

Manganese addition and particle size effects on cobalt-based Fischer-Tropsch synthesis catalysts

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Sustainable aviation fuels (SAF) production is key in recycling carbon within the global energy industry. The Fischer-Tropsch synthesis (FTS) is an attractive and viable route to producing SAF and is of primary interest to CARE-O-SENE, a German-South African project, funded by the BMBF. Cobalt-based catalysts are industrially used in the low-temperature FTS (LTFTS) for the selective production of long-chain hydrocarbons (*i.e.*, C₅₊) that can be further processed (*e.g.*, *via* hydrocracking) to produce the SAF fraction (C₈₋₁₆) [1]. To improve the activity and selectivity to C₅₊ hydrocarbons over Co-based FTS catalysts, promoters such as manganese are typically added to the catalyst. Manganese has long been accepted as a key promoter of Co-based FTS catalysts to improve their C₅₊ selectivity, activity, and turnover frequency [2-4]. There are various Mn promotion mechanisms reported in literature, including the assistance by Mn in removing oxygen from the surface of Co, enhancing CO dissociation, suppressing H₂ uptake, and improving Co dispersion over the support. The other reported influence of Mn is its propensity to reduce the particle size of Co [2-4].

In this study, we investigated the effect of Mn addition on the physicochemical properties and reduction pathway of differently sized Co₃O₄ particles (*i.e.*, 5, 11, and 15 nm). Co₃O₄ was synthesised *via* a surfactant-free hydrothermal method [5], where the ratios of benzyl alcohol and water were adjusted to tune the particle size (Fig. 1). The particles were then promoted with Mn (2 wt.-%) *via* wet impregnation. The resulting Mn-promoted Co₃O₄ particles (5 wt.-%) were supported on Ti-modified SiO₂ spheres *via* ultrasonic deposition [6]. The Mn-Co₃O₄/Ti-modified SiO₂ catalysts were studied using *ex situ* techniques, namely, transmission electron microscopy (TEM) (see Fig. 1 for the TEM results of unpromoted and unsupported Co₃O₄), scanning transmission electron microscopy (STEM) with energy dispersive X-ray spectroscopy (EDS), nitrogen physisorption, and X-ray diffraction (XRD), while *in situ* XRD and magnetometry are being used to determine the effect of Mn addition and Co₃O₄ particle size on the reduction pathway and degree of reduction of Co₃O₄.

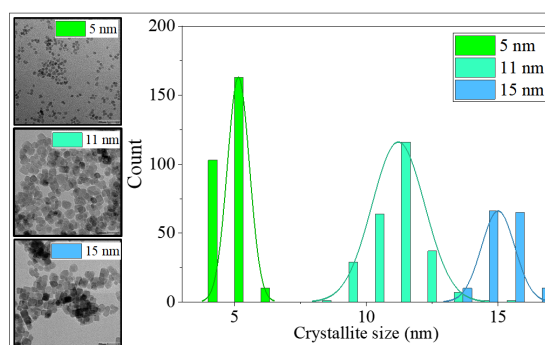


Figure 1. TEM micrographs and particle size distributions of differently sized unpromoted and unsupported Co₃O₄ nanoparticles.

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