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Iron and cobalt catalysts supported on carbon nanotubes for use in the Fischer-Tropsch synthesis

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ABSTRACT

Fischer-Tropsch (FT) synthesis is the catalytic conversion of syngas (a mixture of carbon monoxide and hydrogen derived from coal, natural gas or biomass) into hydrocarbons and oxygenates. At the heart of the FT process is the catalyst, since it provides a surface where the various reactions can take place. In this study, iron or cobalt catalysts, and alkali (Li, Na and K) promoted iron catalysts supported on carbon nanotubes and nitrogen-doped carbon nanotubes were synthesized and tested for their performance in the Fischer-Tropsch process.

The carbon nanotubes (CNTs), used as a support material for the iron and cobalt based FT catalysts, were obtained through the catalytic decomposition of acetylene at 700^{o}C over a 10% Fe-Co supported on calcium carbonate ($CaCO_3$). High quality carbon nanotubes in high yields were obtained under optimum conditions (synthesis time: 1h, temperature: 700^{o}C, acetylene to nitrogen flowrate ratio of 1: 2.67). TEM analysis of the CNTs revealed that they are multiwalled, with outer diameters ranging from 20 to 35 nm and inner diameters ranging from 8 to18 nm. The synthesized CNTs were refluxed at 120^{o}C in 30% $HN0_3$ for 2 and 6 h or in 55% HNO_3 for 2 and 6 h in order to remove residual growth reagents, to introduce surface functional groups and to render the CNTs less hydrophobic. After characterization using TEM, FTIR, TGA, Raman spectroscopy and zeta potential measurements, it was found that the CNT surface roughness, together with the degree of surface functionalization correlated with the harshness of the acid treatment.

Nitrogen-doped carbon nanotubes (N-CNTs) were synthesized by a post-doping method using acetonitrile as the nitrogen source at temperatures ranging from 700 to 900^{o}C. There was no significant change in the morphology of the N-CNTs up to 850^{o}C.The nitrogen content and the % mass increase of the N-CNTs increased almost linearly with increasing reaction temperature whereas the surface area was found to

decrease. The Raman data showed that the graphite layers of the N-doped CNT are more ordered than the purified CNTs as reflected by the decrease in the I_D/I_G ratio.

Iron or cobalt catalysts and alkali (Li, Na and K) promoted iron catalysts supported on CNTs and N-CNTs were synthesized by the deposition precipitation method using urea as the precipitating agent. The catalysts were characterized using TEM, N_2-physisorption, TPR, XRD and TGA. The catalytic testing was carried out in a fixed-bed micro reactor at 220^{o}C (cobalt based catalysts) or 275^{o}C (iron based catalysts), 8 bar, 2400 h^{-1} and at a H_2 : CO ratio of 2.

The FT data of iron metal deposited on differently functionalized carbon nanotubes revealed that the activity correlates with the degree of acid functionalisation of the carbon support. The effect of the catalyst precursor source ($Fe(C_5H_8O_2)_3$, $Fe(OOCCH_3)_2$, $Fe(NO_3)_3 \bullet 9H_2O$ and $Fe(C_2O_4) \bullet 2H_2O$) and solvent (water or acetone) used in the preparation of iron supported on CNTs catalysts has been investigated. Results showed that the precursor and solvent used in the catalyst preparation have an influence on the metal dispersion and the catalyst reducibility and this affects their performance during Fischer-Tropsch.

The effect of alkali (Li, Na, K) promoted Fe/CNT catalysts on the particle size, surface area, catalyst reducibility, activity and selectivity during FTS was studied. It was observed that adding the alkali promoter increased the Fe crystallite size and as a result the catalyst surface area decreased relative to the unpromoted catalyst. This study revealed that Na is an effective promoter for Fe/CNT catalysts, followed by K and lastly Li.

Fe catalysts supported on post-doped N-CNTs revealed that the CNT containing 1.7 % nitrogen is not a suitable support for Fe-based catalysts. However, functionalizing this N-CNT support using 55% HNO_3 resulted in a better catalyst support.