

OVERVIEW OF FISCHER-TROPSCH SYNTHESIS WITH COBALT CATALYSTS

SUMMARY

This review of the use of cobalt catalysts for the Fischer-Tropsch synthesis emphasizes results of the past thirty years. It is primarily intended to define catalyst formulations, both available to the public and of limited use because of patent coverage, that can be utilized in studies to define relationships between catalyst composition and process variables. To accomplish this literature review, two approaches have been utilized. In the first, a summary is provided by research topics: catalyst preparation, catalyst activation, catalytic activity and productivity, and catalyst aging and rejuvenation. Because of the likelihood that these catalysts will eventually be utilized in bubble column reactors, a brief survey of these reactors is presented. The proposed work will involve both fixed-bed and continuous stirred tank reactors (CSTR) and, at this time, the results from these two types of reactors cannot be directly related to large-scale bubble column reactor operations.

FIRST THIRTY YEARS (1925-1955)

The early work on the conversion of synthesis gas to hydrocarbons using cobalt catalysts has been extensively reviewed [1-3]. The Bureau of Mines review [3] of the literature contains 3771 abstracts and the second part covering patents contains 4017 abstracts; each section has an extensive index. The cobalt catalyst compositions center on those that eventually became the "standard" catalyst for the German Synthine process: Kieselguhr supported cobalt and thorium oxide together with other activating materials. This catalyst defined the use of a support and a nonreducible promoter for cobalt catalyst for the Fischer-Tropsch synthesis. It was demonstrated that the presence of copper, up to about 2 wt.%, significantly decreased the

temperature required to reduce the cobalt to the metallic state [4]. This work defined the use of an easily reduced metal oxide as a promoter for reducing cobalt catalysts at lower temperatures than would occur in their absence. However, it was also reported that while the copper allowed reductions to be effected at lower temperatures, the resulting catalyst declined in activity more rapidly [5]. Magnesia has been in use in cobalt catalyst formulation since 1938. The magnesia extends the catalyst life to eight months at normal pressure conditions [6]. The magnesia was added to increase the hardness of the catalyst; it also depressed the methane production and carbon formation.

During this period, the Fischer-Tropsch synthesis was carried out at the commercial scale by the Germans and the Japanese in processes that employed supported cobalt catalysts in fixed-bed reactors [1]. During this period, Köibel and coworkers completed laboratory and pilot plant operations with a bubble column reactor to directly produce products emphasizing gasoline and diesel range materials using what would be considered today to be low-alpha iron catalysts [7].

MORE RECENT REPORTS OF COBALT CATALYST FORMULATIONS

A representative listing of promoters and supports reported in patents that are covered in **Chemical Abstracts** since 1962 are compiled in Attachments I and II.

For the purpose of the proposed study under this contract, the catalyst preparation and compositions of a patent issued in 1978, and now expired, are of interest [4]. This patent describes a process for the conversion of synthesis gas to hydrocarbons having only a minor amount of methane. The process utilizes a catalyst consisting of a major amount of cobalt and a minor amount of ruthenium as the active catalytic components. A sub-claim indicates that the catalyst formulation can contain

an inert support. The standard cobalt catalyst used in this work was prepared following a recipe that is, or is similar to, the standard German cobalt catalyst and consists of Co, Mg and Th on a kieselguhr support. Cobalt can comprise from 1 to 50 wt.% of the finished catalyst for the improved catalyst formulation. The molar ratio of cobalt to ruthenium in the finished catalyst can be from 5:1 to about 200:1. The active catalytic materials are "distended" on a suitable support material. Those metal oxides typically used as support materials can be employed to prepare the Co-Ru catalyst. Examples of suitable supports include oxides of the metals of Groups II, III, IV, V and VIB of the Periodic Chart [Group VIB is obviously intended to be IVB as described in a following sentence]. The oxides of Group II, IIIA, and IVB are preferred, e.g., alumina, boria, zinc oxide, magnesia, calcium oxide, strontium oxide, barium oxide, titania, zirconia and vanadia. It is further stated that a combination of these metal oxides, e.g., silica-alumina, can be used. The support can be natural occurring or synthetic, and examples include: kieselguhr, carbon, attapulgite clays, diatomaceous earth, activated carbon, coke, charcoal, and molecular sieves (both X and Y type). The method employed to deposit the catalytic metals onto the support is not critical, and any technique well known to those having ordinary skills in the art to distend the catalytic metals in an uniform thin layer on the catalyst support is suitable. The catalyst is normally dried, calcined and reduced in a gas such as flowing hydrogen. An interpretation of a phrase from a subclaim, "...with a catalyst consisting essentially of a major amount of cobalt and a minor amount of ruthenium distended in a uniform, thin layer on a catalyst support..." is a demanding task. One could conclude that this patent includes a catalyst with a nonuniform deposition of cobalt within the support particle. The patent covers operating temperatures from 60 to 450°C and pressures from

atmospheric to 300 psig. In the body of the patent it is written that, "...using the catalysts of this invention can occur in a fixed, fluid or moving bed type of operation, and the type of operation would not appear to be critical." A catalyst falling within this description was used in a bubble column reactor that was reported in a 1985 South African patent application [9].

Another report of interest for the proposed work describes the use of Pt and Pd as promoter for Co-alumina catalysts in which the alumina support does not exhibit an XRD pattern [10]. This disclosure permits the use of these noble metals to compare with catalysts containing Ru as disclosed in the Gulf Res. & Dev. Co. patent described above.

The patents described above utilize a range of metal salts, including cobalt carbonyl, to prepare supported cobalt catalysts that contain a variety of promoters - both easily reducible metal oxides including Ru, Pt, Pd and Cu as well as nonreducible metal oxides including zirconia, titania, alumina and silica.

Air Products utilized impregnation techniques to prepare catalysts during their work under DOE contracts in the 1980s. Catalyst precursors and supports were purchased from commercial sources [11]. The supports (γ -Al₂O₃ (Catapal SB, 217 m²/g, 45 μ m), silica (Davison 952, 339 m²/g, 70 μ m), MgO•3.6SiO₂ (Florisil, 298 m²/g, 75 μ m) and titania (Degussa P-25, 50 m²/g, 2 μ m) were calcined at 500°C for 3 hours in air prior to catalyst preparation. The catalysts and precursors were protected from air and moisture using the Schlenk technique and/or dry box. All solvents were distilled from sodium benzophenone detyl in a nitrogen atmosphere. Prior to use, the supports were further dried at 110°C under vacuum for 1-2 hours. Catalysts were prepared using the incipient wetness technique with separate solutions containing the promoter and metal

carbonyl applied to the support in sequential steps. Their patents concerning the preparation of Fischer-Tropsch catalysts contain the following: "The invention was made under DOE Contract No.----- and is subject to government rights arising therefrom."

CATALYST ACTIVATION

Benson et al. [12] indicate that, "Cobalt required carefully conducted prereduction with hydrogen, followed by an equally rigid schedule of induction with synthesis gas." Induction, as utilized in the reports of work at the Bureau of Mines, refers to the protocol followed during the early stages of exposure of the catalyst to hydrogen, or hydrogen and carbon monoxide, after adding the catalyst to the slurry oil/wax, or vice versa, in the reactor.

The majority of laboratory studies utilized hydrogen reduction followed by transfer of the reduced catalyst to the reactor. The transfer could be conducted by transferring the reduced catalyst to an outgassed start-up solvent in the absence of oxygen sources or by first passivating the catalyst with oxygen/air at low temperatures and then re-reducing the catalyst in the reactor [11].

A process that was claimed to provide a catalyst with superior activity involved the reduction of the dried (or calcined) catalyst in hydrogen, reoxidation, and then re-reduction in hydrogen (the ROR method) [13]. When the ROR method is utilized in a fixed-bed reactor, there are no problems in interpreting the approach since the catalyst can be contacted with synthesis gas in the reactor immediately following the re-reduction, and without exposure to oxygen. The ROR method was employed for testing using a bubble column reactor; however, the method used to transfer the catalyst to the

reactor, if indeed it was transferred rather than activated in the bubble column reactor, was not defined in detail [9].

Mitchell [14] claimed a method for activating an essentially fresh, reduced cobalt containing FT catalyst which comprises treating the catalyst with hydrogen or a hydrogen containing gas in the presence of hydrocarbon liquids for a period sufficient to increase substantially the initial catalyst productivity. The induction utilized by the Bureau of Mines workers was to significantly increase the productivity of the catalyst during the early period of catalyst usage.

While there are a number of patents that cover activation of catalysts in hydrogen, none appear to provide specifics as to the mode of operation with respect to catalyst composition.

In a different approach, Nay et al. [15] claimed an activation that involved the oxidation of a cobalt catalyst followed by a reduction using carbon monoxide. This approach was claimed to produce a catalyst which produced less methane and more C₅+ products than when the same catalyst was activated using hydrogen.

Air Products conducted extensive work with cobalt catalysts during the 1980s, and the results are covered in reports and in patents [16-18]. In these studies they utilized both fixed-bed and CSTRs. The catalyst was loaded into the fixed-bed reactor; this was accomplished in a glove-box with air sensitive catalyst precursors. The reactor was then placed in line after the rest of the system had been flushed with nitrogen for at least 10 minutes. After leak testing, the catalyst was activated following two procedures. In the first, the catalyst was activated using CO/H₂ = 1.0. To accomplish this the catalyst precursor was heated to 180°C in a nitrogen flow at atmospheric pressure. At 180°C, the flow was switched to the synthesis gas (CO/H₂ = 1) and then

heated to the reaction temperature. At the reaction temperature, the pressure was increased to the one used for the synthesis. Later in their work, they compared the impact of activation in pure H₂ or syngas (CO/H₂ = 1). For a 4%Co-zirconia promoted alumina catalyst, they found that the sample activated in hydrogen had a significantly higher activity and higher yield of liquid fuels. For the slurry phase tests, catalysts were activated in a separate, 150 cc fixed bed tubular unit using either pure H₂ or 20% syngas in nitrogen. The activated catalyst was then slurried in a deoxygenated paraffin oil in a dry box and transferred to the slurry autoclave under a blanket of nitrogen.

CATALYST ACTIVITY - PRODUCTIVITY

With an iron catalyst the productivity per gram of iron is not independent of CO conversion. Thus, the hydrocarbon productivity is highest at low conversion levels and then declines to about 0.5 g. hydrocarbons/g. Fe/h at the 90%+ CO conversion level (figure 1) [19]. Similar productivity rates are obtained for H₂/CO ratios typical of synthesis gas derived from coal (0.7) or from natural gas (1.7). Based on kinetics, it is anticipated that the productivity of a cobalt catalyst should also be dependent on the CO conversion level, although perhaps not to extent that it is for the iron-based catalyst.

The impact of particle size upon supported catalysts operated in a fixed-bed reactor was demonstrated by work carried out at Gulf Oil (Attachment VIII). As the particle size of the catalyst was decreased in the range from 1.6 to 0.2 mm, the methane production decreased (figure 2) and the C₅+ hydrocarbon fraction increased (figure 3). Likewise, the temperature dependence of synthesis at 185 and 195°C clearly demonstrated that the reaction suffered diffusion limitations in the larger catalyst particle sizes (figure 4). More recent quantitative descriptions of the effect of the

catalyst particle size on product selectivity and on activity has been presented (figure 5) [references 20,21].

The results from synthesis in a bubble column slurry reactor showed that the methane production increased and the C₅+ hydrocarbons decreased as the temperature was increased in the 220-240°C range (figure 6) [9].

It is very difficult to obtain reactor productivity for pilot plant or commercial operations from either the open or patent literature. It is almost always necessary to make one or more assumptions about the operation and this introduces uncertainties in the estimate of productivity. The results summarized in Attachment V suggest that one should be able to obtain productivities in the range of 0.5 g. hydrocarbon/g catalyst/h for either unsupported iron or supported cobalt catalysts.

DECLINE IN CATALYTIC ACTIVITY

Data to define the decline in catalytic activity are not readily available. For a Co-Zr-silica catalyst that is operated with a H₂/CO = 1 at 260°C, the rate of activity decline is about 1% CO conversion per week (figure 7) [22]. On the other hand, a Co-silica catalyst exhibited an activity decline of about 35% CO conversion per week; however, for the same catalyst operated at a higher flow rate so that the CO conversion is only about 10% the activity decline was less than 1% CO conversion per week [23]. This result implies that the activity loss may be conversion dependent, presumably influenced by the partial pressure of water. A recent report indicates that there is a rapid activity decline during the first five days of operation after which the decline becomes much slower (figure 8) [24]. A definition of a series of aging-rejuvenation cycles has been reported (figure 9) [25]. There appears to be a reasonable relationship between the rate of activity decline and the time of the total decline as well as the rate

of activity recovery and the time of the total decline. It should be realized that this patent claims to demonstrate a catalyst rejuvenation technique and that accelerated aging conditions may have been employed during the study.

As important as the initial decline in activity is the regeneration (or rejuvenation) of the catalyst. The early work by the Germans and the U.S. Bureau of mines show that the initial activity of a cobalt catalyst can be attained again, or closely approached, by a brief treatment of the aged catalyst with hydrogen.

KINETICS

Several kinetic equations for synthesis gas conversion have been advanced for both iron and cobalt catalysts. For CO conversion levels to about 50%, both catalysts exhibit little dependence on CO partial pressure and a direct dependence on H₂ partial pressure. Thus, at low conversion the data have been fitted with the equation:

$$\text{rate} = k P_{\text{H}_2} .$$

Several variations of the inhibition effect of the reactants and products, especially H₂O, on the kinetics at higher conversion levels have been proposed. Unfortunately, the scatter in the experimental data at these high conversion levels makes it impossible to settle on a single kinetic expression.

There are several reports of the activation energy for both iron and cobalt catalysts and these are in the 20-25 kcal/mole range.

SLURRY REACTORS

It was recognized soon after the discovery of the Fischer-Tropsch synthesis that a reactor employing the catalyst in direct contact with a cooling oil was an attractive approach to maintain temperature control of the exothermic reaction. U.S. patents were obtained by I. G. Farbenindustrie A.-G., Standard Oil Development Company and

Standard Catalytic Company. The Standard Catalytic Company was established by six U.S. petroleum companies to develop processes for the production of synthetic fuels, and included an agreement with I. G. Farbenindustrie A.-G. Some of these patents are summarized in Attachment VI. Included in Attachments VII and VIII are the claims of several recent patents covering the use of bubble column reactors for the Fischer-Tropsch synthesis.

Recently, Inga [26] has studied the factors involved in relating data obtained in small-scale laboratory reactors to larger ones that would be utilized in industry. In brief, Inga concludes that the data from small reactors can be related **directly** to large commercial reactors only if the mixing in the small reactor will be the same as encountered in the large bubble column reactor. Thus, the usual results from the small-scale reactor is adequate for a definition of the scientific and engineering principles for bubble column operation but is not appropriate for direct application to any commercial scale bubble column reactor.

REFERENCES

1. H. H. Storch, N. Golumbic and R. B. Anderson, "The Fischer-Tropsch and related synthesis," John Wiley & Sons, New York, 1951.
2. B. H. Weil and J. C. Lane, "The technology of the Fischer-Tropsch process," Constable & Co., Ltd., London, 1949.
3. H. C. Anderson, L. L. Wiley and A. Newell, "Bibliography of the Fischer-Tropsch synthesis and related processes (in two parts). I. Review and compilation of the literature on the production of synthetic liquid fuels and chemicals by the hydrogenation of carbon monoxide. II. Patents," Bureau of Mines Bulletin 544, 1954, 1955.
4. F. Fischer, Brennstoff-Chemie, 16, (1935) 1; Petroleum Refiner, 23 (1944) 112).
5. J. F. Schultz, L. J. E. Hofer, E. M. Cohn, K. C. Stein and R. B. Anderson, "Synthetic Liquid Fuels From Hydrogenation of Carbon Monoxide," Bureau of Mines Bulletin 478, 1959.
6. (Technical Oil Mission Report, No. 8, May 15, 1945 (PB 367).
7. H. Kölbel and M. Ralek, Catal. Rev.-Sci. Eng., 21, 225 (1980).
8. T. P. Kobylinski, U.S. 4,088,671, 05/09/1978 (assigned to Gulf Res. & Dev. Co.).
9. H. Beuther, T. P. Kobylinski, C. E. Kibby and R. B. Pannell; "Conversion of synthesis gas to diesel fuel in controlled particle size fluid system," South Africa Patent 855317, 7/15/85; ZA 8505317, issued 02/26/86.
10. R. S. Sapienza, M. Sansone and W. A. R. Slegier, U.S. Patent Application 482372, 06/22/84, (United States), available from NTIS.

11. H. P. Withers, Jr, K. F. Eliezer and J. W. Mitchell, Novel Fischer-Tropsch Slurry Catalysts and Process Concepts for Selective Transportation Fuel Production; DOE/PC/70030-T9, Final Report, December 1987.
12. H. E. Benson, J. H. Field, D. Bienstock, R. R. Nagel, L. W. Brunn, C. O. Hawk, J. H. Crowell and H. H. Storch, "Development of the Fischer-Tropsch oil-recycle process," Bureau of Mines Bulletin 568, 1957.
13. T. P. Kobylinski, C. L. Kibby, R. B. Pannell and E. L. Eddy, U. S. Patent 4,605,679, August 12, 1986.
14. W. N. Mitchell, "Activation of hydrocarbon synthesis catalyst;" U.S. Patent 5,292,705 (Mar. 1994).
15. B. Nay, M. R. Smith and C. D. Telford, "Catalyst treatment;" U.S. Patent 5,585,316, December 17, 1996.
16. P. N. Dyer, R. Pierantozzi and H. P. Withers, Supported Fischer-Tropsch catalyst and method of making the catalyst, US 4,681,867, July 21, 1987.
17. P. N. Dyer and R. Pierantozzi, Catalyst for selective conversion of synthesis gas and method of making the catalyst, US 4,619,910, Oct 28, 1986.
18. P. N. Dyer, R. Pierantozzi and H. P. Withers, Fischer-Tropsch process, US 4,670,472, June 2, 1987.
19. Our work hc/hr vs CO conv
20. E. Iglesia, Appl. Catal. A: General, 161, 59 (1997).
21. E. Iglesia, S. C. Reyes and S. L. Soled, "Reaction-transport selectivity models and the design of Fischer-Tropsch catalysts," "Computer-Aided Design of Catalysts and Reactors," (E. R. Becker and C. J. Pereira, Eds.), Marcel Dekker, Inc., 1992.

22. H. P. Withers, Jr., K. F. Eliezer and J. W. Mitchel, Ind. Eng. Chem. Res., 29, 1807, (1990).
23. Unpublished results, CAER.
24. P. J. van Berge and R. C. Everson, "Cobalt as an alternative Fischer-Tropsch catalyst to iron for production of middle distillates,,: Natural Gas Conversion IV (M. de Pontes et al., Eds.), Studies Surf. Sci. Catal., 107, 207 (1997).
25. W. N. Mitchell, "Rejuvenation of hydrocarbon synthesis catalyst," U.S. Patent 5,283,216, February 1, 1994.
26. J. Inga, Ph.D. Thesis, U. Pittsburgh, 1997.

