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RECENT TECHNOLOGICAL DEVELOPMENTS IN FISCHER-TROPSCH CATALYSIS

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Fischer-Tropsch Synthesis is a promising, long-term, option for environmentally sound production of chemicals and fuels from coal. This paper focuses on catalyst and process developments which have occurred in the past decade. It features three important areas of FT catalysis: chemical modifications (additives, promoters, supports, pretreatments, and preparation methods), interception of intermediates (dual functionalism and secondary reactions), and limitation of chain growth by shape selectivity. Fundamental principles of catalyst design are emphasized. Conventional FT catalyst/process technology suffers from the following limitations: (1) limited selectivity for premium products (e.g. olefins, gasoline, and diesel fuel), (2) catalyst deactivation, (3) high capital cost, (4) heat removal, and (5) less than optimum thermal efficiency. Significant progress toward the solution of deactivation, heat removal, and thermal efficiency problems has been realized in the past two decades; with these innovations improvements in process economics of 30–40% are realizable. Of perhaps even greater significance is the progress made during the same period in the understanding of the relationship of catalyst structure to activity and selectivity properties which provides a scientific basis for catalyst design. Some of the key recent improvements in FT catalyst, reactor and process technology which could significantly impact the efficiency and economical production of fuels and chemicals from coal and natural gas are summarized.

1. Introduction

Fischer-Tropsch Synthesis (FTS), the production of liquid hydrocarbons from synthesis gas (CO and H_2) is a promising, developing option for environmentally sound production of chemicals and fuels from coal. In view of large coal reserves and dwindling petroleum reserves it is projected to play an ever increasing role in coming decades.

Cobalt, iron and nickel catalysts for FTS were first developed in the early 1900's [1–3]. Much of the early catalyst development took place in Germany during the 1930's and 40's; after World War II, developments in Germany and in the U.S. led to the commissioning of the Sasol Plant in South Africa in 1955 which following plant expansions in the 1980's remains the only large scale commercial operation. Renewed activity in the development of FTS catalysts was stimulated in the 70's and 80's by perceived shortages of liquid petroleum. Early developments of FT catalysts and processes have been reviewed by Dry [4] and Anderson [5]; the details of these developments can be found in early reviews referenced in Chapter 1 of Anderson's book on the FTS [5].

These early developments will not be treated here; rather this paper will focus on catalyst and process developments which have occurred during the 70's and 80's with emphasis on examples of recent catalyst developments during the late 1980's. The discussion of catalyst developments will focus on three important areas of FT catalysis: chemical modifications (additives, promoters, supports, pretreatments, and preparation methods), interception of intermediates (dual functionalism and secondary reactions), and limitation of chain growth by shape selectivity. Fundamental principles of catalyst design will also be emphasized.

Many important aspects of the recent developments in FT synthesis are treated in a new book entitled "New Trends in CO Activation" edited by L. Guczi [1]. This paper is a highly condensed treatment of FT technology covered in substantially greater detail in Chapter 5 of that book [2]; that chapter includes references to 225 relatively recent papers, reviews, and patents. Since other chapters in this book [1] treat support and promoter effects (Chapter 4), bimetallics (Chapter 6), alcohol synthesis (Chapter 7), zeolites (Chapter 8), and processing for producing chemicals (Chapter 11), coverage of these topics here will be very brief or nil. Several previous reviews and books have provided perspectives on catalyst and process technologies for the Fischer-Tropsch Synthesis [8–17]. The most recent of these by Mills [17] provides an informative overview of present catalyst/process technology and future directions for indirect coal liquefaction; Mill's review [17] also treats the production of oxygenate fuels, the methanol to gasoline process [18], and the high temperature isosynthesis [19], subjects that are not treated in this paper.

Present FT catalyst/process technology suffers from the following limitations: (1) limited selectivity for premium products (e.g. light olefins, gasoline, or diesel fuel), (2) catalyst deactivation, (3) high capital cost [17], (4) heat removal, and (5) less than optimum thermal efficiency [17].

