Modeling of the Molybdenum Loss in Iron Molybdate Catalyst Pellets used for Selective Oxidation of Methanol to Formaldehyde

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Modeling of the Molybdenum Loss in Iron Molybdate Catalyst Pellets used for Selective Oxidation of Methanol to Formaldehyde

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1. Introduction

Formaldehyde (CH₂O) may be synthesized industrially by selective oxidation of methanol over an iron-molybdate (Fe-Mo) oxide catalyst, known as the Formox process [1]. The fresh catalyst consists of a mixture of Fe₂(MoO₄)₃ and MoO₃. Fe₂(MoO₄)₃ is the active phase and excess MoO₃ must be present to form a surface layer of MoO₃ and make the pellets mechanically stronger. However, under the reaction conditions molybdenum oxide forms volatile species with methanol in the feed gas and migrates through the catalyst bed. The volatile molybdenum species decompose and accumulate downstream in the reactor bed leading to pressure drop build-up and finally plant shutdown. The volatility of the Mo in the catalyst and pressure drop build-up in the industrial reactor is the main reason for the short lifetime of only 1–2 years [2]. In this work the rate of volatilization of Mo from industrial catalyst pellets has been studied as a function of operating conditions and a single pellet model that take the relevant phenomena into account has been developed.

2. Experimental

The molybdenum loss of industrial iron molybdate catalyst pellets (atomic Mo/Fe ≈ 2.6, OD = 4.5 mm, hole diameter 1.7 mm) was investigated using a multitube reactor (ID = 6.5 mm) each exposing a single catalyst pellet. Each cylindrical pellet was placed on the tip of a thermocouple and centered in the middle of the reactor. The feed gas consisted of 4.4 vol.% MeOH and 10 vol.% O₂ in N₂ with a flow of 3 NL/min. Pellets were tested at varying temperatures (250, 300 and 350 °C) and varying time on stream (up to 240 hours). The pellets were recovered after each experiment and cut through the middle. The cross-sections of the pellets were characterized by SEM-EDX for concentration profiles and area analyses, and Mo/Fe elemental ratios were determined.

3. Results and discussion

Figure 1 (Left) shows a SEM image of the cross-section of a catalyst pellet after 70 hours on stream. The bulk of the pellet is light gray indicating a composition similar to the fresh catalyst with excess MoO₃ present. However, a dark gray layer 120 µm thick at the pellet surface indicates a depletion of the excess MoO₃, leaving only the Fe₂(MoO₄)₃ phase present (Mo/Fe = 1.5) at the outer layer of the pellet. To model the influence of operating conditions on the rate of Mo loss, a dynamic 1D model for a single pellet in which methanol oxidation to formaldehyde and simultaneous Mo volatilization takes place was developed and validated. The model considers the diffusion and oxidation of methanol, the reversible volatilization reaction between molybdenum and methanol, and the diffusion of the volatile molybdenum species through the pellet. The model calculates the loss of Mo as a function of radial position as a function of time on stream and reaction conditions. Figure 1 (Right) shows the model prediction of the Mo/Fe ratio in the pellet after 70 hours on stream. At the surface of the pellet a decreasing Mo/Fe ratio is predicted corresponding to the experimentally measured depletion layer thickness.

4. Conclusions

The influence of temperature and time on stream on the molybdenum loss in iron molybdate pellets under reaction conditions was investigated experimentally. The volatilization and diffusion of molybdenum leads to a depletion layer evolving from the surface of the catalyst pellet. A dynamic single particle model was developed which calculates the Mo concentration as a function of radial position in the cylindrical catalyst pellets as function of time. The model is in good agreement with the experimental data.

References