Modeling of the molybdenum loss in iron molybdate catalyst pellets for selective oxidation of methanol to formaldehyde

The loss of molybdenum from industrial iron molybdate (Fe₂(MoO₄)₃) catalyst pellets with an excess of molybdenum oxide was studied during selective oxidation of methanol to formaldehyde for up to about 10 days on stream at varying reaction conditions (MeOH=1.6–4.5%, O₂=2.5–10%, H₂O=0–10.2vol% in N₂ and temperature=250, 300 and 350°C). The changing morphology and the local elemental composition in the pellets were followed for increasing time on stream. Molybdenum was shown to volatilize, leaving a depleted zone starting at the pellet surface and moving inwards with time. For temperatures ≤300°C only volatilization of the excess MoO₃ phase was observed. Increasing concentration of MeOH and temperature enhanced the rate of volatilization, the oxygen concentration had negligible effect, while increasing the H₂O concentration decreased the volatilization rate. At 350°C (MeOH=4.5%, O₂=10%, H₂O=0% in N₂) Mo in the Fe₂(MoO₄)₃ phase was furthermore volatilized leading to the formation of the reduced ferrous molybdate (FeMoO₄). A dynamic 1D mathematical model for a single pellet, in which methanol oxidation to formaldehyde and simultaneous volatilization of free MoO₃ takes place, was developed. The model parameters were fitted using experimental data of the pellet weight loss while the evolution of the MoO₃ depletion layer thickness was used to validate the model. The model describes the data well and additionally predicts that deposition of MoO₃ behind the depletion layer front occurs under certain conditions, leading to a MoO₃ deposition layer, which was verified by scanning electron microscopy (SEM) combined with energy-dispersive X-ray spectroscopy (EDS). Simulations with the model show that the overall loss of molybdenum is significantly slower for large pellets compared to small pellets, which is a key parameter for the success of the industrial process.

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