



Reducibility of alumina-supported cobalt Fischer–Tropsch catalysts: Effects of noble metal type, distribution, retention, chemical state, bonding, and influence on cobalt crystallite size

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ABSTRACT

The distribution, retention, chemical state, and bonding of noble metal (NM) promoters (Pt, Re, or Ru), their influence on Co crystallite size, and the resulting Co reducibility and dispersion were investigated in commercially-representative Co Fischer–Tropsch catalysts (nominally 25 wt% Co and 0 to 0.6 wt% NM on a La stabilized alumina support). NM retention during preparation ranged from complete for Pt and Re to < 50% for Ru. Co concentrations were spatially uniform; however, NM concentration varied dramatically from a sharp concentration gradient at the pellet edge in the case of Ru to a homogeneous distribution for Re and Pt. After 360 °C reduction for 1 h, Pt⁰ bonds directly to Co⁰, Ru forms separate metal crystallites and Re remains as Re₂O₇. Despite these differences, all three NMs substantially improved Co reducibility. Pt is the most effective promoter for increasing cobalt reduction rate and gives the highest extent of reduction (EOR). Preliminary activity tests showed no statistical differences in the CO depletion rates of the four catalysts of this study.

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1. Introduction

The large-scale application of Co catalysts containing noble metal (NM) promoters in the Fischer–Tropsch (FT) process, especially recently in large gas-to-liquid plants operating and under construction around the world, is well established [1]. The previous scientific and patent literatures provide definitive evidence that NM promoters facilitate Co reducibility at lower reduction temperatures leading to Co FT catalysts with higher site density, dispersion, and activity; NM promoters apparently also improve activity stability and regenerability [2–10]. Considering the rising cost of NMs, their efficient use is increasingly critical to achieving favorable economics for Co FT processes.

The previous work shows that reduction of Co oxide to the FT active site (Co metal) occurs in two steps i.e., (1) reduction of Co₃O₄ to CoO, and (2) the reduction of CoO to Co metal [11–13]. Ru and Pt facilitate both steps of this reduction process [14,15]. The significance of reduction improvement involving Ru and Pt is evidenced by a 100–150 °C decrease in the peak temperature of the first reduction step (Co₃O₄ → CoO) [16]. On the other hand, Re has been found to only promote the 2nd

reduction step (CoO → Co) [5,16]. This is explained by the higher temperature required to reduce Re itself (reportedly, 425 °C for Re/Al₂O₃) and thus being unavailable to facilitate reduction until the higher temperature (CoO → Co) step [5,17]. Nevertheless, all three NMs facilitate low temperature reduction to Co metal [6].

Mechanistically, since NM oxides are reduced at lower temperatures than Co oxide [5], once reduced to their metal state, NMs can dissociatively adsorb H₂ to highly mobile H atoms, which subsequently surface diffuse to nearby Co oxide phases and remove O atoms—initiating the reduction of Co oxide to Co metal. Thereafter, Co metal sites can also activate H₂ to H-atoms which then accelerate the reduction of nearby Co oxides. Consequently, reduction to Co metal occurs at a much lower temperature in the presence of nearby NM atoms, thus avoiding high rates of metal atom/crystallite migration and sintering [16]. The chemical state and bonding of NM promoters provides insight into the mechanism of promotion and have been investigated by X-ray absorption fine structure (XAFS) [15,18–20]. Pt bonds to Co following direct reduction (without calcination) at 400–450 °C [21]. In addition, Pt and Re reportedly bond with Co when the Co and NM precursors are calcined in the same step and then reduced at 350 °C (Pt) or 450 °C (Re) [14,19]. Ru's bonding is more controversial; i.e., observations of both Ru–Ru bonds [18,22] and Ru–Co bonds [20] have been reported.

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