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Recent development in heavy paraffin synthesis from CO and H_2

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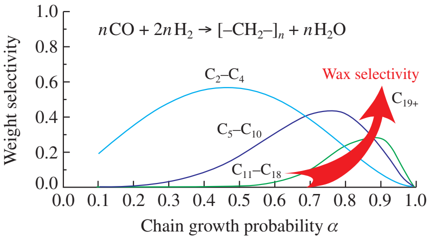
A review of recent studies on the Fischer–Tropsch synthesis of heavy paraffins is presented. The effects of temperature, pressure, feed composition, active metal, promoters and carriers on the formation of heavy products are discussed. New approaches to wax-selective processes such as the application of metallic carriers and supercritical fluids are also described.



Introduction

More than 90 years ago, Franz Fischer and Hans Tropsch discovered the synthesis of higher hydrocarbons from CO and H_2.[1–3] This process referred to as the Fischer–Tropsch synthesis (FTS) attracted more or less attention depending on oil prices and availability in specific regions.[4,5] Nowadays, FTS is mainly regarded as an alternative non-petroleum based route to clean transportation fuels, base oils and chemicals.[6–9] As far as synthesis gas (CO and H_2 mixture) can be readily produced from almost any carbonaceous feedstocks,[10–13] FTS becomes a key part of so-called X-to-liquid (XTL) technologies, where X is G (natural gas),[14] C (carbon)[15] or even B (biomass).[16–18]

The principal FTS reaction is the reductive oligomerization of carbon monoxide:

$$n\mathrm{CO} + 2n\mathrm{H_2} \rightarrow (\mathrm{–CH_2–})_n + n\mathrm{H_2O},\quad \Delta H^{500\,\mathrm{K}} = -165\ \mathrm{kJ\ mol^{-1}} \qquad (1)$$

Products are a mixture of linear paraffins and olefins with a minor amount of branched isomers. Moreover, a number of side reactions occur including the methane formation:

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$$\mathrm{CO + 3H_2 \rightarrow CH_4 + H_2O}, \quad \Delta H^{500\,\mathrm{K}} = -215\ \mathrm{kJ\ mol^{-1}}; \qquad (2)$$

the water gas shift (WGS) reaction:

$$\mathrm{CO + H_2 \rightarrow CO_2 + H_2};$$

and the formation of oxygenates such as alcohols, aldehydes, ketones and carboxylic acids. All these reactions proceed on the surface of solid catalysts such as Ru, Ni, Co or Fe based systems. Ruthenium is considered as the most active catalyst while only cobalt and iron have found commercial application.[19] The FTS products, catalysts, kinetics and proposed reaction mechanisms were described in detail.[3–9,20–28]

Generally, hydrocarbons formed in reaction (1) obey the Anderson–Schultz–Flory (ASF) distribution law:[29]

$$W_n = (1-\alpha)^2 n\alpha^{n-1},$$

where W_n is weight selectivity to C_n hydrocarbon, n is carbon number, and α is so-called chain growth probability postulated according to the formula:

$$\alpha = \frac{k_1}{k_1 + k_2},$$

where k_1 and k_2 are chain propagation and chain termination rate constants, respectively.

Thus, the value of α can vary between 0 and 1: the higher α, the higher the average molecular weight of synthesized hydrocarbons. Methane is usually produced in excess over the value estimated from ASF while C_2 yield is often lower than predicted. Generally, methane selectivity is lower when chain-growth probability becomes higher.

ASF distribution law imposes restriction on the selectivity to particular fractions. Only heavy paraffins (wax) can be obtained with arbitrarily high selectivity provided α value tends to unity. On the contrary, selectivity to gasoline (C_5–C_{10}) and diesel (C_{11}–C_{18}) cuts cannot exceed 44 and 30%, respectively (Figure 1).

Meanwhile, a diesel fraction is the most valuable FTS product possessing a cetane number of about 75 and virtually free from sulfur, nitrogen and aromatics.[28] Selectivity restriction imposed by ASF distribution is an issue in industrial implementation of FTS. Fortunately, there is a way to increase diesel yield greatly by applying a two-step process:

(1) FTS performed under conditions favoring high α value,

(2) mild hydrocracking of heavy FTS products.

