CHAPTER 5

CONCLUSION

5.1 Conclusion

FT synthesis has proved to be an efficient route to the production of high quality synthetic fuels. Despite the high selectivity of FT catalysts to yield the desired products, undesirable products such as carboxylic acids are also sometimes formed during FT processes. These acids are extremely undesirable in FT feed streams as they result in acid leaching of nickel-based hydrotreating catalysts, which are found downstream of FT synthesis. It is therefore desirable to remove the carboxylic acids from the FT streams prior to hydrotreating to circumvent this problem. A potential solution to this problem is to decarbonylate the acids using suitable catalysts prior to hydrotreating.

It has been suggested that metal carboxylate interactions could be used to narrow the field in search of commercial decarbonylation catalysts[1]. Metals that yield carboxylates that decompose at low temperatures may also be capable of decomposing the carboxylic acids at low temperatures. Despite this, literature studies are surprisingly scant in discussing the syntheses and properties of metal carboxylates. Studies of the thermal decomposition behaviour of various metal carboxylates have been undertaken.

In this project, cobalt carboxylates with carbon chain lengths ranging from C_2 – C_{10} were examined. From the data collected, it can be seen that these compounds exhibit strikingly similar physical properties and chemical behaviour. It would appear that the difference in chain length of the carboxylate moiety has only a nominal effect on the behaviour of these compounds.

Elemental analysis results as well as infrared data revealed no indication of traces of free acid or carbonate in the compounds, leading to the conclusion that the compounds were of sufficient purity for the purposes of this study. The infrared spectra of the compounds appeared typical of metal carboxylate species. The two characteristic bands of carboxylate ions were observed for all the compounds. Strong asymmetrical COO^- stretches were observed between 1560 – 1600 cm^{-1} and weaker symmetrical COO^- stretches around 1400 cm^{-1}.

The separation of these two bands (Δv) was determined for each compound and used to make inferences about the possible carboxylate bonding mode in each case by applying the findings of studies conducted by Stoilova et al on a series of metal acetates[2]. They proposed that a separation of 105 – 140 cm^{-1} could be associated with monodentate bonding, 145 – 185 cm^{-1} could be associated with bidentate chelate bonding and 180 – 190 cm^{-1} could be an indication of bidentate bridging bonding. Accordingly, our data suggests that chelating coordination is favoured by the cobalt carboxylates. It should however be borne in mind that the proposed structures are based on data derived for acetates. A close examination of the infrared data reveals that the COO^- peaks appear to be broad. This observation suggests that more than one type of carboxylate bonding mode may be present in a single molecule or that individual carboxylate molecules have linked up to form dimers or trimers. Unfortunately no crystals suitable for X-ray diffraction analysis could be obtained to confirm whether either of these scenarios is true.

Examination of the thermal data shows that the cobalt carboxylates considered in this project are all stable below 200°C. Decomposition occurs between 265°C and 400°C and proceeds quite rapidly. Gravimetric calculations reveal that most compounds studied decompose to yield CoO, as expected[3]. Metallic cobalt is also obtained for the propionate and butyrate and cobalt may be formed as a result of secondary processes whereby H_2 formed during the decomposition of the sample facilitates reduction of CoO to Co[4].

An interesting feature observed in many of the DTG profiles of these compounds is the occurrence of multiple peaks observed over the mass loss step. This would seem to imply that the compounds exhibit more complex decomposition behaviour than suggested by the single step in the TG profiles. The possibility that the compounds decompose via multiple reactions to yield unstable intermediates that further decompose cannot be ruled out. However there are literature reports to suggest that cobalt carboxylates "cake" when heated[5] i.e. fusion occurs forming a crust or diffusional layer that results in apparent discontinuities in the decomposition process. It is also a possibility that the rapid release of gaseous decomposition products during the heating process causes bubbling in the melt which results in spikes in the DTG profile[6]. It is thus proposed that the cobalt carboxylates are also subject to physical effects when heated.

After consideration of the results, it appears that cobalt would not necessarily be a good candidate for use in commercial decarboxylation catalysts. Cobalt forms carboxylate species which are quite stable. The compounds examined decompose in the range 265 – 400°C. These temperatures are well above 205°C, which is the approximate temperature from which fired heaters are required for chemical processes on the plant[7]. Below this temperature conventional steam heaters can be used, which is not only economically advantageous as fired heaters are expensive to run, but also reduces the potential environmental footprint caused by the large amounts of CO_2 generated by fired heaters.

5.2 References

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