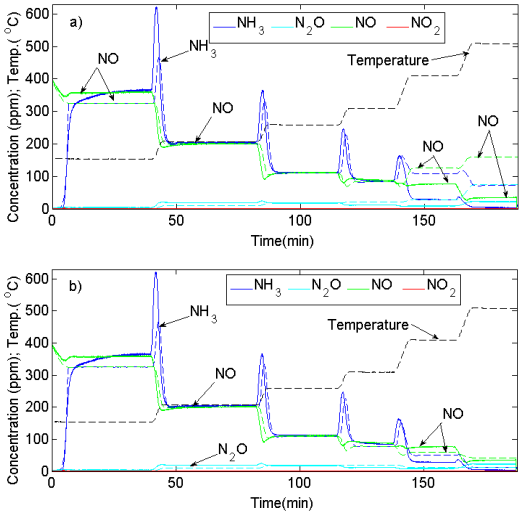


**Figure 1**. Experiments (solid lines) and simulations (dashed lines) for $NH_3$ SCR over Cu/BEA using model 1 (a) and model 2 (b). The catalyst was exposed to 400 ppm $NH_3$, 400 ppm NO, 8% $O_2$ and 5% $H_2O$ and stepwise increasing the temperature.

## Significance

Ammonia SCR is one of the commercially used technologies for removing $NO_x$ from lean burn engines and copper zeolites are extensively used for this method. The catalyst can deactivate after being exposed to high temperature. However, there are today to our knowledge no kinetic models available that can describe hydrothermal aging of copper zeolites used for $NH_3$ SCR, which is the objective with this study. Degreening/aging at 500, 600, 700, 800 and 900°C is used and several reactions are modeled including SCR with different $NO_2$ ratio.

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## References

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