

Supporting Information for:

Migration of Cu ions in SAPO-34 and its impact on NH₃-SCR

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X-ray diffractograms of as-prepared and 750 °C activated Cu-SAPO-34 containing 1.2 wt. % Cu is shown below in Figure S1. No reflections from CuO could be found nor could any significant loss of crystallinity be observed upon the activation treatment.

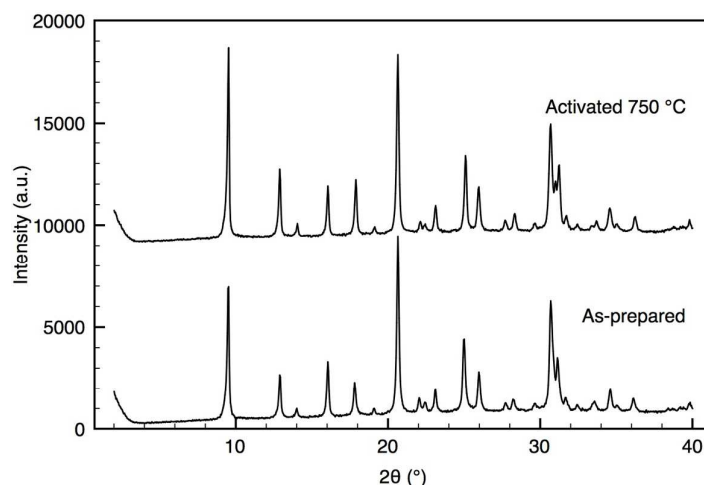


Figure S1 X-ray diffractograms of Cu-SAPO-34 before and after activation at 750 °C

Pseudo-first order rate constants for the NH₃-SCR reaction was calculated assuming isothermal plug-flow conditions and that the pressure drop was primarily caused by the quartz bed in the reactor. This is reasonable as the order of reaction with respect to NH₃ and NO has earlier been investigated and found to be zero and first order respectively [¹]. Furthermore O₂ is present in large surplus. For these reasons we can define the rate as:

$$R_{SCR} = -k_{SCR} \cdot p_{NO} = -k_{SCR} \cdot y_{NO}P = -k_{SCR} \cdot y_{NO,0}P(1 - X)$$

where R_{SCR} is the rate, p_{NO} is the partial pressure of NO, y_{NO} is the mole fraction of NO, k_{SCR} the rate constant and P the total pressure. Using the design equation for a packed bed reactor with the W weight of catalyst and $F_{NO,0}$ inlet molar flow rate of NO and conversion X :

$$W = F_{NO,0} \int_0^X \frac{dX}{-R_{SCR}}$$

we get a rate constant:

$$k_{SCR} = -\frac{F_{NO,0}}{W \cdot y_{NO,0}} \ln(1 - X)$$

$$k_{SCR} = -\frac{F_{total,0}}{W \cdot P} \ln(1 - X)$$

Pseudo-first order rate constants were calculated for various Cu-SAPO-34 catalysts in the NH_3 -SCR reaction and results are shown in Figure S2. The samples shown here consists of various copper loads obtained by ion-exchange and on catalysts with various crystal sizes after activation for one hour at 750 °C.

