



Fischer–Tropsch synthesis: Effect of Pd, Pt, Re, and Ru noble metal promoters on the activity and selectivity of a 25%Co/Al₂O₃ catalyst

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ABSTRACT

The effect of noble metal promoters (atomic ratio of promoter to Co = 1/170) on the activity and selectivity of a 25%Co/Al₂O₃ catalyst was studied at a similar CO conversion level of 50% at 493 K, 2.2 MPa and H₂/CO = 2.1 using a 1-L continuously stirred tank reactor (CSTR). The results show that all promoted catalysts exhibited markedly higher initial CO conversion rates on a per gram catalyst basis than the unpromoted one, which was ascribed to increased Co site density when the promoters were present. This is because the Re, Ru, Pt and unpromoted Co catalysts give essentially the same initial Co TOF values of 0.092–0.105 s^{−1} (based on hydrogen-chemisorption). However, the initial Co TOF value for the Pd-Co catalyst was about 40% lower, which might be caused by Pd atoms segregating on the Co surface and partially blocking Co sites.

At 50% CO conversion, Re and Ru promoters decreased CH₄ selectivity and increased C₅₊ selectivity by nearly the same extent, whereas the opposite effect was observed for Pd and Pt promoters. The Re and Ru promoters had less of an impact on C₂–C₄ olefin selectivity (7.5–60%), but suppressed the secondary reaction of 1-C₄ olefin (from 14.3 to 9%) compared to the unpromoted one; however, the addition of Pd and Pt promoters resulted in lower olefin selectivity (4.4–55%) but higher 2-C₄ olefin selectivity (14.3 to 27–31%). Pt promotion had a negligible effect on C₄ olefin isomerization. The selectivity results were reproducible.

Both Pt and Pd promoters slightly increased WGS activity, whereas Re and Ru promoters had a negligible effect. The Pd and Pt promoters were observed to slightly enhance oxygenate formation, while Re and Ru slightly decreased it.

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1. Introduction

Considerable effort has been made to study supported Co catalysts due to their high activity and selectivity for high molecular weight hydrocarbons in the Fischer–Tropsch synthesis (FTS) reaction [1–5]. Al₂O₃ and SiO₂ are currently used as supports for commercial Co catalysts. To facilitate the reduction of Co, which has strong interactions with Al₂O₃, researchers often add promoters such as Pd, Pt, Re, and Ru to the Co catalysts [3–15]. The effects of loading and type of promoter on Co reducibility and catalyst stability have been reported [3,5,13,14]. The general conclusion is that the noble metal promoters decreased the reduction temperature of Co oxides. Furthermore, Jacobs et al. [16] and Vada et al. [10] observed that Re assisted in the reduction of Co on alumina support in a different pattern relative to Pt and Ru promoters. The temperature of reduction of both steps (Co₃O₄ → CoO and CoO → Co⁰) shifted to lower temperatures in the case of Ru and Pt [3,8,17,18];

however, only the second reduction step was significantly affected in the case of Re. Because the oxides of Ru and Pt were found to reduce at lower temperatures relative to Re oxide, the authors concluded that the metallic state was important for facilitating reduction of Co oxides, possibly by a H₂ dissociation and spillover mechanism or by a chemical effect (e.g., alloying). Pd was reported to facilitate the reduction of cobalt oxides as well [13,19]. Therefore, there is consensus that the noble metal promoters improve the extent of reduction of Co and thus increase CO conversion on a per gram of catalyst basis.

However, the fundamental data on the effect of promoters on cobalt catalyst selectivity and stability at typical FTS conditions are rather rare. In order to make a fair comparison, promoters should be evaluated at a similar atomic loading and conversion level. Moreover, this allows for an equivalent partial pressure of water [6,17,18,20]. Hosseini et al. [14] investigated the effect of Ru loading on the catalyst activity and selectivity under typical FTS conditions. Their results showed that, up to 1.5% loading, Ru promoter enhanced catalyst activity and heavier hydrocarbon selectivity. Similar results over Pd, Pt and Ru-promoted Co catalysts were reported by Xu et al. [13]. However, Vada et al. [10]

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