Selectivity limitations are inherent in the chain growth mechanism for FT synthesis which is governed by Anderson-Shulz-Flory (ASF) kinetics [5,9]. While product molecular weight can be varied by choosing process conditions and/or catalyst to achieve a given degree of polymerization, a wide distribution of products other than methane is inherent, as shown in fig. 1. For example, the maximum obtainable weight percentage of light LPG hydrocarbons (C_2-C_4) is 56%, of gasoline (C_5-C_{11}) is 47%, and of diesel fuel (C_{12}-C_{17}) is 40%. Most attempts to circumvent the selectivity limitations of ASF kinetics have met with failure [9]. Nevertheless, there are new approaches [9] involving (1) shape selective supports, (2) unsteady-state operation, and (3) interception of intermediates which show promise for improving selectivity beyond that predicted by ASF theory. Moreover, the design of catalysts and multistep processes which maximize

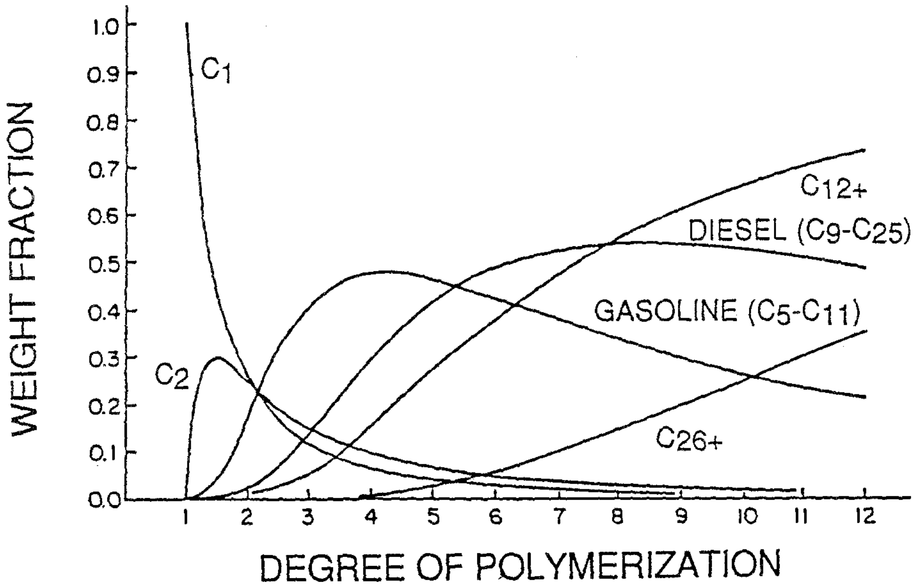

Fig. 1. Selectivity limitations on Fischer-Tropsch synthesis as determined by the Anderson-Schulz-Flory distribution function.

production of light olefins, gasoline, or diesel fuel within the constraints of ASF kinetics has advanced considerably in the past decade.

Significant progress toward the solution of deactivation, heat removal, and thermal efficiency problems has also been realized in the past two decades. With these innovations improvements in process economics of 30–40% are realizable [17]. Of equal or perhaps even greater significance is the progress made during the same period in the understanding of the relationship of catalyst structure to activity and selectivity properties; this understanding provides a scientific basis for catalyst design, some principles of which will be summarized in this short paper.

2. Background

A brief review of some basic definitions and principles relating to the FT synthesis is appropriate here in providing a foundation for the ensuing discussion.

The chemistry of methanation and Fischer-Tropsch (FT) synthesis processes can be described by the following set of reactions:

$$CO + 3H_2 = CH_4 + H_2O \quad (1)$$

$$CO + 2H_2 = \text{-}CH_2\text{-} + H_2O \quad (2)$$

$$CO + H_2O = CO_2 + H_2 \quad (3)$$

$$2CO = C + CO_2. \quad (4)$$

Reaction 1 is the formation of methane, Reaction 2 the synthesis of hydrocarbons heavier than methane, Reaction 3 the water-gas-shift reaction, and Reaction 4 the Boudouard reaction resulting in deposition of carbon. Generally, Ni catalysts are very active for Reaction 1 relative to Reaction 2 and hence most selective for methane relative to Co, Fe, and Ru catalysts; under typical synthesis conditions (e.g. 180–250 ° C, $H_2/CO = 2$) the latter three catalyst types promote Reaction 2 relative to Reaction 1 and are more selective for C_{2+} hydrocarbons. However, the selectivity for C_{2+} hydrocarbons is strongly influenced by reaction conditions and catalyst composition. For example, C_{2+} hydrocarbon make decreases while methane make increases with increasing H_2/CO ratio, increasing reaction temperature, and decreasing pressure.

In Fischer-Tropsch synthesis hydrocarbon product selectivities are determined by the ability of a catalyst to catalyze chain propagation versus chain termination steps. The distribution of hydrocarbon products in Fischer-Tropsch synthesis is general described by a chain polymerization kinetics model ascribed to Anderson, Schulz, and Flory [5,7] henceforth referred to as the Anderson-Schulz-Flory (ASF) model. The ASF product distribution is mathematically represented by the following equation:

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

where n is the number of carbon atoms in the product, W_n is the weight fraction of product containing n carbon atoms, α is the chain growth probability. Generally the value of α is obtained by a least-squares linear regression of the logarithmic form of eq. (16), the slope and intercept yielding α:

$$\ln(W_n/n) = \ln(1-\alpha)^2 + (n-1)\ln\alpha. \tag{2}$$

Values of α are influenced by reaction conditions and catalyst composition. For example, values of α increase with decreasing H_2/CO ratio, decreasing reaction temperature, and increasing pressure. Values of α are higher for Ru and Co catalysts relative to Fe catalysts (see table 1).

