

Fischer-Tropsch Synthesis: Co turnover Frequency Rates over Co/Al₂O₃ Catalysts with Different Reduction Promoters

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Cobalt (Co) turnover frequency (TOF) has been reported to be independent of Co dispersion and support type. However, wide discrepancies in Co TOF values exist in the literature. Differences in catalyst preparation, process conditions, and characterization technique could be major factors that may account for the discrepancies. Therefore, a more accurate assessment of Co turnover frequency (TOF) is needed. In this study, Co TOFs over different Co/Al₂O₃ catalysts promoted with Pd, Ru, Pt and Re at the beginning of reaction and at steady state were determined. The catalysts were prepared in different batches, which resulted in two Co cluster sizes: small Co particle size (~6 nm) and large Co particle size (11.5 nm). Fischer-Tropsch synthesis (FTS) reaction was carried out at different conditions in a continuous stirred tank reactor (CSTR). All promoted Co catalysts were characterized using BET, TPR, H₂-chemisorption and pulse re-oxidation. The FTS was conducted at 220-230 °C, 1.5 MPa, 6-13 NL/gcat/h and H₂/CO = 2.1. Results indicate that catalyst preparation including promoter effect and process conditions significantly impact initial and steady state TOF values. The Co catalysts with larger particles had a larger Co TOF and low space velocity (SV) reduced the number of Co active sites due to severe catalyst deactivation at high CO conversion. For SV of 8.0-13.0 NL/g-cat/h and 1.5 MPa, high Co TOF values (0.074-0.082 s⁻¹, at 210 °C) over the Re and Pt promoted 25%Co/Al₂O₃ were achieved and were in good agreement with recently published value (0.073 s⁻¹) in a few literature. Moreover, these values are about two times the values (0.023-0.045 s⁻¹) reported in some Co related literature under similar conditions. Therefore, true TOF on single Co cluster with the size of 11.5 nm at 210 °C and 1.5-2.0 MPa should be about 0.073-0.082 s⁻¹ (this value is conversion dependent). The effect of promoters (Pd, Ru, Pt and Re) and process conditions on FTS activity and selectivities (hydrocarbons, water-soluble oxygenates and CO₂) was also studied.