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Studies of Deactivation of Methanol to Formaldehyde Selective Oxidation Catalyst

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Introduction

Formaldehyde (CH₂O) may be synthesized industrially by selective oxidation of methanol over an iron-molybdate (Fe-Mo) oxide catalyst according to: CH₃OH + ½O₂ → CH₂O + H₂O. The reaction is normally carried out in a multitubular reactor with excess of air at 250-400 °C (yield = 90-95 %), known as the Formox process [1]. The average lifetime of the industrial catalyst is only 1–2 years depending on the operating conditions. The catalyst consists of a bulk phase of Fe₂(MoO₄)₃ and a surface layer phase of MoO₃. The MoO₃ surface is selective towards formaldehyde while the iron in the sublayer increases the activity of the catalyst [2]. Pure MoO₃ in itself has low activity. Literature from the last decades agrees that the major reason for the deactivation is loss of molybdenum from the catalyst. Molybdenum forms volatile species with methanol, which can leave behind Mo poor zones. The catalyst is usually prepared with excess MoO₃ (Mo/Fe > 1.5) to counter the loss of Mo. This work focuses on understanding the structural changes occurring in the catalyst and its behavior during deactivation via prolonged activity testing and spectroscopic investigations.

Materials and Methods

Fe-Mo oxide with Mo/Fe molar ratio = 2.0 was prepared by hydrothermal synthesis. The fresh catalyst was characterized by ICP-OES, XRD, TEM and SEM-EDX. The catalyst (150-300 μm) was tested in a fixed-bed reactor and in an *in situ* Raman cell [3]. The feed gas consisted of 10 % O₂ and ~5 % MeOH in N₂. Before each experiment the catalyst was thermally treated at 400 °C in air for two hours. The reactors were heated to 375 °C during operation. At the end of the experiment in the fixed-bed reactor, the catalyst was thermal-treated in air followed by reapplying reaction conditions. The spent catalyst from the fixed-bed experiment was characterized by XRD, Raman spectroscopy, SEM-EDX and STEM-EDX.

Results and Discussion

Figure 1 shows the conversion of MeOH, the selectivity towards formaldehyde and the catalyst bed temperature in the fixed-bed reactor for 116 h on stream. Figure 2 shows Raman spectra of the catalyst and conversion of MeOH including the relative presence of α-MoO₃ and Fe₂(MoO₄)₃ (weight parameters determined by linear optimization for selected Raman bands).

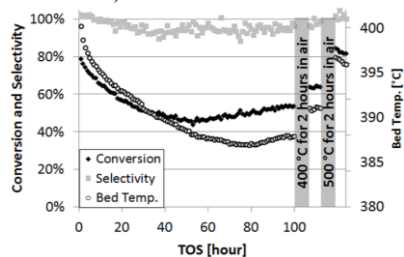


Figure 1. MeOH conversion, formaldehyde selectivity and catalyst bed temp. in the fixed bed reactor. Operating conditions: 25 mg catalyst diluted in 170 mg SiC, ~157.5 NmL/min gas feed: 10 % O₂, ~5 % MeOH in N₂. Other products: DME and small amounts of CO and CO₂ (< 1 C-mol.%).

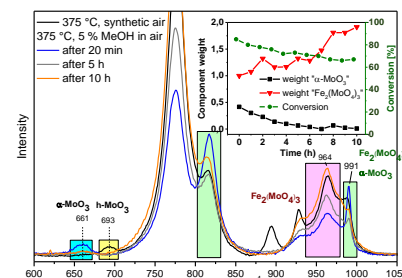


Figure 2. *In situ* Raman spectra after 20 min, 5 h and 10 h on stream during methanol oxidation. Inset: Corresponding MeOH conversion and weight parameters representative for α-MoO₃ and Fe₂(MoO₄)₃.

Operating conditions: TOS = 10 h, 25 mg catalyst diluted in 18 mg Si, ~42 NmL/min gas feed: 10 % O₂, ~5 % MeOH in N₂. Laser: CVI Melles HeNe laser. A 10x objective was used with 5 mW at 633 nm.

For the experiment performed in the fixed-bed reactor, the selectivity was constantly above 90 %. The conversion decreased during the first 53 hours on stream from 80 to 44 % followed by a slight increase to 54 % (100 h). The conversion increased to 64 % after thermal-treatment at 400 °C, and further increased to 81-84 % after thermal-treatment at 500 °C.

For the experiment performed in the Raman reaction cell, the conversion decreased from 85 to 67 % (10 h experiment). The weight parameter assigned to α-MoO₃ decreased to ~0 (Raman bands disappeared) and that assigned to Fe₂(MoO₄)₃ increased with a factor of ~2.

The catalyst was prepared by hydrothermal synthesis, which is a mild synthesis (temp. = 180 °C). The intensity increase in Raman bands related to Fe₂(MoO₄)₃ over time was probably due to crystallization of Fe₂(MoO₄)₃. Surface oxygen is consumed during the reaction and the catalyst must be reoxidized by oxygen from the gas phase. Partial reduction of the catalyst could explain the decrease in Raman bands related to MoO₃ and the decreasing conversion. The SEM-EDX analysis showed that different spent catalyst particles were subject to slightly different degrees of Mo-loss. The XRD analysis showed a composition of mainly Fe₂(MoO₄)₃ with small amounts of FeMoO₄. Raman analysis showed bands from α-MoO₃ and Fe₂(MoO₄)₃. TEM analysis showed particles of ~50 nm in size with few larger particles 200 – 500 nm and a decrease in the Mo/Fe ratio between the fresh and spent catalyst from 2.0 to 1.4. STEM-EDX in addition showed some iron oxide particles.

The results show that Fe₂(MoO₄)₃ is reduced to Mo depleted phases (FeMoO₄ and Fe₂O₃) due to loss of Mo. However, excess MoO₃ (observed with SEM-EDX) acts as a replenishing reservoir, which partly stabilizes the MoO₃ layer on top of the Fe₂(MoO₄)₃ crystals. The reactivation of the catalyst after thermal-treatment is probably due to re-establishment of the molybdenum rich catalyst surface, by replenishing with Mo oxide from the excess MoO₃ crystals.

Significance

This work presents a study of the deactivation behavior of Fe-Mo oxide catalyst during selective oxidation of methanol to formaldehyde in a period of 116 h. The structural changes in the catalyst have been investigated *in situ* for the initial 10 h by Raman spectroscopy, and the structure after 116 h on stream in a fixed bed reactor have been determined by comprehensive characterization.

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