



Fischer-Tropsch synthesis: Anchoring of cobalt particles in phosphorus modified cobalt/silica catalysts



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ABSTRACT

The effect of phosphorus addition on silica-supported cobalt catalyst was investigated for Fischer-Tropsch synthesis (FTS). As shown by STEM images and chemisorption, the addition of phosphorus to cobalt of up to 1 wt% increased the dispersion of cobalt. Further addition of phosphorus (e.g., 3 and 5 wt%), as demonstrated by TPR, pulse reoxidation, and XANES, significantly hindered the reduction of cobalt oxides. The cobalt FTS catalysts containing 0.5 and 1.0 wt% P exhibited greater stability in comparison with undoped and 3.0 wt% P containing cobalt catalysts. Analysis of XANES spectra at the P and Co K-edges, along with DRIFTS results of H₂-activated cobalt catalysts, suggest that cobalt particles interact with PO₄³⁻ ions, indicating a role played by P in anchoring Co particles to the support, thus hindering the cobalt sintering rate. The initial selectivity to methane was slightly higher for 0.5%P-20%Co/SiO₂ and 1.0%P-20%Co/SiO₂ catalysts compared to the undoped catalyst, but at longer times differences were small. At higher loadings of P (3 wt%), FT activity and selectivity were adversely and irreversibly affected.

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1. Introduction

Fischer-Tropsch synthesis (FTS) is a process used for the production of liquid fuels and chemicals from synthesis gas (syngas) derived by gasification of coal, biomass, and reforming of natural gas and other carbon-containing sources [1–3]. Cobalt-based catalysts are widely investigated for FT synthesis in order to obtain high activity and selectivity to heavier hydrocarbons for the gas-to-liquids (GTL) process [4–7]. Several factors are considered to influence the activity and product selectivity of cobalt for FT synthesis [8–10]; these include the nature of the support, promoters, method of catalyst preparation, effect of water, and contaminants in the feed. Promoters also play a vital role in improving catalyst stability [11–13]. Many have agreed that metallic cobalt is the active site for FT synthesis [11,12]. The stability of cobalt catalysts is governed by a number of factors [14,15]. There are many possible routes for deactivation of cobalt, and they depend on reaction conditions, cobalt cluster size, support type, and the level to which the syngas has been cleaned. For example, re-oxidation by water can

be problematic when the cobalt crystallite size is too small [16,17]; this is exacerbated when a strongly interacting support is used [13] and occurs at high water partial pressures (e.g., at the onset of FTS [18]), during excursions to high conversion [19], and with strongly interacting supports during co-feeding of water [20]. Cobalt may also chemically transform to inactive cobalt-support species, which are difficult to reduce [15,21–25]; a complex net reduction and sintering mechanism has been identified in the initial stages of normal catalyst aging [15,26]; at longer times on-stream, carbon deposition may be an issue [14,21,27–30]. Industrially, cobalt FT catalysts have been prepared using a number of different supports, such as Al₂O₃, TiO₂ and SiO₂ and often promoted with noble metals such as Pt, Re, Ru, Ag, Au, etc., [31–47]. The main purpose of adding promoters such as noble metals to cobalt FT catalysts is to facilitate the reduction of cobalt oxides (e.g., Co₃O₄ to CoO and CoO to Co⁰); the reduction promoter generally reduces at a relatively low temperature, which then promotes hydrogen dissociation and spillover from the promoter metal to facilitate cobalt oxide reduction; however, one cannot rule out the possibility of a direct chemical promoting effect.

Support modifiers, such as Zn [48], Group 2 elements (e.g., Mg [49], Ca [50], Ba [51]), La [52], Zr [53], and Th [54] have also been used. The modifiers, when added in the optimized amount, were found to improve pore structure, weaken the interaction between

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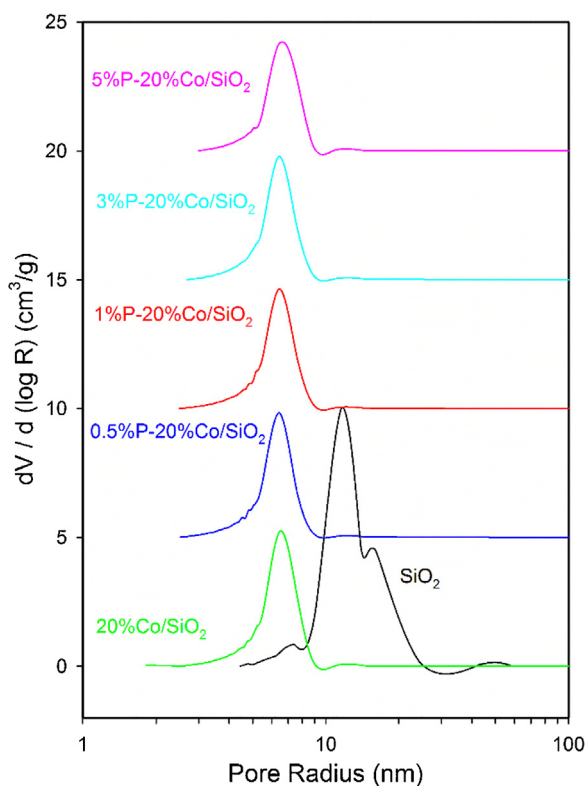


Fig. 1. BJH pore size distributions (desorption branch) of (%P)-20%Co/SiO₂ catalysts.