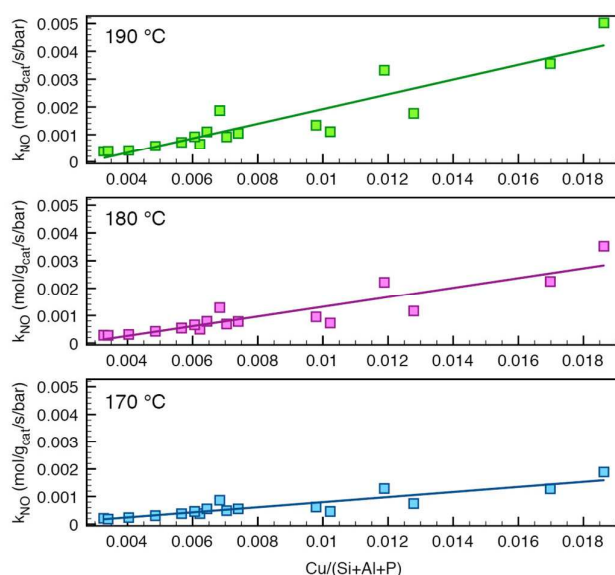


Figure S2 Pseudo-first order rate constants calculated for various Cu-SAPO-34 catalysts in the NH_3 -SCR reaction under steady state conversion at 170, 180 and 190 °C. Conditions were: 500 ppm NO, 530 ppm NH_3 , 10 % O_2 , 5 % H_2O , balance N_2 to a total flow of 300 NmL/min and 20 mg catalyst

Normalization to copper amount and conversion into TOF is straightforward yielding the TOF ($\text{mol}_{\text{gas}}/\text{mol}_{\text{Cu}}/\text{s}$). Based on the above obtained rate constant this is graphically pictured in Figure S3.

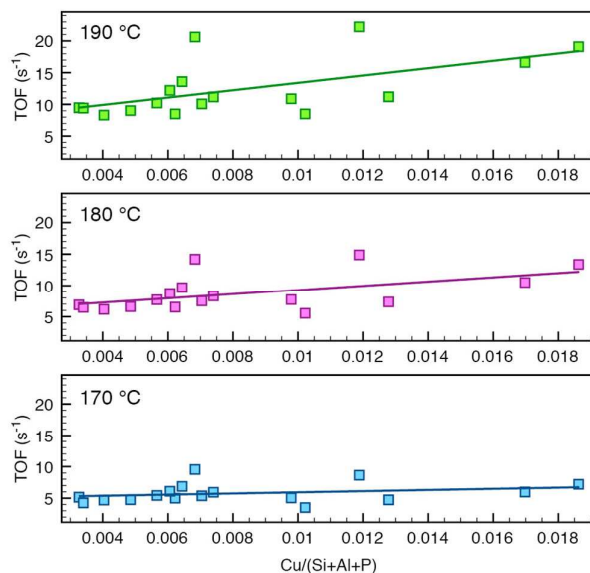


Figure S3 TOFs (s^{-1}) calculated based on the rate constants shown in Figure S2

The fluctuations seen between the data points are believed to be mostly due to the differences in crystal size and microstructural differences. Furthermore the samples were activated for 1h only, and depending on crystal size and Si distribution this might not be sufficient. It is however clear that within the tested Cu range no significant decline in TOF with decreasing Cu-load is seen.

The effect of crystal size was furthermore investigated. Samples with very similar copper loads of 0.66 ± 0.03 wt. % were tested in the activation similar to the procedure used in Figure 3 in the manuscript. Results of from the consecutive activation treatments are shown in Figure S4. The activity herein is reported at 200 °C due to the lower activity of these materials because of the lower Cu load.

As can be seen all materials irrespective of the crystal size experience an increase in catalytic activity upon the activation treatment at temperatures higher than classical calcination treatments. The trade-off between stability and diffusion is also clearly seen. Small crystals are more susceptible to structure collapse and can for this reason not withstand the higher temperatures needed for activation. On the contrary the

larger crystals are diffusion limited and therefore the entirety of the material not exploited in this case. Optimal is therefore the medium sized crystals.

