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L-0 | Poisoning Effects in Methanol Synthesis – The Influence of Oxygen

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The transformation of industrial feedstocks towards renewable sources and off gases from industrial processes carries the challenge of post processing such as purification and trace removal. Methanol synthesis is a well-established industrial process which is suitable for the application of CO_2 from industrial off gases and green H_2 from electrolysis. Since the industrial catalyst is sensitive to trace impurities, the need for purification is to be determined. Oxygen is a common impurity of variable concentration range in H_2 from electrolysis.[1-2]

The industrial copper-zinc-alumina catalyst – an example of dynamic application potential

Considering CO_2 hydrogenation based on steel mill off gases it is important to identify potential catalyst poisons to ensure cost efficient gas purification. The industrial standard for methanol synthesis represented by a Copper-Zinc-Alumina catalyst (CZA) is sensitive to a variety of compounds which will lead to a decrease in the methanol yield by causing either reversible effects or irreversible damage.[3] Oxygen is a special case regarding the known detrimental effects towards the active interface of the catalyst, however the resulting impact is determined by concentration and time of exposure. Further, the catalyst exhibits a dynamic nature regarding the formation of the active interface in different synthesis gas compositions (Fig. 1). A CO rich synthesis gas features a higher reduction potential compared with CO_2 rich synthesis gas. Thus, the impact of oxygen has to be considered in various concentrations and atmospheres.

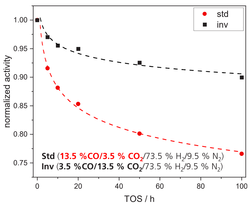

Figure 1: Induction of the commercial methanol synthesis catalyst in clean synthesis gas of different compositions.

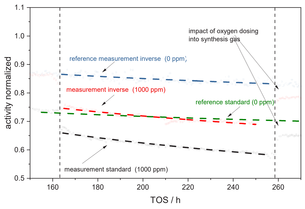

Figure 3: Oxygen poisoning during methanol synthesis – 1,000 ppm O_2 dosed into syngas after induction for 100h.

The effect of oxygen dosing into synthesis gas during methanol synthesis

Investigation of the catalyst featured induction and switching between clean and contaminated synthesis gas (Fig. 2).[4] Oxygen dosing of 1000 ppm after induction for 100 h results in a decrease of activity higher than remaining underlying deactivation (Fig. 3) when switching to clean synthesis gas. The decrease in activity appears similar regarding the investigated atmospheres leading to a complete hydrogenation to water under reactions conditions. The long term effect on the catalyst was revealed by analysis of the spent samples indicating increased sintering in a shorter period of TOS (Fig. 4). However, residual activity and electron microscopy reveal residual microstructure. In conclusion, potential oxygen contamination from, e.g. electrolysis hydrogen is detrimental towards methanol yield and catalyst life time. A certain amount of oxygen can temporarily be handled but a critical threshold for removal has to be determined.

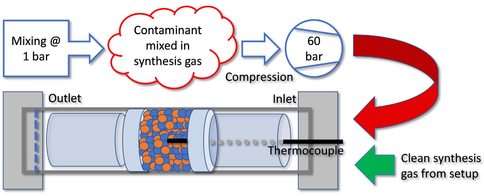

Figure 2: Conceptual design of the long term dosing experiment – Catalytic test setup with two separate and switchable synthesis gas mixing sections.

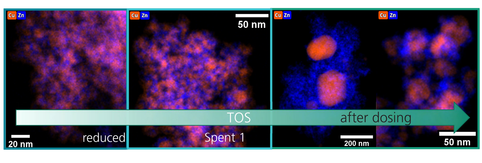

Figure 4: EDX maps of different catalyst lifetime stages – a) reduced catalyst, b) catalyst induced for 24 h TOS and c) spent catalyst after oxygen dosing and recovery in clean synthesis gas.

[1] Schittkowski, J., Ruland, H., Laudenschleger, D., Girod, K., Kähler, K., Kaluza, S., Muhler, M. and Schlögl, R. (**2018**), Chemie Ingenieur Technik, 90: 1419-1429.
[2] Gómez, J.I.S., Takhtehfouladi, E.S., Schlögl, R. and Ruland, H. (**2020**). Chemie Ingenieur Technik, 92: 1574-1585.
[3] Laudenschleger, D., Ruland, H. & Muhler, M. (**2020**) Nature Communications 11, 3898.
[4] Pollok, C.H., Göbel, C., Gómez, J.I.S., Schlögl, R. and Ruland, H. (**2022**), Chemie Ingenieur Technik, 94: 1438-1451.

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