ATTACHMENTS

- I. FT Catalyst Promoter - Patents
- II. FT Supports - Patents
- III. The Preparation of Cobalt Fischer-Tropsch Catalysts - Literature From 1962
- IV. Fischer Tropsch - Examples of Activation
- V. Productivity - Slurry Phase
- VI. Early Slurry Reactors
- VII. Tube-in-Shell Fischer-Tropsch Reactor
- VIII. Cooling Coils in or outside the Fischer-Tropsch Reactor Shell
- IX. Review of Air Products Fischer-Tropsch Synthesis Work
- X. Review of Exxon Patents
- XI. Listing of Open Literature Description of Exxon FT Work
- XII. Review of Fischer-Tropsch Work by Gulf Oil
- XIII. Review of Fischer-Tropsch Work by Statoil
- XIV. Review of Fischer-Tropsch Work by Rentech

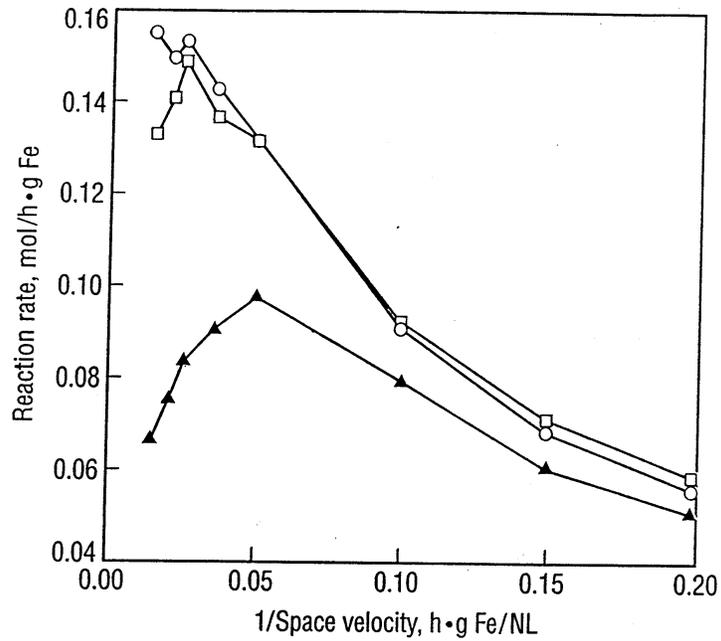


Figure 1. Reaction rate for Fischer-Tropsch synthesis (□,○) and water-gas shift (▲) with an iron catalyst.

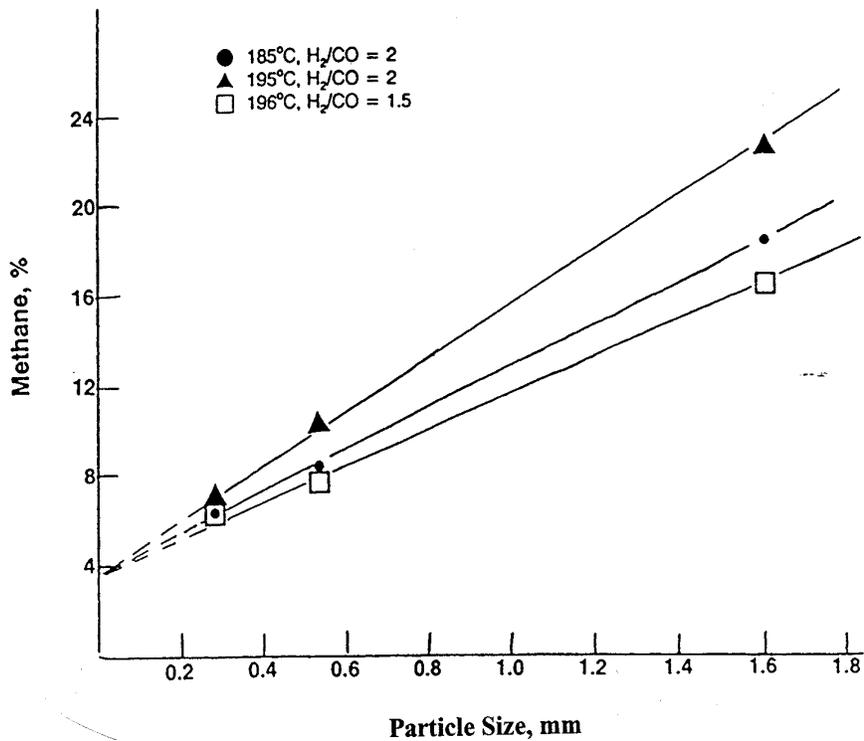


Figure 2. Methane production for synthesis in fixed-bed reactor with different particle size catalysts (from XII.17).

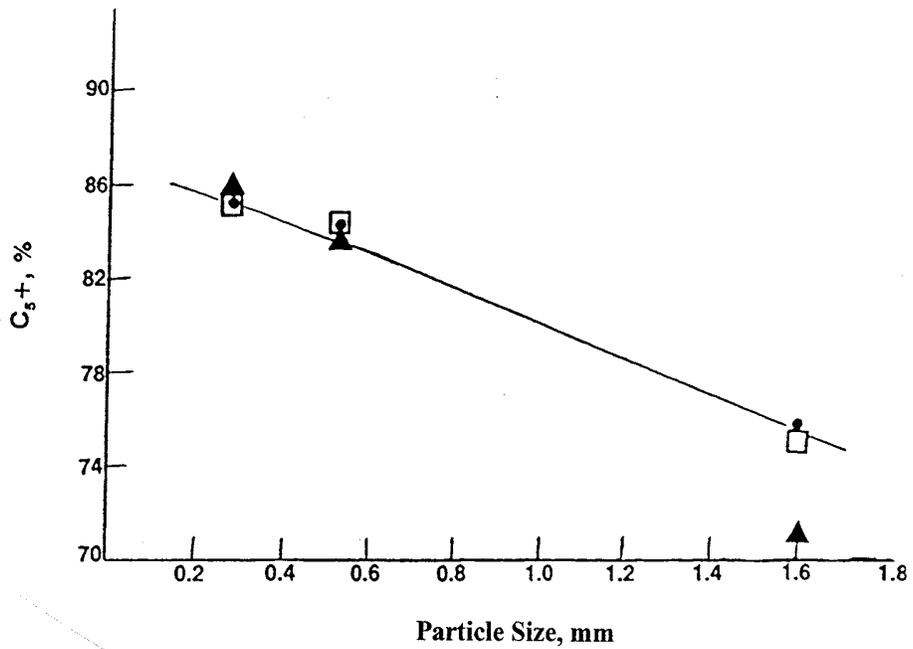


Figure 3. C₅+ product selectivity for three particle size catalysts in fixed-bed reactor (●, 185°C, H₂/CO = 2; ▲, 195°C, H₂/CO = 2; □, 195°C, H₂/CO = 1.5) (from XII.17).

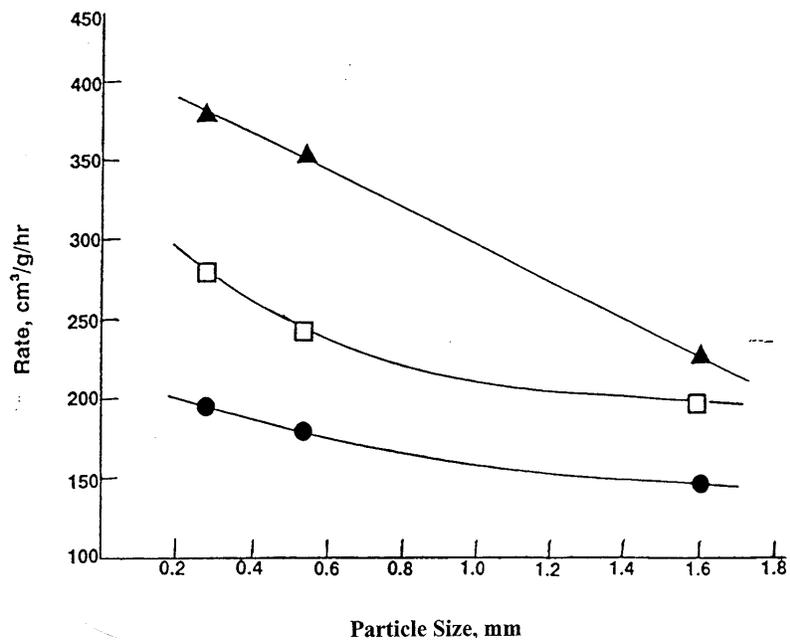


Figure 4. Reaction rate for CO conversion in fixed-bed reactor for three particle size catalysts (●, 185°C, H₂/CO = 2; ▲, 195°C, H₂/CO = 2; □, 195°C, H₂/CO = 1.5) (from XII.17).

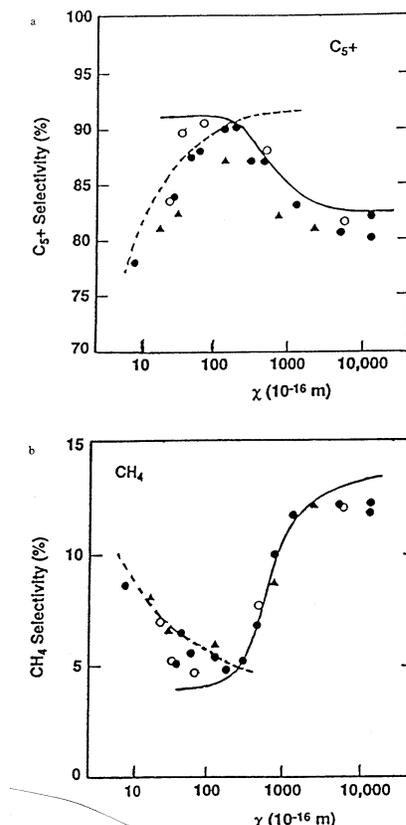


Figure 5. The effect of structural parameters (X) on FTS selectivity. Diffusion-enhanced readsorption (---) and diffusion-inhibited chain growth (—) simulations and experimental data (●, dispersion/support effects; ▲, pellet size variations; ○, eggshell thickness variations). Top) C_5+ selectivity; bottom) CH_4 selectivity [473 K, 2000 kPa, $H_2/CO = 2.1$, 55-65% CO conversion] (X values from eq. 2 with r_p and R_o in m and θ_{Co} in surface Co atoms m^{-2}) (from E. Iglesia in "Natural Gas Conversion IV," (M. De Pontes, R. L. Espinoza, c. Pl. Nicolalides, J. H. Schulz and M. S. Scurrall, eds.), Elsevier, Amsterdam, 1997, pp 153-162).

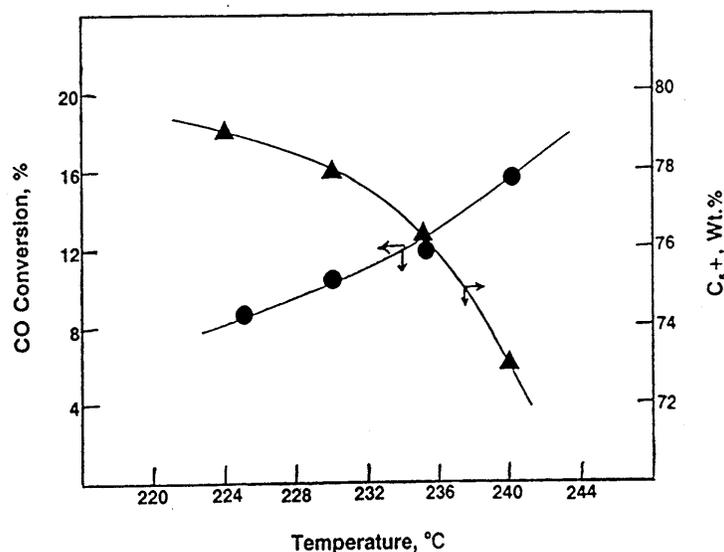


Figure 6. CO conversion and C_5+ product selectivity for FTS using slurry reactor and cobalt catalyst (data from XII.17).

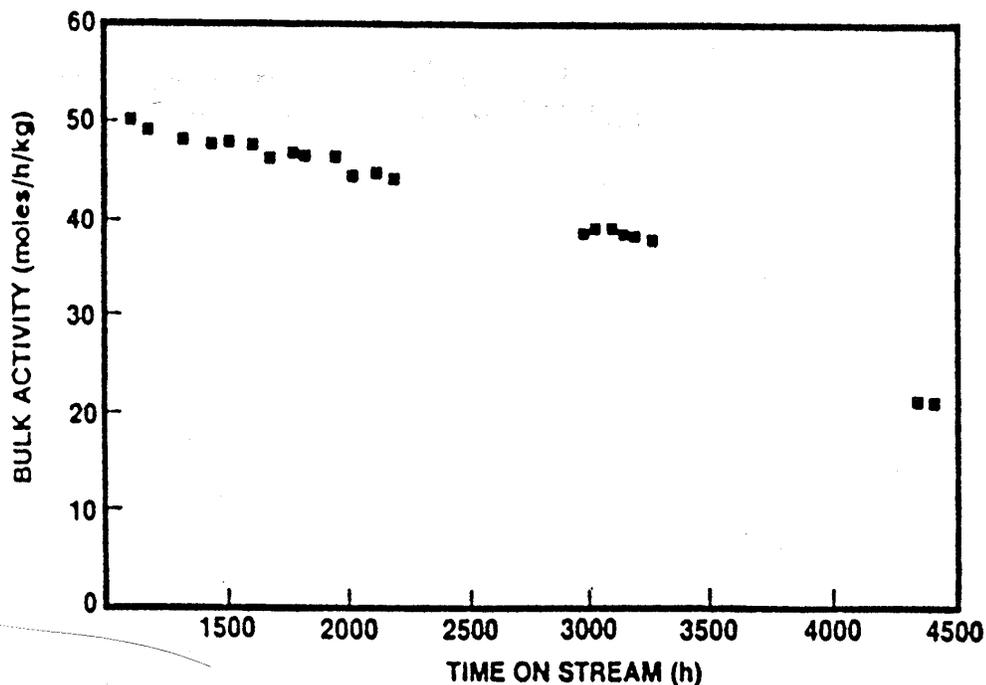


Figure 7. Bulk activity maintenance for extended slurry reactor test of catalyst at baseline conditions (260°C, 2.07 Mpa, CO/H₂ = 1.0, and SV = 2.0 nL/h per g of catalyst).

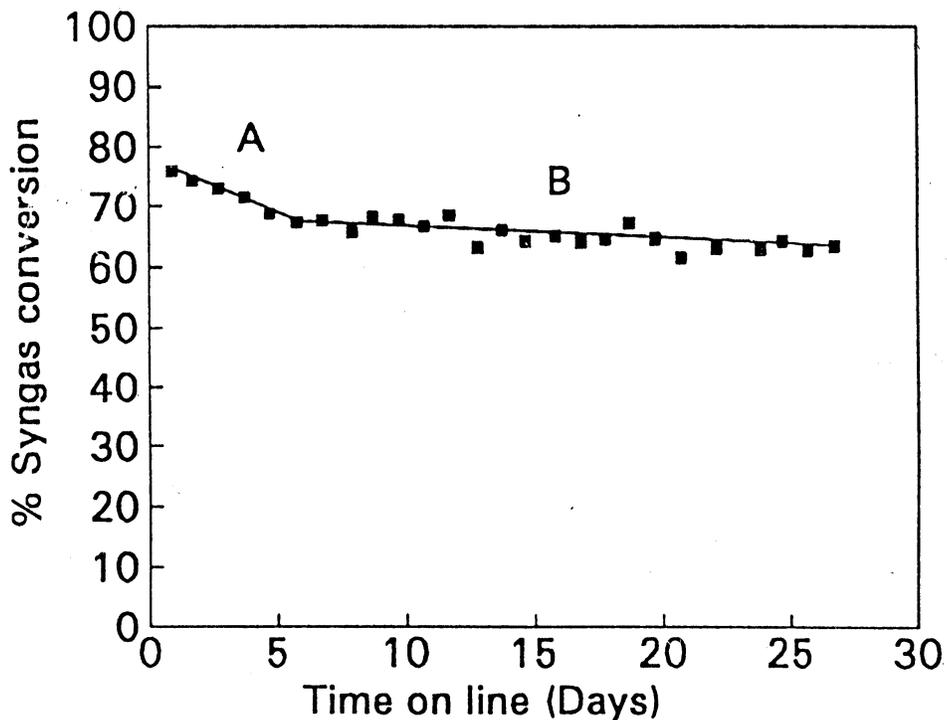


Figure 8. Stability run with a cobalt catalyst (period A, conditioning phase; B irreversible, slow deactivation) (from P. J. van Berge and R. C. Everson, *Natural Gas Conversion IV*, 107, 207 (1997)).

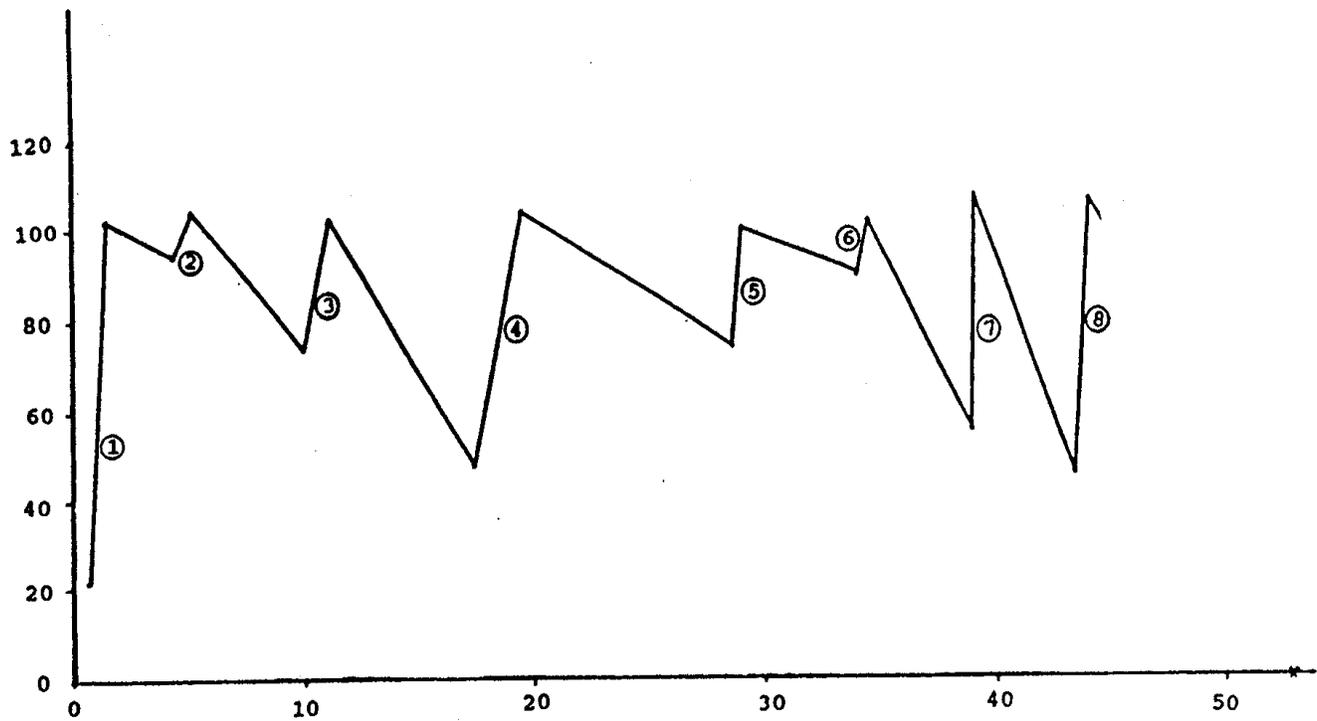


Figure 9. Relative volumetric productivity represented by activity with days on stream with intervals of hydrogen rejuvenation (12 wt.% Co on titania with 6 wt.% Al_2O_3 as binder (from ref. X.96).

