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Cobalt and iron supported on carbon spheres catalysts for Fischer Tropsch synthesis

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ABSTRACT

Gas-to-liquid (GTL) and coal-to-liquid (CTL) technologies are increasingly becoming important in the future of synthetic fuels. Fischer-Tropsch (FT) synthesis, with a history that dates back over 80 years is a promising route for the production of liquid fuels from coal, natural gas and biomass feed stocks. One of the challenging elements in the Fischer-Tropsch synthesis has been the development of active catalysts. In this study we investigate carbon spheres (CSs) and nitrogen doped carbon spheres (NCSs) as potential supports for Co and Fe FT catalysts.

CSs of average size 480 nm, were produced from acetylene gas by a chemical vapour deposition method. It was found that the as-synthesised CSs are thermally stable up to 560 ^{o}C in air and are purely carbonaceous materials (C > 95%). Functional groups (-OH, -COOH, etc), were introduced on CSs using $KMnO_4$ and HNO_3 functionalising agents and were characterised by FTIR spectroscopy, alkalimetry and TGA. Co metal was loaded onto the differently functionalised CSs using the deposition-precipitation (DPU) method and the Co/CS catalysts were tested for FT activity. Fischer-Tropsch (FT) studies, revealed striking differences in activity and selectivity for the HNO_3 and $KMnO_4$ functionalised catalysts. Investigation of the role of Mn (0.05 %) and K (0.05 %) on Co/CS FT catalysts functionalised with HNO_3 revealed that manganese inhibited the cobalt catalysed hydrogenation reactions and increased C_{5+} and olefin product selectivity. The results revealed that residual MnO_4^- ions from the surface functionalisation reaction impacted on the physical (TPR, TGA) and chemical (FT selectivity) properties of the $KMnO_4$ functionalised CS and Co/CS materials.

In other studies CS spheres were synthesised by a hydrothermal synthesis method in an autoclave (CS_{hydr}). The as-synthesised carbon materials were found to contain large amounts of oligomeric and polymeric compounds as by-products. The as-synthesised materials were characterised by Raman spectroscopy, TGA, BET, XRD and TEM. The effect of annealing CS_{hydr} to remove volatile by-products was investigated by varying annealing temperature from 250 to 800 ^{o}C under N_2. It was found that annealing these materials at a temperature higher than 450 ^{o}C completely removes oligomeric and polymeric compounds and in turn increases the surface area from 1.8 to 433 m^2/g. Furthermore, the presence of these by-

products was investigated on the FT activity and selectivity of Co/CS_{hydr} catalysts. The results showed that the use of cleaner CS_{hydr} as Co supports gave more active FT catalysts.

Studies on nitrogen-doped carbon spheres (NCSs) as supports for Fe FT catalysts were also performed. NCSs were synthesised by three different methods; (i) a chemical vapour deposition (CVD) method in a vertically aligned furnace at 900 ^{o}C, for 30 min, (NCS_{ver}) (ii) a CVD method in a horizontally aligned furnace at 950 ^{o}C, for 1 h (NCS_{hor}) and (iii) a hydrothermal synthesis method carried out at 190 ^{o}C for 4 h (NCS_{hydr}). The as-synthesised carbon spheres showed different chemical and physical properties. XPS results showed that NCS_{ver} contained mainly pyridinic nitrogen groups, while the NCS_{hor} sample contained equal ratios of pyridinic and quaternary nitrogen. NCS_{hydr} contained entirely pyrolic nitrogen. Varying amounts of oxygen functionalities were also detected in all these samples. NCS_{hydr} showed the highest oxygen concentration (24.3 %) as a result of using sucrose as a carbon source in this sample. NCS_{hor} and NCS_{ver} samples showed lower oxygen concentrations (5.9 % and 3.6 % respectively). The presence of oxygen in the CVD synthesized NCSs was a result of oxygen uptake from the atmosphere when these materials were exposed to air. The synthesised NCSs were compared for their use as supports for FT Fe catalysts. It was found that Fe/NCS_{ver} catalysts showed the highest FT activity (% CO conversion = 49.1 %) when compared to its counterparts (with % CO conversion = 40.1 % and 43.7 % for NCS_{hor} and NCS_{hydr} respectively) under identical experimental conditions.