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L-II | *In Situ* and *Ex Situ* Poisoning Studies with Thiophene Using a Cu/ZnO/Al_2O_3 Methanol Synthesis Catalyst

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The increasing consumption of fossil fuels promotes the greenhouse effect. Methanol produced from sustainable sources can be a promising alternative to fossil fuels. Industrially, methanol is produced from synthesis gas consisting of CO, CO_2 and H_2 using a Cu/ZnO/Al_2O_3 catalyst. The irreversible poisoning of this catalyst by sulphur-containing molecules has been a known problem for a long time. However, questions regarding the poisoning strength of different sulfur-containing molecules as well as the poisoning mechanism remain unanswered.

IN SITU POISONING STUDIES WITH THIOPHENE

After gas purification processes of synthesis gas from fossil sources had improved around 1960 the poisoning of the Cu/ZnO/Al_2O_3 catalyst, which had previously been outperformed by the much more sulphur-resistant ZnO/Cr_2O_3 catalyst, was no longer a relevant topic. However, with the utilization of new CO_2 sources from highly polluted industrial exhaust gases, the topic is once again of high interest.

H_2S as the simplest S-containing molecule cannot only adsorb on Cu, but also react with Cu and ZnO forming new phases. To achieve a long lifetime of the catalyst, H_2S levels should not exceed 0.1 ppm in the synthesis gas.[1] However, it is assumed that the Cu/ZnO/Al_2O_3 catalyst is able to adsorb up to 1 wt.% S, which is equal to the amount needed to form a monolayer of Cu_2S.

To confirm this assumption and to investigate the poisoning strengths of different S-containing impurities reported in literature,[2] long-term measurements with 10 ppm thiophene are currently being carried out in the MPI Carbon2Chem® laboratories at the Fraunhofer UMSICHT site.

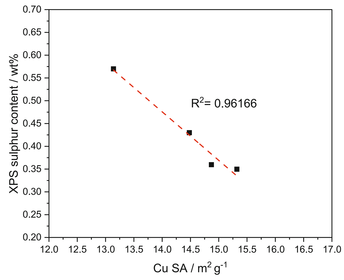

Fig. 1: Correlation between the sulphur content obtained via XPS and the respective copper surface area according to N_2O RFC measurements.

EX SITU POISONING STUDIES WITH THIOPHENE

Since *in situ* long-term experiments are always time-consuming and, in addition, the post-mortem analysis of the used catalyst only permits a certain degree of poisoning (usually complete irreversible poisoning of the surface), *ex situ* poisoning studies are carried out to gain deeper insight. For this purpose, a Cu/ZnO/Al_2O_3 catalyst (provided by Clariant Deutschland GmbH) was poisoned with different concentrations of liquid thiophene, characterized and investigated again with regard to its catalytic activity.[3]

It was found that the sulphur content on the catalyst surface measured by XPS correlates almost linearly with the decreased Cu surface area measured by N_2O RFC (Fig. 1). Under typical MeOH synthesis conditions, the poisoned samples showed a strong decrease in activity even for low molar amounts of sulphur on the catalyst surface, indicating an almost exponential trend (Fig. 2). In order to confirm these observations, however, further samples with very high and low poisoning degrees must be prepared in the future. Furthermore, with this validated method, investigations with other S-components can be carried out.

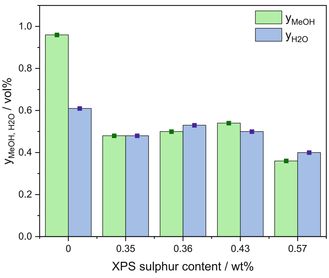

Fig. 2: Methanol and H_2O mole fractions in the product gas stream for the different *ex situ* thiophene-poisoned Cu/ZnO/Al_2O_3 catalysts.

[1] M. V. Twigg, M. S. Spencer, *Top. Catal.* **2003**, 22 (3 – 4), 191 – 203.
[2] B. J. Wood, W. E. Isakson, H. Wise, *Ind. Eng. Chem.* **1980**, 19, 197-204.
[3] M. Wolf, C. Schlüter, O. Hinrichsen, *Journal of CO_2 Utilization*, **2019**, 32, 80-91.

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