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L-II | *In situ* and *ex situ* Poisoning Studies with Thiophene and 1-Propanethiol using a $Cu/ZnO/Al_2O_3$ Methanol Synthesis Catalyst

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In industry, methanol is produced from synthesis gas consisting of CO, CO_2, and H_2 using a $Cu/ZnO/Al_2O_3$ catalyst. Methanol is one of the most important chemical raw materials in the chemical industry. Due to the rising threat of global warming and the resulting need to reduce CO_2 emissions, current research aims at finding new innovative and efficient processes for methanol synthesis. One approach is the synthesis of methanol from CO_2-containing industrial exhaust gases. Here, sulfur-containing impurities in the exhaust gas are a severe problem, since they are irreversible poisons for copper-containing catalysts.[1] *In situ* and *Ex situ* poisoning studies can provide insights about the effect of sulfur-containing impurities on the catalyst activity and selectivity.

In situ poisoning studies with Thiophene

Thiophene is an impurity present in industrial exhaust gases and acts as a poison for the industrially used $Cu/ZnO/Al_2O_3$ methanol synthesis catalyst. Therefore, the poisoning strength of thiophene was investigated under industrially relevant conditions.

Methanol synthesis was performed alternating between two different conditions. Since under equilibrium-controlled conditions the catalyst still produced methanol even though it showed no activity under kinetically controlled conditions, it was postulated that S_{ads} diffusion from Cu^0 to ZnO at higher temperatures is fast recreating active sites which had been previously poisoned at lower temperatures. Since thiophene is preferentially adsorbed on Cu^0, ZnO acts as an indirect sulfur trap depending on the applied temperature and therefore the diffusion of S_{ads}.
In addition, CO_2 hydrogenation was poisoned stronger compared with the water-gas shift reaction providing evidence for the bifunctionality of the $Cu/ZnO/Al_2O_3$ catalyst. Since COS is also an impurity in industrial exhaust gases, *in situ* poisoning studies with COS are planned in the near future.

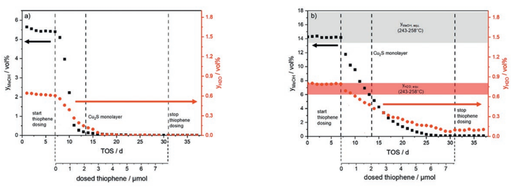

Figure 1: Mole fractions of methanol (black squares, left y-axis) and water (red circles, right y-axis) a) under kinetically controlled conditions (195 °C oven temperature, 4000 Nml min^{-1}) and b) under equilibrium-controlled conditions (235 °C oven temperature, 400 Nml min^{-1}) for the $Cu/ZnO/Al_2O_3$ catalyst poisoned with 10 ppm thiophene. Equilibrium mole fractions within the product gas stream were calculated using ChemCad8®.

Ex situ poisoning studies with 1-Propanethiol

Ex situ poisoning studies are a less time- and cost-intensive alternative to *in situ* poisoning studies. In addition, *ex situ* poisoning allows the variation of the sulfur coverage which would be too costly with *in situ* methods. In this work, a $Cu/ZnO/Al_2O_3$ catalyst was poisoned with different amounts of 1-propanethiol at room temperature, characterized and investigated with regard to its catalytic activity.

By the applied *ex situ* poisoning method catalyst samples with different poisoning degrees were obtained. In most cases the loss of activity is proportional to the decrease in copper surface area indicating that the poisons do not modify the nature of the active sites but rather their number.[2] Correspondingly, the catalyst activity did sufficiently correlate not only to the copper surface area but also to the amount of sulfur added, the sulfur content measured by CHNS analysis, and sulfur on the catalyst surface detected by XPS. With this poisoning method the poisoning strength of other sulfur compounds (e. g. DMSO) can be investigated in the future.

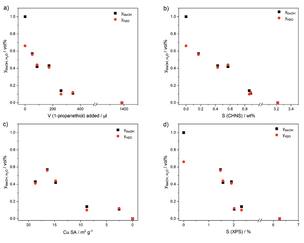

Figure 2: Mole fractions of methanol and H_2O in the product gas stream during methanol synthesis for the *ex situ* poisoned samples correlated to the amount of sulfur added and the results characterizing the poisoning degree. Methanol synthesis was performed at 210 °C and 60 bar using a synthesis gas consisting of $CO/CO_2/H_2/N_2$ (13.5 vol%/ 3.5 vol%/ 73.5 vol%/ 9.5 vol%) with a volumetric flow rate of 66 Nml min^{-1}.

[1] M. V. Twigg, Topics in Catalysis 2003, 22, 191.
[2] E. Heracleous et. al., Chemical Engineering Journal 2022, 444, 136571.

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