ATTACHMENT I

FT Catalyst Promoter - Patents

1. J. J. C. Geerling, A. Hoek, H. M. Huisman, and P. W. Lednor, WO 9825870 A1, 06/18/98 (Shell International). A supported (e.g., titania) cobalt/manganese with a Co/Mn molar ratio of 7-14/1 - shows, at high GHSV and low Co/Mn ratios, a high activity and C₅+ productivity even at relatively high gas hourly space velocity (GHSV).
2. J. J. C. Geerlings, M. F. Goes, H. M. Huisman, J.-P. Lange, H. Oosterbeek, P. J. M. Paulus and D. Schadenhorst, WO 9700231 A1, 01/03/97 (Shell International). Co + Mn and/or V is supported on a carrier, e.g., TiO₂ is effective for use in a process for the manufacture of hydrocarbons from synthesis gas.
3. P. J. M. Rek and P. Blankenstein, EP 583837 A1, 02/23/94 (Shell International). This patent application provides a method for the preparation of a catalyst or catalyst precursor that comprises a refractory oxide, solvent and peptizing agent that are mixed and neutralized with salt of catalytic active component (e.g., Group VIII metals).
4. C. J. Kim, U.S. Patent 5,227,407, 07/13/93 (Exxon R&E Co.) A syngas with added water is passed over a catalyst containing Co, Ru, or their mixtures, preferably on a TiO₂ support, produces an increased amount of C₅+ and a decreased amount of CH₄, compared to conversions with the same catalyst without added water.
5. B. Sandra and A. L. Chaffee, WO 9305000 A1, 03/18/93 (Broken Hill Pty. Co. Ltd., Australia) A catalyst consists of Co and scandium incorporated into a zeolite.

6. D. Reinalda and P. Blankenstein, EP 510770 A2, 10/28/92 (Shell International).
A catalyst composed of a Group VIII metal (Fe, Co, Ni) on refractory oxide (e.g., alumina, silica, titania, zirconia or mixtures of these) and then extruded into shapes is suitable for producing hydrocarbons from syngas.
7. S. L. Soled, E. Iglesia and R. A. Fiato, U.S. Patent 5,162,284, 11/10/92 (Exxon Res. & Eng. Co.). Cu promoted Co-Mn spinel ($\text{Co}_{3-x}\text{Mn}_x\text{O}_4$ with $x = 0.5$ to 1.2) are effective for converting syngas to a product rich in low molecular weight alkenes. The synthesis includes the use of an α -hydroxy aliphatic carboxylic acid (e.g., citric or glycolic acid) and Cu = 0/1-5 g-atom% of Co + Mn.
8. J. W. Geus and E. Boellaard, EP 466268 A1, 01/15/92 (Shell International).
Alloys of 2 or more Group VIB, VIIB and VIII elements, in which the alloys (metals) have negative heat of formation and the metal may be in the form of carbide, are suitable catalyst or catalyst precursor for hydrocarbon synthesis from syngas.
9. J. T. Miller and C. A. Radlowski, CA 2018611 AA, 12/13/90 (Amoco Corp.).
Nitrates of Co, Zn and Na were precipitated at pH 10 and calcined and these solids are effective catalysts for the production of olefins or higher alcohols from synthesis gas.
10. Anon. UK, Res. Discl (1991), 323, 180. A honeycomb support for Co promoted with ZrO_2 or Pt or Pd is used to prepare a Fischer-Tropsch catalyst.
11. S. Eri, T. Riis, G. Marcelin and J. G. Goodwin, Jr., WO 9007377 A1, 07/12/90 (Statoil). Co with a second metal (Pt, Ir and/or Rh) on alumina support is used for hydrocarbon synthesis.

12. S. Eri, J. G. Goodwin, Jr., G. Marcelin and T. Riis, U.S. Patent 4,889,763, 11/14/89 (Statoil). Co, Re and alkali (K) are supported on alumina; a metal oxide promoter may also be present. The composite may be used to convert synthesis gas to hydrocarbons.
13. S. Eri and J. G. Goodwin, Jr., U.S. 4,857,559, 08/15/89 (Gas-to-oil, Inc., U.S.A.) Co-Re-alumina which may contain another metal oxide promoter is useful to produce hydrocarbons from synthesis gas.
14. J. G. Miller, G. M. James and J. A. Rabo, ZA 8806952, 05/30/89 (Union Carbide). Co containing LZ-210 zeolite that contains a Mo oxide promoter produce products that exhibit lower methane yield, higher C₅+ hydrocarbons, increased olefins and longer catalyst life..
15. S. L. Soled, R. A. Fiato and E. Iglesia, EP 319625 A1, 06/14/89 (Exxon Res. & Dev. Co.) A catalyst comprised of Co-Ru on TiO₂ support can be regenerated without removal from the reactor: it produces 7.9% CH₄ and 85.7% C₅+ at GHSV 1200 h⁻¹. Co and Ru are dispersed within the same crystallite.
16. S. Eri, J. G. Goodwin, Jr., G. Marcelin and T. Riis, U.S. 4,801,573, 01/31/89 (Statoil). Co-Re on alumina, to which a metal oxide promoter may be added, exhibits a higher activity than either Co or Re alone.
17. W. C. Behrmann, C. H. Mauldin, K. B. Arcuri and M. Herskowitz, EP 266898 A1, 05/11/88 (Exxon Res. & Dev. Co.). A catalyst consisting of a metal film of 0.02-0.25 mm thickness is deposited on the surface of a particulate support; Co and Re are repeatedly deposited on preheated TiO₂ substrate as thin layer (60-160 μm) to prepare the catalyst which is suitable for hydrocarbon production from

- syngas. The composite has very high hydrocarbon productivity and low CH₄ selectivities.
18. E. Iglesia, S. L. Soled and R. A. Fiato, U.S. 4,738,948, 04/19/88 (Exxon Res. & Dev. Co.). Co-Ru is deposited on a refractory oxide, and then oxidized and reduced to form a catalyst with the Co and Ru in intimate contact. This catalyst produces 93 mol% C₅+ and 3.4 mole% methane whereas a similar catalyst without Re produces 85 mol% C₅+ and 7 mole% methane.
 19. P. N. Dyer, R. Pierantozzi and H. P. Withers, U.S. 4,670,472, 06/02/86 (Air Products & Chemicals, Inc.). An inert carrier was treated with a Group IVB metal compound, then impregnated with decomposable metal compound (e.g., Co, Fe or Ru carbonyls) to produce a catalyst precursor. Reactions with air or water and calcination are specifically avoided. Instead the catalyst was contacted with the synthesis gas.
 20. K. P. De Jong, J. H. E. Glezer and M. F. M. Post, EP 221598 A1, 05/13/87 (Shell International) Fe, Ni or Co is deposited on SiO₂ along with one or more Group VIII noble metal promoters and, in addition, may contain Zr. The specific example is Pt-Co-Zr-SiO₂ with 0.1:10:0.9:100 weight parts.
 21. C. H. Mcateer and B. Nay, WO 8607350 A1, 12/18/86 (British Petroleum Co.) A catalyst with Co_aA_bL_{ac}CeO_x (A, alkali metal with a = 0-0.25%; b = 0-5%, x = number to satisfy equation) is prepared. A procedure for preparing a pellet also includes an activation procedure.
 22. C. J. Kim and R. A. Fiato, U.S. 4,624,968, 11/25/86 (Exxon Res. & Dev. Co.) Fe/Ce/Zn/K, Re-Mn-K or Fe-Co-K catalysts are used in first stage and then the

exit gas is converted to heavier produces over Ru/TiO₂, Ru/SiO₂ or Ru/Al₂O₃ catalyst in a second stage.

23. J. H. Brophy, F. J. J. Font, M. Helena, D. J. H. Smith and C. D. Telford, WO8605775, 10/09/86 (British Petroleum Co.). Hydrocarbons are preferably produced by Fischer-Tropsch reaction over a Group VIII metal oxide or sulfide in presence of 1-40 mole% unsaturated hydrocarbon, preferably ethylene. Support utilized include: alumina, C, silica, zirconia, titania, MgO, ceria, gallia and can contain an acidic component such as a zeolite or amorphous silica-alumina.
24. H. Beuther, T. P. Kobylinski, C. L. Kibby and R. B. Pannell, U.S. 4,585,798, 04/29/86 (Gulf Oil). Co and Ru are impregnated by nonaqueous technique on alumina support and can contain another promoter (Ca, Mg, Th, or rare earth or rare earth mixtures).
25. D. Bode and S. T. Sie, EP 188304 A1, 07/23/86 (Shell International). Co + 0-100 wt. parts of element Zr, Ti, Cr and Ru are supported on alumina, silica or silica-alumina and the material formed to be suitable for fixed-bed catalyst.
26. P. K. Coughlin, WO 8600296 A1, 01.16/86 (Union Carbide Corp.). Co with or without Th (1-50 mol%) and an additive (Mo and/or W) on a zeolite or non-zeolite molecular sieve is used as catalyst for converting synthesis gas to hydrocarbons.
27. H. Beuther, T. P. Kobylinski, C. E. Kibby and R. B. Pannell, ZA 8505317, 03/26/86 (Gulf Res. & Dev. Co.) Diesel fuel is produced from synthesis gas using a Co(5-25%)-Ru(0.01-0.5) on a support. The support can be alumina or silica and is in the 10-110 μm size range. Data show diffusion limitations in large

catalyst particles in fixed bed reactors but not with the small particles in the slurry reactor.

28. M. F. M. Post and S. T. Sie, EP 153781 A2, 09/04/85 (Shell International). In first step, syngas is converted to hydrocarbons using a Co(3-60)-Zr(0.1-100)/SiO₂ (100) under specified conversion levels, the water removed and the gaseous products passed to second step using a mixture of two catalysts [Co-Zr/silica and Cu-Zn/alumina].
29. J. K. Minderhoud, M. F. M. Post, S. T. Sie and E. J. R. Sudholter, EP 142887 A2, 05/29/85 (Shell International). A catalyst containing silica 100, Co (15-50) and 2nd metal (Zr, Ti, Ru or Cr) is prepared by sequential impregnations with Co and the 2nd metal.
30. J. K. Minderhoud, M. F. M. Post, S. T. Sie and E. J. R. Sudhoelter, EP 142888 A2, 05/29/85 (Shell International). A first stage Ni-Ca-K-alumina catalyst and a second stage Co-Zr-silica catalyst are employed.
31. J. K. Minderhoud and S. T. Sie, GB 2146350 A1, 04/17/85 (Shell International). Zr-Co-silica was used for hydrocarbon synthesis in the first stage of the process.
32. J. K. Minderhoud and M. F. M. Post, EP 127220 A2, 12/05/84 (Shell International). A three-step impregnation of silica with Zr and one-stem impregnation with Co was followed by kneading/calcining to produce catalyst particles active for hydrocarbon synthesis from syngas.
33. J. K. Minderhoud, M. F. M. Post and S. T. Sie, EP 109702, 05/30/84 (Shell International). Zr- or Ti-promoted Co-silica are used to produce hydrocarbons.
34. A. Hoek, J. K. Minderhoud, M. F. M. Post and P. W. Lednor, EP 110449 A1, 06/13/84 (Shell International). a catalyst is prepared in which a Zr or Ti

compound is added to silica by impregnation, then calcined and then impregnated with a Co compound, calcined and reduced.

35. H. Beuther, C. L. Kibby, T. P. Kobylinski, and R. B. Pannell, U.S. 4,413,064, 11/01/83 (Gulf Oil). Finely divided alumina is impregnated with a Co salt, the product is dried and then contacted with aqueous or nonaqueous solution of salts of Ru and Group IIIB or IVB metals is active for the production of hydrocarbons from synthesis gas.
36. T. P. Kobylinski, U.S. 4,088,671, 05/09/1978 (Gulf Res. & Dev. Co.). A process for the conversion of synthesis gas to hydrocarbons having only a minor amount of methane utilizes a catalyst consisting of a major amount of cobalt and a minor amount of ruthenium as the active catalytic components. A sub-claim indicates that the catalyst can contain an inert support. The standard cobalt catalyst was prepared following a recipe that is, or is similar, the standard German cobalt catalyst and consists of Co, Mg and Th on kieselguhr support. Cobalt can comprise from 1 to 50 wt.% of the finished catalyst. The molar ratio of cobalt to ruthenium in the finished catalyst can be from 5:1 to about 200:1. The active catalytic materials are "distended" on a suitable support material. Those metal oxides typically used can be employed to prepare the Co-Ru catalyst. Examples of suitable supports include oxides of the metals of Groups II, III, IV, V and VIB of the Periodic Chart [old style; Group VIB is obviously intended to be IVB as described in a following sentence]. The oxides of Group II, IIIA, and IVB are preferred, e.g., alumina, boria, zinc oxide, magnesia, calcium oxide, strontium oxide, barium oxide, titania, zirconia and vanadia. It is further stated that a combination of these metal oxides, e.g., silica-alumina, can be used. The

support can be natural occurring or synthetic, and examples include: kieselguhr, carbon, attapulgite clays, diatomaceous earth, activated carbon, coke, charcoal, and molecular sieves (both X and Y type). The method employed to deposit the catalytic metals onto the support is not critical, and any technique well known to those having ordinary skills in the art to distend the catalytic metals in a uniform thin layer on the catalyst support is suitable. The catalyst is normally dried, calcined and reduced in a gas such as flowing hydrogen. The interpretation of a phrase from a subclaim is critical: "...with a catalyst consisting essentially of a major amount of cobalt and a minor amount of ruthenium distended in a uniform, thin layer on a catalyst support..." One interpretation of the meaning of the phrase enclosed in quotes is that it includes "rim-loaded" catalysts. The patent covers operating temperatures from 60 to 450°C and pressures from atmospheric to 300 psig. In the body of the patent it is written that, "...using the catalysts of this invention can occur in a fixed, fluid or moving bed type of operation, and the type of operation would not appear to be critical." This patent expired after 17 years from the issue date so that it now falls within the public domain and does not restrict its use. A catalyst falling within this description was used in a bubble column reactor that was reported in a 1985 South African patent application.

ATTACHMENT II

FT Supports - Patents

1. P. Blankenstein, J. J. C. Geerlings, H. M. Huisman, P. W. Lednor and B. J. Van Liemt, WO 9811037 A1, 03/19/98 (Shell International). A catalytically active metal (e.g., Co) is supported on titania having a rutile/anatase ratio less than 2/3 and surface area $< 75 \text{ m}^2/\text{g}$ is used to prepare C_5+ hydrocarbons from synthesis gas.
2. L. A. Rivas, E. Peluso, D. Rojas, J. J. A. Garcia, U.S. 5,648,312, 07/15/97, (Intevep, S.A., Venez.). Spherical particles of a homogeneous mixture of two refractory inorganic carbides, nitrides or mixtures, with surface area $> 30 \text{ m}^2/\text{g}$ and a particle size $> 0.1 \text{ mm}$ can be used as a support Group IVB and VIII metals in a catalyst system active for the conversion of synthesis gas to C_2+ hydrocarbons.
3. R. Zennaro, A. Gusso and M. G. Clerici, EP 756895 A2, 02/05/97 (Agip Petroli S.P.A., Italy; Institut Francais Du Petrole). A method to prepare a catalyst utilizes an inert support and Co, Ru and a third element, scandium or yttrium. The process includes a sequence of steps for preparation and then calcination, reduction, and passivation steps.
4. J. J. C. Geerlings, M. F. Goes, H. M. Huisman, J.-P. Lange, H. Oosterbeek, P. J. M. Rek and D. Schadenhorst, WO 9700231 A1, 01/03/97, (Shell International). Co and Mn and/or V is supported on a carrier, eg, titania, and is used to convert synthesis gas to hydrocarbons.
5. R. L. Espinoza, J. J. Visagie, P. J. Van Berge and F. H. Bolder, EP 736326 A1, 10/09/96, (Sastech Proprietary Ltd.). A process for preparing Fischer-Tropsch

catalysts is prepared by impregnating alumina with an aqueous salt of Co, Fe and mixtures thereof. The sample is dried below atmospheric pressure, and then calcined.

6. D. Reinalda and P. Blankenstein, EP 510770 A2, 10/18/92, (Shell International). Hydrocarbons are produced by contacting a synthesis gas at 125-350°C and 5-100 bar pressure with a catalyst comprising a Group VIII metal (Fe, Co or Ni) on a refractory oxide carries (alumina, silica, titania, zirconia and mixtures thereof). The catalyst particles are helical lobed shape made by extrusion through a die plate such as a 2 mm helical trilobe.
7. S. L. Soled, E. Iglesia, R. A. Fiato and G. B. Ansell, U.S. 5,169,821, 12/08/92, (Exxon Res. & Eng. Co.). A stable high-temperature Fischer-Tropsch catalyst has the general formula $\text{Co/Ti}_x\text{M}_{1-x}\text{O}_2$ where $x = 0.01$ to 0.14 selected from Si, Zr, and Ta where titania is anatase. Activation of the composite includes drying and calcining followed by reduction of the Co.
8. D. Reinalda, P. Blankenstein and A. Derking, EP 510771 A1, 10/28/92, (Shell International). A process for the preparation of extruded SiO_2 -based catalysts, containing elements from Group VIIB or Group VIII and a promoter from elements in Group IVB is described.
9. A. H. Joustra and B. Scheffer, EP 455308 A1, 11/06/91 (Shell International). The preparation of alumina-based extrudates containing Co, Fe, or Ni is described.
10. E. Iglesia, H. Vroman, S. L. Soled, J. Baumgartner and R. A. Fiato, EP 434284 A2, 06/26/91 (Exxon Res. & Dev. Co.). Supported Co catalysts are prepared by depositing a metal on a suitable support, eg, silica. Rim-loaded catalysts are

obtained by contacting the support with a molten salt. Non-rim-loaded catalysts may be prepared in a similar manner.

