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Publication date:
2019

Document Version
Peer reviewed version

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Citation (APA):

Raun, K. V., Thorhauge, M., Gaur, A., Grunwaldt, J-D., Jensen, A. D., & Høj, M. (2019). *Experimental Investigations and Modelling of the Molybdenum Loss from Iron Molybdate Methanol Selective Oxidation Catalysts*. Abstract from 14th European Congress on Catalysis, Aachen, North Rhine-Westphalia, Germany.

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Experimental Investigations and Modelling of the Molybdenum Loss from Iron Molybdate Methanol Selective Oxidation Catalysts

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Introduction

Formaldehyde (CH₂O) can be synthesized by selective oxidation of methanol over an iron molybdate (FeMo) catalyst according to: $\text{CH}_3\text{OH} + \frac{1}{2}\text{O}_2 \rightarrow \text{CH}_2\text{O} + \text{H}_2\text{O}$. Industrially, the reaction is carried out with stoichiometric excess of oxygen (10% MeOH, 10% O₂, 5 % H₂O, balance N₂) near atmospheric pressure and 270-400 °C, known as the Formox process [1]. The fresh catalyst consists of two crystalline phases: Fe₂(MoO₄)₃ and MoO₃. Fe₂(MoO₄)₃ is the active phase and excess MoO₃ must be present to form a surface layer of MoO_x. However, under reaction conditions Mo forms volatile species with methanol, which migrate through the catalyst bed. The volatile molybdenum species decompose to MoO₃ downstream in the reactor leading to pore blocking and pressure drop increase, resulting in a short process lifetime of only 1–2 year [2]. To understand and model the MoO₃ volatilization, migration and deposition we have studied the molybdenum volatilization from the catalyst in three forms: Finely ground and diluted particles used for operando X-ray diffraction and absorption spectroscopy, 150-300 μm sieve fractions studied by operando Raman spectroscopy and in laboratory reactors for up to 600 h with extensive Mo loss and whole, ring shaped, cylindrical pellets exposed in single pellet reactors.

Results and Discussion

A FeMo catalyst with Mo/Fe = 2.0 was prepared by a hydrothermal method and calcined at 535 °C in air. The fresh catalyst contained Fe₂(MoO₄)₃ and α-MoO₃ according to XRD and Raman and had a surface Mo/Fe ratio of 6.09 according to XPS, showing significant MoO_x surface enrichment. Laboratory reactor studies using sieve fractions showed complete evaporation of MoO₃ after 10 h on stream, with a concurrent decrease in XPS surface Mo/Fe ratio to 0.81 and decrease in catalytic activity.

The formaldehyde/DME selectivity remained above 99 % [3]. When exposing the catalyst for up to 600 h, Mo evaporated from $\text{Fe}_2(\text{MoO}_4)_3$, forming FeMoO_4 and eventually Fe_2O_3 , with a surface Mo/Fe ratio of 0.44 as determined by XPS. However, the catalytic activity increased to above the initial activity from 10 to 250 h, then remained constant, and the selectivity to formaldehyde/DME was still above 96 %, showing that the catalyst may suffer significant Mo loss and still be active and selective [3].

Operando Raman spectroscopy confirmed the complete MoO_3 evaporation, decreased activity, but maintained selectivity and $\text{Fe}_2(\text{MoO}_4)_3$ phase, within 10 h on stream. Using finely ground and diluted catalyst particles for operando XAS and XRD showed complete MoO_3 evaporation and decreased activity within 1-2 h. Increase of the MeOH concentration or temperature and decrease of the O_2 concentration led to a higher rate of MoO_3 volatilization.

Exposing industrial pellets, shaped as cylinders with a hole in the middle (outer diameter = 4.55 mm, hole diameter = 1.70 mm and length = 4.00 mm) showed depletion of MoO_3 in a front from the surface towards the center as seen by dark contrast, where the Mo concentration is lower, in Fig. 1 [4].

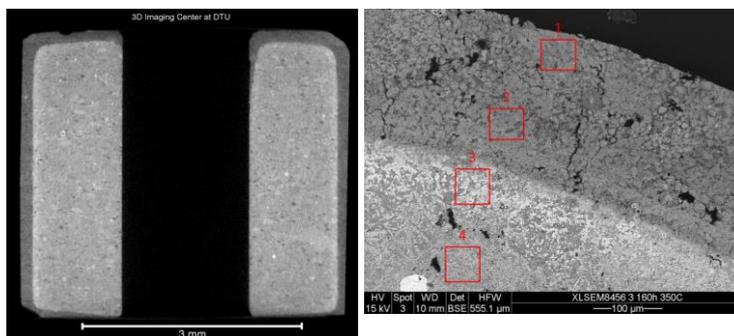


Fig. 1: X-ray absorption tomography image of pellet axial cross section and SEM image of radial cross section

A mathematical model for the kinetics of MeOH oxidation, MoO_3 evaporation and deposition, as well as diffusion of all species was successfully applied. This described the amount of excess MoO_3 present in the pellet as function of radial position, MeOH and H_2O concentrations and temperature (Fig. 2) [4]. This model was additionally implemented in a reactor model for predicting the pressure drop increase with time on stream and thus the industrial process lifetime, including improvement strategies [5].

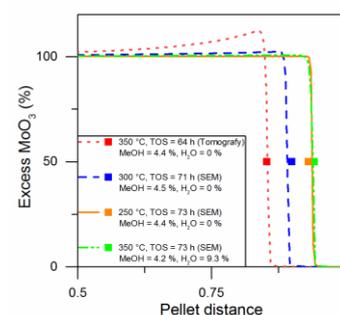


Fig. 2: Pellet model

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