Understanding the Deactivation of the Iron Molybdate Catalyst and its Influence on the Formox Process

The industrial production of formaldehyde from methanol is an important chemical process. The majority of the produced formaldehyde is processed into higher-valued synthetic resins, making formaldehyde an important chemical building block. In 2017 approximately 52 million ton were produced, and the demand is increasing.

Formaldehyde is primarily synthesized industrially by selective oxidation of methanol over an iron molybdate catalyst. The industrial catalyst is composed of Fe₂(MoO₄)₃ with an excess of MoO₃ corresponding to a molar ratio of Mo/Fe of 2-3. However, the process life-time is only 1-2 years due to loss of molybdenum from the catalyst leading to a loss of selectivity and pressure drop increase over the bed due to transport and downstream deposition of the volatilized molybdenum. The relative short lifetime of the process leaves great room for improvements.

This thesis is dedicated to study the performance of the iron molybdate catalyst under reaction conditions and propose strategies to stabilize the catalyst and mitigate molybdenum transport taking both catalyst preparation and reactor design into account.

The first part of the thesis investigates the catalytic performance of a synthesized iron molybdate catalyst with a particle size of 150-300 μm during selective oxidation of methanol to formaldehyde for a period up to 25 days. The structural and compositional changes of the catalyst were characterized and it was shown that free MoO₃ quickly (around 10 hours) volatilized leaving a MoO₃-depleted catalyst. At longer operating time, also the Fe₂(MoO₄)₃ lost molybdenum successively forming FeMoO₄ and finally Fe₂O₃. However, even at significant changes in the catalyst composition, it maintained a rather satisfactory selectivity towards formaldehyde (above 92 %). Surprisingly, formation of β-MoO₃ was observed after 25 days, indicating that this species might be stable to some extent under reaction conditions.

The second part of the thesis investigates volatilization and loss of MoO₃ from industrial catalyst pellets under varying reaction conditions for a period up to 10 days. Molybdenum was shown to volatilize, leaving a depleted zone starting at the pellet surface and moving inwards with time. The rate of volatilization was shown to be enhanced by increasing methanol concentration and operating temperature, while water was shown to inhibit the rate of volatilization. The experimental data was used to develop and validate a dynamic single pellet mathematical model, which considers the diffusion and oxidation of methanol, the reversible volatilization reaction between molybdenum (MoO₃) and methanol, and the diffusion of all gaseous species including the volatile molybdenum species through the pellet. The model calculates the loss of Mo as a function of the position in the pellet, time on stream and reaction conditions and compared favorably with the experimental data.

In the third part of the thesis the developed single pellet model is implemented in a reactor model, where transport of the volatilized MoO₃ and deposition downstream in the reactor bed takes place. As methanol is converted through the bed, the volatilized Mo species decompose into MoO₃ and methanol in the void space between the pellets due to the reverse volatilization reaction. The deposition decreases the void space leading to pressure drop buildup, which is calculated as a function of the catalyst shape and molybdenum content, reaction conditions and time on stream. The reactor model is fitted to experimental measurements of increasing pressure drop in a pilot scale reactor at Haldor Topsøe A/S. Finally the model is used to predict the effect of different strategies to extend the process lifetime. By reducing the molybdenum content or changing the shape of the catalyst pellets from open to filled cylinders in the initial part of the reactor, optimization of the pressure drop increase is achieved.

This thesis contributes with new insight into the structural changes and catalytic performance of the iron molybdate catalyst under reaction conditions over a time period long enough to achieve significant degradation. The developed catalyst pellet model implemented into a reactor model was used to analyze different strategies to extend the process lifetime with respect to catalyst preparation. Redesigning the catalyst in the initial part of the reactor was shown to potentially extend the lifetime of the formaldehyde process significantly.

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