Modified product selectivity in Fischer-Tropsch synthesis by catalyst pre-treatment☆

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ABSTRACT

Fischer-Tropsch Synthesis (FTS) yields a spectrum of products with carbon lengths of 1 to upwards of 100 units. In order to make use of the full spectrum of hydrocarbon fractions, particularly the heavier units, secondary processing is required. Modifying the FTS product distribution and catalyst activity in order to decrease the amount of long chain hydrocarbons (C_{25+}) may allow significant simplification of FTS based processes. To this end we report the results of *in-situ* pre-treatment of alumina supported cobalt catalysts (Co/Ru/La – Al_2O_3) with acetylene in a fixed-bed reactor. It is postulated that acetylene dissociation and dehydrogenation resulted in the generation of carbidic and C_xH_y species on the catalyst surface. The formation of these carbonaceous species on different active sites of the catalyst surface following pre-treatment also significantly altered the FTS product distribution by affecting the extent and pathway of 1-olefin secondary reactions. It is thought that these changes resulted from decreased incorporation of 1-olefins in further chain growth and a decrease in secondary hydrogenation rate. The amount of heavy hydrocarbons (waxes) produced was reduced by more than two-fold.

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1. Introduction

The Gas-to-Liquids (GTL) process, for the conversion of natural gas into "drop-in" transport fuels (diesel, gasoline, jet fuels) and other chemicals *via* syngas generation and the Fischer-Tropsch reaction has been known for many decades and provide an alternative for the use and conversion of natural gas reserves, which are vast in many parts of the world. While the products of GTL are more valuable and transportable than the natural gas itself, the lack of product selectivity in the Fischer-Tropsch synthesis (FTS) step, an essential part in the GTL process, adds to the cost and complexity of the overall process, and thus reduces the commercial attractiveness of GTL for utilisation of natural gas. Indeed, waxy hydrocarbons (C_{22+}) require further hydroprocessing and hydrocracking. However, in some locations, such as on offshore oil and gas producing platforms, it is undesirable to locate hydrocracking facilities due to weight, space and economic limitations.

A shift in the selectivity of FTS toward the liquid product end has certain advantages [1], and would simplify the post-FTS processing (*e.g.* cracking) operations. It would also decrease the operating and capital costs of the GTL process, as well as the overall GTL plant footprint. This would also benefit small scale applications of the GTL process, such as floating GTL (*e.g.* floating production, storage and offloading, GTL-FPSO) or small scale GTL in remote locations.

The FTS process yields a wide range of hydrocarbon and oxygenated products, the formation of which is controlled by mechanistic and kinetic factors. It is widely accepted that FTS proceeds *via* a methylene insertion mechanism [2–6]. In this process, methyl monomer (CH_x), produced on the catalyst surface from CO adsorption, dissociation and hydrogenation with H_2, is added stepwise to a growing aliphatic chain to give a wide spectrum of hydrocarbon products (C_1–C_{100+}). These products are generally referred to as syncrude. The growing hydrocarbon chains can be terminated by either β-hydrogen removal, forming 1-olefins, or by hydrogenation to form *n*-paraffins.

The formation of hydrocarbons through a stepwise insertion or addition of CHx intermediates with constant chain growth probability (α) should result in an ideal Anderson–Schulz–Flory (ASF) distribution, as described by Eq. (1). However, for most FTS catalysts, including iron

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and cobalt catalysts, a clear deviations from this ideal distribution is generally observed [2,6].

$$w_n = n(1-\alpha)^2 \cdot \alpha^{n-1} \tag{1}$$

w_n is the weight fraction of the species with carbon number n, and α is the chain growth probability, assumed to be independent of n [2].

1-Olefins formed by primary reactions can re-adsorb on the catalyst surface to form metal alkyl, and undergo further competitive reactions: (1) dehydrogenation to 1-olefins, (2) hydrogenation to produce n-paraffins, (3) hydrogenolysis, and (4) reinsertion to initiate new growing chains to produce larger hydrocarbons, as shown in Fig. 1 [7,8]. Hydrogenation of the 1-olefins into *n*-paraffins of the same carbon number will change the paraffin to olefin ratio. In contrast, secondary re-adsorption and reinsertion of 1-olefins in chain growth will modify the chain growth probability α, resulting in higher hydrocarbons and a deviation from a typical ASF distribution. It will also reverse the original β-dehydrogenation process, decreasing the selectivity to light products [9,10]. Controlling the pathway of secondary reactions thus becomes important for increasing the selectivity for higher liquid hydrocarbons.

A large body of research has shown that catalyst activity and product selectivity is highly sensitive to catalyst parameters such as support, metal type and loading, particle size, preparation method, and degree of reduction (see for example Rytter et al.'s review [11]). In addition to catalyst pre-treatment prior reduction (*e.g.* [12]), catalyst activation (reduction) and gaseous pre-treatment prior to FTS have been studied. The effect of successive reduction-oxidation-reduction (ROR) treatments have been shown to improve Ru-Co catalysts reducibility by increasing the catalyst's surface area and Co dispersion [13], increasing CO conversion and increasing selectivity toward liquid hydrocarbon [11]. In addition to standard H_2 reduction, CO and synthesis gas have also been used for pre-treatment [14–17]. Bukur et al. [17] demonstrated that the presence of CO in the pre-treatment stream favoured the production of higher molecular weight hydrocarbons (C_{5+}). This alos suppressed secondary reactions, due to the formation of metal carbides and the build-up of inactive carbonaceous species on the catalyst surface. Optimisation of reaction conditions [8,18,19], and promoted catalysts [20,21] have also been investigated in an attempt to modify the FTS product distribution and improve the selectivity toward higher molecular weight hydrocarbons.

