

Fischer-Tropsch Synthesis Catalysis: Low-Temperature Fe Catalysts and the Mechanism for CO Dissociation on Fe and Co

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Introduction

The Fischer-Tropsch synthesis (FTS) provides the most effective route for the conversion of natural gas to liquid products via synthesis gas intermediates. This process uses Fe and Co catalysts (1). Here, we report optimal protocols for promoter addition to Fe-based catalysts, leading to materials with unprecedented reactivity and high C₅₊ selectivities and able to work at 470-520 K, temperatures used for typically more active Co-based catalysts. We also report indirect experimental evidence and supporting theoretical calculations for the kinetic-relevant steps in CO hydrogenation and for the role of chemisorbed hydrogen in CO dissociation steps. This study provides evidence for a set of elementary steps consistent with the kinetic dependence of hydrocarbon synthesis rates on CO and H₂ partial pressures and for the respective roles of these reactants on the removal of chemisorbed oxygen atoms as H₂O or CO₂. The results are also consistent with rate equations and isotopic studies on Co-based catalysts.

Materials and Methods

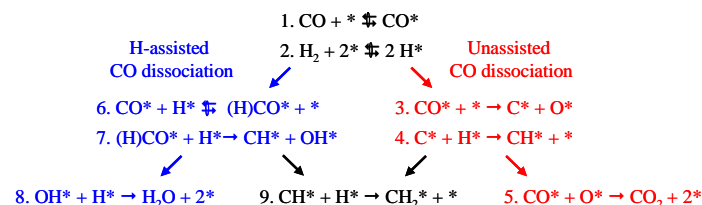
Fe-based catalysts were prepared by coprecipitation of Fe and Zn oxides (2). The precipitated powder was washed with isopropanol to avoid pore collapse during drying in ambient air at 393 K for 16 h and at 543 K in flowing dry air for 4 h. K and Cu (or Ru) promoters were added by incipient wetness impregnation. Rates and selectivities were measured as a function of CO and H₂ concentrations in a microreactor with plug-flow hydrodynamics at pressures relevant to industrial practice. Reactants and products were analyzed *on line* with a gas chromatograph. Samples were characterized by N₂ physisorption and X-ray absorption spectroscopy.

Results and Discussion

The sequence in which promoters (K, Cu, Ru) were introduced into Fe-Zn oxides influenced the uniformity of the promoters and, as a result, their reactivity in FTS. Impregnation with Cu²⁺ or Ru³⁺ solutions (pH<3) and thermal treatment before K impregnation prevented recrystallization processes that prevailed for the reverse sequence. The resulting Fe-based materials give FTS rates and selectivities (C₅₊) similar to those on Co-based catalysts.

Several different elementary steps (direct CO dissociation, hydrogenation of C* or CH* species) have been proposed to be kinetically-relevant in previous studies to explain the measured dependence of hydrocarbon synthesis rates on CO and H₂ pressures. These proposals, however, cannot account for the relative rates at which oxygen is removed as H₂O or CO₂ as H₂ and CO pressures vary. We find that these data reveal the involvement of two parallel processes for CO dissociation. One path involves unassisted dissociation and leads to O* removal exclusively as CO₂; the other path dissociates CO after H-addition and leads to the direct formation of OH*, which is removed as H₂O (Scheme 1). Both routes ultimately form a CH_x monomer required for chain growth. A *pseudo*-steady-state analysis of this set of elementary

steps accurately describes the rates of formation of hydrocarbons, CO₂ and H₂O as a function of H₂ and CO pressures on both Fe and Co catalysts. On Co catalysts, CO dissociation occurs only via H-assisted pathways and leads to O* removal exclusively as H₂O.



Scheme 1. Elementary steps proposed for the FTS mechanism.

On Fe, H-assisted pathways also prevail, but smaller contributions from direct dissociation lead to detectable rates of primary CO₂ formation via a sequence of steps that also accounts for secondary water-gas shift reactions as H₂O concentrations increase with CO conversion. These proposals are consistent with theoretical slab calculations on model Fe and Co surfaces, which find a lower energy barrier for H-assisted than direct CO dissociation steps; on Co, the direct dissociation barrier actually exceeds the binding energy of chemisorbed CO. These simulations also show that O* removal as H₂O via reactions with H* shows a very high activation barrier, suggesting that the formation of OH* and its ultimate evolution as H₂O requires H-assisted CO dissociation steps, and that any O* formed is removed instead as CO₂ via reactions with CO*.

Measured and calculated kinetic H₂/D₂ isotope effects are consistent with the involvement of H* species in kinetically-relevant steps. Measured inverse kinetic isotope effects (KIE=0.57) reflect contribution of both kinetic and thermodynamic origin. Consistent with this proposal, no isotope effects are measured for CO₂ formation rates because of its formation via direct CO dissociation, while H₂O formation rate presents KIE values identical to those for the term in the hydrocarbon synthesis rate expression corresponding to the H-assisted activation route.

This mechanism also accounts for the kinetic rate equation and for the exclusive rejection of O* as H₂O on Co catalysts. On Co surfaces, calculated CO dissociation barriers are even higher than on Fe, and therefore, H-assisted activation is a much more favorable route. Measured kinetic isotope effects are also inverse (KIE=0.80) and in quantitative agreement with those estimated from theoretical treatments. We conclude that only H-assisted CO dissociation pathways prevail during the Fischer-Tropsch synthesis on Co catalysts.

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