11. D. Reinalda and J. Dars, EP 421502 A2, 04/10/91, (Shell International). A Co compound is applied on a porous inert support, dried and then calcined in an atmosphere with greater than 20 volume% NO_x.
12. C. H. Mauldin and K. L. Riley, U.S. 4,977,126, 12/11/90, (Exxon Res. & Eng. Co.). A film layer of catalytically effective amounts of Co is deposited on the peripheral outer surface of a porous inorganic oxide, especially TiO₂.
13. E. Iglesia, S. L. Soled and R. A. Fiato, U.S. 4,960,801, 10/02/90 (Exxon Res. & Dev. Co.). A catalyst with Co present on a TiO₂ support that contains up to 15 wt.% SiO₂ is described.
14. C. H. Mauldin and K. L. Riley, EP 370757 A1, 05/30/90, (Exxon Res. & Dev. Co.). A catalyst support with 0.1-20% of inorganic metal oxide binder (alumina, silica, zirconia or titania) is utilized. A Group VIII metal, preferably Co or Co plus additional metal or metals, is deposited on the support.
15. J. G. Miller and J. A. Rabo, U.S. 4,874,732, 10/17/89, (UOP). A catalyst having improved selectivity for C₅+ hydrocarbons consists of a Co containing acid zeolite that additionally contains Mn oxide or Mn oxide and Zr oxide promoters.
16. E. Iglesia, S. Soled and R. A. Fiato, U.S. 4,794,099, 12/27/88, (Exxon Res. & Dev. Co.). Silica (to 15%) or silica precursor is incorporated into a Co-containing catalyst on an inorganic refractory titania support. Re can also be present.
17. W. C. Behrmann, C. H. Mauldin, B. K. Arcuri and M. Herskowitz, EP 266898 A2, 05/11/88, (Exxon Res. & Dev. Co.). Metal is deposited alone or with a promoter as film on support.

18. K. P. De Jong, J. H. E. Glezer and M. F. M. Post, (Shell International). A Fischer-Tropsch catalyst contains Fe, Ni or Co deposited on silica with additional Group VIII metal(s). The catalyst may also contain Zr.
19. T. P. Kobylinski, C. L. Kibby, R. B. Pannell and E. L. Eddy, U.S. 5,605,679, 08/12/86, (Chevron Res. Co.). A Co-based catalyst is prepared by impregnation of Co carbonyl on alumina or silica and then activating in sequential steps of reduction in hydrogen, oxidation, and re-reduction in hydrogen.
20. P. F. Meier and F. Pennella, U.S. 4,623,669, 11/18/86, (Phillips Petroleum Co.). A metal is vaporized in the presence of a solvent and condenses to form a solid mixture; this is warmed to form a metal-solvent slurry which is then contacted with a support and then the solvent is removed. Co evaporation into toluene followed by deposition on a silica support was the example preparation.
21. H. Beuther, C. L. Kibby, T. P. Kobylinski and R. B. Pannell, U.S. 4,605,680, 08/12/86, (Chevron Research Co.). Alumina is used to support Co and one or more Group VIII or IVB metal oxide promoters.
22. E. J. R. Sudhoelter, EP 180269, 05/07/86, (Shell International). Co-silica catalyst preparation procedure is described wherein silica is obtained from a Si halogen, alkoxy and/or acyloxy).
23. A. I. Foster, R. W. Joyner, J. J. McCarroll, S. R. Partington, R. G. L. Spiers and S. R. Tennison, WO 8601499 A1, 03/13/86, (British Petroleum Co.). Co or Fe (with option of including Pt) is deposited on a C support.
24. D. Bode and S. T. Sie, EP 188304 A1, 07/23/86, (Shell International). Co, and one or more of Zr, Ti, Cr and Ru is deposited on a silica, alumina or silica-alumina support.

25. P. K. Coughlin, WO 8600296, 01/16/86, (Union Carbide Corp.). Co with Th promoter and 1-50 mole% (based on Co) of an additive (e.e, Mo and/or W) supported on a zeolite, SAPO or non-zeolite molecular sieve.
26. H. Beuther, T. P. Kobylinski, C. L. Kibby and R. B. Pannell, ZA 8505317, 03/26/86, (Gulf Res. & Dev. Co.). Co (5-25 WT.%) and Ru (or other promoters, 0.01-0.5 wt%) is deposited on a support. The average particle diameter is 10-110 micron size and is suitable for use as slurry phase conversion of synthesis gas to hydrocarbons.
27. V. L. Payne and C. H. Mauldin, U.S. 4,595,703, 06/17/86, (Exxon Res. & Eng. Co.). Co is dispersed on a TiO₂ or ThO₂ support that, when titania, has greater than 2:3 rutile-anatase ratio.
28. M. F. M. Post and S. T. Sie, EP 153781 A2, 09/04/85, (Shell International). A two step process for converting synthesis gas to diesel range fuels. In the first stage a Fischer-Tropsch catalyst containing Co (3-60)-Zr(0.1-100)-SiO₂(100) so that conversion is in range $(F - 0.5)/(F + 2)(150) < C < (F - 0.5)/(F + 1)(250)$, where F is syngas flow and C is syngas conversion. After water removal, the gaseous products are separated and contacted in the second step with two catalysts (e.g., Co-Zr-SiO₂ (I) and Cu-Zn-alumina (II)).
29. J. K. Minderhoud, M. F. M. Post, S. T. Sie and E. J. R. Sudholter, EP 142887 A2, 05/29/85 (Shell International). Hydrocarbon steam reforming produces a syngas that is converted with a Fischer-Tropsch catalyst containing SiO₂ (100), Co (15-50) and a second metal (chosen from Zr, Ti, Ru or Cr) (> 0.1). The catalyst is prepared by sequential impregnation.

30. J. K. Minderhoud, M. F. M. Post, S. T. Sie and E. J. R. Sudholter, EP 142888 A2, 05/29/85, (Shell International). C₉+ hydrocarbons are manufactured in a two stage process consisting of steam reforming of C₁-C₄-hydrocarbons with a Ni-containing catalyst followed by Fischer-Tropsch synthesis with a Co-containing catalyst (e.g., Co:Zr:SiO₂ = 25:18:100).
31. J. K. Minderhoud and M. F. M. Post, EP 127220 A2, 12/05/84, (Shell International). Fischer-Tropsch catalysts were prepared by a three-step impregnation of silica with a solution of zirconium tetrapropoxide in a propanol-benzene, then aqueous cobalt nitrate, kneading and then calcination.
32. R. S. Sapienza, M. Sansone and W. A. R. Slegier, U.S. Patent Application 482372, 06/22/84, (United States). A catalyst for converting synthesis gas to hydrocarbons contains 0.1-10:10-70 (wt.%) Pd or Pt-Co-alumina where alumina does not show an XRD peak for alumina. The catalyst was prepared by impregnating a Pd/Al₂O₃ catalyst with Co₂(CO)₈ in the reactor and then heating with synthesis gas to the reaction temperature.
33. J. K. Minderhoud, M. F. M. Post and S. T. Sie, EP 109702 A1, 05/30/84, (Shell International). A catalyst with the composition 0.9:25:100 wt Zr-Co-silica was used for Fischer-Tropsch synthesis.
34. H. Beuther, C. L. Kibby, T. P. Kobylinski and R. B. Pannell, U.S. 4,413,064, 11/01/83, (Gulf Res. & Dev. Co.). A catalyst suitable for use in a fluidized reactor was prepared by impregnating finely divided alumina support with a Co salt, drying, and then contacting with a nonaqueous solution containing salts of Ru and a Group IIIB or IVB metal.

ATTACHMENT III

**The Preparation of Cobalt Fischer-Tropsch Catalysts -
Literature from 1962**

Yong-qing Zhang and Burtron H. Davis

ATTACHMENT III

The Preparation of Cobalt Fischer-Tropsch Catalysts -

Literature from 1962

Cobalt Fischer-Tropsch catalysts has been widely investigated in recent years due to its high activity and selectivity for the synthesis of long-chain hydrocarbons. In this review, we summarize preparation methods of cobalt Fischer-Tropsch catalysts. The effect of precursors, promoters, support materials and pretreatment conditions are covered. These effects arise at the level of a catalytic site and reflect the influence of site structure, composition and electronic properties on the rate of the primary chain growth and the selectivity of catalysts. Such modifiers for metal catalysts have been hypothesized to act by the structural modification of the metal surfaces that is induced by a promoter (III.1-III.3), by blockage of the active catalytic sites by the modifier (III.4), by charge transfer between the modifier and the metal (III.5,III.6), by direct chemical interactions between the modifier and the active intermediates (III.7) and/or by the effect of the electrostatic field of the modifier ions (III.8-III.10). As to cobalt catalysts, work has been done on the promotion effect of potassium, zirconium, ruthenium, platinum, rhenium, etc.

The noble metal promoter has been suggested to have a number of different ways of affecting catalyst performance. It has been proposed that it acts as a source of hydrogen spillover (III.11), that it increases the reducibility of cobalt (many), that it preserves activity by preventing the buildup of carbonaceous deposits (III.12), that it exhibits cluster and ligand effects (III.13), and that it provides a combination of enhanced cobalt reducibility and dispersion (III.14). It has even been reported that the

addition of a second metal component may have no, or a detrimental, effect on CO hydrogenation activity (III.15).

Ruthenium promoters have been reported (III.13, III.16-III.20). Two papers (III.16,III.20) indicate the use of alumina as support material and the preparation of the catalyst using an incipient wetness impregnation method. Cobalt nitrate hexahydrate, ruthenium nitrosyl nitrate and ruthenium chloride were used as precursors. The incipient wetness impregnation was carried out in a single step followed by drying and calcination. Some catalysts, however, were prepared by sequential impregnation of cobalt and ruthenium with intermediate drying, calcination, or reduction in order to determine the ways that differences in catalyst preparation influence catalyst performance. Co-Ru/Al₂O₃ catalysts described in these references contained 20 wt% cobalt and 0.5 wt% ruthenium. Their results indicate that the addition of small amounts of ruthenium on alumina-supported cobalt catalysts facilitate the reduction of the cobalt. This conclusion was based on the lowering of the reduction temperatures during temperature programmed reduction (TPR) by approximately 100°C and essentially complete reduction of the Ru-promoted catalyst (CoRu/Al₂O₃) at 350°C compared to only a 60% reduction of the unpromoted Co/Al₂O₃ catalyst. In parallel, the amount of metal atoms exposed on the surface, determined by hydrogen chemisorption, increased by a factor of three upon ruthenium promotion.

Catalyst activity was obtained by the conversion of a helium diluted H₂/CO mixture (H₂/CO = 10; 20 cc/min H₂; 2 cc/min CO; total flow 100 cc/min; H₂ = 8 NL/hr•g-cat.; CO = 0.8 NL/hr•g-cat; total flow 40 NL/hr•g-cat). The catalyst bed consisted of 15 mg catalyst diluted with 15 mg of quartz powder. The reaction was conducted in a fixed-bed reactor at 220°C and 1.8 atm. The catalyst contained 20 wt.% cobalt and, if

present, 0.5 wt.% ruthenium. If the rate ($\mu\text{mole/gCo}\cdot\text{s}$) is assumed to be based on CO, we calculate that $25 \mu\text{mole/gCo}\cdot\text{s}$ corresponds to $0.25 \text{ gCH}_2/\text{hr}\cdot\text{g-cat}$ and $50 \mu\text{mole/gCo}\cdot\text{s}$ corresponds to $0.5 \text{ gCH}_2/\text{hr}\cdot\text{g-cat}$ (Figure III.1). From the data shown in Figure III.2, the temperature of reduction (300, 350 and 400°C) does not impact the reaction rate; however, the calcination temperature does and the catalyst calcined at 300°C is about twice as active as the material after calcination at 400°C .

An increase in surface exposed metal atoms was paralleled by an equivalent increase in the rate of CO hydrogenation, yielding practically constant turnover frequencies (Figure III.3). Steady-state isotopic transient kinetic analysis (SSITKA) results indicated constant intrinsic activities but an increase in the number of reaction intermediates at constant coverages when a Ru-promoted catalyst was compared to the unpromoted cobalt catalyst. There was little change in product selectivity. Promotion with more than 0.5% Ru improved the catalyst characteristics only marginally. From these results they conclude that ruthenium acts only as a reduction promoter for cobalt by increasing the reducibility and dispersion of the cobalt. These results for Ru promotion are compatible with those recently reported for Pt-promoted cobalt FTS catalysts (III.21).

As shown in Figure III.4, the presence of ruthenium increases the rate of hydrocarbon production by up to a factor of four. Iglesia et al. (III.13) reported that ruthenium promotion of silica- and titania-supported cobalt catalysts caused a synergistic effect since the specific rates for CO hydrogenation, expressed as turnover frequencies (TOFs) based on hydrogen chemisorption, increased with addition of small amounts of ruthenium. They attributed this improvement to the hydrogenation activity of ruthenium and its ability to decrease, or prevent, carbon formation on the surface of

cobalt. In contrast to Iglesia et al., Kogelbauer et al. (III.16) conclude that surface enrichment of ruthenium is unlikely for the alumina supported cobalt-ruthenium catalysts.

Belambe et al. (III.20) reported methane selectivities in the range of 70-85% for the cobalt catalysts tested in Goodwin's laboratory (Table III.1) and attributed this to the high H_2/CO ratio (=10) that they used. The Anderson-Schulz-Flory (ASF) alpha values obtained by Belambe et al. were in the range of 0.37 for the aged, steady-state catalysts and 0.4-0.42 for the fresh catalyst (Table III.1). Ruthenium appeared to inhibit the formation of highly irreducible cobalt species (cobalt oxide strongly interacting with the support to form cobalt aluminates) or to promote their reduction, indicated by the absence of the broad, high-temperature TPR feature observed with Co/Al_2O_3 and the greater degree of reduction. Calcination of Ru/Al_2O_3 or Co/Al_2O_3 precursors prior to a sequential impregnation of cobalt or ruthenium, respectively, impeded the intimate mixing of the metal components. Coimpregnation of the metal salts appeared to produce catalysts slightly more active for CO hydrogenation.

They (III.20) also investigated the effect of calcination and reduction temperatures on the activity of a Ru-promoted 20 wt% Co/Al_2O_3 catalyst for the CO hydrogenation reaction by steady-state reaction and SSITKA (III.20). While reduction temperature in the range 300-450°C had at most a negligible effect, calcination temperature was found to have a significant effect on the overall activity of this catalyst. The overall catalyst activity decreased with increasing temperature of calcination (Figure III.2). However, pretreatment temperatures did not affect the intrinsic activity of the catalyst sites. The decrease in CO hydrogenation rate with increasing calcination temperature was found to be attributable to a decrease in the number of surface active

sites due to a decrease in the reducibility of the catalyst. The SSITKA results, which showed no change in the surface residence time for CH_4 intermediates with increasing calcination temperature, as well as the TOF results, confirmed that there was no change in the intrinsic activity of the sites producing methane. Neither the reduction nor the calcination conditions had any effect on chain growth probability. Calcination temperature did have, however, a small effect on CH_4 selectivity.

A study of CO hydrogenation on La^{3+} -promoted Co/SiO_2 catalysts (La/Co atomic ratios of 0-0.75; Cab-O-Sil silica support) has been performed by Haddad et al. (III.21) using both global rate measurement and SSITKA. The prereduced and passivated base catalyst containing 20% cobalt was impregnated by incipient wetness with the appropriate amount of an aqueous solution of $\text{La}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ to obtain catalysts with La/Co atomic ratios of 0.0, 0.05, 0.1, 0.2, 0.3, 0.5 and 0.75. After impregnation, the catalyst was allowed to dry in an oven overnight at 90°C . Finally, it was re-reduced in hydrogen at 350°C for 22 h and passivated at 25°C .

Aqueous impregnation of Co/SiO_2 with La^{3+} led to a significant decrease in the number of intermediates leading to methane during CO hydrogenation (Figure III.5), but it did not alter the nature of the active sites (III.21). In a previous characterization paper (III.21a) La^{3+} promotion of Co/SiO_2 was shown to moderate strong Co-support interactions brought about by aqueous impregnation of the Co/SiO_2 and to enhance the reducibility of the cobalt oxide. La^{3+} addition to the Co/SiO_2 catalyst was found to lead to a significant increase in the activity for Fischer-Tropsch synthesis (on a per gram cobalt basis) (Figure III.6). It appears that the impregnation to produce the B-La0 (0 means no La^{3+} promoter) catalyst from the B catalyst caused a decrease in the amount of CO adsorbed and in the TON; the reason for this was not given. The SSITKA results

showed that the concentration of active intermediates leading to methane increased with increase in La/Co ratio. However, the TOF, the pseudo-first-order rate constant, the reactivity distribution function, and the activation energy were not affected by La³⁺ addition. Thus, it can be concluded that La³⁺ did not change the nature of the active sites, just their concentration. This increase in the concentration of active sites follows exactly the increase in surface Co⁰. La³⁺ promotion also caused the chain growth probability (Figure III.7) and the olefin/paraffin ratio (Figure III.8) to increase significantly at 220°C for H₂/CO=2.

Ali et al. (III.22) also investigated the influence of zirconia promotion of 20 wt% Co/SiO₂ on FTS using catalysts prepared in different ways and having different loadings of zirconia (up to 8.5 wt%). The catalysts were investigated using FTS (H₂/CO=2), H₂-D₂ exchange, and CO dissociation to provide insight into how zirconia modifies the cobalt properties. The Zr-promoted catalysts exhibited higher overall rates of FTS compared to unpromoted Co/SiO₂ (Figure III.9). The sequentially impregnated Co/Zr/SiO₂ catalysts appeared to be the most active. However, the coimpregnation method of preparation appeared to result in higher cobalt dispersion. While zirconia promotion did not appear to promote or inhibit hydrogen activation, hydrogen spillover may have been partly responsible for enhancing the activity of the sequentially impregnated Zr/Co/SiO₂ catalysts. Zirconia also possibly created an active interface with cobalt that increased catalyst activity by facilitating CO dissociation. Although high levels of promotion tended to increase the selectivity for higher hydrocarbons, zirconia appears to primarily function as an excellent rate promoter for Co/SiO₂.

Huffman et al. (III.23) studied the promotion effect of potassium on cobalt catalysts. The K-promoted Co/Al₂O₃ catalyst was prepared by impregnating the

passivated 9.0 wt% Co/Al₂O₃ catalyst with a solution of potassium nitrate in order to have an atomic ratio of K/Co=1. In situ XAFS spectroscopy studies were conducted at reaction conditions on the potassium-promoted cobalt catalysts supported on SiO₂ and Al₂O₃, and on similar samples without potassium. Measurements were conducted at temperatures up to 200°C under both reducing and simulated FTS reaction conditions. Potassium and cobalt K-edge XANES spectra indicate that potassium interacts with both the cobalt phase and the SiO₂ support, and that potassium promotion inhibits the reduction of the Co/SiO₂ catalyst in hydrogen at 200°C. However, under CO hydrogenation conditions in the presence of water vapor, the differences in degree of reducibility are less since the unpromoted catalyst becomes more oxidized. For the K-promoted Co/Al₂O₃ catalyst, Co K-edge XANES and EXAFS spectra show that cobalt is initially present as a mixture of Co₃O₄ and CoO. Under hydrogen at 200°C, these oxides are reduced to a mixture of CoO and cobalt metal. During reaction at 200°C in H₂/CO, the cobalt phases are reconverted to a mixture of Co₃O₄ and CoO. Without potassium, the cobalt in Co/Al₂O₃ is reduced almost completely to cobalt metal under hydrogen at 200°C and remains in that form even during reaction at 200°C in H₂/CO. Only a minor trace of CoO is observed.