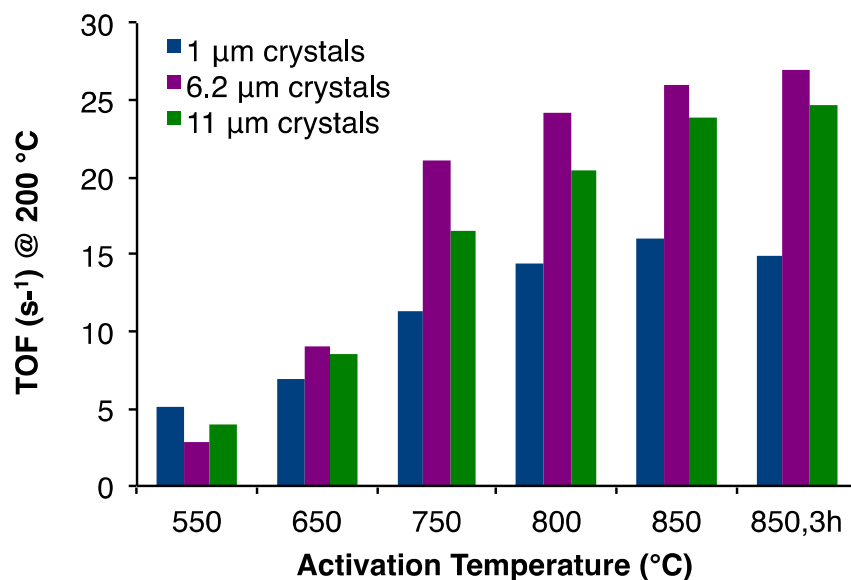
