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## Development of a chemical selective iron Fischer Tropsch catalyst

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### ABSTRACT

In the chemical industry C<sub>2</sub>–C<sub>4</sub> olefins are critical building blocks for high value commodity products. One of the key challenges in Fischer Tropsch Synthesis (FTS) technology development is to manipulate process conditions and/or catalytic systems in order to suppress methane selectivity while still producing mainly C<sub>2</sub>–C<sub>4</sub> products with maximum olefin content. Sasol developed an iron catalyst promoted with sodium and sulphur that yielded a fairly high proportion of C<sub>2</sub>–C<sub>4</sub> products with lower than expected methane selectivity. Due to the unexpected low methane selectivity in combination with high olefin selectivity necessitated the evaluation of other promoters similar to sulphur in combination with alkali promoters (i.e. sodium and potassium) in order to understand whether the combination of sulphur and sodium is unique or whether other alkali and non-metal promoters will yield similar results or even improve the selectivity further. By employing high throughput experimentation, a total of 306 catalysts were synthesised and tested in order to identify whether other possible non-metal FTS promoters could either match or improve the selectivities observed for sodium and sulphur and to also identify potential optimum promoter levels for maximum C<sub>2</sub>–C<sub>4</sub> olefin selectivity and minimum methane formation. The results showed that from the series of catalysts evaluated sulphur and sodium yielded the highest olefin selectivity in combination with low methane selectivity and that a mole ratio of at least 2:1 Na:S is required for optimum C<sub>2</sub>–C<sub>4</sub> selectivity. Apart from the statistical analysis of data and subsequent comparison of catalyst selectivity, the catalysts were also evaluated based on the expected Schulz Flory selectivity correlation. For unique catalyst selectivity a significant shift should be observed. In this paper the results of high throughput experimentation are presented and discussed using the direct relations of C<sub>2</sub>–C<sub>4</sub> selectivity and methane selectivity in order to distinguish unique catalyst systems that are selective towards C<sub>2</sub>–C<sub>4</sub> olefin production.

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### 1. Introduction

Iron-catalysed Fischer Tropsch Synthesis (FTS) has been used commercially from the early 1950s by Sasol in South Africa to produce fuel and commodity chemicals such as wax. The advantage of this technology is that the product spectrum can be manipulated either *via* process conditions or choice of catalyst system to yield a range of high value products *e.g.* waxes, liquid hydrocarbon fuels and chemicals *e.g.* olefins and oxygenates. The wide range of products produced by FTS can be advantageous especially if product types and volumes could be manipulated to capitalise on current market demand. Due to recent fluctuations in the oil price the need for flexibility in product selectivity is becoming more critical and could provide opportunities to shift production to higher value

commodities. Ideally, this should be achieved using existing hardware with limited modifications and capital expenditure. Research should thus focus on possible manipulation of the catalyst system and/or process conditions. Sasol uses both low and high temperature iron-based FTS in its operations, with the high temperature process focused on producing liquid fuel and commodity chemicals while the low temperature process produces mainly waxes. Although Sasol has extensive knowledge of maximising chemical production from iron catalysed Fischer Tropsch Synthesis, the main challenge remains producing commodity chemicals such as C<sub>2</sub>–C<sub>4</sub> olefins with minimum methane and paraffin selectivity. In the chemical industry C<sub>2</sub>–C<sub>4</sub> olefins are critical building blocks for high commodity products and one of the key challenges in FTS technology development is to manipulate process conditions and/or catalytic systems in order to suppress methane selectivity while maximising C<sub>2</sub>–C<sub>4</sub> olefin products. The ideal catalyst should also exhibit high activity and allow for high CO conversion rates. The Schulz Flory distribution is a mathematical function that is

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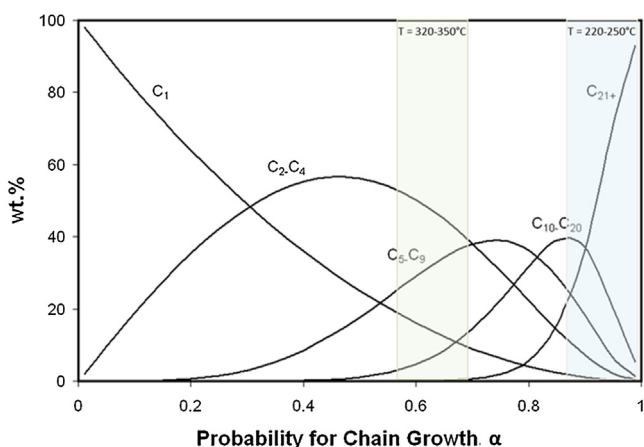


Fig. 1. Influence of  $\alpha$ -value on product distribution. Highlighted areas show the influence of temperature on the selectivity of iron based Fischer Tropsch Synthesis.

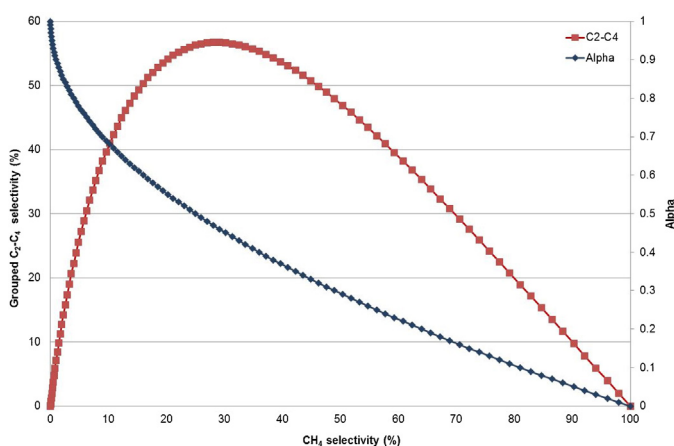


Fig. 2. Fixed relationship between grouped  $C_2$  to  $C_4$  selectivity and methane selectivity as predicted by the ideal Schulz-Flory model.