Schanke et al. (III.24) undertook studies directed toward explaining the role of platinum as a promoter for hydrocarbon synthesis on alumina-supported and silica-supported cobalt catalysts. In addition to conventional measurements of kinetics and metal surface areas, direct information on reaction rates and surface coverage of reaction intermediates has been obtained by the use of SSITKA experiments. Al₂O₃ and SiO₂ supported catalysts containing 9 wt% cobalt and 0 or 0.4 wt% platinum were prepared by incipient wetness coimpregnation of the supports with aqueous solutions of

$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$. At $T = 483\text{K}$, $P = 1\text{ bar}$ and $\text{H}_2/\text{CO} = 7$, CO hydrogenation rates (based on weight of cobalt) of Pt-promoted catalysts were 3-5 times higher than those on their unpromoted analogues. The selectivity was not influenced by the presence of platinum. TPR-studies shown that the presence of platinum strongly influences the reducibility of the catalysts, with TPR-peaks shifting to lower temperatures for all catalysts. This effect is most pronounced on the Al_2O_3 supported catalysts, where the highly dispersed and otherwise difficult to reduce surface cobalt oxides are readily reduced at normal reduction temperature in the presence of platinum. The dispersion of metallic cobalt for platinum promoted catalysts increased compared to that on the unpromoted catalysts, with Al_2O_3 supported catalysts showing the largest effect due to the reduction of highly dispersed surface cobalt oxide. Apparent turnover numbers (based on H_2 -chemisorption) were higher for Pt-promoted catalysts than for their unpromoted analogues by a factor of two. Decoupling coverage and intrinsic reactivity effects on the apparent turnover number by the use of SSITKA revealed essentially constant true turnover numbers on all catalysts. Thus, the increased apparent turnover numbers on Pt-promoted catalysts are due to a higher surface coverage of reactive intermediates.

In another paper (III.15), they reported the preparation of Pt- and Re-promoted 8.7 wt% $\text{Co}/\text{Al}_2\text{O}_3$ (1.0 wt% platinum or 1.0 wt% rhenium) by impregnating Al_2O_3 with an aqueous solution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ using the incipient wetness technique. The sample was dried and calcined for 2 h at 573 K. Portions of the calcined base catalyst were then modified by impregnating with an aqueous solution of $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ or Re_2O_7 . An investigation of the CO hydrogenation of the two promoted catalysts has been carried out at two different conditions: 473 K, 5 bar, $\text{H}_2/\text{CO}=2$ and 493 K, 1 bar, $\text{H}_2/\text{CO}=7.3$.

The addition of platinum or rhenium significantly increases the CO hydrogenation rate (based on weight of cobalt), but the selectivity was not changed by the presence of platinum or rhenium. The results show that the observed increases in the reaction rates are caused by increased reducibility and increased number of surface exposed Co-atoms. SSITKA with carbon tracing was used to decouple the effects of the concentration of active surface intermediates and the average site reactivity of intermediates during steady-state CO hydrogenation. The SSITKA results show that the concentration of active surface intermediates leading to CH₄ increased as a result of the addition of a noble metal promoter. However, the average site activity was not significantly affected upon rhenium or platinum addition.

Holmen (III.25) also studied the effect of small amounts of Re on the reduction properties of alumina supported cobalt catalysts by TPR. An intimate mixture of Co/Al₂O₃ and Re/Al₂O₃ catalysts showed a promoting effect of rhenium similar to that for coimpregnated Co-Re/Al₂O₃. A loose mixture of Co/Al₂O₃ + Re/Al₂O₃ did not show any effect of rhenium on the reduction of cobalt. However, when the loose mixture of Co/Al₂O₃ + Re/Al₂O₃ was pretreated with argon saturated with water before the TPR, a promoting effect of rhenium on the reduction of cobalt was observed. It is suggested that rhenium promotes the reduction of cobalt oxide by hydrogen spillover, and that no direct contact between rhenium and cobalt seems to be necessary in order to obtain the promoting effect as observed by TPR. It is also shown that the presence of a high temperature TPR peak at 1200 K assigned to cobalt aluminate is mainly a result of Co-ion diffusion during the TPR and not during calcination. It would appear that another possibility would be water assisted transport of rhenium onto the Co-Al₂O₃ particles.

Iglesia (III.13) has reported work on TiO_2 and SiO_2 supported Ru-promoted cobalt catalysts. The catalytic activity was obtained using a fixed-bed reactor with $\text{H}_2/\text{CO} = 2.05$, 453-523 K, 0.01-2 MPa and 2-10 g catalyst with an average diameter of less than 0.2 mm to avoid diffusional effects. Their Co-Ru/ TiO_2 catalysts were prepared by adding a ruthenium nitrate/acetone solution to an acetone slurry containing the pretreated, calcined, reduced and passivated Co/ TiO_2 catalyst, followed by evaporation of the acetone solvent while stirring. The cobalt and ruthenium contents were 11.6 and 0.14% wt., respectively, corresponding to an atomic Ru/Co ratio of about 0.0067. SiO_2 supported bimetallic Co-Ru/ SiO_2 catalyst was prepared from formerly prepared Co/ SiO_2 using the synthesis and pretreatment procedures described above for TiO_2 -supported catalysts. Cobalt and ruthenium contents were 23.0 and 0.26 wt.%, respectively, corresponding to an atomic Ru/Co ratio of about 0.0070. It seems the addition of small amounts of ruthenium to Co/ TiO_2 or Co/ SiO_2 catalysts (Ru/Co, 0.008 atm) increase their turnover rate (Figure III.10) and C_5+ selectivity (Figure III.11) for FTS. The methane make was much lower than Kogelbauer et al. (III.16) reported and the alpha-values were much higher. Also, deactivated bimetallic Co-Ru catalysts can be regenerated by a hydrogen treatment at the reaction temperature whereas monometallic cobalt catalysts cannot. On Co/ TiO_2 , ruthenium addition increases the turnover rates by a factor of three and C_5+ selectivities from 84.5 to 91.1%, without an apparent change in cobalt dispersion. Activation energies (88 ± 6 kJ/mol) and kinetic pressure orders ($n = 0.6-0.65$ for CO) are unaffected by ruthenium addition. These data suggest that the presence of ruthenium leads to higher cobalt site density during reaction without modifying the chemical reactivity of exposed cobalt surface atoms. Ruthenium appears to inhibit the deactivation of surface cobalt ensembles. Ruthenium

atoms at the surface of cobalt crystallites increase the rate of removal of carbon and oxygen species during reaction and during regeneration of deactivated cobalt catalysts. The resulting higher cobalt site density leads to higher apparent turnover rates and to enhanced readsorption of olefins. As a result, Co-Ru catalysts yield a heavier and more paraffinic product than monometallic cobalt catalysts with a similar initial dispersion. The observed bimetallic interactions require intimate contact between cobalt and ruthenium, a state that forms during oxidation of the bimetallic precursors at high temperature. This treatment induces migration of ruthenium oxide species and leads to mixed Co-Ru oxides. The reducibility and the carbon deposition rates on well-mixed bimetallic Co-Ru catalysts are very different from those of monometallic cobalt catalysts. Electron microscopy, X-ray absorption spectroscopy, and thermogravimetric studies confirm the intimate mixing required for catalytic rate and C₅+ selectivity enhancements, for faster reduction of the cobalt oxide precursor, and for inhibition of carbon deposits during reactions of H₂/CO mixtures.

Turney (III.19) prepared a Ru-promoted coprecipitated cobalt/ceria catalyst. A mixture of ammonium ceric nitrate and cobalt nitrate hexahydrate in water was slowly added to an aqueous solution of ammonium carbonate, while stirring vigorously and bubbling carbon dioxide through the reaction vessel. After addition, the pH dropped to 7.1; the resultant dark brown precipitate was collected by centrifugation and washed five times with 4 L aliquots of water and then twice with 2 L aliquots of acetone. Residual acetone was removed in vacuo at ambient temperature. Further drying at 120°C for 16 h in air and then calcination at 600°C gave a black powder. Promotion was effected by adsorption of Ru₃(CO)₁₂ from solution in n-heptane onto the support; on stirring under nitrogen for 2 h, the solution was fully decolorized, indicating complete

uptake of the ruthenium carbonyl. FTS using the catalysts indicates the addition of ruthenium lowers the reduction temperature of both Co_3O_4 and CeO_2 further, presumably via hydrogen spillover reduction. Consequently there is more Co^0 in the ruthenium-promoted catalyst than the unpromoted catalyst leading to higher activity.

Bianchi et al. (III.18) prepared a Ru-doped cobalt titanium silicate (ETS-10) catalyst by a slurry impregnation of the ion-exchanged ETS-10 with a solution of $\text{Ru}(\text{NO})(\text{NO})_3$ in pure ethanol. The result indicates that the presence of small amounts of ruthenium introduced by wet-impregnation leads a complete reduction of the surface cobalt species and an increase of CO conversion and of the selectivity to iso-products. Upon increasing the amount of ruthenium, a further increase of the CO conversion and an interesting decrease of the C_1 fraction was found.

Kiviaho et al. (III.17) prepared a Co-Ru/ SiO_2 catalyst from the carbonyl cluster. $\text{Co}_{4n}\text{Ru}_n\text{H}_n(\text{CO})_x/\text{SiO}_2$ and $(\text{Co}_4(\text{CO})_{12}+\text{Ru}_4\text{H}_4(\text{CO})_{12})/\text{SiO}_2$ catalysts were prepared and their TPR and FT-IR properties were studied. $\text{Co}_{4n}\text{Ru}_n\text{H}_n(\text{CO})_x/\text{SiO}_2$ and $(\text{Co}_4(\text{CO})_{12} + \text{Ru}_4\text{H}_4(\text{CO})_{12})/\text{SiO}_2$ catalysts were prepared from the carbonyl cluster and their TPR and FT-IR properties were studied by Kiviaho et al. (III.17). The FT-IR studies suggested that $\text{Ru}_4\text{H}_4(\text{CO})_{12}$, $\text{CoRu}_3\text{H}_3(\text{CO})_{12}$ and $\text{Co}_3\text{RuH}(\text{CO})_{12}$ clusters on silica were more stable in room temperature than $\text{Co}_4(\text{CO})_{12}$, $\text{Co}_2\text{Ru}_2\text{H}_2(\text{CO})_{12}$ and $\text{Co}_2\text{Ru}_2(\text{CO})_{13}$ clusters. The FT-IR measurements also indicated that all precursors decomposed during thermal treatment, but the distinct temperature of decarbonylation was not necessarily noticeable. On the other hand, in TPR, the CO desorption peak maxima for the precursors were 123°C for $(\text{Co}_4(\text{CO})_{12}+\text{Ru}_4\text{H}_4(\text{CO})_{12})$, 127°C for $\text{CoRu}_3\text{H}_3(\text{CO})_{12}$, 133°C for $\text{Co}_2\text{Ru}_2(\text{CO})_{13}$, 137°C for $\text{Co}_4(\text{CO})_{12}$, 144°C for $\text{Co}_2\text{Ru}_2\text{H}_2(\text{CO})_{12}$, 148°C for $\text{Co}_3\text{RuH}(\text{CO})_{12}$ and 185°C for $\text{Ru}_4\text{H}_4(\text{CO})_{12}$. Thus, the catalysts with 1:1 atomic ratio of

Co:Ru decarbonylated at different temperatures. The temperature of decarbonylation was lower for $\text{Co}_2\text{Ru}_2(\text{CO})_{13}/\text{SiO}_2$ than for $\text{Co}_2\text{Ru}_2\text{H}_2(\text{CO})_{12}/\text{SiO}_2$, i.e., cobalt influenced the decarbonylation more in the first case. In accordance, the CO hydrogenation activity and selectivity results for the decarbonylated catalysts suggested that $\text{Co}_2\text{Ru}_2(\text{CO})_{13}/\text{SiO}_2$ exhibited the characteristics of cobalt more than $\text{Co}_2\text{Ru}_2\text{H}_2(\text{CO})_{12}/\text{SiO}_2$ did.

Effects of activation on the surface properties of silica-supported cobalt catalysts were studied by Coulter and Sault (III.26). Drying and calcining effects for 16-19 wt% Co/SiO₂ FTS catalysts, prepared by impregnation with cobalt nitrate, have been examined using ultrahigh vacuum surface analysis and conventional catalyst characterization techniques. Drying in air at 110°C or under vacuum at 100°C and then calcining in air at 400°C causes large Co₃O₄ particles to form, which easily reduce under hydrogen at 300°C. In contrast, dried samples annealed under UHV prior to calcining exhibit dramatically different characteristics. The decomposition of cobalt nitrate during drying initiates the formation of a surface cobalt silicate. Prolonged air drying eventually converts the surface silicate into Co₃O₄, while vacuum drying disperses the nitrate precursors on the support, forming cobalt silicate islands. Annealing air-dried samples in UHV stabilizes the surface silicate against reduction or oxidation through the migration of Co²⁺ ions into the support to form a well-ordered bulk cobalt silicate. Annealing of vacuum dried samples to 200°C in UHV produces a continuous, conductive surface silicate that sinters upon heating to temperatures above 250°C. Analysis of species generated during the decomposition of the $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ precursor indicates that the concentration of gas phase CO near the surface determines the nature of the cobalt surface phase. The formation of an intermediate

surface cobalt silicate under specific activation conditions maximizes the amount of reducible cobalt surface area available for FTS reactions.

The precursor can significantly influence the property of the catalyst.

Loosdrecht et al. (III.27) prepared alumina-supported cobalt catalysts from different cobalt precursors to study its influence on the ultimate metal particle size. Furthermore, the effect of the particle size on the catalytic performance (activity and selectivity) during FTS was investigated. The preparation by incipient wetness impregnation, using cobalt EDTA and ammonium cobalt citrate precursors, of low-loaded cobalt catalysts (2.5 wt%) resulted initially in very small cobalt oxide particles, as determined by XPS. The small oxide particles reacted during the thermal treatment in a reducing gas flow with the alumina support to form cobalt aluminate, which was neither active nor selective during FTS. The catalysts prepared with cobalt nitrate had larger particles that could be easily reduced to metallic cobalt. These catalysts were active under reaction conditions (fixed-bed reactor, 523 K, $H_2/CO = 2$, 30 ml/min, 1 atm). Higher-loaded cobalt catalysts (5.0 wt%) prepared using ammonium cobalt citrate showed a larger particle size than the lower-loaded catalyst prepared from the citrate precursor. The extent of reduction to metallic cobalt that could be achieved with the higher-loaded catalyst was significantly higher than that with the lower-loaded catalyst, as shown by magnetic measurements. Accordingly, the authors report that "the higher-load catalyst exhibited a reasonable activity and, in addition, an interesting and remarkably high selectivity toward higher hydrocarbons, and also a very high Schulz-Flory parameter." This statement must be viewed as a relative comparison since the methane selectivities varied from 36 to 64% and the alpha values were in the range of 0.45 to 0.69, low values for a cobalt catalyst.

The effect of the precursor on the characteristics of the Co/SiO₂ catalysts prepared from Co(NO₃)₂, Co(CO)₈ and Co₄(CO)₁₂ was determined by Niemela et al. (III.28). The near-surface reduction was clearly lower for the Co₂(CO)₈ derived catalyst than for the Co₄(CO)₁₂ based one. The hydrogen chemisorption, CO desorption, XRD and XPS measurements indicated that the dispersion of the metallic species decreased in the precursor order Co₂(CO)₈ > Co₄(CO)₁₂ >> Co(NO₃)₂. The TPD studies showed that CO was more strongly adsorbed on catalysts derived from carbonyls than on those based on nitrate, resulting in greater initial activity for CO hydrogenation. In pulsed CO hydrogenation reactions, the selectivity of the Co₂(CO)₈ derived catalyst differed from the other two. Thus, despite the well documented transformation of the Co₂(CO)₈ to Co₄(CO)₁₂ on the silica support, the supported catalysts derived from these two precursors exhibited distinct characteristics and reactivity.

The activity of the Co/SiO₂ catalyst in relation to pretreatment of the catalyst was investigated by Niemela et al. (III.29). With increasing reduction temperature (300-450°C), the extent of reduction increased. The increase was not, however, accompanied with increased chemisorption capacity. Namely, the hydrogen chemisorption was highest at a reduction temperature of approximately 300°C. Also, carbon monoxide adsorption was almost constant at 200-400°C, and decreased drastically when the catalyst was heated to higher temperatures. Thus, the results suggest that cobalt agglomerated at temperatures above 400°C. The activity for toluene hydrogenation correlated well with the hydrogen uptake for reduction temperatures above 300°C. Also, the CO hydrogenation activity (235°C; 5 bar, H₂/CO/Ar = 3/1/3, GHSV = 2600 h⁻¹) of the catalyst increased with increasing temperature of reduction (400-450°C) due to the decrease in the number of active sites

(figure III.12). These results are in contradiction to the results of Moon and Yoon (III.30) who obtained a higher extent of reduction and catalytic activity by increasing the reduction temperature in the range 325-525°C. Johnson et al. (III.31) also obtained increasing activity (expressed as CO turnover frequency) with increasing percentage of reduction, although the specific activity of the well reduced catalyst sample did not depend upon cobalt dispersion.

Iglesia (III.32) found that catalyst productivity and selectivity to C₅+ hydrocarbons are critical design criteria in the choice of FTS catalysts and reactors. Cobalt-based catalysts appear to provide the best compromise between performance and cost for the synthesis of hydrocarbons from CO/H₂ mixtures. Optimum catalysts with high cobalt concentration and site density can be prepared by controlled reduction of nitrate precursors introduced via melt or aqueous impregnation methods. FTS turnover rates are independent of cobalt dispersion and support identity over the accessible dispersion range (0.01-0.12) (Figure III.10) at typical FTS conditions. At low reactant pressures or conversions, water increases FTS reaction rates and the selectivity to olefins and to C₅+ hydrocarbons. These water effects depend on the identity of the support and lead to support effects on turnover rates at low CO conversions. Turnover rates increase when small amounts of ruthenium (Ru/Co < 0.008 atm) are added to cobalt catalysts. C₅+ selectivity increases with increasing cobalt site density because diffusion-enhanced readsorption of α-olefins > β-hydrogen abstraction steps and inhibits chain termination. The readsorption of α-olefins merely has the effect of reversing the predominant chain termination pathways of small surface chains (β-hydrogen abstractions) by reinitiating surface chains that continue to grow and ultimately desorb as larger hydrocarbons. In effect, termination of alkyl chains via β-hydrogen abstraction becomes increasingly

reversible as olefin concentration or residence time increases; the readsorption reaction also becomes faster as reactive olefins are retained longer within liquid-filled catalyst pellets. This well known secondary reaction leads to an increase in the selectivity to C₅+ hydrocarbons and to lower selectivities to methane and olefins as bed residence time increases. Clearly, readsorption effects become more influential as olefin concentrations increase with increasing bed residence time and CO conversion. Severe diffusional restrictions, however, can also deplete CO within moderate diffusional restrictions. Diffusional constraints depend on pellet size and porosity and on the density and radial location of cobalt sites within catalyst pellets. Slurry bubble column reactors and the use of eggshell catalyst pellets in packed-bed reactors introduce design flexibility by decoupling the characteristic diffusion distance in catalyst pellets from pressure drop and other reactor constraints.

