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Chemistry of the active metal center in the selective catalytic reduction of NO by NH₃

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NO_x emissions from power plants and mobile combustion engines are a global concern due to the detrimental effects of NO_x on the environment and public health. The current best technology for removal of NO_x from the exhaust of both types of emission sources is based upon the selective catalytic reduction of NO_x by ammonia. The commercial catalytic systems are based on the redox active metals vanadium, copper or iron, but to this point the reaction mechanism for all of the catalytic systems are still under discussion.

We present a new reaction scheme for the SCR reaction exemplified by copper exchanged zeolites and adaptable to iron exchanged zeolites and vanadia (V₂O₅) on TiO₂.

The new reaction scheme is compatible with previous suggestions [1,2,3] but is the first to fully comply with the constraints usually put upon chemically consistent reaction schemes at moderate temperatures.

1 Experimental/methodology

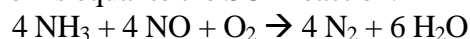
Transient intermediates in catalytic reactions are often impossible to trap and to investigate spectroscopically. At the same time a large number of different metal containing species are present in the activated catalysts giving a multitude of spectator sites and sites that participate in side-reactions. Recent investigations [4,5,6] have elucidated and quantified the copper species present in dehydrated Cu-SSZ-13. The method used includes Fourier Transform Infrared (FTIR), Electron Paramagnetic Resonance (EPR) spectroscopy and X-ray Absorption Spectroscopy (XAS). Using the same spectroscopic investigation techniques and the same Cu-SSZ-13 material under *in-situ* and *operando* conditions the resting states of the Cu-SSZ-13 catalyst under reducing SCR relevant conditions (NH₃ + NO) and oxidizing conditions (NO + O₂) have been identified.

2 Results and discussion

The experimental investigation identify Cu⁺ bound to the zeolite framework in the reduced resting state and Cu²⁺NO₃⁻ in the oxidized resting state.

When connecting these resting states to a chemically consistent cycle the following constraints were applied:

1. Only stable neutral molecules are adsorbed or desorbed during the reaction.
2. The total reaction is equal to the SCR reaction:



The approach was successful resulting in a consistent reaction cycle for the SCR reaction on a mononuclear metal site. This includes two separate cycles each with an oxidation and a reduction step with the fast SCR reaction being identified as being an integral part of the SCR reaction.

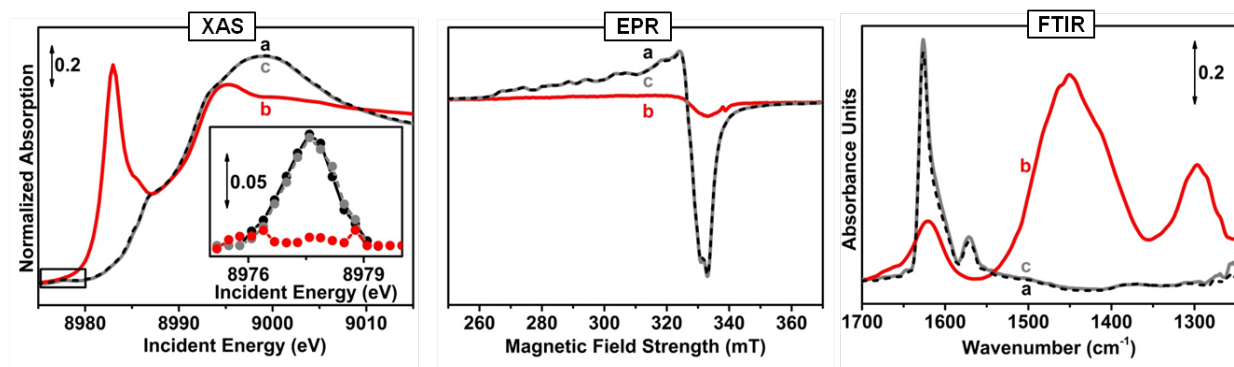


Figure 1: Spectra of Cu-SSZ-13 (Cu/Al = 0.44, Si/Al = 14) at flow conditions at 250 °C exposed first to NO + O₂ (a) then to NH₃ + NO (b) and finally to NO + O₂ (c).

3 Conclusions

A consistent cycle for the SCR reaction of NO with NH₃ is suggested. The implications on the chemical requirements of the metal of the active site can be summarized as follows:

1. Able to perform one-electron redox reactions.
2. Able to coordinate a NO molecule in both the reduced and the oxidized state.
3. Able to support an OH⁻ ligand in the oxidized state under reaction conditions.

These requirements are all fulfilled by V⁵⁺/V⁴⁺, Cu²⁺/Cu⁺ and Fe³⁺/Fe²⁺, which are active in the SCR reaction.

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