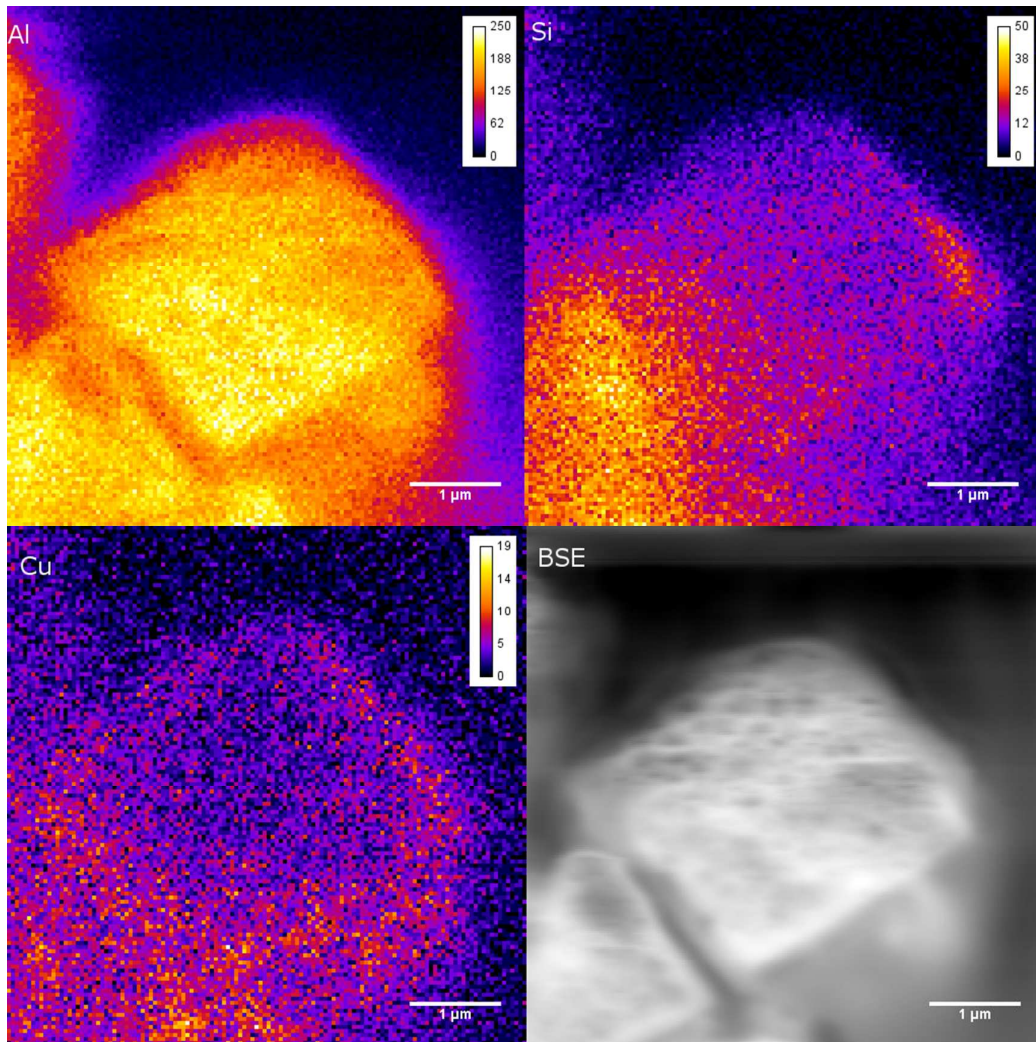
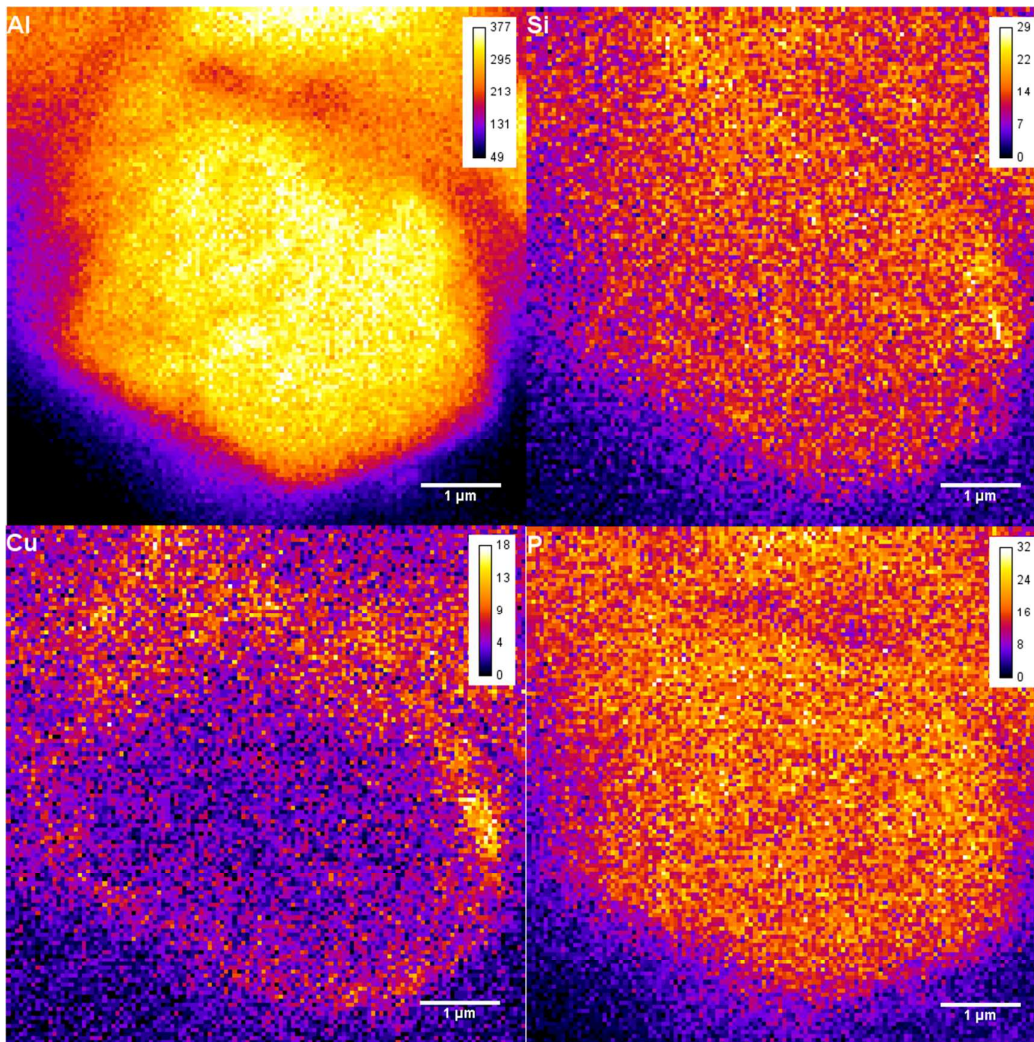