Catalytic rates and selectivity can reflect the intrinsic behavior of a metal surface. Sometimes, this surface chemistry changes because metal crystallites of different size expose surface ensembles with unique structures (III.33); strong interactions with a metal oxide support can also perturb the electronic density and structure of metal crystallites (III.34). The effect of titania, silica, alumina, zirconia and ZSM-5 on the specific activity and selectivity properties of cobalt for carbon monoxide hydrogenation has been studied by different authors under different conditions.

Bessell (III.35) examined a range of cobalt catalysts supported on kieselguhr, silica, alumina, bentonite, Y-zeolite, mordenite and ZSM-5 for catalytic activity and product selectivity for FTS at 240°C, 2 MPa using a GHSV of 1000 h⁻¹ in a microreactor. These results were correlated with catalyst reducibility and adsorptive properties, as well as support acidity, surface area and structure. In order to maximize the activity of

cobalt-based Fischer-Tropsch catalysts, it is necessary to choose high surface area supports and to obtain high cobalt dispersions. However, possible interactions between cobalt and the support must be taken into account as they can lead to lower catalyst activity. This was evidenced by the alumina, Y-zeolite and mordenite supported catalysts which did not undergo complete reduction under standard conditions due to the formation of irreducible surface species or ion exchanged cobalt within the support. Incomplete reduction, while producing a more dispersed catalyst, will limit the availability of active cobalt sites. Pore structure of the support is also important as pore diffusion or blocking effects can prevent reactants accessing active cobalt sites. All supports examined showed similar methane, carbon dioxide and higher hydrocarbon selectivities, and in all cases carbon dioxide selectivity was low. However, the nature of the higher hydrocarbons depended very much on the acidity of the support. The low acidity kieselguhr, silica, alumina and bentonite supports produced the traditional straight chained Fischer-Tropsch products, and are thus the preferred type of support if a straight chained product, such as a wax or diesel fuel, is desired. If gasoline production is targeted, zeolite supported catalysts are to be preferred as a lighter, more highly branched, and at sufficiently high temperatures aromatic, product results. However, the primary formed Fischer-Tropsch products must have access to the zeolitic acid sites if these secondary isomerization and aromatization reactions are to occur. This places some constraints on the channel system and ion exchange properties of the zeolite in question.

Reuel and Bartholomew (III.36) investigated the effect of support and dispersion on the CO hydrogenation activity/selectivity properties of cobalt. Specific activities and selectivities of unsupported cobalt and cobalt supported on alumina, silica, titania,

carbon, and magnesia carriers for CO hydrogenation were measured in a single-pass differential reactor at low conversion, 1 atm, and 175-350°C. The results indicate that specific activity and selectivity of cobalt vary with support, dispersion, metal loading, and preparation method. The order of decreasing CO hydrogenation activity at 1 atm and 225°C for catalysts containing 3 wt% cobalt is Co/TiO₂, Co/SiO₂, Co/Al₂O₃, Co/C, and Co/MgO (Figure III.13). The specific activity of cobalt decreases significantly with increasing dispersion (Figure III.14). Product selectivity is best correlated with dispersion and extent of reduction (Figure III.15), i.e., the molecular weight of hydrocarbon products is lower and the CO₂/H₂O ratio is higher for catalysts having higher dispersions and lower extent of reduction. This effect may be due to stable oxides in the well-dispersed, poorly reduced catalysts, which catalyze the water-gas-shift reaction thereby increasing the H₂/CO ratio at the surface. In the Co/Al₂O₃ system, activity and selectivity for high molecular weight hydrocarbons increase very significantly with increasing cobalt loading. A 15% Co/Al₂O₃ is 20 times more active than 3% Co/Al₂O₃; moreover, 86 wt% of its hydrocarbon fraction is in the C₅-C₁₂ (gasoline) range compared to 18 wt% for 3% Co/Al₂O₃.

Silica is a very popular support for cobalt; it exhibits high surface area and it does not readily form spinels during the reduction process. However, according to Goodwin's results (III.37), the formation of cobalt silicates in Co/SiO₂ has been found to occur during FTS, whether conducted in gaseous or the liquid phase. In order to explore the role of vapor in causing this formation, the Co/SiO₂ catalyst was studied using conditions simulating those present during FTS. It was found that, depending on exposure time and gas phase concentration, a loss of the catalytically active phase and the formation of cobalt silicates occurred. The cobalt silicates formed were not

completely reducible even during TPR to 900°C. The formation of silicates occurred rapidly for the in situ reduced catalyst and even more rapidly in the presence of hydrogen. The presence of air retarded this effect. On the contrary, when the cobalt was present as the oxide, hydrothermal treatment had little effect. It is concluded that the presence of cobalt metal is necessary for Co-silica reactions to occur forming both 'reducible' and 'nonreducible' (<900°C) cobalt silicate. The results point out a type of catalyst change which can occur during reaction. The authors did not indicate how Co_o can react to form a cobalt silicate.

Khodakov et al. (III.38) studied the reducibility of cobalt species that are present in silica-supported Fischer-Tropsch catalysts using in situ XRD, in situ EXAFS, and FTIR spectroscopy with carbon monoxide as a molecular probe. Crystalline cobalt phases in the oxidized catalysts were characterized using XRD. In the oxidized samples with a large concentration of amorphous phase, EXAFS showed the presence of small oxide clusters including several cobalt atoms. It was found (in-situ XRD, EXAFS) that calcination of oxidized cobalt catalysts under an inert atmosphere resulted in a selective transformation of Co₃O₄ to CoO at 623-673 K. FTIR spectroscopy, with CO as a molecular probe, revealed the presence of different sites associated with cobalt after the reduction of the catalysts with hydrogen at 723 K: cobalt metal sites, Co²⁺ ions in the crystalline phase of CoO, and Coⁿ⁺ species in an amorphous phase. The results (XRD, EXAFS, FTIR) showed that the hydrogen reduction properties of particles of cobalt oxide on silica depended on the size of the Co₃O₄ crystallites. The ease of reduction to metal decreased from larger (200-700Å) to smaller (60Å) particles.

The long-term performance of Co/SiO₂ catalysts in CO hydrogenation was investigated by Neimela and Krause (III.39). The catalysts were prepared from nitrate

(N) and carbonyl (CO) precursors. The activity in terms of conversion of carbon monoxide was determined over a reaction time of 120 h. The activity was obtained using a fixed-bed reactor, 0.5 MPa, 235-290°C, Ar:CO:H₂ = 3:1:3 and GHSV = 5200 h⁻¹. The conversion decreased rapidly during the first five hours (**Figure III.16**), and thereafter at a moderate rate that was related to dispersion, i.e, the higher the dispersion the higher the rate of decrease. These catalysts produced 58-65 mole% methane and had alpha values in the range of 0.69-0.81. The active sites were blocked by wax and coke formed during the reaction, although some agglomeration of particles probably took place on the Co(CO)/SiO₂ catalysts. More carbon was accumulated on Co(CO)/SiO₂ during the reaction suggesting a need for frequent regeneration. The reduction-oxidation-reduction treatments indicated, however, that the regenerability of the Co(CO)/SiO₂ in terms of hydrogen uptake is poor, although the amounts adsorbed still remained higher than those for Co(N)/SiO₂.

The influence of water on alumina-supported cobalt catalysts has been studied by Schanke et al. (III.40). The deactivation of supported cobalt catalysts was studied in a fixed-bed reactor using synthesis gas feeds containing different concentration of water vapor. Supporting model studies were carried out using H₂O/H₂ feeds in conjunction with XPS and gravimetry. Rapid deactivation occurs on Re-promoted Co/Al₂O₃ catalysts when H₂/CO/H₂O feeds are used, whereas unpromoted Co/Al₂O₃ shows more stable activity (**Figure III.17**). The results from the gravimetric studies suggest that only a small fraction of the bulk cobalt metal initially present reoxidizes to cobalt oxide during reaction. However, the XPS results indicate significant reoxidation of surface cobalt atoms in highly dispersed cobalt phases, which is likely to be the cause of the observed deactivation. Rhenium is shown to have a marked effect by

decreasing the extent of reoxidation of alumina-supported cobalt catalysts and a smaller decrease in the catalytic activity.

Lapidus and co-workers (III.41-III.43) studied the physical properties and FT performance of 10% cobalt catalysts supported on alumina, silica and alumina-silica, respectively. They found that properties of impregnated cobalt catalysts depend on the nature of the support and on the temperature of pretreatment. The decomposition of dried 10% Co/Al₂O₃ and 10% Co/SiO₂ in an inert gas proceeds in two steps: water evolution and decomposition of cobalt nitrate. In a reducing atmosphere, the endothermic decomposition was accompanied by exothermic reduction of cobalt nitrate, and the whole process strongly depended on the nature of the support. On SiO₂, the formation of cobalt surface compounds with the support was much more limited than on Al₂O₃. The amount of adsorbed CO increases with calcination temperature, while both the degree of cobalt reduction and the cobalt dispersion decrease. CO was adsorbed in four different states on the 10% Co/Al₂O₃ catalyst: as linear forms on Co²⁺, Co.δ.⁺, and CoO, bridged form on CoO. Their relative amounts depended on the temperature of pretreatment. Catalyst pretreatment with a CO and hydrogen mixture under hydrocarbon synthesis conditions causes a certain modification of the metal surface which leads to variations of the CO adsorption states. The influence of the nature of the support and the pretreatment temperature on the activity of cobalt catalysts in FTS at atmospheric pressure are presented. Pretreatment by calcination in air led to a decrease in cobalt reducibility and dispersion. The degree of reduction was higher with Co/SiO₂ than with Co/Al₂O₃ at all calcination temperatures. Except for the dried samples, cobalt dispersions were higher with Co/Al₂O₃. The variations in the catalytic properties of Co/Al₂O₃ and Co/SiO₂ in FTS with the pretreatment temperature differed

for both supports. When the calcination temperature was increased, the total hydrocarbon yield decreased over Co/SiO₂ catalysts and increased over Co/Al₂O₃ catalysts. The C₅₊ fraction selectivities over Co/Al₂O₃ catalysts increased with the pretreatment temperature, whereas over Co/SiO₂ catalysts, they remained practically constant. The resistance of cobalt catalysts to the action of air was higher with samples previously used in Fischer-Tropsch synthesis than with freshly reduced ones. For freshly reduced Co/Al₂O₃ catalysts, an increase of catalytic activity was found up to a certain level after repeated doses of air were passed through the catalyst bed. The nature of the oxide phases are thought to be responsible for the variation of catalytic properties. On the Co/SiO₂ catalyst surface, the formation of Co₃O₄ supposedly reduces the total hydrocarbon yield. In spite of the decrease of cobalt dispersion, the Co-support surface compounds cause an increase in the total hydrocarbon yield and the C₅₊ fraction selectivity on the Co/Al₂O₃ catalysts.

The physicochemical properties of 10% Co/SiO₂-Al₂O₃ catalysts prepared by impregnation were studied by temperature programmed reduction, thermoanalysis and CO adsorption (III.41-III.43). The temperature at which the catalyst was pretreated has a great influence on its adsorption capacity for CO. Both reduced and unreduced samples calcined in air at relatively high temperatures adsorbed CO, but the reduced ones adsorbed much larger amounts. The adsorption capacity tended to increase with increasing pretreatment temperature. The character of CO temperature programmed desorption profiles and the proportions of the individual adsorption forms depend on the pretreatment temperature and the degree of cobalt reduction. CO was adsorbed in three forms on species originating in Co-support interactions, metallic cobalt, and on Co₃O₄. Calcination in air caused a decrease of both cobalt reduction and the activity for

hydrocarbon synthesis. While the yield of gaseous products remained constant, liquid yield decreased substantially with increasing pretreatment temperature, reaching a maximum value when the degree of cobalt reduction was approximately 40-50%. The average carbon number decreased with increasing cobalt reduction. The catalytic properties of $\text{Co/SiO}_2\text{-Al}_2\text{O}_3$ are resemble more closely those of Co/SiO_2 than of $\text{Co/Al}_2\text{O}_3$, but $\text{Co/SiO}_2\text{-Al}_2\text{O}_3$ catalysts are less efficient in polymerization than either Co/SiO_2 or $\text{Co/Al}_2\text{O}_3$. The hypothesis, suggesting that the adsorption centers of weakly bonded CO were involved in the production of liquid hydrocarbons and that the cobalt oxide species act directly in this synthesis, was confirmed.

A particularly interesting scheme is to react synthesis gas mixture over a bifunctional catalyst (III.44-III.46). The catalyst would be a combination of Fischer-Tropsch catalyst and a shape-selective zeolite. For example, the combination of metal oxides with the medium pore (ca. 6.0 Å) ZSM-5 zeolite (III.47-III.50) and the use of metal nitrate or organometallic impregnated ZSM-5 (III.51-III.55) catalysts have been shown to produce gasoline range hydrocarbons containing a high percentage of aromatics from synthesis gas. Physical and chemical properties as well as the activity and selectivity of Co/HZSM-5 zeolite bifunctional catalysts have been studied by Calleja (III.56) for conversion of synthesis gas. These catalysts were prepared by incipient wetness impregnation with different conditions of drying, calcination and reduction. The cobalt content in the catalyst and the effect of thoria, as a promoter, were also studied. The catalysts were characterized and tested in a fixed bed continuous reactor system. The results show that drying is the most important step in the preparation, having more active catalysts with fast drying conditions, probably due to the formation of smaller cobalt particles. The interaction between the metal and the zeolite surface seems to

contribute significantly to the catalyst activity. Maximum activity of the catalyst is obtained with 1.5 wt% of thorium, resulting in an increase of C_{6+} selectivity. This was explained in terms of a shift in chemisorption properties of the catalyst. The basic character of the promoter affects the zeolite acidity, decreasing the aromatic proportion in the liquid hydrocarbon fraction. [It is not clear how either ThO_2 or Rh^{4+} can exchange could do this. For example, exchange of a zeolite with La^{3+} does not appreciably change the number of acid sites of a zeolite.] Finally, the optimum bifunctional catalyst selected in this study is compared with a physical mixture of a commercial Fischer-Tropsch catalyst and HZSM-5 zeolite. The results achieved under the usual reduction conditions with both catalysts show that, for the same value of conversion, selectivity towards C_{6+} hydrocarbons was notably greater for the optimum catalyst. Although the amount of aromatic hydrocarbons was slightly lower, the percentage of C_{6+} hydrocarbons was about two-fold higher. Also, an increase could be observed in the olefinic nature of C_3 hydrocarbon fraction obtained using the selected catalyst. The most important reason for these differences may be a decrease in the acidity of the zeolite due to the basicity of ThO_2 , which reduces aromatization reactions of light alkenes. Therefore, the selected catalyst yields a higher liquid hydrocarbon fraction compared to physical mixture catalyst. Moreover, the mixture of hydrocarbons had an acceptable composition to be used as high octane number fuel.

Yin et al. (III.57) studied CO hydrogenation with PdCo/NaY catalysts. NaY-encapsulated Pd-Co bimetallic catalysts of various Co/Pd ratios and pretreatment conditions were used for carbon monoxide hydrogenation. Preparation conditions have an overwhelming effect on the active phases and the catalyst selectivity. In Pd/NaY and bimetal samples with very a low extent of cobalt reduction, the formation of

palladium carbide is detected by XRD. On these catalysts, methane is formed when particles are very small, but after some agglomeration, methanol is the dominant primary product of CO hydrogenation; secondary reactions (MTG) on strong Brønsted-acid sites lead to dimethyl ether and heavier hydrocarbons. For bimetallic PdCo/NaY samples, calcination and reduction conditions are critical for the formation of PdCo alloy particles, which prevents the formation of palladium carbide, and methane selectivity is high. For higher cobalt contents, alloy particles are obtained following reduction at high temperature; these samples show a signature reminiscent of Fischer-Tropsch catalysts.

McMahon et al. (III.58) studied dispersed cobalt-containing zeolite Fischer-Tropsch catalysts. Microwave discharge methods were used to prepared highly dispersed cobalt clusters in zeolites. Ferromagnetic resonance, electron microscopy, and hydrogen chemisorption experiments have been used to determine the particle sizes of the cobalt clusters. These materials were also studied as Fischer-Tropsch catalysts. Catalytic results suggest that these cobalt zeolite catalysts show high selectivity for the production of low-molecular-weight olefin. Evidence of shape selective catalysts with a cut off at the C₆ chain length has also been observed according to their analysis. McMahon et al.'s data indicate that CO hydrogenation on Co/zeolite catalysts is a structure-sensitive reaction. These highly dispersed catalysts are not as active as catalysts with larger cobalt particles but show higher selectivities toward light hydrocarbons than cobalt-alumina catalysts. FTIR, SEM, and hydrogen chemisorption experiments indicate that the cobalt clusters are extremely small. H₂ chemisorption experiments indicate a 100% dispersion and a particle size of about 9Å prior to catalytic experiments. At 512 K, the hydrocarbon product is 26% C₂-C₄ olefins. A tail-off in Anderson-Schulz-Flory plots at C₆-C₉ is indicative of a shape-selective

effect. However, in a later review, Bartholomew (III.59) provided data obtained by Ungar and Baird that is still unpublished that conclusively show that because of the holdup of heavy hydrocarbons in the zeolite structure, one must wait for a longer time period than most of the reported data to ensure that steady-state products are obtained.

Stencel et al. (III.60) prepared a metal-impregnated Co/ZSM-5 catalysts with $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ using an incipient wetness technique. These catalysts were shown to contain highly dispersed, ion-exchanged, non-reducible Co^{2+} species in the interior of the ZSM-5 particle, and large, reducible cobalt oxide crystallites on the exterior as determined from the number of pyridine molecules that coordinately bond to each of these ions, estimated using infrared data. The crystalline forms of cobalt on the surface of the ZSM-5 are identified and their sizes estimated after O_2 calcination, H_2 reduction, and $\text{CO}+\text{H}_2$ exposure. These data are then scrutinized for correlations of chemical and physical properties of the Co/ZSM-5 catalysts with conversion activity and selectivity for synthesis of hydrocarbons from $\text{CO}+\text{H}_2$ gas. The use of surface sensitive and bulk experimental techniques have enabled the differentiation of two distinct cobalt species in Co/ZSM-5 catalysts. Cobalt interior to the ZSM-5 is in an irreducible, ionic Co^{2+} form created during ion exchange for H^+ , cobalt exterior to the ZSM-5 is in the form of large Co_3O_4 crystallites that are reducible under hydrogen at 350°C to hcp cobalt metal and CoO . By varying the preparation methods, either of these cobalt forms can be obtained. It may now be of interest to study the conversion of other reactants over these types of catalysts and possibly to investigate the effect of particle size of the exterior-located cobalt on $\text{CO}+\text{H}_2$ conversion activity and selectivity.

