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Deactivation Mechanisms of Co/Al₂O₃ Catalyst in Fischer-Tropsch Synthesis: A Study on Sintering, Coke Formation, and Temperature Control Strategies

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Abstract

The Co/Al₂O₃ catalyst was applied in a Fischer-Tropsch (FT) reaction aiming to obtain synthetic fuel. During the reaction, under conditions of 20 bar and 220 °C, a significant temperature increase (> 500 °C) was observed due to the exothermic nature of the process [1]. Consequently, the catalyst underwent severe changes, directly affecting its activity. According to the diffractogram of the fresh catalyst, the phases of Co₃O₄ (ICDD 01-074-165) and Al₂O₃ (COD 96-901-2254) were identified. It is important to highlight that the main active phase is Co⁰ (metallic cobalt), which forms after the in situ reduction process in the catalytic bed under a reducing gas (H₂) atmosphere at 400 °C for 10 hours. In addition to Co⁰, the spent catalyst also showed the presence of a C phase (ICDD 01-075-1621), identified as coke. According to Rietveld refinement, the crystallite diameter of the active Co phase increased from 20 nm to 82.7 nm, indicating sintering. In the scanning electron microscopy analysis of the spent catalyst, coke formation was identified, including the presence of carbon filaments. The thermogravimetric analysis of the spent catalyst indicated a mass loss of 47.2% in a burning event between 293-640 °C. In this context, it can be inferred that the main deactivation pathways of the catalyst in the FT reaction are related to sintering and coke formation. The formation of carbonaceous species (coke) in the active phase was the main deactivation factor, leading to a loss of catalyst activity and selectivity. At temperatures below 260°C, amorphous carbon is formed; on the other hand, wax formation is also a serious deactivation issue. During catalytic deactivation due to carbonaceous species deposition, theoretical studies [2] suggest the formation of multiple branched chains or graphitic layers, resulting in a completely blocked catalyst surface. Another possible deactivation pathway is related to the oxidation of the Co phase. These sites can easily oxidize from the oxygen source derived from CO (mainly) and the formed water. The direct contact of oxygen with the Co-active phase is favored in areas with low coke deposits. Regarding the sintering of active metals, over time, under conditions of temperature and pressure, the growth of small metallic particles occurs via migration of these sites followed by the coalescence of these particles [3]. Therefore, the results indicate that the Co/Al₂O₃ catalyst experienced both coking and sintering during the Fischer-Tropsch reaction due to the high exothermic heat release, resulting in gradual deactivation through coking, blocking access of the reagents to the active sites, as well as the possible oxidation of the active phase, ultimately leading to a reduction in catalytic activity. In this sense, to prevent a temperature increase during the reaction process, it becomes advantageous to employ possible strategies: the use of inert sweep gas to dissipate heat and modifications in catalyst preparation to enhance resistance to sintering.

Key words: Fischer-Tropsch reaction, Deactivation, coke formation, Co/Al₂O₃

References

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