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In situ x-ray diffraction analysis of Fischer Tropsch synthesis.

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ABSTRACT

Fe-Co/$CaCO_3$ catalysts for the synthesis of multi walled carbon nanotubes were synthesised by an incipient wetness impregnation method. This catalyst was then characterised by in situ variable temperature X-ray diffraction (XRD) and in situ XRD reduction. Other characterisation techniques such as temperature programmed reduction (TPR), thermal gravimetric analysis (TGA) and transmission electron microscopy (TEM) were used to analyse the catalyst. As the temperature was raised $CaCO_3$ decomposed to CaO and also a Ca_2FeCoO_5 phase could be identified. Upon reduction an FeCo alloy was also identified.

MWCNTs were synthesised by pyrolysis of acetylene at 700 ˚C over this 10% Fe-Co/$CaCO_3$ catalyst. The synthesis was carried out for 1 hour with nitrogen as the carrier gas in a ratio N_2: C_2H_2 (1: 2.7). The product was then purified by nitric acid to remove the Fe-Co/$CaCO_3$ catalyst particles as well as amorphous carbon. Purification was done by refluxing the product in 55% nitric acid at 120 ˚C for 6 hours. The as-grown and purified MWCNTs were analysed by various techniques such as, Raman spectroscopy, TEM, surface area analysis and TGA. TEM confirmed that MWCNTs had indeed been synthesised. The as grown MWCNTs had an average outer diameter of 29 nm whilst the diameter of the purified sample was 24 nm. TGA showed that most of the catalyst particles had been removed after acid purification. Fourier Transform infra-red spectroscopy confirmed that functional groups such as carboxylic groups had been introduced by acid treatment.

These MWCNTs were used as support for a ruthenium catalyst. 10% Ru/MWCNTs were synthesised by the incipient wetness impregnation (IMP) method and deposition precipitation (DPM) method using urea as deposition agent. TEM analysis revealed that the dispersion of the ruthenium metal on the MWCNTs was better on the DPM catalyst than on IMP. The DPM catalyst had smaller Ru particles (2.4 nm) with a narrower size range than Ru particles produced by the IMP method (5.2 nm). Addition of Ru metal onto the MWCNT surface aided in the thermal decomposition of the MWCNTs in air. TPR revealed that the DPM catalyst was easier to reduce than the IMP catalyst. The catalyst was heat treated under N_2 at 400 ˚C to decompose the precursor salt. It was observed that RuO_2 was reduced

to Ru metal under these conditions with the extent of reduction for the DPM catalyst reaching 100% whereas for the IMP catalyst was 80%.

The catalysts were tested for FT using syngas at reaction temperatures of 220 ˚C and 250 ˚C and 8 bar pressure, in the ratio 2:1 of H_2: CO. As expected the activity at 250 ˚C was greater than at 220 ˚C and selectivity to heavier hydrocarbons was realised at the lower reaction temperature. The preparation method influenced the dispersion and the Ru particle size but it only had a slight impact on the activity and selectivity of the FT synthesis reaction.