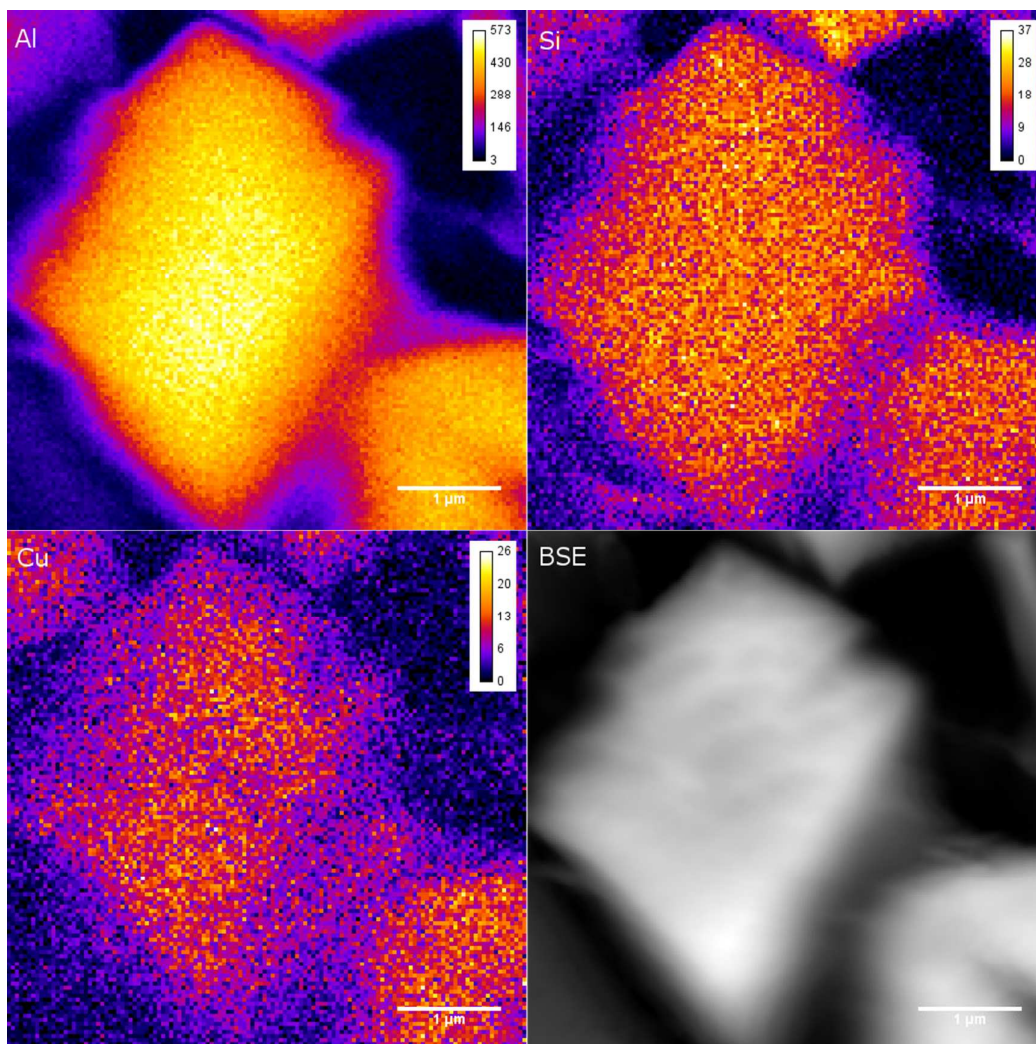


