

Combustion synthesized cobalt catalysts for liquid fuel generation via Fischer Tropsch reaction

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This thesis is concerned with studies on the conversion of syngas to liquid hydrocarbons. A major part of the effort is aimed at synthesising the catalyst and use of it in a specifically designed high pressure-high temperature reactor to produce liquid hydrocarbons with Fischer-Tropsch synthesis. This study was motivated by two important considerations: (a) The predominant need to produce biomass derived liquid fuels such as gasoline and diesel. (b) Identify the key catalyst properties that influence the hydrocarbon yield and accordingly synthesize catalysts that compare with the data available in the literature. The specific areas of this research are: (i) Produce active, efficient Co based catalysts using different methods and characterise them for Fischer-Tropsch process, (ii) Build a reactor for operations at suitable pressure and temperatures and test the conversion process that involves various catalysts depending on the process used for producing them with the principal control parameter being the residence time and (iii) Examine the overall biomass to liquid fuel conversion and the economics of building such systems at smaller throughputs of particular reference to India (or other developing countries).

Based on a review of the literature on catalysts, amongst the two FT active metals, iron and cobalt, the latter was chosen for its high activity (60 - 70% conversion in a single pass) along with high selectivity and stability in the synthesis of linear hydrocarbons. The catalysts were supported on alumina and silica-doped alumina (SDA) catalyst carriers and synthesized by incipient wetness impregnation (IWI) method and combustion synthesis (CS)

method. During the course of this study, the functionality of IWI catalysts were compared to that of CS catalysts and also the effect of supports on FT reaction were investigated. Several sets of experiments were conducted with each spanning for a duration of 150 - 160 hours to address the syngas conversion and the liquid fuel generation.

The first part of this thesis deals with the synthesis of supported catalysts that contain cobalt loading of 20 wt.% (expected range of 15 - 25% from literature), the Co^0 crystallite size in the range of 15 - 25 nm, and metal dispersion in the range of 9 - 16%. The selected cobalt loading level was due to the fact that loadings less than 10% results in the formation of surface cobalt aluminates (due to the diffusion of cobalt ions into the first few layers of aluminate lattice) and at loadings greater than 25 - 30 wt.%, no additional increase in the FT activity is observed. Further, the cobalt crystallite sizes below 6 nm show reduced activity due to larger rates of deactivation and carbide formation and crystallite sizes larger than 50 nm show reduced fraction of active sites available for the FT reaction.

The Al_2O_3 (1 mm diameter spheres, BET surface area = $158 \text{ m}^2/\text{g}$, pore volume = 0.45 ml/g) supported cobalt catalysts were synthesized using the CS method and compared with the conventionally synthesized IWI catalysts. CS catalysts were synthesized using hexamethylenetetramine (HMT) as the fuel. While the CS catalysts have been developed and used for several industrial reactions, especially environmental catalysts, its use for FT reaction has been limited to a few laboratory scale studies. The major limitation for CS process is the high heat release and the consequential high temperature rise rates, resulting in the evolution of combustion products with uncontrolled explosion, eventually powdering the catalysts and in most cases resulting in the loss of active components. Such vigorous behaviour of CS reaction is distinctly evident for metal loading above 5%. The use of these powdered catalysts in a fixed bed reactor demands either re-pelletizing or re-moulding which is considered very disadvantageous. The two instances in the literature that have reported CS catalysts for FT reactions have metal loadings limited to 15% and exist in powdered form, for use in a slurry type reactor or in micro-channel reactors [Shi et al., 2012, LeViness et al., 2014].

The performance of FT catalysis using CS is limited and unavailable in the open literature. In particular, investigations related to the increase in Co_3O_4 reduction temperatures and the effect of CS process on the cobalt support interaction and the metal dispersion still need further probing.