Discussion of the effects of promoters, supports, additives, pretreatments and preparation is only meaningful in the context of baseline catalytic properties in the absence of these effects. Table 1 compares the activity and selectivity properties of representative, unpromoted Co, Fe, and Ru catalysts at 480 K, 1 atm, $H_2/CO = 2$ and low CO conversions (1–10%) such that heat/mass transport processes did not influence the measured rate; these data were obtained for catalysts of high metal loading and low dispersion so that effects of support and dispersion were minimized; both Co and Ru catalysts were prepared by wet aqueous impregnation of the metal salts. The data for the Co and Fe catalysts [20,21] were obtained after 20–30 hours of reaction and hence represent steady-state activity/selectivity data; while those for Ru [22] were obtained after only 20 minutes, but the activity and selectivity data are in good agreement with those obtained under similar conditions but after 20 hours of reaction for a 3%

Table 1
CO hydrogenation activities and propagation probabilities of representative unpromoted Co, Fe and Ru synthesis catalysts at 480 K ($H_2/CO = 2$, 1 atm)

Catalyst	$N_{CO} \times 10^3$ [a] (s^{-1})	%CO_2 in Prod [b]	% Olefin C_2-C_7 [c]	α [d]	Ref.
15% Co/Al_2O_3	17	1	54	0.90	[20]
Unsupported Fe	1.4	31	94	0.44	[21]
11% Ru/Al_2O_3	1.8	–	88	0.69	[22]
3% Ru/Al_2O_3	1.5	4	65	0.70	[23]

[a] Turnover frequency in molecules of CO converted per catalytic site per second.
[b] Mole percentage of CO_2 in product (excluding unconverted reactants).
[c] Mole percentage of olefins in C_3-C_7 product.
[d] Propagation probability determined from the slope of a mole % hydrocarbon versus carbon number plot.

Ru/alumina catalyst of comparable dispersion prepared by carbonyl decomposition [23].

The data in table 1 show in accordance with previous experience [5,16] that Co is significantly more active than Fe or Ru; Co and Ru catalysts produce heavier products consistent with the larger values of α of 0.90 and 0.70 relative to that of 0.44 for unsupported, unpromoted iron. In line with its higher activity for the water-gas-shift reaction, iron rejects as significant fraction of the oxygen in the form of CO_2 rather than H_2O; accordingly iron catalysts can be operated at significantly lower H_2/CO ratios, e.g. 0.6–1.0 [17], compared to values of 2 for Co and Ru catalysts without significant deactivation due to carbon formation due to Reaction 4.

3. Fundamental design principles

The rates of production of hydrocarbons and product selectivity in FT synthesis can be controlled in large degree by careful choices of (1) catalyst properties (chemical and physical), (2) process conditions (temperature, pressure, reactant concentrations, and space velocity), (3) reactor design, and (4) process design. The fundamental chemical levers to affect selectivity are (1) chemical modifications of the catalyst (additives, promoters, supports, pretreatments, and preparation methods) and (2) interception of intermediates (dual functionalism and secondary reactions).

Some of the *important design principles* include the following:

1. FT technology suffers from limitations in regard to (1) product selectivity, (2) high capital cost, (3) heat removal, (4) thermal efficiency, and (5) catalyst deactivation. The extent to which a given FT process is affected by these limitations depends on catalyst, reactor, and process design.

2. Hydrocarbon selectivity in steady-state FT synthesis is generally governed by Anderson-Schulz-Flory (ASF) polymerization kinetics which limit the production of premium products by carbon number; accordingly the maximum obtainable weight percentages of C_2-C_4 hydrocarbons, gasoline, and diesel products are 56, 47 and 40% respectively. However, it is possible to obtain up to 70% waxes operating at a polymerization probability of 0.95. Attempts to circumvent ASF statistics by means of promoters, interacting supports, high metal dispersions, and shape-selective supports have generally met with failure.