At the latter step, wax is catalytically converted into middle distillates (kerosene or diesel fractions) while light fractions remain relatively intact (skeletal isomerization partially occurs). Thus, the higher wax content of FTS syncrude, the higher final middle distillates yield. Practically, a diesel yield may be up to 60%, much more than that ruled by ASF distribution.[30]

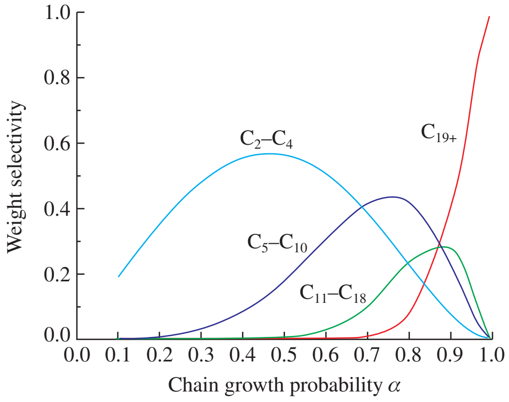

Figure 1 Calculated weight selectivity of hydrocarbon cuts depending on α value.

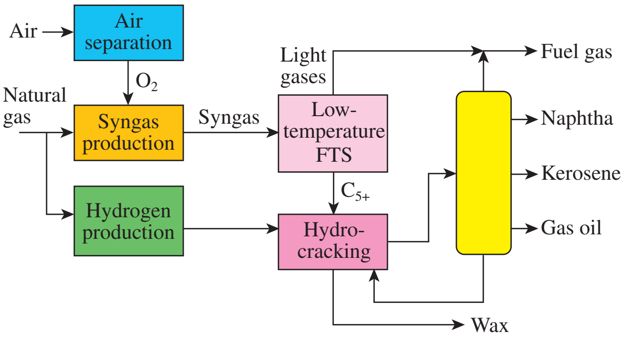

Figure 2 Simplified flow scheme of a Shell GTL plant.

This concept was studied at Sasol in the mid-1970s.[31–33] However, at that time diesel engines were not widespread and the technology was rejected as uneconomical. Later, Shell implemented the same idea at its Bintulu plant (Malasia) commissioned in 1993. Since that, most new GTL facilities are built in accordance with this middle distillates scheme (Figure 2). Shell's Pearl plant in Qatar, Sasol's Oryx GTL in Qatar and Escravos GTL in Nigeria should be mentioned in this context.[4,7] Target products of these facilities are diesel and jet fuel blends. Shell also produces synthetic lubricant base oils *via* hydroisomerization of heavy paraffins (PurePlus technology).

Many variables have an effect on chain growth probability. The most important are temperature and pressure. In general, α value decreases rapidly with temperature and increases with synthesis gas pressure. This is why heavy paraffin synthesis is performed at a relatively low temperature of 190–240 °C and a pressure up to 30–40 bar. Such conditions are referred to as low-temperature Fischer–Tropsch (LTFT). Another important factor is a catalyst. The active metal, promoter(s), support and preconditioning procedure affect the catalyst activity, selectivity and heavy paraffin yield. Other variables such as feed composition, space velocity, and reactor type may also be substantial. In this review, we summarize recent achievements in the elaboration of wax-selective catalysts and processes.

FTS wax

FTS wax is not only feedstock for middle distillates and base oil production but also an important commercial product. Due to the absence of aromatics and sulfur impurities, it is especially suitable for food industry, cosmetics and medicine applications. Wax is also used in the manufacture of glues, paints, candles, rubber, paper and phlegmatizer for explosives.[34–36] The world wax market is relatively small, and it can be easily overwhelmed by few large FTS plants.[14]