The CS catalysts used in this thesis have been deposited over Al_2O_3 support spheres with a metal loading of 20 wt.% and without affecting the integrity of the support structure using a novel technique. The synthesized catalysts resulted in an average cobalt oxide crystallite size of 7 - 10 nm and metal dispersion ranging from 11 - 13.5%. The X-ray photoelectron spectroscopy and the H_2 chemisorption analysis of the synthesized catalysts showed that the CS catalysts display reduced metal support interaction in comparison to the IWI catalysts. Strikingly, the Al_2O_3 supported CS catalysts reduced at temperatures that are ~ 350 K higher than reduction temperatures of IWI catalysts, a feature not explicit in literature. The high reduction temperatures were associated to the reduction of surface Co^{2+} ions in the $\text{Co}^{2+}\text{-Al}^{3+}$ spinel structure.

A further effort was made to synthesize cobalt catalysts directly in a single step without the need for further reduction by employing fuel rich conditions (equivalence ratio (ϕ) of 1.2 and 1.5). However, the XRD analyses of these catalysts revealed the presence of Co_3O_4 . It was observed that, even under the fuel rich conditions, the redox mixture interacts with the atmospheric oxygen, yielding Co_3O_4 . These catalysts (CS- $\phi = 1.2$, and CS- $\phi = 1.5$) were characterised by higher degree of reduction (DOR = 75% and 77% respectively) and higher dispersion (D = 12.8% and 13.2% respectively) compared to the CS catalysts synthesized with unity equivalence ratio (DOR = 69% and D = 11%).

The Al_2O_3 supported CS catalysts resulted in an increased FT activity, as the CO conversion increased from 32% for IWI catalysts to 41% for CS catalysts. Similarly, enhanced CO conversion rates were observed for CS catalysts synthesized with $\phi = 1.2$ and 1.5, with a highest CO conversion of 61% for CS ($\phi = 1.2$) catalysts. Strikingly, the FT product spectrum reported a maximum weight fraction of wax hydrocarbons (C_{24+}), allowing for higher degree of surface polymerization for CS catalysts. The formation

of waxes reduced with increasing equivalence ratios.

Al₂O₃ supported cobalt catalysts showed a strong cobalt support interaction. The maximum metal dispersion that could be attained was limited to 12 - 13% and the degree of metal reduction extended to a maximum of 77% (CS- $\phi = 1.5$). In order to further examine the influence of the support material on catalytic activity, cobalt was impregnated into 40 wt.% silica doped alumina supports by IWI and CS method. The earlier literature study that reported investigations on the effect of 30 - 40 wt.% SiO₂ doping into Al₂O₃ supports, revealed a silica enriched surface containing phases of only SiO₂ and aluminosilicate. A lower concentration of SiO₂ doping (1.5 - 30 wt.%) showed phases of silica, alumina and a minimum concentration of aluminosilicate, while higher concentration of silica doping (>40 wt.%) showed a silica enriched surface [**Daniell et al.,2000**]. Invariably, the least cobalt support interaction for an Al₂O₃ characteristic support is bound to occur for 40 wt.% silica doping, due to the maximum concentration of aluminosilicate. Therefore, the second part of this thesis investigates the effect of 40 wt.% silica doping in alumina support on the properties of the synthesized catalysts and thereupon the FT activity and selectivity. The effect of metal support interaction and its consequent effect on the FT activity and hydrocarbon selectivity were investigated. The XRD spectra of SDA support when compared to γ -Al₂O₃ and SiO₂ support indicated silica coverage of alumina support, in a way that exposed only minimum fraction of γ -Al₂O₃ phase on the support surface. Consequently, the SiO₂ doping reduced the formation of cobalt aluminates, resulting in lower metal support interaction as compared to cobalt deposited in Al₂O₃ supports. A 34% increase in the degree of cobalt reduction is observed for SDA-CS catalysts, compared to Al₂O₃-CS catalysts. In addition, the fraction of active cobalt sites, as measured by the H₂ chemisorption experiments, increases by a margin of 48% for SDA-CS catalysts. A 16% increase in the CO conversion was recorded for SDA-CS catalysts compared to Al₂O₃-CS catalysts, with a 12% increase in the C₅₊ hydrocarbon yield.

