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Article · December 2012

DOI: 10.1016/j.apcbee.2012.06.055

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Further Investigation into the Formation of Alcohol during Fischer Tropsch Synthesis on Fe-based Catalysts

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Abstract

The Fischer Tropsch (FT) synthesis is a complex polymerization reaction characterized by competing intermediates reaction steps. The various termination steps may result in the formation of different product classes, such as olefins, paraffins, alcohols, etc. While high synthesis gas conversion is important; a high selectivity is much desirable, which may result in.improved economics. This mechanistic study further elaborates on the elementary reaction steps for the formation of product compounds in the Fischer-Tropsch synthesis. The effect of space velocity on the products distribution, particularly on the formation of oxygen containing organic product compounds was investigated. The reactions were carried out at industrially relevant conditions on Fe-based catalyst promoted with Cu, K and alumina. The resulting catalyst precursor was characterized using TPR, XRD, BET and SEM/EDX. The alcohol/hydrocarbon ratio remains fairly constant at very high space velocity (i.e. low conversion) where secondary reactions become insignificant. This implied primary formation of alcohols in the Fischer-Tropsch synthesis.

Chemical, Biological & Environmental Engineering Society

Keywords: Fischer Tropsch; Space velocity; Fe catalyst; Secondary reactions; Oxygenated hydrocarbons.

1. Introduction

Sabatier and Senderens [1] published probably the first documented work on the synthesis of hydrocarbons via the catalytic hydrogenation of carbon monoxide. Methane and water were produced when a mixture of

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hydrogen and carbon-monoxide were passed over finely-divided nickel, iron and cobalt at 250^{o}C and elevated

pressure [2, 3]. The basis for industrial hydrogenation of carbon monoxide to fuel-type of organic product compounds is credited to Franz Fischer and Hans Tropsch [4, 5]. The Fischer-Tropsch synthesis is the catalytic step that converts synthesis gas (a mixture of CO and H_2) to liquid fuels and chemicals. It provides a route for the production of fuels not only from natural gas but as well from coal, biomass and other carbonaceous materials. The Fischer-Tropsch process converts simple feedstock (CO and H_2) into a wide range of organic products, predominantly linear paraffin and Ţ-olefins. Oxygen-containing organic product compounds or oxygenates including 1-alcohols, aldehydes, ketones and carboxylic acids are produced as side products [4-9].

The FTS is a complex polymerization reaction characterized by numerous competing reaction steps with the formation of a wide products spectrum resulting in poor selectivity. It requires a well-defined choice of catalysts, reactors and process conditions to obtain the desired products distribution [5, 7, 8, 10-13]. Improved economics may result from a well-defined products distribution, with a high selectivity for higher value products. Since its discovery, much research has been focused towards gaining better insights into the fundamental chemistry of the Fischer Tropsch synthesis. A full elucidation of the various mechanistic reaction pathways describing all the observed FT products will yield a model incorporating a complete kinetics description of the rates of products formation [7, 12]. There are still uncertainties on the mechanism of product formation [14, 15] and the type ofof the monomeric units [16] in the Fischer Tropsch polymerization reaction. Consequently, numerous and sometimes divergent reaction pathways have been proposed to explain the observed FT product distribution [7, 12]. This is partly due to the very broad spectrum of products that has been observed during the FT reactions. It is now widely accepted that to account for the all the products, an *interplay* of the various elementary reaction steps must actually exist on the catalyst surface. Several authors [5, 9, 17] have reviewed the mechanism of hydrocarbons and oxygenates formation during the Fischer-Tropsch synthesis. It should be noted that none of these postulated mechanisms have satisfactorily account for the FT synthesis broad product distribution taking into account all types of products formed.

Of particular interest is the mechanism that leads to the formation of oxygenates during the Fischer-Tropsch synthesis. Thermodynamic considerations show that the amount of ethanol for instance, produced during the Fischer-Tropsch synthesis exceeds quantity possible from secondary reactions. This will then imply a primary reaction pathway for the formation of oxygen containing organic product compounds. It further implies that the reaction and that different pathways are responsible for the formation of hydrocarbons and alcohols during the FT process, possibly alkyl/OH-insertion mechanism etc. Classically, space velocity studies have been used to elucidate reaction pathways in cases of numerous and competing reactions. At very low conversion, the primary reactions are expected to dominate. Hence any product observed at this condition is regarded as primary or a pseudo primary product (in the latter case when the secondary reaction is very fast). This paper presented the results obtained when the space velocity is varied on the FT process products distribution over promoted and unpromoted Fe-based catalysts.