Fischer–Tropsch wax can be obtained only in LTFT, when a low reaction temperature allows high α value to be achieved. (On the contrary, high-temperature FTS performed at 300–340 °C over iron-based catalysts does not produce wax but some amount of aromatic heavy ends.[37]) Depending on the process conditions and α value, the upper range of hydrocarbons in wax is generally above C_{60}, but may exceed C_{120}.[37] Wax contains mainly alkanes (95%), smaller amounts of alkenes and oxygenates and neither sulfur nor much aromatics.[38] Distillation is used to separate so-called medium and hard waxes. They may be characterized by congealing point. Various wax grades are produced by Sasol and Shell LTFT facilities (Tables 1, 2).[39,40]

Catalysts

Both iron and cobalt based catalysts are suitable for heavy paraffin synthesis, provided they are working in LTFT conditions. A Shell proprietary cobalt based catalyst possesses high selectivity to heavy hydrocarbons and α value of >0.90.[30] The

Table 1 Properties of the main wax grades originally produced at Sasol-1.[37]

Wax	Carbon range	Average molecular formula	Linear paraffin content (%)	Congealing point/°C	Oil content (wt%)
Sasolwax L1	C_{13}–C_{36}	$C_{23}H_{48}$	84	37	15
Sasolwax M	C_{19}–C_{38}	$C_{28}H_{58}$	96	58	1.4
Sasolwax H1	C_{33+}	$C_{50}H_{102}$	90	98	0.8

Table 2 Properties of the main wax grades produced by Shell at Bintulu plant.[37]

Wax	Congealing point/°C	Oil content (wt%)
SX30	31	5
SX50	50	2.5
SX70	70	0.4
SX100	98	0.1

practically achievable wax selectivity for iron and cobalt based catalysts seems to be very similar, and α values of about 0.94 and 0.95 were reported for cobalt and iron based catalysts, respectively.[41,42] Importantly, for iron based catalysts, pressure variation in a range of 10–40 bar has almost not effect on chain growth probability while cobalt based catalysts are more responsive to pressure variation.[27,42]

The active phase of cobalt based catalysts is metallic cobalt distributed on the surface of a carrier.[25–27] Cobalt is known to crystallize in hexagonal close-packed (hcp) or more stable face-centered cubic (fcc) forms. A number of investigations have focused on comparative activity and selectivity of these two Co^0 phases. Recently,[43] 20% Co-hcp/SiO_2 and 20% Co-fcc/SiO_2 catalysts were prepared using different activation procedures:

– for Co-fcc, reduction in a mixture of H_2:He (1:3) at 623 K for 10 h;

– for Co-hcp, reduction in a mixture of H_2:He (1:3) at 623 K for 10 h; then explosion to pure CO at 503 K for 15 h followed by treatment under H_2 at 503 K for 24 h.

Microstructure of Co^0 in both catalysts was verified by XRD. In line with earlier works, Co-hcp catalysts exhibited much higher CO conversion on a catalyst weight basis compared to Co-fcc. In addition, Co-hcp catalysts produce more heavy hydrocarbons as compared to Co-fcc: selectivity to C_{5+} was 90 and 83%, respectively. XRD analysis of spent catalysts revealed that the individual phases of cobalt (either hcp or fcc) remain stable under LTFT conditions.[43] Higher catalytic activity of the hcp phase of cobalt was demonstrated.[44,45]

Bezemer *et al.*[46] shed light on a strong influence of cobalt crystallite size on intrinsic activity and selectivity of Co/CNF (carbon nanofibers) catalysts. Site-time yield (*i.e.* moles CO converted per mole of surface Co atoms per second) and C_{5+} selectivity decreases drastically when average cobalt particle size decreased below 6–8 nm. Similar regularities were observed for Co/Al_2O_3 catalysts.[47] It was hypothesized that, on small crystallites, the metal domains combining different active sites are not stable or they contain a non-optimum ratio of the different sites.[46]

Selectivity to heavy hydrocarbons generally increases with the average cobalt crystallite size. The latter, in turn, is generally in proportion to cobalt loading.[48–51] However, the volcano-type dependence of C_{5+} selectivity on average cobalt particle size was reported.[52] The highest molar selectivity of 88–90% with respect to the target C_{5+} hydrocarbons was observed for catalysts with a cobalt particle size of 5–9 nm. The same samples demonstrated the lowest methane selectivity (Figure 3). Cobalt particle size, in turn, could be controlled by choosing carrier (alumina or amorphous silica–alumina) with appropriate texture. In particular, carriers with 7–12 nm average pore diameter provide the optimal crystallite size and the highest selectivity to heavy hydrocarbons.[52]