In the available literature, the effect of SDA (5% SiO₂ in Al₂O₃ [**Jean-Marie et al., 2009**]) catalysts on the FT reactions have been only limited to

the CO conversion and the C₅₊ hydrocarbon selectivity. The effect of these catalysts on the nature of product spectrum was notably lacking. Hence, studies were carried to identify the major components of the FT reaction that are predominantly a function of the catalyst apart from the process conditions employed. The results of the product spectrum of SDA supported cobalt catalysts explicit the formation of middle distillate hydrocarbons (C₁₀-C₂₀) as the primary liquid hydrocarbon product, compared to waxes (C₂₄₊) for Al₂O₃ supported cobalt catalysts. The difference in the product spectrum for alumina and SDA supported catalysts was attributed to the enhanced surface acidity of the SDA support. NH₃-TPD analysis of the SDA support showed a 91% excess surface acidity compared to the Al₂O₃ support. The SDA surface acidity, which was observed as the summation of Lewis and Bronsted acidity, occurs due to the formation of hydroxyl group formation across aluminium and silica atoms. The aluminosilicate behaviour of SDA support was further supported by the FT-IR spectrum. Also, the SDA supported catalyst displayed higher selectivity to (C₂ - C₅ hydrocarbons (~ 2.4 times higher than Al₂O₃ supported catalysts) owing to its aluminosilicate structure, rendering it a zeolite like behaviour.

The third part of this thesis deals with the overall energy balance and presents an economic assessment of biomass to liquid fuel for an annual consumption of a nominal 10000 tonne woody biomass system with an expected liquid hydrocarbon output of 1500 tonnes, a size if found economical would be of great importance to the field. Cost analysis involving a 1000 kg/h steam-oxy biomass gasification plant paired with FT plant has been evaluated. The system configuration uses an oxy-steam gasifier, a gas cleaning system, CO₂ separation system, a compressor to raise the pressure to 3 MPa and a single-pass FT reactor. Detailed capital cost estimates for each section involved in the BTL system are set out, on the basis of which future commercial large-scale facilities producing fuel and/or power are evaluated. Several elements of the total system are available as off-the-shelf items and the gasifier itself has originated from long experience of such systems for air-gasification at the laboratory (see <http://cgpl.iisc.ernet.in>). The oxy-steam gasifier operates with an equivalence ratio of 0.1 and a steam to biomass ratio

in the range of 0.8 - 1.2. The exit syngas from the gasifier comprises 47% H₂, 22% CO, 27% CO₂ and 4% CH₄ (by volume; H₂/CO ratio of 2.1:1). The FT reactor consists of a single casing enclosed multi-tubular reactor maintained at 503 K and 3 MPa. Syngas conversions using the combustion synthesised SDA supported cobalt catalysts were considered for this analysis for varying space velocities (WHSV ranging from 2610 ml/h·g_{cat} - 873.3 ml/h·g_{cat}). The syncrude (C₂₄₊, C₆-C₁₂ and aqueous products) are separated and processed in a hydrocracker for conversion into high quality liquid transportation fuel. For a once-through FT reactor configuration, substantial energy exists in the gas phase, which includes C₁- C₅ hydrocarbons and unconverted syngas; the BTL system was therefore designed such that, the fuel-gas energy is converted to electricity using an internal combustion engine, either for in-house electricity consumption or for sale to the grid. The analysis elucidates that the fuel ratio, which is the ratio of mass of the liquid fuel to the mass of the gas phase hydrocarbons (including the unconverted syngas), decreases with a reducing WHSV, affecting the net electricity cost or the gross electricity units sold to the grid. Furthermore, the analysis shows that a market competitive liquid fuel can be produced with a CO conversion greater than 60%, at a cost ranging from 35 to 40 Rs/litre (0.5 - 0.6 USD/litre). The investment of Rs 45,000/ton of liquid fuel (681 USD/tonne) will have a will have a payback of 3.5 years. These results emphasize that an economically affordable and environmentally favourable BTL system can be produced even at the levels discussed here.