2. Experimental

2.1. Catalyst Preparation

The required amount of $Fe(NO_3)_3.9H_2O$ (Sigma-Aldrich, 98+%); $Al(NO_3)_3.9H_2O$ (SigmaAldrich 99+%) and $Cu(NO_3)_2.3H_2O$ (Kimix, 99%) to give a Fe/Al/Cu ratio of 100gFe/30gAl/5gCu were introduced into a 4L flask and deionized water added. The solution was heated to 90 ^oC over a hot plate fitted with a thermocouple (Heidolph EKT 3001) to control the temperature. The required amounts of boiling ammonium carbonate solution (Merck 34%, 1.5M) for precipitation and to keep the pH at 7.0 ± 0.02, is added to the boiling nitrate

solutions. The mixture is stirred starting at about 1500rpm and increase as the nucleation process proceeded to 2500 rpm with a Ultra-Turrax T25 overhead stirrer. The pH was controlled with a Thermo Orion Bench top pH and pH/IST meter (Model 410Aplus) fitted with a Thermo Orion Ag/AgCl Sure-Flow combination pH electrode. A make-up Cu salt solution was added in drops to keep the pH at the desired value.

The solution is maintained at 90 ^{o}C and stirred vigorously for about 15 minutes to promote the nucleation-precipitation processes. The suspension is filtered and the precipitates washed with boiling distilled water until the filtrate is free of nitrate (confirmed with the brown ring test. The precipitate is subsequently dried in the oven overtime at 110 ^{o}C. Potassium was added via the incipient wetness method. The dried cake is crushed into particles of pre-determined size and an aqueous solution of KNO_3 (Sigma-Aldrich 99+, 1.0M) at the concentration required to obtain a Fe/K atomic ratio of 20 is added. The impregnated slurry was vacuum dried in a rotatory vaporiser (Buchi Rota vapour Model R-205) equipped with a Buchi controller V-800 and a water/oil bath, at variable pressures until dryness. During the nucleation process, some of the Cu added will inevitably be lost as $Cu(NH_3)_4^{2+}$ giving blue colour to the filtrate. This is due to the difficulty in controlling and maintaining the pH at 7 within a narrow band of ± 0.2 resulting in formation of Cu complexes. A specific amount of make-up $Cu(NO_3)_2$ is added to some of the samples using the same method as was done with potassium above.

The resulting oxyhydroxides were calcined in a fluidized bed reactor using Ar (flow rate 60ml/min at NTP) at 350^{o}C for 16 hrs. using a heating rate of 1^{o}C/min. The calcination step involves thermal decomposition, crystallization and re-crystallization processes and some degree of sintering. The step will remove interstitial water in the sample and other volatiles from the solid precursor. The resulting catalyst sample is then sieved to obtain desired particles size. These samples were tested in a fixed bed reactor fitted with an on-line TCD to study the activity in the Fischer-Tropsch synthesis and selectivity of interest

2.2. Catalyst Characterization

Nitrogen chemisorption, SEM-EDX and AAS analyses were employed to obtain the surface area, pore size, the pore volume distribution, particle size, elemental distribution and the elemental composition respectively. The bulk phases present was studied with XRD while the reducibility and the maximum degree of reduction of the metal oxides to the metallic state under the FT condition was studied using the TPR method.

Temperature Programme Reduction - The reduction behaviour of catalyst samples was investigated by means of temperature programmed hydrogen reduction (TPR) with a tubular fixed bed reactor fitted to an online GC (Varian 3000) fitted with a thermal conductivity detector and HP auto-integrator TCD. The required amount of the catalysts powders were first dried in-situ using Argon gas (flow rate 30ml/min NTP) for about 12 hours to 300 ^{o}C at a ramping rate of 10^{o}C/min. The gas flow was then switched to 10% H_2 in Ar at a flow rate of 30 ml/min NTP, and the temperature ramped from 250 to 1000^{o}C with a constant heating rate of 10^{o}C/min.

BET Characterization - The specific surface area, pore volume and pore volume distribution were determined via N_2 adsorption/desorption according to the BET method using a Micromeritrics ASAP 2000 analyzer (Micromeritrics Instruments Corp., USA). BET surface area analysis was used to obtain a rough estimate of the average crystallite size of the catalyst.

