# Comparison of Cu-CHA type catalysts performance in the $NH_3$-SCR reaction of nitrogen oxides

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## Introduction

Copper loaded CHA-type zeolites and zeotypes are among the most promising catalysts for the selective catalytic reduction of nitrogen oxides with ammonia ($NH_3$-SCR). In particular their high hydrothermal stability, excellent low-temperature performance, better resistance against poisoning by hydrocarbons, and a lower selectivity to unwanted $N_2O$ compared to other Cu-zeolite systems, makes them very attractive candidates for various automotive SCR applications where traditional vanadium based formulations cannot be used.[1] Furthermore, the CHA structure allows for an unprecedented opportunity to study in detail the role of Cu in an industrially relevant zeolite catalyst, due to its relatively simple crystal structure, and well defined Cu sites.

CHA-materials can be synthesized in various compositions. Of particular interest in this study are the classical silicon rich aluminosilicate zeolite SSZ-13, its alumina rich counterpart synthetic Chabazite and the silicoaluminophosphate SAPO-34 zeotype. Each composition leads to a different performance in SCR, as will be shown in the presentation.

## Materials and Methods

Cu-CHA materials with similar copper loadings were either obtained from commercial suppliers or synthesized for the purpose of comparison. The Cu-CHA catalysts were characterized by HR-PXRD, *in situ* XAFS-techniques, physisorption and TGA methods. Additionally, DFT calculations were used to support the findings. For the assessment of catalytic performance (activity, stability and poisoning by hydrocarbons) powder-tests (150-300 µm fraction) were performed in fixed bed reactors (2mm i.d.) at a high space velocity (W/F typically at 120 mol/g/h) using a typical gas composition for SCR (500 ppm NO, 530 ppm $NH_3$, 5% $H_2O$, 10% $O_2$ in $N_2$).

## Results and Discussion

Conventional ion exchange of Cu-CHA materials usually leads to a homogenous distribution of copper ions. However, in SAPO-34, Cu remains in the outer regions of the crystals, and a treatment at about 750°C is required to redistribute the Cu-ions throughout the crystals.[2] After the pretreatment the Cu-SAPO-34 catalyst activity becomes several times more active (**Figure 1a**), whereas minor increases in activity for Cu-SSZ-13 is experienced at most. Furthermore, we note that the activity per Cu-atom is consistently higher (in the low temperature region < 250°C) for the Cu-SAPO-34 compared to Cu-SSZ-13.

The resistance of Cu-SAPO-34 and Cu-SSZ-13 catalysts towards hydrocarbons has been studied by adding 250 ppm propylene to the SCR feed gas. Below 250°C the influence is governed by an unselective adsorption of the propylene, affecting the Cu-SSZ-13 and Cu-SAPO-34 only to a small extent and in a similar way. Above 250°C differences in adsorption of propylene (and/or products thereof) becomes visible, and Cu-SAPO-34 is clearly less affected by the propylene, compared to Cu-SSZ-13 (**Figure 1b**). We currently ascribe this to differences in polarity and copper speciation in these frameworks.

The hydrothermal stability and deactivation of Cu-SAPO-34, Cu-SSZ-13, and Cu-Chabazite was measured by following the activity during ageing at 600 °C in 10% $H_2O$/10% $O_2$/$N_2$ for up to 200 h. The stability follows the trend Cu-SAPO-34>Cu-SSZ-13>Cu-Chabazite and some differences in the low- and high-temperature performances (**Figure 1c**) are observed. Interestingly, all three catalysts in **Figure 1c** show a bimodal $NO_x$ conversion profile. We ascribe this to changes in copper speciation with temperature, which affects the $NH_3$-SCR mechanism. The changes in copper speciation with temperature and different gas atmosphere are discussed based on density functional theory calculations.

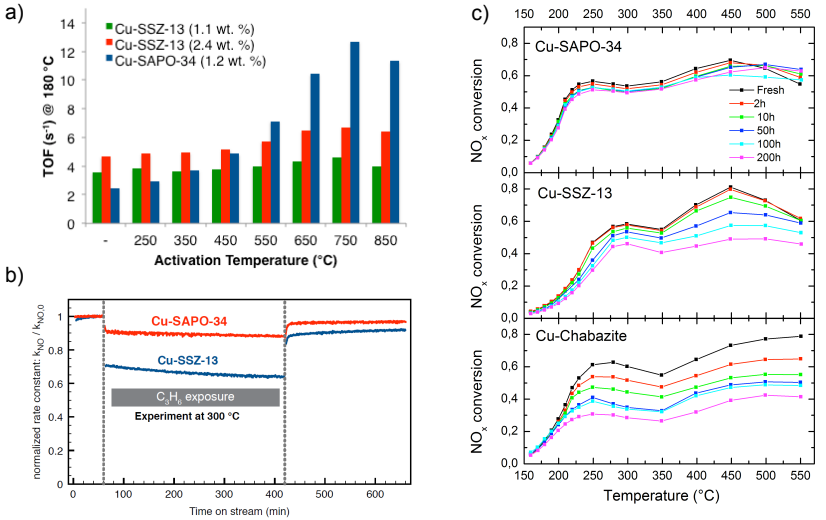


**Figure 1**. Performance of various Cu-CHA type catalysts in the $NH_3$-SCR reaction: a) activity depending on pre-treatment (adapted from [2]), b) resistance towards propylene and c) development up catalytic performance with hydrothermal ageing (10% $H_2O$ at 600°C) with ageing time between 0 and 200 h.

## Significance

Further details on the copper speciation shed light on the mechanism of $NH_3$-SCR over Cu-CHA zeolites and zeotypes, which may be altered slightly by choice of the chemical composition of the zeolite framework.

## References

1. F. Gao, J. H. Kwak, J. Szanyi, C. H. F. Peden, *Top. Catal.* **2013**, *56*, 1441–1459
2. P. N. R. Vennestrøm, A. Katerinopoulou, R. R. Tiruvalam, A. Kustov, P. G. Moses, P. Concepcion, A. Corma, *ACS Catal.* **2013**, *3*, 2158–2161.