Effect of Manganese promoter on Cobalt-based catalyst structure and reduction behaviour for Fischer-Tropsch Synthesis <u>F.T. Tinkamanyire¹, A.W. Walton², K.P. Polus³</u>

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Abstract

The Fischer-Tropsch (FT) process is a catalytic reaction which transforms a feedstock of syngas (CO/H2) into liquid hydrocarbons (CxHy). Syngas can be from diverse sources such as natural gas, biomass and more recently solid municipal waste (SMW) into liquid fuels and chemicals, which would otherwise ended up as landfill [1]. The key bottleneck preventing further adoption of FT in the energy sector is the poor selectivity of the catalysts. Cobalt-based FT catalysts promoted with manganese are particularly desirable for FT due to their stability and high selectivity towards production of C5+ hydrocarbons and long-chain alcohols, yet the role of Mn and its interaction with Co are still uncertain[2,3]. The presence of high Mn promoter loadings (on Co/TiO2) has shown to shift the selectivity away from traditional long-chain paraffins to short chain olefinic and long chain (linear) alcohol products[2,4,5]. However, the promotion mechanism of Mn is not understood, inhibiting further catalyst development. The goal is therefore to develop a better understanding of the dynamic nature between the catalyst, promoter and the environment using state-of-art operando/in situ characterisation techniques. Conventional XPS, NAP-XPS and Raman spectroscopy have been employed to investigate the oxidation state changes and reduction behaviour of Mn doped Co Fischer-Tropsch catalysts in the high Mn-loading regime (>5%) and a profound change in the structure, dispersion and reduction behaviour at high Mn loadings has been observed as shown in figure 1 (oxidation state changes where Co spinel or Co₃O₄ reduces to CoO at high Mn doping before heat treatment) and figure 2 (Co oxide reduction stages in H₂).



Fig.1. XPS spectra displaying the effect of Mn doping on cobalt oxidation states before reduction. Y denotes a satellite peak after Co $2p_{3/2}$ as a key feature for Co²⁺spetrum observed for 5wt and 10wt%Mn doped samples, and no satellite is clearly visible for 0wt% & 2wt%Mn samples. This relates to Co³⁺ spectrum.

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Fig.2.Lab source NAP-XPS Co 2p spectra showing reduction of the 0% Manganese catalyst in H_2 from $Co^{3+} - Co^{2+} - Co^{0}$