3. It is possible to achieve the maximum yield of a given hydrocarbon product within the constraints of ASF kinetics, for example, nearly 100% olefin yields in the C_2-C_4 range, about 70% waxes at $\alpha = 0.95$ and a large fraction of branched products by (1) careful design of the catalyst through promoters, supports, gaseous additives, interstitial compounds, and bimetallics and (2) careful choice of reaction conditions, i.e. temperature, pressure, and H_2/CO ratio. Additives such as promoters, supports, interstitial additives, and alloying metals are thought to change the chemistry of the reaction by changing the localized chemical/electronic structure of the active metals. For example, basic promoters such as K and Mn oxides favor production of olefins probably due to their presence on the metal or carbide surface where they locally promote CO dissociation while inhibiting hydrogen adsorption and thus hydrogenation to paraffins; at the same time they lower methane production by neutralizing acidic sites on the support which would otherwise crack hydrocarbon intermediates to methane.

4. It is possible to circumvent ASF-predicted hydrocarbon yields through the use of zeolites and other promoters/supports which intercept reaction intermediates and convert them via hydrocracking, isomerization, oligomerization and/or hydrogenation to lighter, branched, heavier, or saturated products. It is also possible to cut off the heavier hydrocarbons of the predicted distribution by transient selective adsorption on the support over short periods of operation; the ASF distribution can also be sharpened by introducing olefins into the feed.

5. Variations in pretreatment, preparation, and reaction conditions enable almost infinite variations in the composition/structure of Group VIII metal catalysts; this is especially true of iron catalysts, for which bulk compositions can range from carbides to oxides and mixtures in between. These unique compositional/structural properties, when fixed by a unique choice of these preparation/operational variables, determine in turn the catalyst's unique activity and selectivity properties.

6. While metal loading, extent of reduction to the metal, extent of carbiding in the case of iron, and coverage of the surface with promoter or support species are important structural parameters which affect activity and selectivity in FTS, there is strong evidence that variations in surface metal structure and dispersion (at constant extent of reduction) have no effect on activity or selectivity; in other words, CO hydrogenation on Group VIII metals is probably not structure-sensitive.

7. In bifunctional metal/zeolite FT catalysts, there are trends of increasing methane and isobutane selectivities and decreasing olefin/paraffin ratio with increasing zeolite acidity as a result of increasing activity for hydrocracking, isomerization, and hydrogenation reactions on the zeolite.

8. There are basically three reactor types used in FT synthesis: fixed, fluidized, and slurry beds. The choice of reactor depends upon its (1) throughput, (2) capital and operating costs, (3) thermal efficiency, (4) heat removal, (5) product selectivity, (6) operational flexibility, (7) catalyst activity maintenance/easy of regeneration, and (8) reactor ideality/stability. Fluidized beds currently lead in system throughput per unit volume of reactor while both fluidized and slurry bed reactors are highly selective for high octane gasoline products. The fixed bed has a high throughput, the best operational flexibility, and is most selective for diesel and waxy hydrocarbons. The slurry bed, while having the lowest system throughput, involves the lowest capital and operating costs, the highest thermal efficiency and a capacity to operate at low H_2/CO ratio with minimum activity loss due to carbon formation. Overall, the slurry reactor appears to be the most efficient, economical system for production of light olefins and gasoline and the best match for syngas from advanced gasifiers.

9. Although FT synthesis cannot achieve in one step greater than 40–50% selectivity for a given premium product such as light olefins, gasoline, or diesel fuel, it is now possible through a combination of two or three reaction/separation stages to achieve selectivities on the order of 70–90% for almost any desired product.

4. Conclusions and recommendations

ASSESSMENT OF CURRENT TECHNOLOGY AND CONCLUSIONS

This paper briefly summarizes representative Fischer-Tropsch catalyst, reactor and process developments of the past decade with an emphasis on design principles. It is evident from the work reviewed in detail elsewhere [2] that significant progress has been made in both understanding and the application of this understanding to the development of more efficient catalyst and process technologies.

Some of the *key recent improvements in FT catalyst, reactor and process technology* which could significantly impact the efficiency and economical production of fuels and chemicals from coal and natural gas include:

1. *Catalysts*

a. Improvements in Fe/Mn catalysts prepared from mixed oxides, spinels and carbonyls and promoted with Ce, for highly-selective production of olefins and low methane production [24–29].

b. Co and Ru catalysts promoted with Zr, Ti or Cr for production of waxes which in turn can be cracked to diesel fuel and olefins [30].

c. Co/TiO_2 catalysts promoted with lanthanides [31,32] having improved thermal stability towards regeneration and a Co-Ru/TiO_2 catalyst [33] which can be regenerated in situ, both having high activities and selectivities for premium transportation fuels.

d. High activity and olefin-selective $Fe_2O_3C_x$ catalysts [34].

e. Co borides of high activity and high sulfur resistance [35].

f. More sophisticated preparation techniques involving, for example, non-aqueous impregnations [36–39], controlled-pH precipitations [40–46], and decomposition of metal carbonyl on dehydrated supports to produce highly-dispersed, highly-reduced, contaminantfree supported metals [23,47–64].

g. Bifunctional or mixed metal/zeolite catalysts which due to interception of intermediates produce aromatics and gasoline in yields higher than predicted by ASF theory [65–73].