Investigation of bifunctional zeolite supported cobalt Fischer-Tropsch catalysts has been done by Bessell (III.61). ZSM-5, ZSM-11, ZSM-12 and ZSM-34 were examined as supports for cobalt bifunctional Fischer-Tropsch catalysts in order to determine the influence of zeolite pore structure on the synthesis. All supports produced reasonably active catalysts, with the activity increasing with the channel size of the zeolite support (i.e, in the order of ZSM-34 < ZSM5, ZSM-11 < ZSM-12 supported catalysts). Lack of observable differences in methane and higher hydrocarbon selectivities indicated that this increased activity was not due to an electronic cobalt-support effect. It was more likely a result of increased cobalt dispersion due to an enhancement of some small cobalt crystallite formation within the larger-channeled zeolites. The absence of a channel-size dependent cut-off in the product distributions indicated a lack of shape selective behavior, and that significant hydrocarbon chain growth was occurring on cobalt crystallites on the zeolite surface. Ammonia TPD measurements indicated that the acidity of these zeolites, in terms of both acid strength and acid site concentration, decreased in the order ZSM-34 > ZSM-5 > ZSM-11 > ZSM-12. Contrary to initial expectations, the hydrocarbon products became lighter, and contained less n-alkanes, as the acidity of the zeolite was reduced (which was in the same order as when the channel size of the zeolite was increased). This indicated that for this strongly acidic series of zeolites, accessibility to internal acid sites was more important in influencing the degree of secondary acid catalyzed restructuring reactions of the primary Fischer-Tropsch products than was the strength or concentration of these acid sites.

Metal dispersion and support effects on FTS rate and selectivity were studied at conditions that favor the formation of C₅+ hydrocarbons (>80% selectivity) by Iglesia et

al. (III.62). On cobalt, hydrocarbon synthesis rates are proportional to metal dispersion (0.0045-0.095) and independent of the metal oxide support (SiO_2 , Al_2O_3 , TiO_2 , and ZrO_2 -modified SiO_2 and TiO_2). Site-time yields ($1.6\text{-}3.0 \times 10^{-2}\text{s}^{-1}$) are independent of cobalt dispersion and support (473 K, 2.0 MPa, $\text{H}_2/\text{CO}=2.1$). Dispersion and support influence C_5+ selectivity slightly; these changes reflect transport-enhanced secondary reactions and not modifications of intrinsic chain growth kinetics. Specifically, transport restrictions imposed by the physical structure of the support and by a high site density within catalyst pellets increase the residence time and the readsorption probability of reactive α -olefins and lead to higher C_5+ yields and more paraffinic products.

FTS site-time yields and intrinsic chain growth kinetics depend only weakly on cobalt dispersion and on the oxide support (SiO_2 , Al_2O_3 , TiO_2). Dispersion and support effects on C_5+ selectivity arise from changes in the extent of α -olefin readsorption as changes in site density and support structure modify the rate of intrapellet olefin removal (III.63).

Fu and Bartholomew (III.64) determined the activities and selectivities of cobalt/alumina catalysts for CO hydrogenation as a function of metal loading, reduction temperature, and preparation. Specific activities and average carbon number of the hydrocarbon product were found to significantly vary with metal loading, reduction temperature, and preparation. These changes were also found to be linearly correlated with changes in dispersion indicating that CO hydrogenation on $\text{Co}/\text{Al}_2\text{O}_3$ is structure-sensitive (Figure III.18). The changes in specific activity with dispersion can be explained by variations in the distribution of low and high coordination sites and by changes in the nature of adsorbed CO species available for reaction. High specific activity is apparently favored on sites to which CO is strongly coordinated. Variations in

the average carbon number of the product can be explained by changes in the rate of termination relative to the rate of propagation. High-molecular-weight products are favored by catalysts having high rates of propagation and low rate of termination.

REFERENCES

- III.1. Marbrow, R.A., Lambert R.M., *Surf. Sci.*, **61**, 319 (1976).
- III.2. Marks, L.D., Heine, V., *J. Catal.*, **94**, 570 (1985).
- III.3. Iyagba, E.T., Hoost, T.E., Nwalor, J.U., Goodwin, J.G., Jr., *J. Catal.*, **123**, 1 (1990).
- III.4. McClory, M.M., Gonzalez, R.D., *J. Catal.*, **89**, 392 (1984).
- III.5. Massardier, J., Bertolini, J.C., Raiz, P., Delichere, P., *J. Catal.*, **112**, 21 (1988).
- III.6. Praliaud, H., Dalmon., J.A., Mirodatos, C., Martin, G.A., *J. Catal.*, **97**, 344 (1986).
- III.7. Angevaere, P.A.J.M., Hendrickx, H.A.C.M., Ponec, V., *J. Catal.*, **110**, 11 (1988).
- III.8. Luftman, H.S., White, J.M., *Surf. Sci.*, **139**, 369 (1984).
- III.9. Uram, K.J., Ng, L., Yates, J.T., Jr., *Surf. Sci.*, **177**, 253 (1986).
- III.10. Norskov, J.K., Holloway, S., Lang, N.D., *Surf. Sci.*, **137**, 65 (1984).
- III.11. Goodwin, J.G., Jr., *Prep. ACS Div. Petr. Chem.*, **36**, 156 (1991).
- III.12. Takeuchi, K., Matsuzaki, T., Arakawa, H., Hanaoka, T., *Appl. Catal.*, **48**, 149 (1989).
- III.13. Iglesia, E., Soled, S.L., Fiato, R.A., Via, G.H., *J. Catal.*, **143**, 345, (1993).
- III.14. Shpiro, E.S., Tkachenko, O.P., Belyatskii, V.N., Rudnyi, Y., Telegina, N.S., Panov, S.Y., Gryaznov, V.M., Minachev, K.M., *Kinet Catal.*, **31**, 832 (1990).
- III.15. Vada, S., Hoff, A., Adnanes, E., Schanke, D., Holmen, A., *Topics Catal.*, **2**, 155 (1995).

- III.16. Kogelbauer, A., Goodwin, J.G., Jr., Oukaci, R., *J. Catal.*, **160**, 125 (1996.)
- III.17. Kiviaho, J., Niemela, M.K., Reinikainen M., Pakkanen, T.A., *Appl. Catal.*, **149**, 353 (1997).
- III.18. Bianchi, C.L., Carli, R., Merlotti, S., Ragaini, V., *Catal. Lett.*, **41**, 79 (1996).
- III.19. Bruce, L.A., Hoang, M., Hughes, A.E., Turney, T.W., *Appl. Catal.*, **100**, 51 (1993).
- III.20. Belambe, A.R., Oukaci., R., Goodwin, J.G., Jr., *J. Catal.*, **166**, 8 (1997).
- III.21. Haddad, G.J., Chen, B., Goodwin, J.G., Jr., *J. Catal.*, **161**, 274 (1996).
- III.21a. Haddad, G.J., Chen, B., Goodwin, J. G., Jr., *J. Catal.*, **160**, 43 (1996).
- III.22. Ali, S., Chen, B., Goodwin, J.G., Jr., *J. Catal.*, **157**, 35 (1995).
- III.23. Huffman, G.P., Shah, N., Zhao, J., Huggins, F.E., Hoost, T.E., Halvorsen, S., Goodwin, J.G., Jr., *J. Catal.*, **151**, 17 (1995).
- III.24. Schanke, D., Vada, S., Blekkan, E.A., Hilmen, A.M., Hoff, A., Holmen, A., *J. Catal.*, **156**, 85 (1995).
- III.25. Hilmen, A.M., Schanke, D., Holmen, A., *Catal. Lett.*, **38**, 143 (1996).
- III.26. Coulter, K.E., Sault, A.G., *J. Catal.*, **154**, 56 (1995).
- III.27. Loosdrecht, J., Haar, M., Kraan, A.M., Dillen, A.J., Geus, J.W., *Appl. Catal.*, **150**, 365 (1997).
- III.28. Niemela, M.K., Krause, A.O.I., Vaara, T., Kiviaho, J.J., Reinikainen, M.K.O., *Appl. Catal.*, **147**, 325 (1996).
- III.29. Niemela, M.K., Backman, A.O.I., Krause, Vaara, T., *Appl. Catal.*, **156**, 319 (1997).
- III.30. S. H. Moon and K. E. Yoon, *Appl. Catal.*, **16**, 289 (1985).

- III.31. B. G. Johnson, C. H. Bartholomew and D. W. Goodman, *J. Catal.*, **128**, 231 (1991).
- III.32. Iglesia, E., *Appl. Catal.*, **161**, 59 (1997).
- III.33. Van Hardeveld, R., Hartog, F., in "Advances in Catalysis and Related Subjects", Vol. 22, P. 75. Academic Press, New York, 1972.
- III.34. Tauster, S.J., Fung, S.C., *J. Catal.*, **55**, 29 (1978).
- III.35. Bessell, S., *Appl. Catal.*, **96**, 253 (1993).
- III.36. Reuel, R.C., Bartholomew, C.H., *J. Catal.*, **85**, 78 (1984).
- III.37. Kogelbauer A., Weber, J.C., Goodwin, J.G., Jr., *Catal. Letters*, **34**, 259 (1995).
- III.38. Khodakov, A.Y., Lunch, J., Bazin, D., Rebours, B., Zanier, N., Moisson, B., Chaumette P., *J. Catal.*, **168**, 16 (1997).
- III.39. Niemela, M.K., Krause, A.O.I., *Catal. Letters*, **42**, 161 (1996).
- III.40. Schanke, D., Hilmen, A.M., Bergene, E., Kinnari, K., Rytter, E., Adnanes, E., Holmen, A., *Catal. Letters*, **34**, 269 (1995).
- III.41. Lapidus, A., Krylora, A., Kazanskii, V., Borovkov, V., Zaitsev, A., Rathousky, J., Zukal, A., Jancalkora, M., *Appl. Catal.*, **73**(1), 65 (1991).
- III.42. Lapidus, A., Krylova, A., Rathousky, J., Zulkal, A., Jancalkova, M., *Appl. Catal.*, **80**(1), 1 (1992).
- III.43. Rathousky, J., Zukal, A., Lapidus, A., Krylova, A., *Appl. Catal.*, **79**(2), 167 (1991).
- III.44. Chang, C.D., Lang, W.H., Silvestri, A.J., *J. Catal.*, **56**, 268 (1979).
- III.45. Caesar, P.D., Brennan, J.A., Garwood, W.E., Criric, J., *J. Catal.*, **56**, 274 (1979).
- III.46. Melson, G.A., Crawford, J.E., Crites, J.W., Mbadcam, K.J., Stencel, J.M., Rao, V.U.S., *ACS Symp. Ser.*, **218**, 397 (1983).

- III.47. Bruce, L.A., Hope, G.J., Mathews, J.F., *Appl. Catal.*, **9**, 351 (1984).
- III.48. Dwyer, F.G., Garwood, W.E., in Herman, R.G., *Catalytic Conversions of Synthesis Gas and Alcohols to Chemicals*, Plenum, New York, 1984, pg. 167.
- III.49. Penniline, H.W., Gormley, R.J., Schehl, R.R., *Ind. Eng. Chem. Prod. Res. Dev.*, **23**, 388 (1984).
- III.50. Varma, R.L., Bakhshi, N.N., Mathews, J.F., Ng, S.H., *Can. J. Chem. Eng.*, **63**, 612 (1985).
- III.51. Rao, V.U.S., Gormley, R.J., *Hydrocarbon Proc.*, **59**, 139 (1980).
- III.52. Shamsi, A., Rao, V.U.S., Gormley, L.J., Overmyer, R., Schehl, R.R., Stencel, J.M., *Ind., Eng. Chem. Prod. Res. Dev.*, **23**, 513 (1984).
- III.53. Rao, V.U.S., Gormley, R.J., Shamsi, A., Petrick, T.R., Stencel, J.M., Schehl, R.R., Chi, R.P.H., *J. Mol. Catal.*, **29**, 271 (1985).
- III.54. Shamsi, A., Rao, V.U.S., Gormley, R.J., Obermyer, R.T., Schehl, R.R., Stencel, J.M., *Appl. Catal.*, **27**, 55 (1986).
- III.55. Gormley, R.J., Rao, V.U.S., Anderson, R.R., Schell, R.R., Chi, R.P.H., *J. Catal.*, **113**, 193 (1988).
- III.56. Calleja, G., Lucas, A.D., Van Grieken, R., *Appl. Catal.*, **68**, 11 (1991).
- III.57. Yin, Y., Zhang, Z., Sachtler, W.M.H., *J. Catal.*, **138**, 721 (1992).
- III.58. McMahon, K.C., Suib, S.L., Johnson, B.G., Bartholomew, C.H., Jr., *J. Catal.*, **106**, 47 (1987).
- III.59. C. H. Bartholomew in "New Trends in CO Activation," (L. Guzzi, Ed.) *Studies in Surface Science and Catalysis*, **64**, 159, (1991)

- III.60. Stencel, J.M., Rao, V.U.S., Diehl, J.R., Rhee, K.H., Dhere, A.G., DeAngelis, R.J.,
J. Catal., **84**, 109 (1983).
- III.61. Bessell, S., *Appl. Catal.*, **126**, 235 (1995).
- III.62. Iglesia, E., Soled, S.L., Fiato, R.A., *J. Catal.*, **137**, 212 (1992).
- III.63. Iglesia, E., Soled, S.L., Fiato, R.A., Via, G.H., in Curry-Hyde, H.E., Howe, R.F.,
(editors), *Natural Gas Conversion* pg. 433.
- III.64. Fu, L., Bartholomew, C.H., *J. Catal.*, **92**, 376 (1985).

Table III.1

Effect of Calcination Temperature on CO Hydrogenation (reduction temperature = 300°C, H₂/CO = 10, T = 220°C, P = 1.8 atm) (from ref. III.20)

T _c (°C) ^a	% CO conversion		Rate ^d (μ mole/g Co _{Tot} /S)		CH ₄ Selectivity (%)		α		TOF ^e x 10 ² (1/s)	
	Initial ^b	S-S ^c	Initial	S-S	Initial	S-S	Initial	S-S	Initial	S-S
Uncalcined	9.7	7.5	44.0	32.2	70	75	0.42	0.37	---	---
200	15.1	11.1	68.6	50.4	86	84	0.40	0.36	---	---
250	12.3	9.2	55.9	41.9	86	80	0.41	0.36	3.0	2.2
300	10.9	8.4	49.8	38.2	73	76	0.40	0.38	2.9	2.3
350	8.2	6.4	37.2	29.2	70	74	0.42	0.37	3.0	2.3
400	6.4	5.1	29.2	23.0	68	73	0.41	0.37	3.3	2.6

- a. Calcination temperature.
 b. After 5 min. of reaction.
 c. After 7 hr. of reaction.
 d. Error in rate measurement was \pm 5%.
 e. Based on total hydrogen chemisorption.

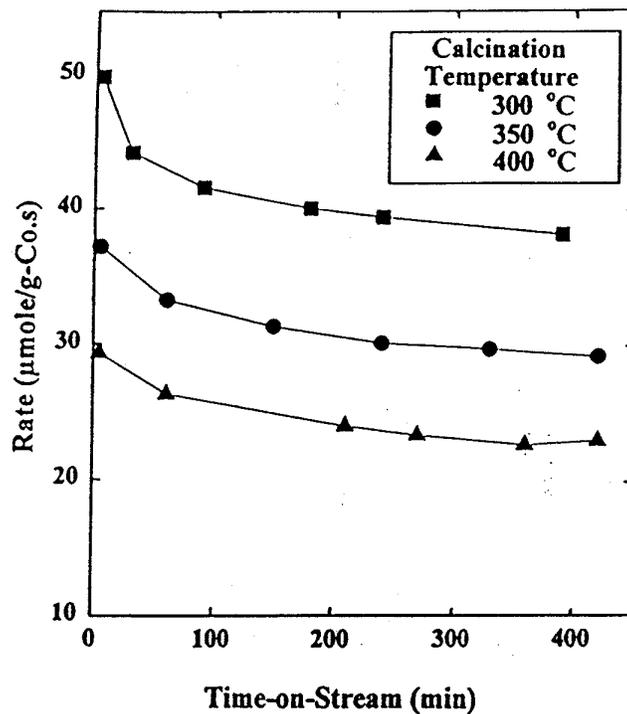


Figure III.1. Time-on-stream behavior of the overall rate of CO hydrogenation for the catalyst reduced at 300°C and calcined at various temperatures (from ref. III.20).

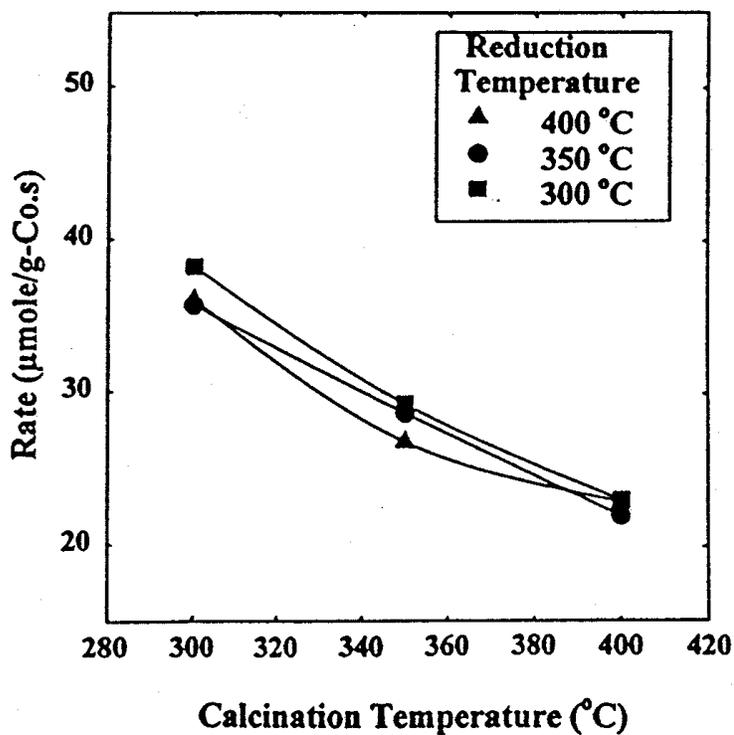


Figure III.2. Effect of pretreatment temperatures on overall catalyst activity of Ru/Co/Al₂O₃ (from ref. III.20).

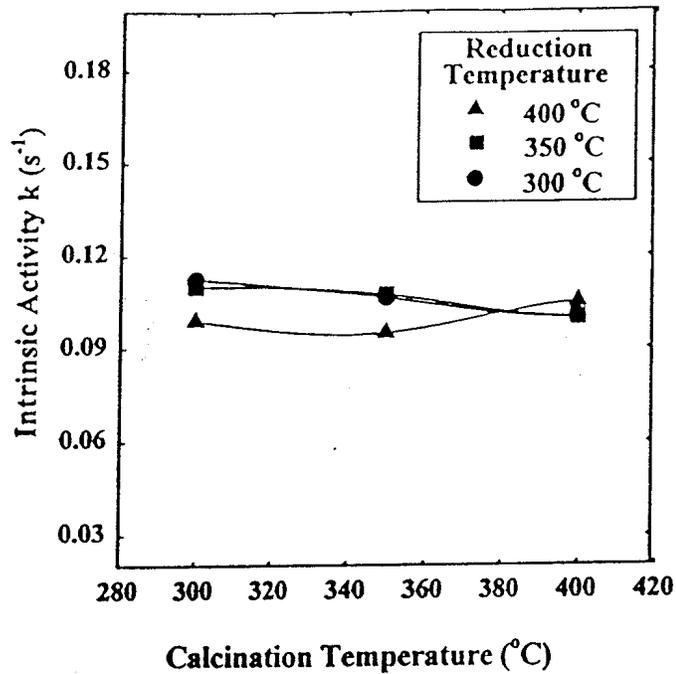


Figure III.3. Effect of pretreatment temperatures on intrinsic activity of Ru/Co/Al₂O₃ for methane formation (from ref. III.20).