This work is organized into six chapters and Fig 1 shows the schematic of the thesis organization.

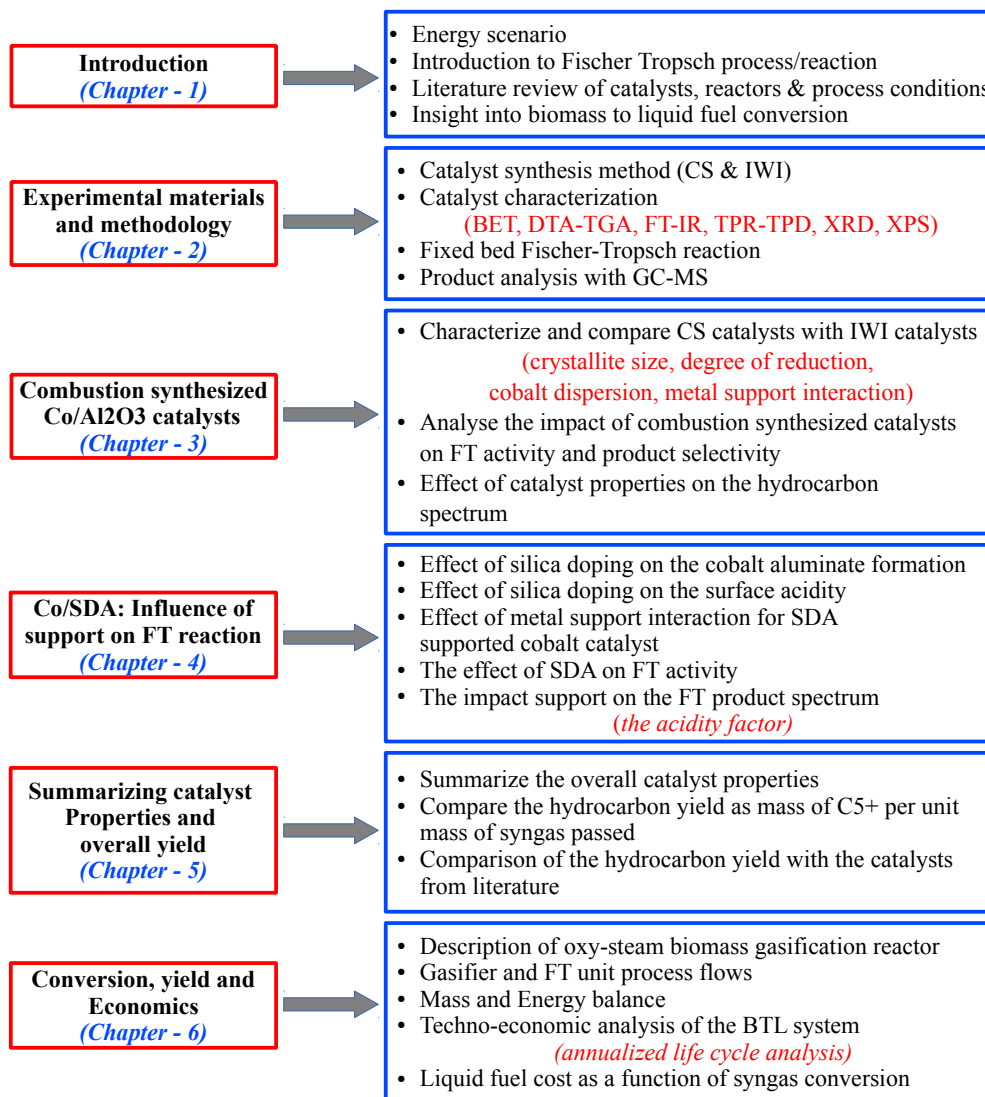


Figure 1: The thesis layout

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