NH_3-SCR chemistry for NOx abatement: Influence of zeolite support on N_2O formation & phosphorus species addition

Joonsoo Han

Department of Chemistry and Chemical Engineering
Chalmers University of Technology, Gothenburg 2021

Abstract

Different lattice arrangements of Si, Al, and O atoms result in a variety of pore dimensions and zeolite channel network systems, giving rise to different physicochemical environments inside the catalyst cage. The objective of the thesis work was to understand the influence of zeolite topology on NH_3-assisted SCR chemistry over CHA, MFI, and BEA frameworks, on the formation of N_2O and the addition of phosphorus species to attain fundamental insight into NOx emission control. A variety of characterization techniques and mechanistic experimental protocols were used to examine Cu^{2+} ions coordinated with 1Al and 2Al in frameworks, denoted as Z2Cu and ZCuOH, respectively. Catalytic activity tests were performed to investigate the influence of ammonium nitrate (AN)-forming N_2O and phosphorus species on DeNOx performance over the Cu-impregnated CHA, MFI, and BEA.

In Paper I, ammonium nitrate (AN) formation and decomposition were thoroughly investigated to see the effect of zeolite topology, copper species, and water vapor on the N_2O formation in NH_3 SCR of NOx at low temperatures. Three different Cu/zeolites (CHA, MFI, and BEA) were used, and these were compared with H/zeolites as the reference. H_2 temperature programmed reduction and in-situ IR spectroscopy suggest that the CHA framework structure is more favorable than MFI and BEA to form AN inside the catalyst cage. AN formation was enhanced in the presence of Cu ions over the Cu/zeolites. Catalyst activity tests demonstrated that Cu/CHA has a potential for uncontrolled N_2O emission in transient conditions despite it shows lower N_2O formation over standard and fast SCR reaction due to a highly stabilized AN inside the catalyst cage at low temperatures. This indicates pros and cons of AN stability over CHA in NH_3-SCR systems. The critical effect of water vapor on AN formation and decomposition was found. The water vapor causes the cleavage of Cu dimers into Cu^{2+}-OH groups, which are responsible for NO oxidation forming NO^+ and surface nitrates. Thus, it results in the formation of fewer surface nitrates, leading to less AN and less N_2O formation in wet conditions.

In Paper II, phosphorus poisoning of different zeolite topologies was investigated. Fresh Cu/zeolites (CHA, MFI, and BEA) were used as the reference, and these were compared with P-poisoned Cu/zeolites. X-ray powder diffraction (XRD) revealed that the MFI framework was vulnerable to phosphorus species attack, resulting in the deformation of the framework structure. A variety of phosphorus species, such as PO_3^-, PO_4^{3-}, and P_2O_5 populations, were observed over Cu/zeolites with X-ray photoelectron spectroscopy. Transient response methodologies suggest that ZCuOH sites were significantly poisoned by PO_3^- and PO_4^{3-}over Cu/CHA. Accordingly, a promoted or deteriorated redox feature of Cu ions (i.e., Z2Cu and ZCuOH) was suggested. A significant drop in catalytic activity was demonstrated over Cu/MFI in catalytic activity tests. It is suggested that MFI framework deformation, such as pore-blockage, local expansion, and cracking, impedes the mobility of $Cu^+(NH_3)_2$ complexes at low temperatures under standard SCR conditions. Consequently, we hypothesize that MFI framework degradation hinders the formation of NH_3-solvated Cu dimer complexes, which are responsible for O_2 activation.

Keywords: NH_3 SCR chemistry, Zeolite topology, Copper, N_2O, Phosphorus poisoning