generally used to describe and/or predict the selectivity profile for various iron FT catalysts. It describes the probability of chain growth on specific catalyst sites. Fig. 1 shows the selectivity of various product fractions as a function of chain growth probability. For low alpha FT catalysts (alpha < 0.5) it is shown that the  $C_2$ – $C_4$  selectivity increases, through a maximum  $C_2$ – $C_4$  weight percent with a concomitant decrease in methane selectivity. As the alpha value increases beyond 0.5 both methane and  $C_2$ – $C_4$  selectivity are inhibited. The product selectivity as described by the Schulz Flory correlation is also responsive to variation of process parameters *i.e.* temperature, pressure and  $H_2/CO$  ratio and predicts product profiles for most known FTS catalysts. For lower temperature iron FTS catalysts alpha values as high as 0.94 is observed yielding mainly wax products.

Based on the Schulz Flory distribution the challenge is to identify a catalytic surface which will both increase hydrogenation rate *i.e.* limit chain growth while limiting paraffin and specifically methane selectivity. From Fig. 1 it can be observed that the higher the temperature, the lower the chain growth probability of the catalyst, but this has a significant impact on the effectiveness of the FTS process *i.e.* high volumes of methane being produced that needs to be recycled back into the system. The current high temperature iron FTS process produces only ~40% of  $C_2$ – $C_4$  products (mainly paraffins) with methane selectivities of ~10–15%. The ideal Schulz Flory correlation of iron FTS catalysts predicts a fixed relationship between methane and the grouped  $C_2$ – $C_4$  selectivity

(Fig. 2). The corresponding alpha values are also presented in this graph. As the probability of chain growth decreases, the methane selectivity increases up to 100% for a catalyst with an alpha value of zero. The grouped  $C_2$ – $C_4$  selectivity goes through a maximum at a corresponding  $C_1$  selectivity of just below 30%. According to this ideal relationship, at a maximum, iron high temperature FT catalysts can yield a grouped  $C_2$ – $C_4$  selectivity of  $\pm 57\%$ , but with the cost of an appreciable methane make. Due to the somewhat higher-than-expected methane selectivity usually observed experimentally, the actual grouped  $C_2$ – $C_4$  selectivity is anticipated to lie below the curve of Fig. 2. That is clearly not an ideal situation from an industrial perspective if the aim is to selectively produce light chemicals and optimisation is required in order to alter the fixed relationship between  $C_2$ – $C_4$  olefins and methane from the standard Schulz Flory distribution.

A recent review by Torres and de Jong highlighted the renewed focus on developing a FT catalyst that yields mainly  $C_2$ – $C_4$  olefins [1]. Primarily iron based catalysts have shown the greatest propensity to produce olefins and therefore have been the basis for most studies focused on producing chemicals from syngas. Several studies in literature focused on developing catalyst systems with optimum  $C_2$ – $C_4$  selectivity while minimising methane selectivity [2–4]. These include combinations of metal oxides/sulfides other than iron and cobalt (molybdenum, platinum, nickel, etc.) with alkali metals [5]. In the field of iron FTS catalysis it was noted that sulphur in combination with promoters such as manganese, phosphorous, etc. could also yield improved  $C_2$ – $C_4$  selectivity [6]. In a study by Van Dijk *et al.* [7] an iron/manganese catalyst containing sulphur showed improved ethylene selectivity at temperatures above 350 °C. However, in spite of the various approaches to obtain an improved yield of short chain products described in literature, the main challenge remains to develop a catalyst that can selectively produce  $C_2$ – $C_4$  olefins, while keeping the methane formation as low as possible. Early work by Bromfield and Coville [8] indicated that the addition of small quantities of sulphide induced a modification of the morphology of the iron oxide catalyst surface resulting in enhanced surface area and porosity and thus yielding higher conversions. In addition to this the sulphide promoted catalysts also yielded a higher percentage of olefins in the product profile. However, the product distribution followed a typical Schulz Flory correlation and did not afford the desired minimum methane selectivity. In this regard Sasol developed an iron FTS catalyst that showed a high propensity towards  $C_2$ – $C_4$  olefins, while simultaneously suppressing excess methane formation, by combining alkali and/or alkaline earth metal promoters with sulphur [9]. The catalyst yielded up to 68% of olefins in the  $C_2$ – $C_4$  fraction with a relatively low methane selectivity of 13% and CO converted to hydrocarbons of 40%. This catalyst showed a high affinity for  $C_2$ – $C_4$  products (~55%) and lower than expected methane selectivity (<15%) and was used as a reference catalyst for further optimisation. Torres Galvis *et al.* [10] confirmed this observed increase in olefin selectivity while evaluating the effect of sodium in combination with sulphur on supported iron FTS catalysts. The group showed that these promoters added to  $Fe/\alpha-Al_2O_3$  catalysts yielded high  $C_2$ – $C_4$  olefin selectivity (~50%), enhanced catalytic activity, and decreased methane production (<20%) relative to  $Fe/\alpha-Al_2O_3$  catalysts not promoted with sodium and sulphur.

The question to be answered was whether the combination of sulphur and sodium was unique in achieving these results or whether other possible promoter combinations could yield even higher olefin selectivities. Due to the potential technology impact of an olefin selective FTS catalyst, Sasol decided to expedite the development *via* high throughput experimentation, which is an enabling technology that allows for the rapid and parallel evaluation of numerous catalyst formulations. The hardware associated with high throughput screening has evolved rapidly over recent

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