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Characterizing Intrinsic Deactivation in Cobalt-Catalyzed Fischer-Tropsch Synthesis

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Three intrinsic deactivation modes observed in experimental cobalt Fischer-Tropsch synthesis (Co FTS) catalysts are investigated via ex-situ TEM [1]. These include: cobalt oxidation reversible by mild hydrogen treatment, cobalt agglomeration, and cobalt-support mixed oxide formation. All three mechanisms involve redox transformation of the catalytically active cobalt metal.

Earlier studies [2] have shown that (a) Co^0 is the catalytically active entity in Co FTS and (b) the site activity is not influenced by the support or the metal particle size in catalysts containing metal particles larger than ~5 nm. Steady-state isotope transient studies with similar catalysts [3] confirmed these conclusions. Consequently, transformations that reduce Co^0 surface by agglomeration or by oxidizing Co particles will reduce catalytic activity. Bulk thermodynamic data [4,5] suggests that CoO would not form under typical Co FTS conditions. However, reactor studies and TEM observations prove that the behavior of nanoscale metal particles deviates from that of the bulk and that cobalt oxidation does occur during commercially relevant Co FTS conditions. The exact nature of the oxidized species is not clear, but it is shown that the process is enhanced by higher CO conversion (higher $\text{H}_2\text{O}/\text{H}_2$ ratio) and smaller metal particle size. This oxidation is fully reversed by hydrogen reduction at Co FTS temperature and pressure.

Once the cobalt metal is oxidized, it wets the support surface and thus allows nearby oxidized cobalt particles to contact each other. Subsequent reduction can lead metal agglomeration. Since this growth mechanism starts with metal oxidation, it is also enhanced by CO conversion and smaller particle size. However, due to the spatial proximity requirement, metal particle distances on the support surface also play a role. In this regard, the reduction-oxidation-reduction (ROR) treatment of Co FTS catalysts is also instructive. ROR treatment is known to boost Co FTS activity [6] and increase Co dispersion [7,8]. This work shows that the ROR process involves the formation of hollow oxide domes that break up into smaller Co particles upon re-reduction.

Thermodynamic calculations suggest that cobalt-support mixed oxide formation with SiO_2 , Al_2O_3 , and TiO_2 is favored at ~70% or even lower conversion of stoichiometric syngas in Co FTS. This path is kinetically open as soon as Co is converted to Co^{2+} via byproduct water. Indeed, evidence for various degrees of mixed oxide formation is presented. In general, this solid-state chemistry is slow, although in the case of Co/ SiO_2 , crystalline mixed oxide needles of well-defined stoichiometry formed rapidly at high CO conversions [9].

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