2. *Reactor developments*

a. Recent investigations of fixed-fluidized-bed reactors indicating likely improvements in performance over the early Brownsville reactor and the circulating Synthol reactor [74,75].

b. Recent studies of slurry-bed reactors providing new, fundamental understanding of principles that can be used in optimizing their performance [76–93].

3. *Process developments*

a. Conceptual and experimentally-tested two-step processes for highly-selective production of diesel fuel [74a,94].

Table 2
Summary of some technology options for production by FTS of premium products

Premium product	Catalysts	Reactors	Processes
C_2-C_4 olefins	Fe/K, Fe/Mn, Fe/Mn/Ce Fe/K/S, Ru/TiO_2, $Fe_2O_3C_x$ Fe/C, Mo/C	Slurry, fluid-bed	Synthol, Koelbel, Rheinpreussen-Koppers DowLPG
Gasoline	fused Fe/K	Fluid-bed	Synthol
	Co/ThO_2/Al_2O_3/Silicalite,	Fixed-bed	Gulf-Badger
	Fe/K/ZSM-5, Co/ZSM-5, Ru/ZSM-5	Slurry/fixed-bed	Mobil One-Stage
	Fe/Cu/K and ZSM-5		Mobil Two-Stage
Diesel fuel	Fe/K, Ru/V/TiO_2 Co/Zr, Ti or Cr/Al_2O_3 Co/Zr/TiO_2 Co-Ru/Al_2O_3	Fixed-bed (low T) Slurry-bed (low T)	Sasol-Arge, Gulf-Badger Sasol-Two Stage Shell-Middle Distillate Eisenlohr/Gaensslen
Waxes	Fe/K, Fe/Cu/K Co/Zr, Ti or Cr/Al_2O_3 Co/R/Al_2O_3, Prom. Fe/Ru	Slurry-bed (low T) Fixed-bed (low T)	Mobil (First Stage) Shell-Middle Distillate (First Stage)

b. Successful pilot testing of a Mobil two-stage promoted-Fe-slurry FTS/ZSM-5 upgrading process for converting H_2-poor syngas to high quality gasoline [88,95].

c. Development and commercialization of the multi-stage Shell Middle Distillate Synthesis process to produce jet fuel kerosine and diesel gas oil from natural gas feeds [96–98].

Technology options for production of premium hydrocarbons by various combinations of these catalyst, reactor, and process technologies are summarized in table 2.

RECOMMENDATIONS FOR FUTURE RESEARCH AND DEVELOPMENT

Based on the work reviewed in the more detailed chapter [2] and on recommendations by Mills [17] several areas of technology are listed below which if further researched and developed could contribute significantly to more efficient, economical production of synthetic fuels and chemicals from FTS:

1. *Catalyst Technology*

a. Further improvements in catalysts which greatly reduce methane formation.

b. Catalysts with higher resistance to deactivation by sulfur and by carbon deposits and/or coke, particularly in high-wax and slurry reactor processes and which are more easily-regenerable.

c. Catalysts with higher attrition resistance for application in fixed-fluid-bed reactors.

d. Catalysts of higher activity for slurry-bed processes.

e. Catalysts with improved selectivity and stability for production of waxy hydrocarbons.

f. Continued research on metal/zeolite combinations and second-stage zeolites for upgrading FT products.

2. *Reactor technology*

a. More quantitative characterization and modeling of the kinetics and mechanisms of essential reaction and transport processes in each stage of the combined slurry phase FTS/ZSM-5 upgrading process. This should be followed by optimization studies.

b. Investigation into the causes and prevention of catalyst settling and stability-loss in slurry reactors.

c. Experimental/modeling studies of the performance and detailed kinetics of fixed-fluid bed FTS reactors.

3. *Process technology*

In view of the trend to natural gas as a feedstock for the next 3–4 decades, increased emphasis on integrated processes such as the Shell Middle Distillates Synthesis which produces premium products from natural gas via autothermal reforming to a H_2-rich syngas is recommended.

The long-term potential for substantial improvements in scientific understanding and technology leading to a substantial, cost-effective FTS industry is very promising [17]. Accordingly, it is hoped that the present shortsightedness in government and industry leading to a radical decline in FTS R&D will give way to a more enlightened, long term view.

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