Addition of CO_2 to the syngas stream has also been shown to have some effect on the product distribution [22–25], generally decreasing the catalyst's activity and selectivity toward C_{5+} hydrocarbons, with a shift to lower molecular weight hydrocarbons. Other materials such as alcohols [4,26,27] and alkenes [10,28,29], especially ethylene [30,31] and acetylene [32–34], have been used as probe molecules, incorporated in the syngas stream, to study the FTS mechanism over cobalt catalysts [35]. It was found that these molecules generally act as chain initiators, and are incorporated in the final products. However, they do not serve as chain propagators. In particular, acetylene used as a probe molecule is more strongly adsorbed on FTS catalysts than light alkenes, making it a more efficient chain initiator at lower temperatures [34,36–38].

Although most of the studies mentioned above focused on increasing liquid hydrocarbon product selectivity (C_{5+}), none of them focused on reducing the amount of very heavy hydrocarbons (waxes; C_{22+}), which require further processing (hydrocracking). Therefore, our research efforts (this paper and previous publications) focus on a way of reducing the amount of waxes produced during the FTS, to reduce costs and improve the attractiveness of the GTL process, especially for small-scale applications (<200bpd). Rather than developing new or modified catalysts to achieve this goal [1], we use a commercial FTS catalyst. The novelty in our approach lies in pre-treating the catalyst *in-situ* prior to FTS, a route that could easily be retrofitted to existing process.

Our previous studies have shown that addition of unsaturated C_2 hydrocarbons to the syngas feed of the FTS resulted in a narrower product distribution, reducing the portion of long chain, waxy hydrocarbons compared to conventional FTS, with a deviation from the ASF distribution [39,40]. In some cases, heavier and gaseous fractions are reduced and fuel range (diesel and gasoline) fractions are increased. Similar results were observed when a cobalt-based FTS catalyst was pre-treated under appropriate conditions with acetylene prior to FTS [41]. According to the authors, carbonaceous species are formed from acetylene during pre-treatment, and deposited on highly active sites responsible for chain growth during the FTS reaction. It is thought that deactivation of highly active polymerization sites by carbonaceous deposits during pre-treatment leads to a smaller extent of chain growth during subsequent FTS, resulting in smaller amounts of heavy hydrocarbons and an increase in middle distillates.

In this paper we studied the effect of catalyst pre-treatment by an unsaturated C_2 hydrocarbon (acetylene) on the product distribution of
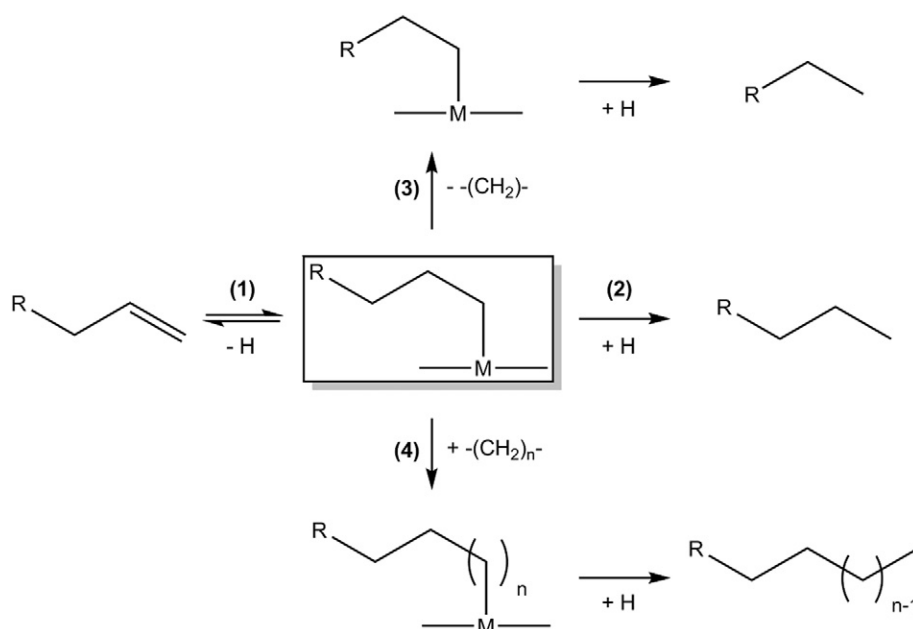

Fig. 1. Secondary reactions of *in-situ* formed 1-olefins: (1) dehydrogenation, (2) hydrogenation to *n*-paraffin, (3) hydrogenolysis, (4) chain growth [8,10].