XRD Profile - Analyses of metal oxide phases present in the calcined samples as well as average crystallite sizes were determined by means of X-ray analysis. X-ray diffraction measurements were done on a Rigaku Multiflex X-ray diffractometer (Rigaku America Corporation, USA) with Cu-KĮ radiation of wavelength 1.540 ÛA at 40 kV and 20 mA. The scan range was 15^{o} through 85^{o} at a scanning rate of 1 ^{o}C/min. All diffraction patterns were recorded in the continuous scan mode with a sampling with of 0.04 degrees.

Scanning Electron Microscopy/Energy Dispersive X-ray spectroscopy - This was done with a high

resolution conventional scanning electron microscope, Hitachi S-3000N Standard VP-SEM (Hitachi High Technologies, USA) equipped with a four quadrant solid state Back Scatter Electron Detector, BSED and a thermionic electron source. The S-3000N is fitted with an energy dispersive x-ray spectrometer, ISIS 300 EDX microanalysis system which allows a macroscopic investigation of the distribution of the oxides crystallites and to determine the actual amount of the metals in the catalyst. A Denton vacuum desk II cold sputtering unit (Denton Vacuum, USA) fitted with a gold sputter cathode was used to clean the surface of the sample and to deposit an ultra-thin layer of a heavy metal conductive coating (Au in this case).

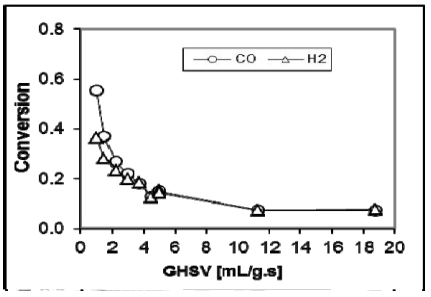
2.3. Reactions

The reactions were conducted in a fixed-bed tubular reactor fitted with an online GC-TCD and an ampoule sampling point (for offline GC-FID analysis) at 20 bars and 240^{o}C. 2g of the catalyst was calcined in argon at 350^{o}C for 16 hrs and subsequently reduced in-situ with hydrogen flowing at 60ml/min (STP) at a temperature of 350^{o}C. The required flow rate of CO and H_2 were supplied to give different SV. A GC-TCD is used to obtain the CO and H_2 conversions and the methane and CO_2 yield. A nitrogen-cyclohexane mixture was used as internal standard for the GC-FID analysis

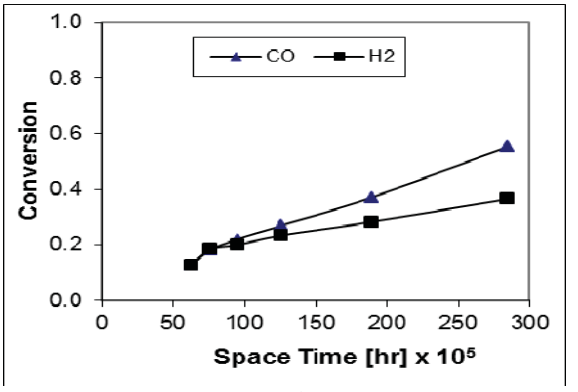
3. Results

The XRD pattern confirmed that the dominant phase in the calcined samples was haematite. No diffraction peaks attributable to a copper or potassium containing phase was observed. This could be due to their relatively small concentration of these elements in the sample (~3wt%). Their weight percent was however confirmed with AAS and EDX studies. It is evident from the TPR spectra that a high degree of reduction (~ 85%) was obtained for the samples reduced at …?.

Products Distribution - A plot of conversion against space velocity (and space time) presented in Fig 1 revealed that the overall CO (and H_2) conversion decreasing as the space velocity increases (or as the space time decreases) as expected. At space velocity greater than 18 mL/g.s, the conversion is deemed sufficiently low enough to make any secondary reactions insignificant. The full products spectrum is then carried out for the samples obtained from SV= 12mL/g.s onwards.