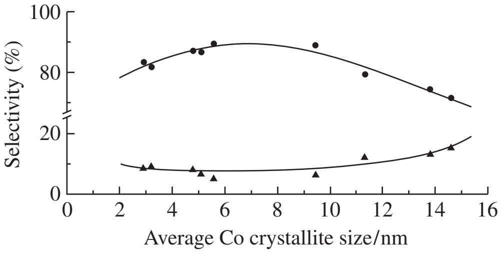

Figure 3 Selectivity to methane and C_{5+} hydrocarbon as a function of cobalt crystallite size.

A monotonic decrease of the chain growth probability with cobalt particle size in a range of 5–150 nm was reported.[53]

Recently, a new class of polymetallic catalysts with high cobalt loading was proposed.[54,55] The catalysts were obtained by leaching complex intermetallic compounds (aluminides) produced by self-propagating high temperature synthesis (SHS):

$$Ox_1 + Ox_2 + \ldots + Al \rightarrow \text{multicomponent intermetallic alloy} + Al_2O_3,$$

where Ox_i is a metal oxide.

The method gives an opportunity to include any metal active in FTS (Fe, Co or Ni) together with a wide variety of promoters (Zr, Ce, La, Mn) in catalyst composition. The structure of catalysts surfaces is complex (Figure 4).

The catalysts were tested in a fixed-bed reactor at a pressure of 20 bar in a temperature range of 160–240 °C at a synthesis gas (CO:H_2, 1:2) flow rate of 2.5 nl g_{cat}^{-1} h^{-1}. Some results are given in Table 3. Best samples possess specific activity close to or even more than that for conventional Co–Re catalyst prepared by an incipient wetness impregnation (IWI) method. However, selectivity to C_{5+} hydrocarbons wax amount in product is much higher for the new catalysts. A chain growth probability up to 0.94 was reached.[54,55] Possible explanation of these results is both high cobalt loading and good thermal conductivity of metal catalyst. Indeed, FTS is a highly exothermic reaction, and

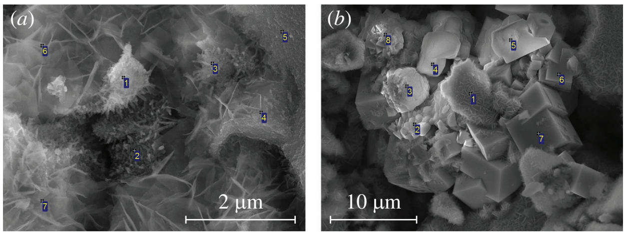

Figure 4 SEM images with electron probing sites of (*a*) Co–Ce and (*b*) Co–Ce–Zr catalysts obtained by SHS.

Table 3 Activity and selectivity characteristics of SHS intermetallide catalysts.[54]

Catalyst	Activity/ μmol_{CO} g_{cat} s^{-1}	Selectivity on a carbon basis (%)			ASF α
		CH_4	C_{5+}	CO_2	
Co	1.29	7.2	92.8	0.0	0.90
50Co-50Ni	2.11	6.7	92.6	0.5	0.91
95Co-5V	1.27	7.1	92.9	0.0	0.92
95Co-5Zr	0.97	7.5	91.8	0.0	0.91
95Co-5Ce	4.64	12.7	73.7	1.1	0.82
95Co-5La	3.37	4.0	93.8	1.1	0.94
90Co-5Ce-5Zr	2.63	12.3	82.0	2.0	0.85
90Co-5La-5Zr	3.24	8.0	87.6	1.4	0.88
20%Co-0.5%Re/Al_2O_3 (conventional catalyst)	3.95	7.0	88.0	1.5	0.83

