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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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Highlights

- Volatilization of molybdenum in iron molybdate pellets tested under reaction conditions
- MoO_3 forms volatile species with methanol and migrates away from the catalyst
- Loss of MoO_3 leads to formation of a depletion layer evolving at the pellet surface
- Modeling of the MoO_3 loss in a single pellet by a 1D mathematical model

1. Introduction

Formaldehyde (CH_2O) may be synthesized industrially by selective oxidation of methanol over an iron-molybdate (Fe-Mo) oxide catalyst according to: $CH_3OH + ½O_2 \rightarrow CH_2O + H_2O$. The reaction is normally carried out in a multitubular reactor (tube length = 1-1.5 m) with stoichiometric excess of oxygen (10% MeOH, 10% O_2, 5 % H_2O, balance N_2) at atmospheric pressure and 270-400 °C (overall plant yield = 88-92 %), known as the Formox process [1]. The fresh catalyst consists of two phases $Fe_2(MoO_4)_3$ and MoO_3. $Fe_2(MoO_4)_3$ is the active phase and excess MoO_3 must be present to form a surface layer of excess MoO_x and make the pellets mechanically stronger. Pure MoO_3 in itself has low activity.
However, under the reaction conditions molybdenum oxide forms volatile species with methanol in the feed gas and migrate through the catalyst bed. The volatile molybdenum species decompose and accumulate downstream in the reactor bed leading to significant 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 depending on the operating conditions [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. Methods

The molybdenum loss of industrial iron molybdate catalyst pellets (atomic Mo/Fe ≈ 2.6, OD = 4.5 mm) was investigated in a single pellet reactor (ID = 6.5 mm). The 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 % MeOH and 10 % O_2 in N_2 with a flow of 3 NL/min. Different 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 Scanning Electron Microscopy (SEM) combined with Energy Dispersive X-ray spectrometry (EDX) for concentration profiles and area analyses, and Mo/Fe ratios were determined.

3. Results and discussion

Figure 1 shows a SEM image of the middle cross-section area of a catalyst pellet after 70 hours on stream at 300 °C. The bulk of the pellet is light gray indicating a composition similar to the fresh catalyst with excess MoO_3 present. However, a dark gray layer 120 µm thick at the pellet surface indicates a depletion of the excess MoO_3, leaving only the $Fe_2(MoO_4)_3$ phase present at the outer layer of the pellet. The corresponding Mo/Fe ratios of the respective phases were confirmed by SEM-EDX.

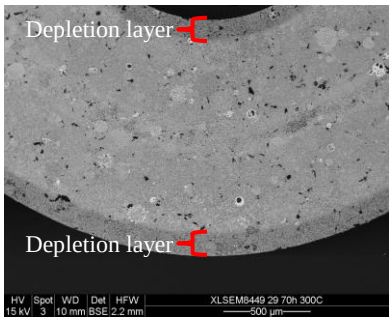

Figure 1. SEM image of catalyst pellet after 70 h on stream, at reaction conditions: temp. = 300 °C, feed = 4.4% MeOH, 10% O_2 in N_2. Light gray indicates Mo rich composition (Mo/Fe = 2.6) and dark gray stoichiometric composition (Mo/Fe = 1.5).

To model the influence of operating conditions on the rate of Mo loss, we developed and validated a dynamic 1D mathematical model for a single pellet in which methanol oxidation to formaldehyde and simultaneous Mo volatilization takes place. Figure 2 (Left) shows a drawing of the cylindrical pellet geometry. For simplification the pellet geometry was assumed to be a slap with no contribution from the top and bottom as shown in the figure. The model considers the diffusion and oxidation of methanol, the volatilization reaction between molybdenum and methanol, and the diffusion of the volatile molybdenum species through the pellet. The diffusion was modeled using an effective diffusion coefficient calculated from the bulk diffusion coefficient, catalyst porosity and tortuosity. The reaction rate of methanol to formaldehyde was based on kinetic studies performed in a laboratory reactor elsewhere, and was independent of the MoO_3 depletion in the pellet. The reversible volatilization reaction between methanol and molybdenum was modeled by a simple power law expression. The equilibrium constant and reaction order were fitted to describe the experimentally measured evolution of the depletion layer thickness. The model calculates the Mo/Fe ratio through the pellet in the radial direction as a function of time on stream and temperature at a feed composition of 4.4 % MeOH, 10 % O_2 in N_2. Figure 2 (Right) shows the model prediction of the Mo/Fe ratio in the pellet after 70 hours on stream at the respective conditions. At the surface of the pellet a decreasing Mo/Fe ratio is predicted corresponding to the experimentally measured depletion layer thickness.

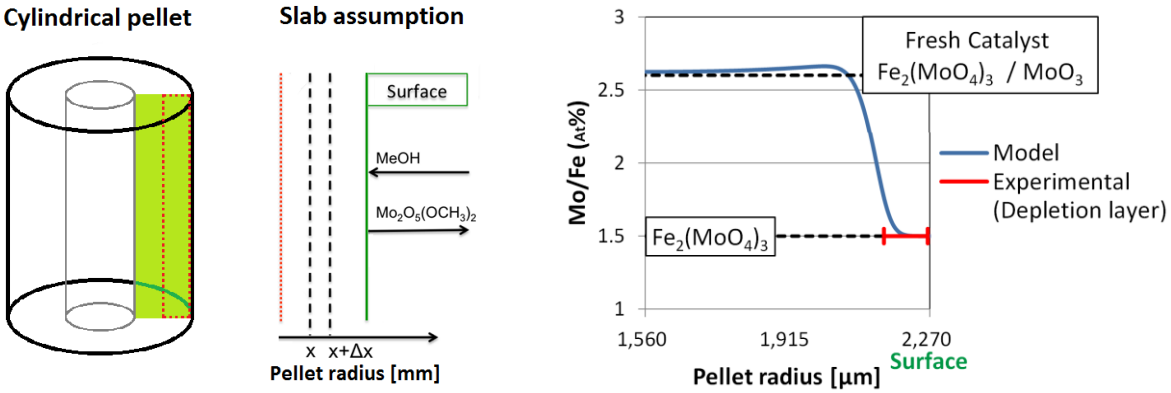

Figure 2. Left: Drawing of the catalyst pellet and 1D slab assumption model.
Right: Model prediction of the depletion layer for the pellet showed in figure 1 (TOS = 70 h, Feed = 4.4 % MeOH, 10 % O_2 in N_2.

Furthermore, at 350 °C deposition of MoO_3 inside the pellet due to inwards diffusion and deposition of the volatile Mo species forming a layer with increased Mo/Fe ratio was observed. This feature is also correctly predicted by the model.

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/Fe ratio in the radial direction of the cylindrical catalyst pellets as function of time. The model parameters were fitted to describe the thickness of the depletion layer at varying temperatures and time on stream at a feed composition of 4.4 % MeOH, 10 % O_2 balance N_2. The fitted model is capable of describing the molybdenum loss and corresponding depletion layer thickness of a single catalyst pellet.

References

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Keywords
Methanol oxidation to formaldehyde, catalyst, loss of molybdenum oxide, modeling