

Reaction mechanism of selective catalytic reduction of NO with NH₃ over Cu-exchanged SSZ-13

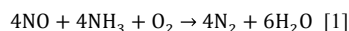
Wenkang Su,¹ Huazhen Chang,¹ Yue Peng,¹ Junhua Li^{1*}

¹State Key Joint Laboratory of Environment Simulation and Pollution Control, School of Environment, Tsinghua University, Beijing 100084, P. R. China

*corresponding author: lijunhua@tsinghua.edu.cn

Introduction

Selective catalytic reduction (SCR) of nitrogen oxides with NH₃ is considered an effective way to control NO_x emission from mobile sources. Among available catalytic formulations, metal exchanged zeolites have shown superior SCR performance. In general, the overall “standard SCR” reaction between NO and NH₃ can be expressed as follows:



In spite of some arguments, most agree that the reaction follows two competitive mechanisms, Langmuir-Hinshelwood and Eley-Rideal[2], in which the adsorbed ammonia reacts with the NO_x adspecies or gaseous NO to form N₂ and H₂O. The two competitive L-H and E-R mechanism are all possible over zeolites based catalysts.

Recently, Cu(II) exchanged zeolites, Cu/SSZ-13 with the chabazite (CHA) structure have been commercialized as NH₃-SCR catalysts in diesel engines for their broadened activity window and stable performance, as well as their high selectivity to N₂. However, detailed research about the reaction mechanism, including the active intermediates and reactive sites, has not been studied thoroughly.

Materials and Methods

The Cu/SSZ-13 catalysts were prepared by aqueous ion exchange. 5g NH₄/SSZ-13 were added to CuOAc solutions with pH adjusted to 3.5, and stirred at 80°C for 24 hours followed by calcination at 550°C for 4 hours. The in situ infrared spectra were collected in the range of 4000-800 cm⁻¹ at a resolution of 2 cm⁻¹ and 32 scans of accumulation. The spectra during the reactions between i) adsorbed ammonia and gaseous NO+O₂, ii) adsorbed NO_x and gaseous ammonia, iii) adsorbed ammonia and NO_x and gaseous NO+O₂ were recorded. Simultaneously, temperature programmed surface reaction (TPSR) about the three mentioned reaction were carried out to monitor the gas concentration in the outlet.

Results and Discussion

Figure 1 shows the reaction scheme of SCR of NO with ammonia on Cu/SSZ-13 at lower temperature. **Figure 2** shows the infrared spectra collected during reaction i) and iii). The results reveal that two competitive pathways for NO reduction are possible at low temperature. One involves the formation of intermediate (NH₄)₂NO₃ and its subsequent reduction by NO via the formation of N₂O₃. Another involves the formation of intermediate NH₂NO on Lewis acid sites (namely Cu sites) which easily decomposes to N₂ and H₂O.

The chemisorbed ammonia on Bronsted and Lewis acid sites all participate the reaction following different pathway. The roles of copper include creating Lewis acid sites for NH₃ coadsorption and oxidation of NO to mononitrosyl and nitrate.

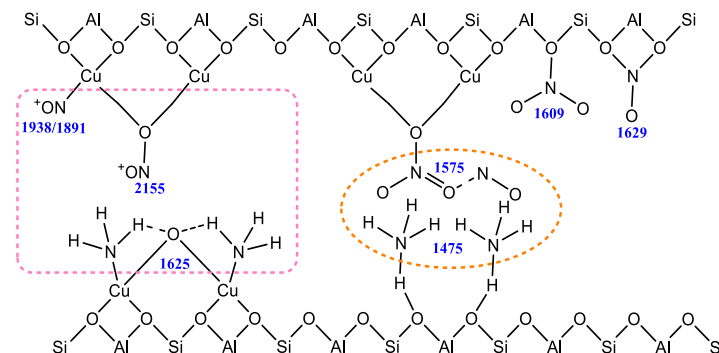


Figure 1. Reaction scheme of SCR of NO with ammonia on Cu/SSZ-13 at lower temperature

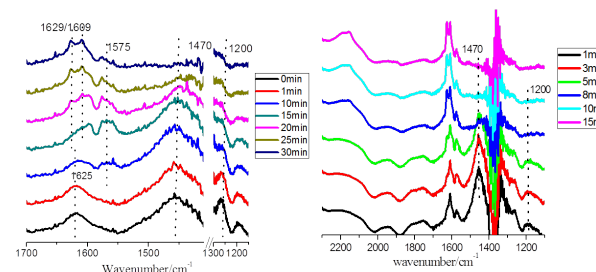


Figure 2. DRIFTS spectra taken at 150°C upon passing 500ppm NO + 5% O₂/N₂ over NH₃ pre-adsorbed(left) and NO+ NH₃-presorbed(right) 1.7wt% Cu/SSZ-13 catalyst for 0-30 min.

Significance

Two possible SCR reaction mechanisms over Cu/SSZ-13 are proposed. The active adspecies of ammonia involve both coordinated ammonia on Cu sites and NH₄⁺ ions on Bronsted acid sites. The active adspecies of NO_x are (Cu-NO⁺) reacted with coordinated ammonia and (Cu-O-N₂O₃) reacted with NH₄⁺ ions. The rate controlling steps are the formation of nitrate and activation of coordinated ammonia.

References

- [1] R.Q. Long, R.T. Yang, Journal of Catalysis 198 (2001) 20-28.
- [2] D. Wang, L. Zhang, K. Kamasamudram, W.S. Epling, ACS Catalysis 3 (2013) 871-881.