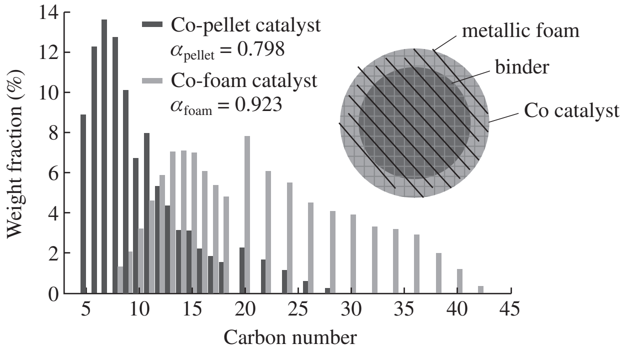

Figure 5 Co-foam catalyst and hydrocarbon product distribution. Reproduced with permission from ref. 56. © 2010 Elsevier.

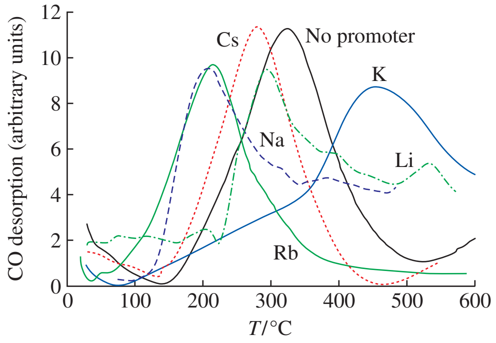

Figure 6 TPD CO spectra of alkali-promoted Co/Al_2O_3 catalysts.

hot spots emerging in a catalyst bed increase methane formation. Therefore, good heat withdrawal gives rise to improvement in C_{5+} selectivity.

Another approach to metal-supported cobalt catalyst was demonstrated by Yang *et al.*[56] They prepared a powdered $Co/\gamma\text{-}Al_2O_3$ catalyst and coated the surface of sphere shaped metallic foam (Ni 75%, Cr 25%) granules with it. For comparison, a pelletized $Co/\gamma\text{-}Al_2O_3$ catalyst was also prepared. The Co-foam catalyst seemed highly selective toward liquid hydrocarbon production. Furthermore, the liquid hydrocarbon productivity and chain length probability α of Co foam were much higher than those of Co pellet (Figure 5). High effectiveness of Co-foam catalyst was attributed to enhanced mass and heat transfer properties from the egg–shell structure and the inner metallic foam, respectively.

High thermal conductivity of silicon carbide foam ceramic was used to prepare a cobalt catalyst selective to heavy hydrocarbons.[57] Chain growth probability obtained on SiC-based catalyst was 0.91, as compared to 0.85 on conventional Co/Al_2O_3. The improvement of the C_{5+} selectivity was attributed to the high efficiency of the support to evacuate heat generated during the course of reactions (1) and (2) and also to the presence of meso- and macro-porosity of the support. An additional catalytic test conducted on a hybrid support, *i.e.* alumina-coated SiC foam, confirmed the high C_{5+} selectivity.

Hexagonal mesoporous silica (HMS) was claimed as a suitable support material for cobalt catalysts to produce long chain hydrocarbons.[58] Supposedly, the high yield is conditioned by uniform mesopore characteristics of the support. A positive effect of MnO additives, apparently caused by the fact that MnO segregates partially the active Co sites and prevents the formation of methane, was also revealed.

Other mesoporous materials, MCM-41 and SBA-15, were used for the preparation of cobalt and iron FTS catalyst.[59,60] Very high α value of 0.92–0.93 was reported for Co/SBA-15 catalyst at a reaction temperature of 503 K. Interestingly, iron analogue Fe/SBA-15 gave α of only 0.84 under the same conditions.

