

Developing Stable NO_x Removal Catalysts for Environmental Protection

Expected outcome – as specified in the grant application

In this project we set out to understand an important phenomenon that we had observed in our previous work. When using the catalyst Cu/SAPO-34, a common catalyst used to reduce NO_x in vehicle exhausts, we observed that the catalyst deactivated when water was present in the atmosphere below 100 °C. These conditions are encountered frequently in vehicles during start up, when the engine temperature is low, so this catalyst inactivation is a major problem for the car industry aiming to comply with the current legislation on environmental protection. Therefore, our objective in this project was to understand which part of this complex catalyst is responsible for deactivation, and clarify as far as possible the mechanisms of its deactivation by water. Further, provided that we could demonstrate some mechanistic insight, our ambition was to identify parameters which can be tuned to improve catalyst stability, and propose means to synthesise a more stable version of the catalyst Cu/SAPO-34.

Achieved results

The applicant, Dr. Kirsten Leistner, employed in Prof. Louise Olsson's group at Chalmers University of Technology, Department of Chemistry and Chemical Engineering, Division of Chemical Reaction Engineering, has been working on the synthesis and characterisation of SAPO-34 catalysts for the entire duration of the project. Postdoctoral fellow Mafalda Lancinha joined in May 2017, as communicated to Åforsk Foundation Executive Director Anders Snell and approved on 13 March 2017. The main achievements of our work are summarized below.

- We have first of all sought to understand why Cu/SAPO-34 catalysts containing both copper and protonic sites deactivate when exposed to water at 70 °C. The general approach has been to expose catalysts to water for differing durations and characterize them using XRD, NMR, nitrogen physisorption, DRIFT spectroscopy and reactivity testing to understand what is happening, over time, to copper species, protonic sites and framework aluminium.
- Both H/SAPO-34 (containing protonic sites only) and Cu/SAPO-34 catalysts have been characterised, with the goal of understanding the impact of copper sites vs protonic sites, as well as different types of copper sites. Cu/SAPO-34 is the actual catalyst used in engine exhaust after treatment, and the H/SAPO-34 was used as a control without copper. We have discovered that SAPO-34 deactivation occurs in two stages. First, during the water-based deactivation phase, a (small) loss of catalyst structure is observed. After the water-based deactivation phase, H/SAPO-34 catalysts become very unstable when exposed to temperatures above room temperature, and also due to atmospheric moisture with storage time. We found that the presence of Cu (Cu/SAPO-34) clearly stabilizes the catalyst against structural degradation. However, this difference in inactivation made H/SAPO-34 very challenging to characterise using many common methods, and by consequence a comparison between H/SAPO-34 and Cu/SAPO-34 became challenging. We have

therefore focused on characterisation using X-ray diffraction and MAS NMR, to avoid raising the temperature in H/SAPO-34. Nevertheless, even in a room temperature atmosphere, damage to the catalysts was considerable. Notwithstanding these challenges, we were able to conclude that there is a major difference in both speed and extent of deactivation between H/SAPO-34 and Cu/SAPO-34. This means that incorporated copper, besides being known to reduce the proportion of available protonic sites, also slows or reduces the extent of degradation.

- During the water-based deactivation process itself, the extent of damage to the catalyst varied considerably depending on the duration of this phase. We have identified from XRD and N₂ physisorption that the largest loss of long-range crystallinity occurs at the very shortest exposure times. This has important consequences for preparation of stabler SAPO-34 - containing catalysts, as both ion exchange and washcoating steps include immersing the catalyst in an aqueous solution. Similarly, storage of the catalyst in normal atmospheric conditions exposes it to atmospheric humidity, also damaging the catalyst as we have now established.
- As to the mechanism of inactivation, BET, XRD and ²⁷Al-NMR measurements performed on degraded/inactivated samples indicated that loss of aluminium is occurring from the unit cell. The NMR measurements show that the largest proportion of this aluminum loss occurs at the shortest exposure time, correlating perfectly with loss of activity. Hence, we can conclude that loss of aluminium from the CHA lattice is an important consequence of water-based deactivation. One assumption that can be inferred from this finding is that the presence of copper somehow reduces access of inactivating water to aluminium ions in the SAPO-34 structure. This underscores that copper content is a key parameter, which has a significant impact on the stability of the catalyst.
- Another important optimization parameter we discovered for reducing water-based catalyst inactivation is the crystal particle size. We have discovered that a catalyst with large particle size (above 100 μm) is very resistant to water-based deactivation. Further investigation of the effect of particle size as a parameter for tuning catalyst stability is indicated. Large particle size corresponds to reduced surface, which would logically reduce access of water to aluminium sites inside the lattice.

In conclusion, we have identified aluminium loss as the basis of water-based deactivation of Cu/SAPO-34 catalysts. We clarified the protective effect of copper and beneficial effect of larger particle sizes. The last year of the project was spent consolidating the findings with further characterisation methods. Based on these results, we can confidently propose that the way forward to synthesizing more stable Cu/SAPO-34 catalyst would be to increase copper content, and consider reducing the surface (this has to be balanced with achieving optimal catalytic activity). We are optimistic that these findings will lead to synthesizing Cu/SAPO-34 catalyst with significantly improved stability post project. A paper detailing the results will be published, and the financial support from ÅForsk acknowledged therein. We are very grateful to ÅForsk for the financial support.

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