Hydrothermal stability of Cu-SSZ-39 compared to Cu-SSZ-13 in NH_3-SCR of NO_x

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Introduction

The advantage of small-pore zeolites in selective catalytic reduction (SCR) of NO_x is their exceptionally high hydrothermal stability at high temperatures, high NO_x conversion and high N_2 selectivity. Cu-SSZ-13 has been extensively studied as catalyst for NH_3-SCR of NO_x but also Cu-SSZ-39 showed very good hydrothermal stability. Both zeolite structures are similar, the difference is the arrangement of the double 6-rings in a mirror symmetry for SSZ-39, while they are arranged parallel in SSZ-13. This results in a more tortuous channel structure and in a different size of the cavities. The focus of our work was on kinetic studies of the small-pore zeolite SSZ-39 (AEI structure) with different Cu loadings and the influence of hydrothermal ageing on the Cu-species compared to Cu-SSZ-13 (CHA structure).

Materials and Methods

SSZ-39 with Si/Al=10 and 15 were synthesized hydrothermally via inter-zeolite conversion (IZC) with gel compositions of SiO_2 : 0.033 Al_2O_3 : 15 H_2O : 0.2 NaOH : 0.2 OSDA and SiO_2 : 0.016 Al_2O_3 : 4 H_2O : 0.2 NaOH : 0.2 OSDA (OSDA: 1,1,3,5-tetramethylpiperidinium hydroxide). SSZ-13 was purchased commercially. Both zeolites were ion-exchanged with an aqueous ammonia nitrate solution to obtain Na^+-free zeolites and aqueous copper acetate solution to achieve the desired Cu loading. Atomic absorption spectroscopy (AAS) was used to determine the Cu and Na content. The catalysts were hydrothermally aged via steaming at 800°C, 850°C and 900°C for 16h with 10 % H_2O in syn. air. Kinetic measurements were carried out at high GHSV≈430,000h^{-1} with the following gas composition: 500 ppm NO, 550 ppm NH_3 and 5 vol% H_2O in N_2. The effluent feed composition was measured using a *FTIR Antaris IGS* by *Thermo Fisher*. The crystallinity of the zeolite structure was verified by X-ray diffraction (XRD) using a *MiniFlex600-C* by *Rigaku* with scanning ranges from 5°2θ to 50°2θ and increments of 0.01°. H_2 temperature programmed reduction (TPR) was carried out using 10 % H_2 in N_2. The samples were ramped from 30°C to 1000°C with 10 K/min using a *ChemStar* by *Quantachrome Instruments* and H_2 was detected with a thermal conductivity detector (TCD).

Results and discussion

After hydrothermally aging Cu-SSZ-39 (AEI) and Cu-SSZ-13 (CHA) catalysts at 800°C, 850°C and 900°C, we observed an exceptional high stability for both zeolite types. High catalytic activities were observed after aging up to 850°C at all Cu loadings for both AEI and CHA, the 3 wt% Cu-SSZ-39 still showed a NO conversion of 94 % at 325°C. Even though both zeolite types are very similar we observed a difference in Cu-ion stability and zeolite structure stability for the AEI and CHA based catalysts. Cu-ion and structure stability also strongly depends on the Cu loading and Si/Al ratio, therefore we mainly focused on 3wt% Cu and a Si/Al=10.

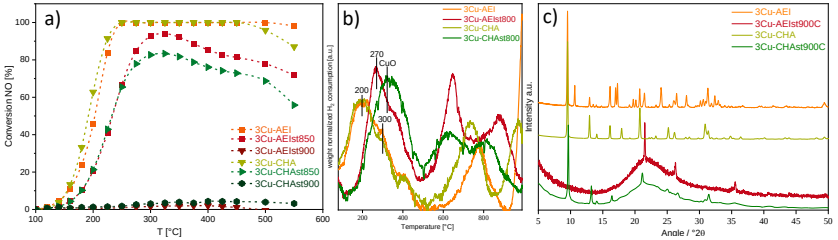

Figure 1: a) NO conversion of 3 wt% Cu-SSZ-13 and 3 wt% Cu-SSZ-39 before and after hydrothermal aging at 850°C and 900°C. b) H_2-TPR before and after hydrothermal aging at 800°C. c) XRD before and after hydrothermal aging at 900°C

For the fresh 3 wt% Cu-AEI and CHA the same type of Cu species were observed. The zeolite structures were hydrothermally stable up to 850°C for both, AEI and CHA. After steaming a relocation of the Cu^{2+}-ions from the windows of the six-membered rings (6MR) and $ZCu^{2+}(OH)$ can be observed, Cu oxide formation was found to depend on the hydrothermal aging temperature and zeolite type. This relocation is postulated to be the primary reason for the catalyst deactivation in both, NH_3-SCR of NO and NH_3-oxidation while the formation of Cu oxide is increasing the activity for NH_3-oxidation. The 3 wt% Cu-AEI shows a high hydrothermal Cu^{2+} stability without forming Cu oxides up to 800°C, whereas the Cu oxide formation in 3 wt% Cu-CHA already started at lower temperatures. This results in a higher activity in NH_3-oxidation and a faster decrease in NH_3-SCR activity for Cu-CHA. After aging at 900°C the NO conversion decreased to 5% due to the collapse of the zeolite structures. With lower Cu loadings, less Cu oxide is formed and the hydrothermal stability for both, Cu-ions and zeolite structure increases. The trend regarding the zeolite type remained the same for all Cu loadings.

Significance

Hydrothermal stable catalysts are from great importance for their application in NO_x removal regarding their need for a long lifetime as diesel catalysts. The identification of Cu species after hydrothermal aging is essential for the development of catalysts with a long durability.

Acknowledgement

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