The effect of the pore structure of silica–alumina (AS-37) on the catalytic performance of 19% Co/AS-37 has been studied.[61] It was found that the reaction rate and selectivity to C_{5+} hydrocarbons are strongly affected by diffusion factors. However, their influence is ambiguous. The acceleration of reactant transport with an increase in pore diameter hinders the readsorption of olefins and diminishes the performance with respect to high-molecular-weight products. The latter is confirmed by the increased olefin content of products synthesized on catalysts with a high degree of transformation of the pore structure and, accordingly, with large pore diameter.[61]

A promoter is an important part of cobalt and, especially, iron catalysts.[19,26,27] Perhaps, the strongest influence on heavy products selectivity is exerted by alkali promoters. They are usually introduced in a nitrate or carbonate form. Potassium is a well-known promoter for iron catalysts.[19] Chain growth probability ranges from 0.72 to 0.95 depending on less or more potassium content in iron catalyst. An analogous effect was found for cobalt catalyst.[27] Unfortunately, for cobalt catalysts, improved selectivity to heavy products is usually accompanied by decrease in activity.[27] For iron ones, the effect of alkali on activity is controversial.[62] Alkali additives were reported to enhance the catalytic activity due to facilitating CO dissociation for the formation of iron carbide (considered to be active phase in FTS) by electron donation.[63]

Both deposition order and potassium precursor nature affect the activity and selectivity of Fe–K/AC catalyst. Iron-time yield in FT synthesis is higher for catalysts with a preliminarily alkalized carrier, likely due to their higher active surface. The highest α value of 0.90 was reached when potassium was introduced in the form of K_2CO_3.[62]

For alkali-promoted Co/Al_2O_3 catalyst, nature of alkali (Li, Na, K, Rb or Cs) greatly affects the CO adsorption strength, based on TPD CO data (Figure 6). The most amount of strongly bonded CO is observed on potassium-promoted catalyst. This sample also demonstrated the highest selectivity to C_{5+} hydrocarbons (92%) and the highest α value (0.91) among the catalysts promoted by various alkali metals.[64]

Alkali-earth metals exert a similar promoting effect on the formation of heavy products.[65,66] Adding calcium to a Co/Al_2O_3 catalyst was reported to enhance C_{5+} selectivity.[65] For $Co\text{-}M/Al_2O_3$ catalysts (M = Mg, Ca, Ba), selectivity to C_{5+} increases in the order Mg < Ca < Ba and selectivity to CH_4 decreases in the same order.[66]

Adding Al_2O_3 to Co/SiO_2 provides high yield of heavy hydrocarbons.[67–69] The largest promotion effect was observed for the catalysts with 1 wt% of alumina loading. The modification of the catalyst with alumina (1 wt%) changes molecular weight distribution of the resultant C_{5+} paraffins with increasing the fraction of C_8–C_{25} and decreasing the fraction of longer chain hydrocarbons.[67]

The addition of Re leads to significant improvements in cobalt-time yield and C_{5+} selectivity of Co/TiO_2. Rhenium was found the best promoter as compared to Ag, Pt and Ru.[70]

Recently,[71] combustion synthesized cobalt catalysts were reported. A redox reaction between $Co(NO_3)_2$ and hexamethylenetetramine was performed in the pores of a carrier (alumina or silica–alumina) to afford cobalt oxide:

$$27\,Co(NO_3)_2 + 7\,C_6H_{12}N_4 \rightarrow 9\,Co_3O_4 + 41\,N_2 + 42\,H_2O + 42\,CO_2.$$

The catalysts thus prepared were activated in an H_2 flow at an unusually high temperature of 927 °C followed by testing in FTS at 230°C and 30 bar. Reportedly, α value of these catalysts reached 0.96 and was higher than that of the samples prepared for comparison by a conventional IWI procedure. Therefore, this new preparation method may be suitable for wax production.

Process variables

The total pressure of synthesis gas is known to provide a positive impact on heavy hydrocarbon selectivity. Conversely, temperature increase normally shifts the product slate lo lighter products.[72,73] However, recently,[74,75] an unexpected increase in C_{5+} selectivity over a Co-Al_2O_3/SiO_2 catalyst with temperature was revealed. Whereas at a moderate pressure (20 bar), the catalyst response to temperature was typical of FTS, *i.e.*, an increase in activity concurrent with a decrease of C_{5+} selectivity, the C_{5+} selectivity at a high pressure grew up in parallel with reaction temperature and catalyst activity (Figure 7). Selectivity to C_{35+} hydrocarbons was an order of magnitude greater in FTS at 60 bar compared to 20 bar. At a temperature of 205°C and a synthesis gas pressure of 60 bar, the chain growth probability reached 0.96.[75] This was explained by a known positive effect of water (formed in FTS) on heavy hydrocarbon selectivity.[76,77]