Figure S4 Catalytic TOF ($\text{mol}_{\text{gas}}/\text{mol}_{\text{Cu}}/\text{s}$) of Cu-SAPO-34 (0.66 wt. %) after consecutive activation treatments. Catalytic test conditions were: 500 ppm NO, 530 ppm NH_3 , 10 % O_2 , 5 % H_2O , balance N_2 to a total flow of 285 NmL/min and 40 mg catalyst

Elemental mapping was carried out in several crystals of Cu-SAPO-34 (1.2 wt.% Cu). All maps were consistently showing similar elemental distribution. Two examples of the as-prepared and activated samples respectively are shown in Figure S4







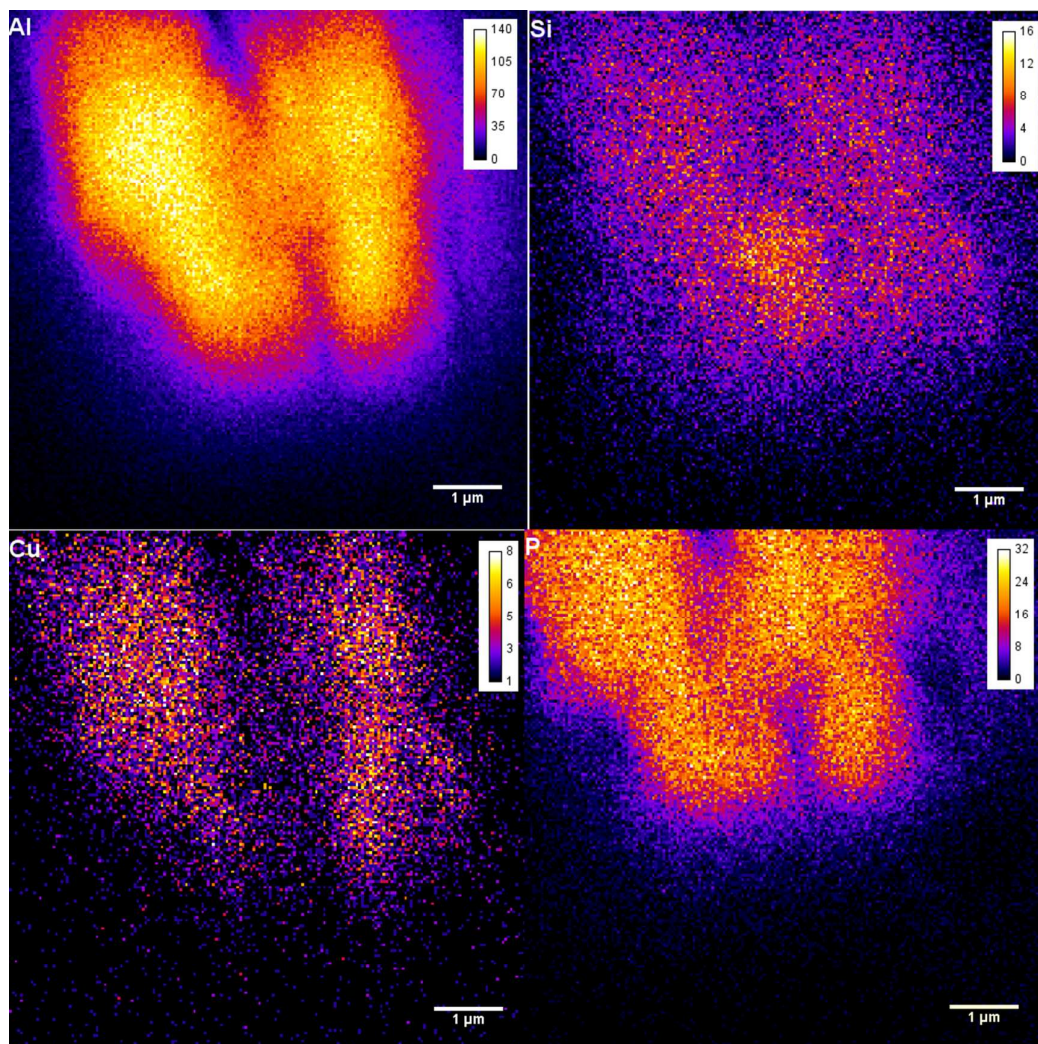


Figure S5 Element maps of Cu-SAPO-34 a,b) before and c,d)after activation. The distribution of Al, Si and P is even on the sample surface. Cu maps of as-prepared samples show a distinct rim around the grain, whereas Cu distribution is even on the grain after activation.

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