(a)



(b)

Fig. 1. Plot of conversion versus the GHSV and space time

For comparison, the molar per cent of the linear hydrocarbons and alcohols in the FT products were measured and plotted at different SV as shown in Figure 2. Low SV resulted in high synthesis gas conversion. At this condition, the secondary reactions are assumed to be competing with the primary reactions. Figures 2 (a) and (b) represent this point. Figure 2 (c) and (d) are obtained at very high SV and low conversion and hence predominantly primary reactions. It could be seen that the hydrocarbons/oxygenates ratio is more or less constant.

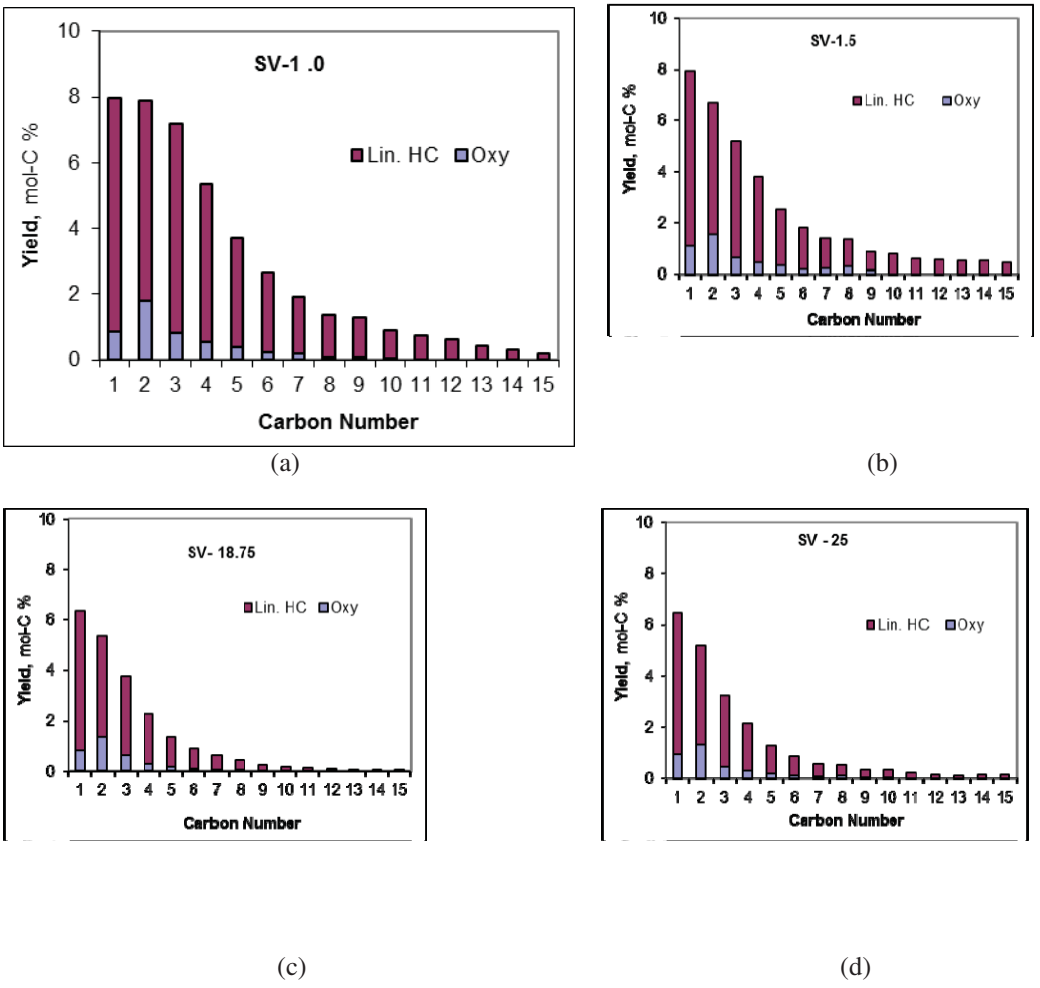


Fig. 2. Linear hydrocarbons and oxygen containing organic product compounds in FT products for different SV (a) 1 mL/g.s (b) 1.5 mL/g.s (c) 18.75 mL/g.s (d) 25 mL/g.s

4. Conclusions

This conclusively proved that oxygenates, and primarily the alcohol compounds are primary products. Hence the postulation that the alkyl mechanism is the sole mechanism during the FT process is wrong. The existence of parallel and separate mechanistic pathway(s) for oxygenates like the CO-insertion or OH-

insertion mechanism is strongly supported by these results.

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