Wax yield depends on gas hourly space velocity (GHSV). Productivity to C_{35+} hydrocarbons was found to increase profoundly when GHSV was decreased from 200 to 60 h^{-1}. A less pronounced effect of GHSV on wax formation was revealed in a range of 200–300 h^{-1}.[78]

Decreasing H_2/CO ratio in feed synthesis gas leads to an increase in C_{5+} selectivity.[65,79] Such a gas with low hydrogen content is usually formed in high-temperature coal and biomass gasification processes. Selectivity of Co-Re/Al_2O_3 catalyst to C_{5+} hydrocarbons increased from 80 to 87% when the H_2/CO ratio was reduced from 2.1 to 1.0. Lower H_2/CO ratios decreased CH_4 selectivity and raised the olefin/paraffin ratio in synthesized hydrocarbons.[79] For alumina-promoted Co/SiO_2 at a synthesis gas pressure of 20 bar and a GHSV of 1000 h^{-1}, a change in H_2/CO from 2 to 1 twice increased C_{35+} yield, and α reached 0.93.[74] These effects of H_2/CO ratio should be attributed to higher CO concentration on catalyst surface, which favors chain growth and restrains hydrogenation reactions.

Water promotes hydrocarbon chain growth.[76,77,80] As far as water is the product of FTS, increasing CO conversion (by varying synthesis gas space velocity rather than temperature or pressure) leads to an increase in C_{5+} selectivity.[81] Adding water vapor in the feed gas markedly enhances wax selectivity.[82] Moreover, a substantial deviation of hydrocarbon weight distribution from an ASF pattern was reported. These effects of water were explained by suppressing secondary hydrogenation of 1-olefins and facilitating their readsorption and chain growth.[82]

Transport limitations of synthesis gas and, especially, products affect FTS selectivity and wax formation.[72,83] The formation of C_5–C_{60} and C_{60+} hydrocarbons proceeds in the external and internal diffusion regions, respectively, over a cobalt catalyst with a particle size of 3–4 mm. It was presumed that the selectivity of the process can be controlled by regulating the distribution of the pore radii of carrier particles.[84]

Performing FTS in supercritical media is known to affect catalyst activity and selectivity (Figure 8).[85] According to many reports, the overall product distribution shifts towards heavier products in comparison with those under conventional (gas phase) conditions.[86–91]

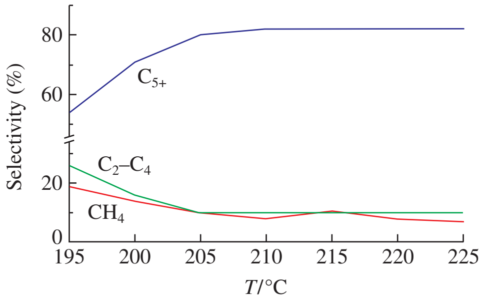

Figure 7 Effect of temperature on FTS selectivity of Co-Al_2O_3/SiO_2 at P = 60 bar.

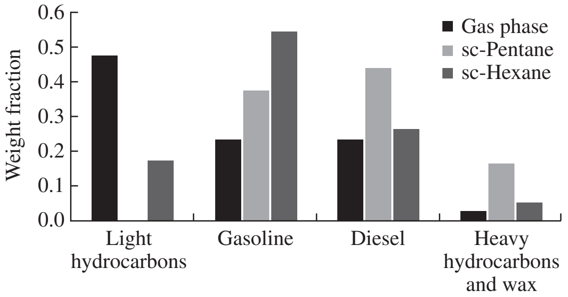

Figure 8 Hydrocarbon distributions in gas phase, supercritical hexane and supercritical pentane media. Reproduced with permission from ref. 85. © 2009 Elsevier.