Co and support, and/or improve cobalt reducibility, resulting in improved catalytic activity on a per gram catalyst basis and in some cases good stability. Some have suggested that addition of the modifier suppresses sintering of cobalt particles during the FTS reaction by forming stable surface species with supports [53]. Zirconium addition to silica had the opposite effect on reducibility of cobalt oxides than when it was added to alumina; however, the greater interaction between cobalt oxides and the support led to a greater dispersion and improved active site densities [55], decreasing the average diameter of Co from 50 to less than 20 nm; higher activ-

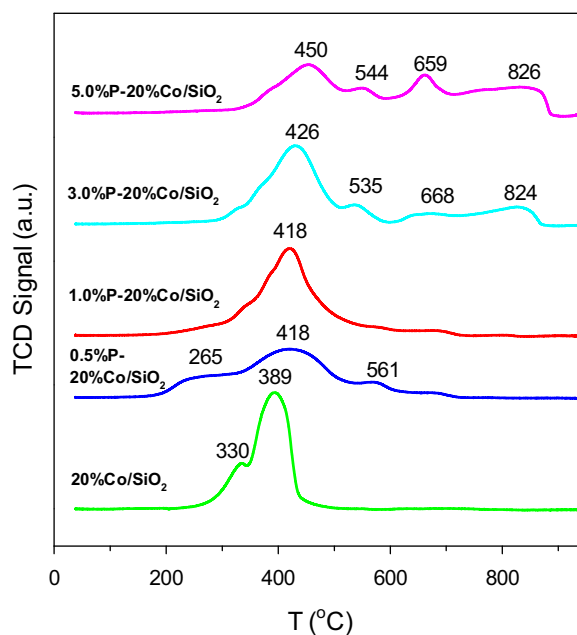


Fig. 2. H₂-TPR profiles of (%P)-20%Co/SiO₂ catalysts.

ity was observed in previous catalytic tests with Zr-modified silica [53].

Phosphorus modified Al₂O₃ was found to enhance the FTS activity of cobalt [56], and the authors attributed this to the formation of homogeneously distributed small cobalt clusters and redispersion of cobalt species during the reaction [56]. Recently, Bae et al. [57] observed some positive effects of zirconium phosphate on silica supported Ru/Co catalysts for FTS, in which the authors showed high catalytic activity and stability during reaction.

In all these cases, phosphorus was added to a support before cobalt addition such that phosphorus was primarily interacting with the support to alter metal-support interactions with cobalt. Although phosphorus was found to be a promoter to cobalt for FT synthesis only in the presence of supports/modifiers like Al₂O₃ and ZrO₂, to the best of our knowledge there are no reports

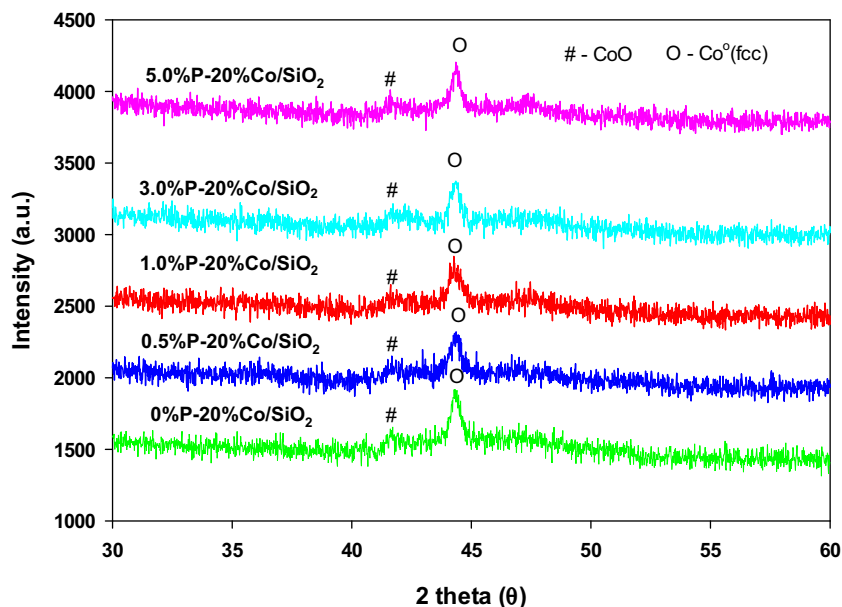


Fig. 3. XRD patterns of the reduced samples of (%P)-20%Co/SiO₂ catalysts.

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