
Abstract

Legislation to remove nitrogen oxides (NO_x) and other pollutants is becoming increasingly more stringent in every part of the world. One of the largest contributions comes from mobile sources, where NO_x and soot particles are generated during combustion. In order to remove these harmful compounds catalytic solutions are needed and especially zeolite-based systems are considered amongst the most promising candidates for selective catalytic reduction of NO_x using ammonia as reductant (NH_3 -SCR) in diesel exhaust after treatment systems.

This thesis explores the use of copper exchanged zeolites in the NH_3 -SCR reaction. Zeolites are crystalline microporous aluminosilicates where many framework topologies have already been discovered. For this reason several known frameworks were initially used to screen for activity- and deactivation-structure-relationships. More specifically similar amounts of copper was introduced into zeolites of the type MFI, BEA, FAU, MOR, FER, CHA, SZR and LEV with similar aluminum contents. It was shown that zeolites with three-dimensional pore systems gave the highest NO_x conversion and that the activity of zeolites with small pores were confirmed to be more stable under hydrothermal conditions. Additionally, it was shown that pore size and dimensionality of the pore system dictate the formation of unwanted N_2O during NH_3 -SCR so that large pores and dimensionality enhance N_2O formation.

Deactivation by unburnt hydrocarbons (HCs) can also be detrimental to the

use of zeolites. By using zeolites (BEA, MFI and CHA) a window-size effect was shown to dictate the degree of HC influence on the NH₃-SCR performance. In this way the severity of HCs followed the order Cu-BEA > Cu-MFI > Cu-CHA. To better understand the influence of HCs on small pore zeolites Cu-SSZ-13 and Cu-SAPO-34 was chosen to investigate the effect of framework polarity. Adsorption experiments showed that similar amounts of propylene (and products thereof) are adsorbed on Cu-SSZ-13 and Cu-SAPO-34 up to 250 °C. However, above this temperature Cu-SAPO-34 showed less propylene uptake than the Cu-SSZ-13, which was ascribed to the differences in chemical composition of the two catalyst materials leading to different framework polarities. The influence of propylene poisoning on the catalytic performance was tested by co-feeding propylene during the NH₃-SCR reaction at 250 and 300 °C that showed a higher resistance for Cu-SAPO-34 towards hydrocarbon poisoning at higher temperatures than did the Cu-SSZ-13 as expected from the differences in propylene uptake. Despite the differences in HC resistance all catalytic activity of all materials investigated could be recovered by heating to high temperatures e.g. 550 °C that are experienced under automotive operating conditions.

Small-pore zeotype Cu-SAPO-34 is an interesting candidate for future NH₃-SCR purposes, because it exhibits high hydrothermal stability and industrial production is already available. Therefore, its use was investigated and it was found that an activation at 750 °C is needed in order to exploit this material's full potential. The activation was shown to involve migration of Cu from the near-surface region into the crystals. The migration of copper was also modeled by DFT calculations whereupon further improvements to the activation atmosphere were discovered and verified experimentally. Best results were obtained when water was added to the activation atmosphere. In fact, the activity per copper atom at low temperatures (180 °C) in properly activated Cu-SAPO-34 was shown to be approximately double that of the aluminosilicate counter-part Cu-SSZ-13, which makes Cu-SAPO-34 a promising candidate for industrial applications.

To better understand the hydrothermal deactivation mechanism of copper based zeolites, Cu-ZSM-5 and Cu-IM-5 were lastly used as model materials. These materials exhibited very similar catalytic activity in the fresh state, but because the aluminum is more stable in the IM-5 structure the influence of framework stability and cation migration could be decoupled by use of various characterization techniques. Especially the migration of copper ions from CuO into zeolite ion exchange positions was found to be facile under typical SCR conditions.

Based on the findings a deactivation mechanism was suggested to rationalize the results including reversible copper migration and irreversible formation of a Cu-Al phase related to the aluminum stability in the framework. Furthermore, this mechanism could also explain the differences in deactivation iron and copper exchanged zeolites under hydrothermal conditions.