Yokota and Fujimoto[86] compared FTS in a gas phase, supercritical hexane (T_C = 470 K, P_C = 30.2 bar) and a liquid phase over a Co/SiO_2 catalyst. They found that the carbon number of products under the supercritical conditions was extended to higher values compared with other reaction phases. In the liquid phase, the heaviest hydrocarbon produced was C_{26}, but in sc-hexane the carbon number went up to C_{40}.

By performing FTS in sc-pentane (T_C = 470 K, P_C = 33.3 bar), waxy hydrocarbon formation rate was significantly increased while light hydrocarbon formation was suppressed.[88] Namely, the selectivity to C_{20}–C_{45} cut over 29% Co/SiO_2 at 473 K in sc-pentane was of 55.8% while it was 38% over the same catalyst in a gas-phase reaction (N_2). The calculated chain growth probability was as high as 0.96 in sc-pentane. Selectivity to methane was 3 and 7% for supercritical and gas-phase conditions, respectively. Notably, CO conversion was approximately the same in both cases. These finding was attributed to improved heat and mass transfer in supercritical media. Supercritical fluids can enhance thermal conductivity leading to improved heat transfer. Local overheating in the catalyst bed is eliminated thus decreasing methane formation and increasing selectivity to heavy products. Reverse dependence of wax selectivity on the catalyst activity was also revealed.[88]

In supercritical media, the effective H_2/CO ratio on catalyst surface can decrease thus leading to lower methane selectivity and higher chain propagation rate. Moreover, according to an olefin readsorption model,[83] extraction of wax from the catalyst pores by supercritical fluid liberates active sites for re-adsorption and enhanced chain growth. Moreover, the lower diffusivity of olefins in the condensed heavy hydrocarbons inside the catalyst pores of GP-FTS brings about longer residence times for α-olefins on the active sites. This increase in residence time can lead to hydrogenation and isomerization reactions, which lower α value in the gas phase FTS comparatively to sc-FTS.[85]

Effect of the dilution of synthesis gas with nitrogen on FTS has been studied extensively.[92–96] Such a nitrogen-rich gas (about 50 vol% of N_2) arises when air is used as an oxidant instead of pure oxygen in synthesis gas manufacture. Using air eliminates the need in air separation facility and, therefore, reduces the capital costs of FTS plants. Although nitrogen is chemically inert under FTS conditions, its presence in the feed improves heat and mass transfer in the catalyst bed and affects process indexes. In particular, methane selectivity decreases and C_{5+} selectivity increases.[95,97] Dilution of synthesis gas with nitrogen improves selectivity to C_{5+} and C_{35+} fractions and suppresses the formation of gaseous hydrocarbons.[97] These effects can be explained by improving heat withdrawal from the reaction zone and decreasing temperature gradient across the catalyst bed. A loss of process efficiency upon the dilution of synthesis gas can be partly compensated by increasing gas space velocity.[97]

Conclusions

Selectivity to heavy paraffins is a key property of modern FTS implemented in XTL processes. Heavy paraffins (wax) synthesized from CO and H_2 over iron or cobalt catalysts are sent to mild hydrocracking yielding high quality diesel and kerosene blends. Hydroisomerization of heavy paraffins gives synthetic lubricant base oils. Due to its high paraffinicity and the absence of aromatics and nitrogen- and sulfur-containing impurities, synthetic wax is also valuable feed for food industry, cosmetics and medicine. Other applications include the manufacture of glues, paints, candles, rubber, paper and explosives.

Significant progress has been achieved in heavy paraffin synthesis from CO and H_2 in the last decade. Modern catalysts provide a chain growth probability value of 0.90–0.96, which means wax selectivity of 60% or higher. Both iron and cobalt are suitable for the synthesis of heavy paraffins in low-temperature FTS. Note that the metal crystallite size for cobalt catalysts should be controlled to obtain high specific activity and selectivity of the catalyst. Temperature and pressure are principal variables regulating chain growth probability and selectivity. Moreover, wax formation may be essentially improved by the use of special promoters such as alkali and alkali earth metals and rhenium. Fast removal of reaction heat is also important. For this, special carriers with high thermal conductivity (some metals and silicon carbide) have been proposed. Performing FTS in supercritical media and using nitrogen-rich synthesis gas may also be beneficial for heavy product formation.

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