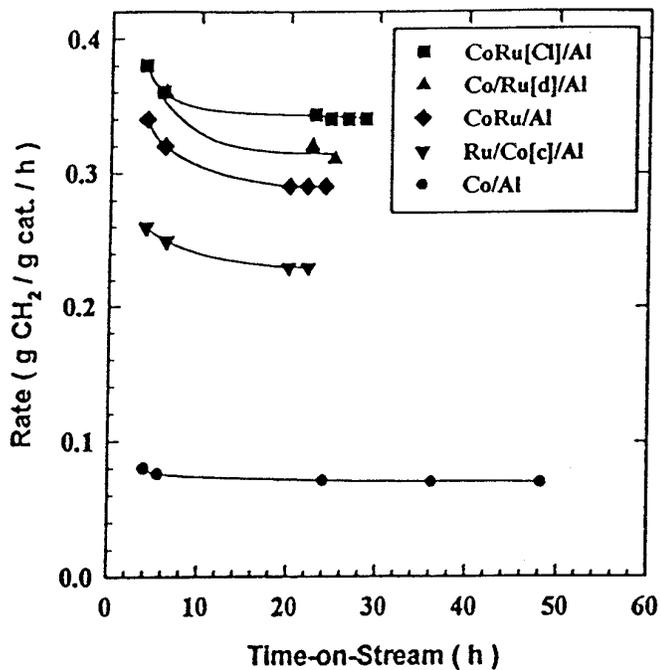


Figure III.4. Rates of F-T synthesis at 220°, 1 atm. and H₂/CO = 2 versus time-on-stream for selected catalysts (in inset d = dried, c = calcined, r = reduced, Cl = prepared from RuCl₃) (figure from ref. III.16).

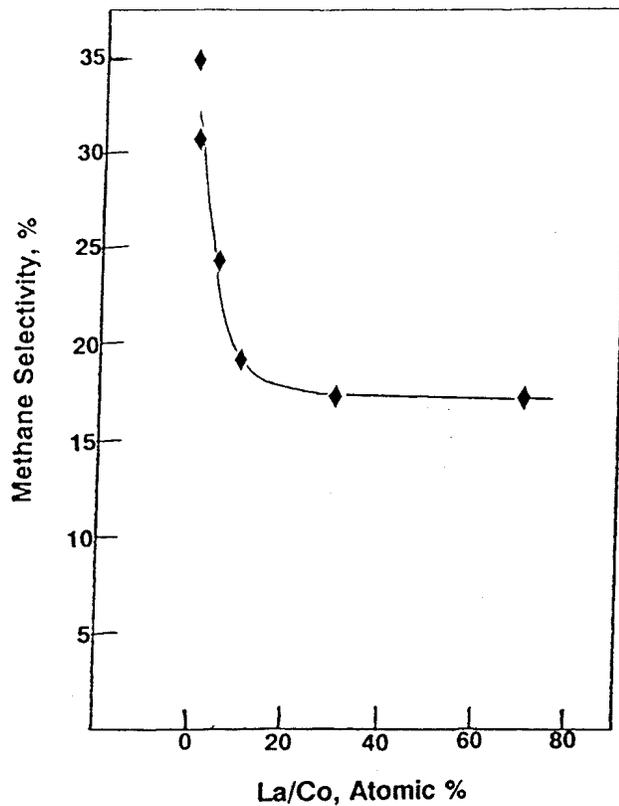


Figure III.5. Influence of La^{3+} content on the fraction of methane produced by a Co/SiO_2 catalyst (220°C , 1 atm., $\text{H}_2/\text{CO} = 2$) (from ref. III.23) Plot from table 2 of reference.

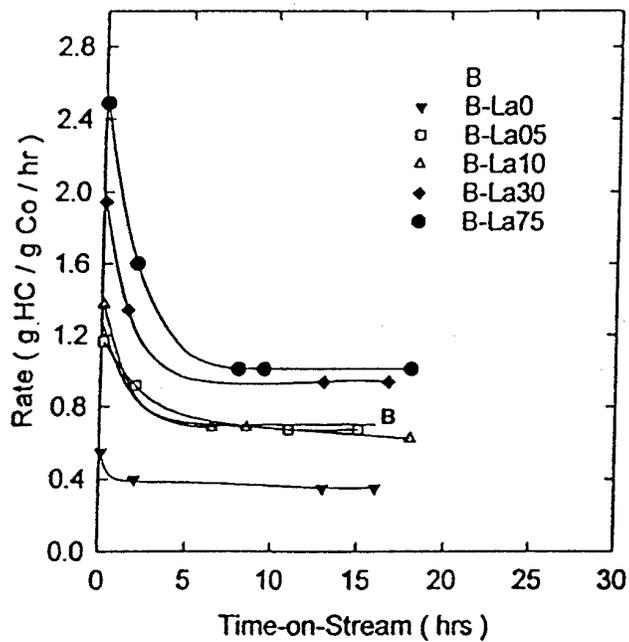


Figure III.6. Initial CO hydrogenation reaction for $(\text{La})\text{Co/SiO}_2$ catalysts (220°C , 1 atm., $\text{H}_2/\text{CO} = 2$) (from ref. III.23).

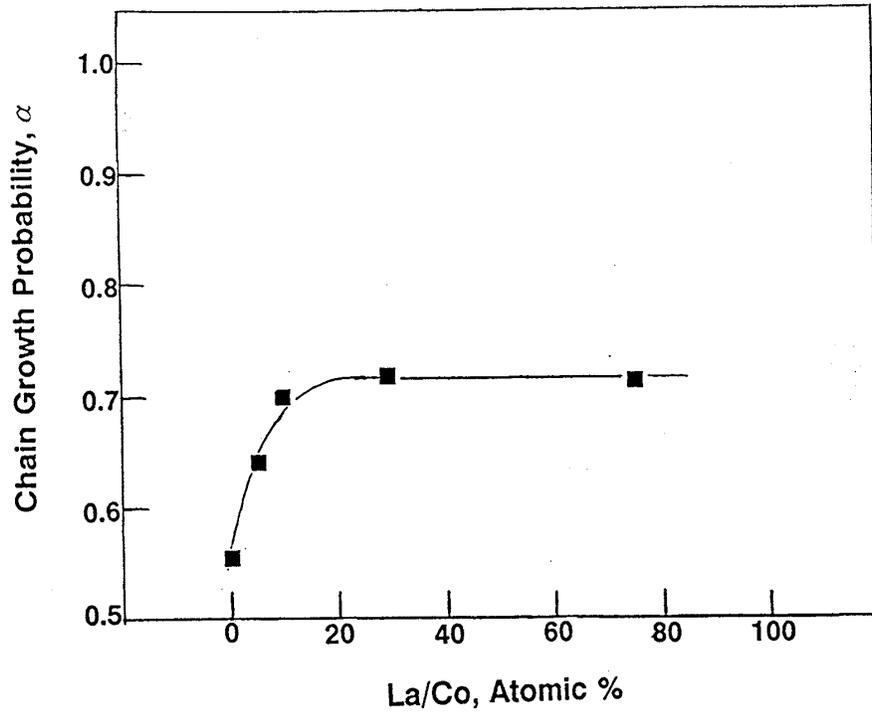


Figure III.7. Dependence of the chair growth probability (α) on the La^{3+} content for a Co-SiO_2 catalyst (220°C , 1 atm., $\text{H}_2/\text{CO} = 2$) (from ref. III.23). drawn from table 2.

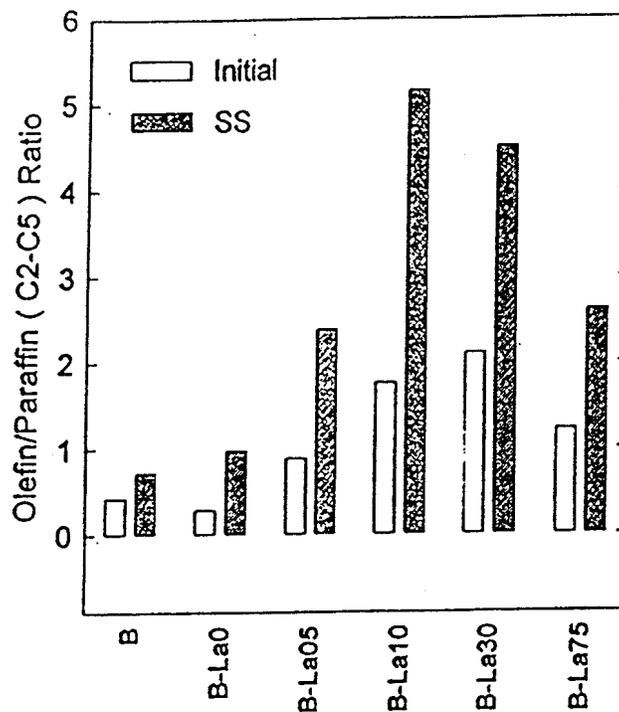


Figure III.8. $\text{C}_2\text{-C}_5$ olefin/paraffin ratios for La-promoted Co/SiO_2 catalysts (220°C , 1 atm., $\text{H}_2/\text{CO} = 2$) (from ref. III.23).

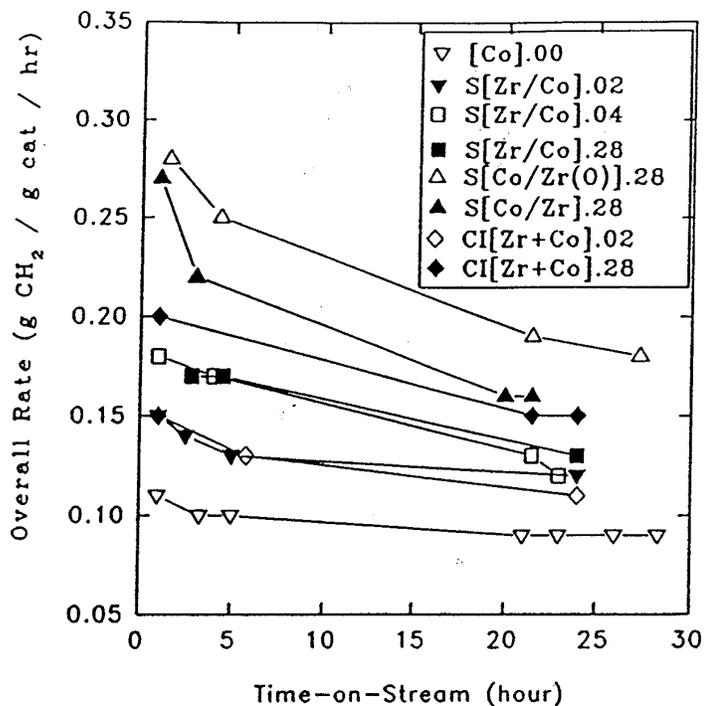


Figure III.9. Overall rate vs time-on-stream during FTS (220°C, 1 atm., H₂/CO = 2) (from ref. III.24).

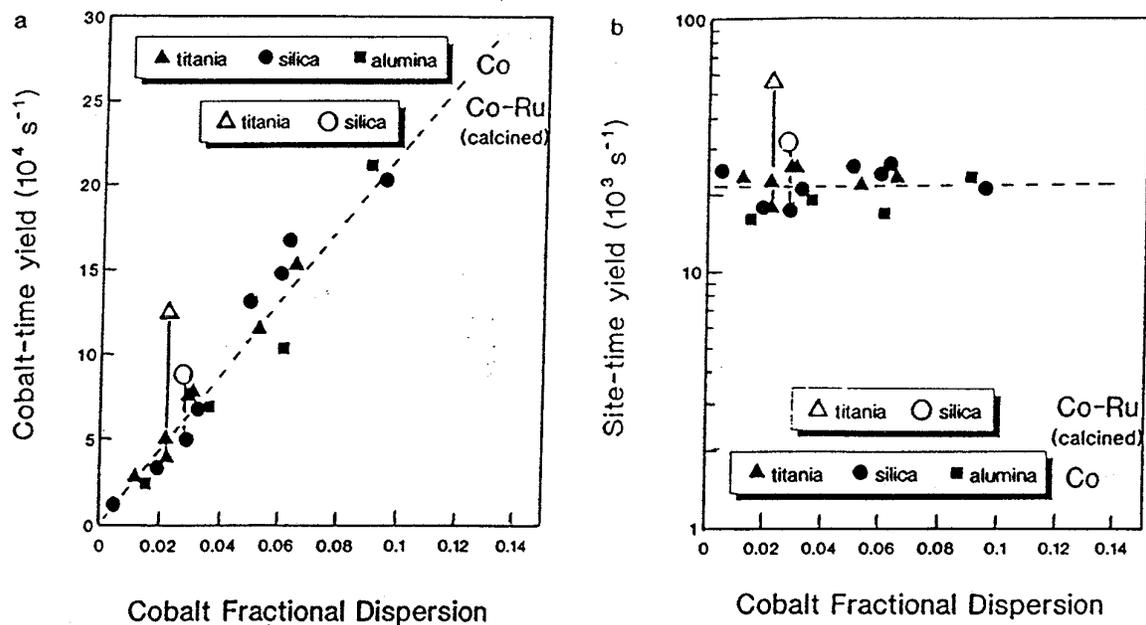


Figure III.10. Effects of cobalt dispersion and support on Fischer-Tropsch synthesis rates (473 K, H₂/CO = 2.1, 2.0 MPa, 50-60% CO conversion: (a) metal-time yields and (b) site-time yields (from ref. III.13).

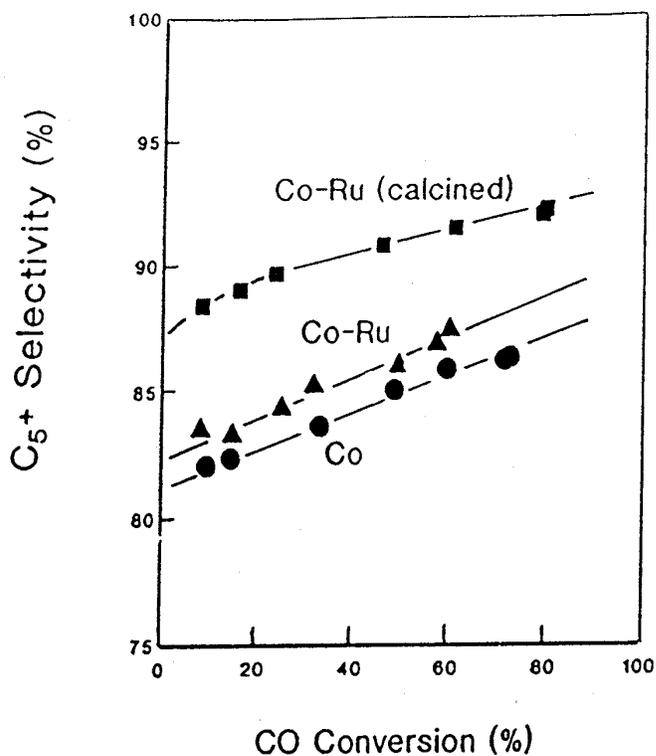


Figure III.11. C₅+ selectivity on Co/TiO₂ and Co-Ru/TiO₂ (Ru/Co = 0.0067 at.) catalysts (473 K, 2.0 MPa, H₂/CO = 2.05, 11.6 wt.% Co) (from ref. III.13).

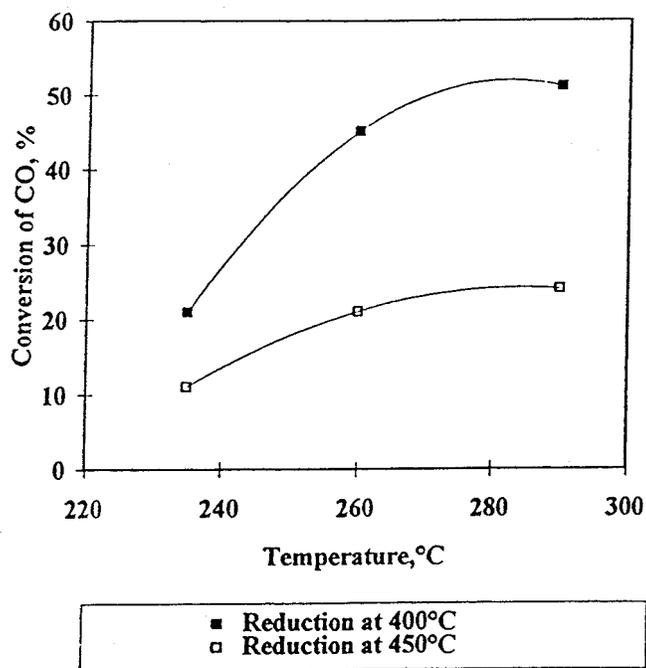


Figure III.12. The effect of reduction temperature on the activity of Co/SiO₂ hydrogenation at 235°C, 5 bar, 1g of catalyst, GHSV of 2600 h⁻¹ and H₂:CO:Ar = 3:1:3 (from ref. III.29).

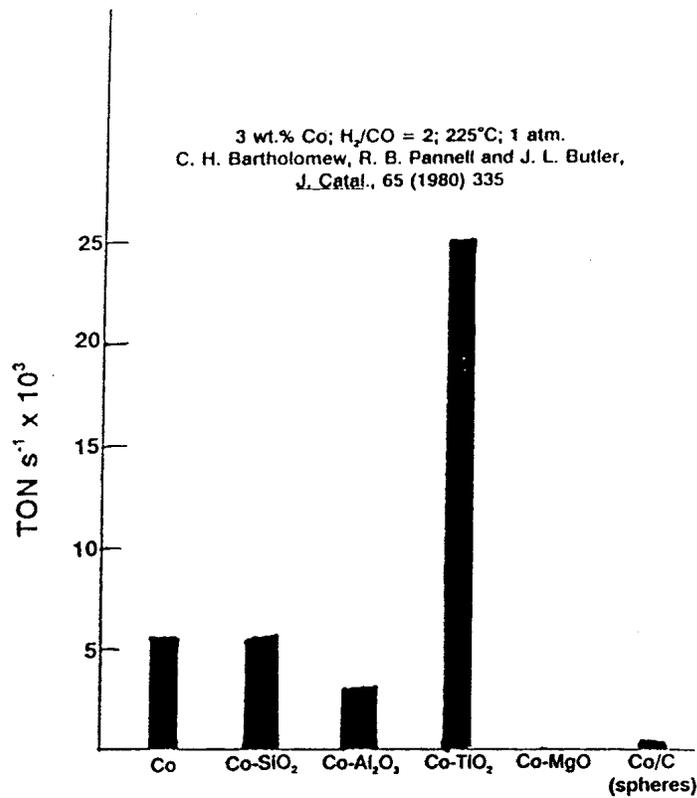


Figure III.13. The activity of the indicated catalysts for CO hydrogenation at atmospheric pressure (drawn using data in C. H. Bartholomew, R. B. Pannell and J.L. Butler, *J. Catal.*, 65 (1980) 335).

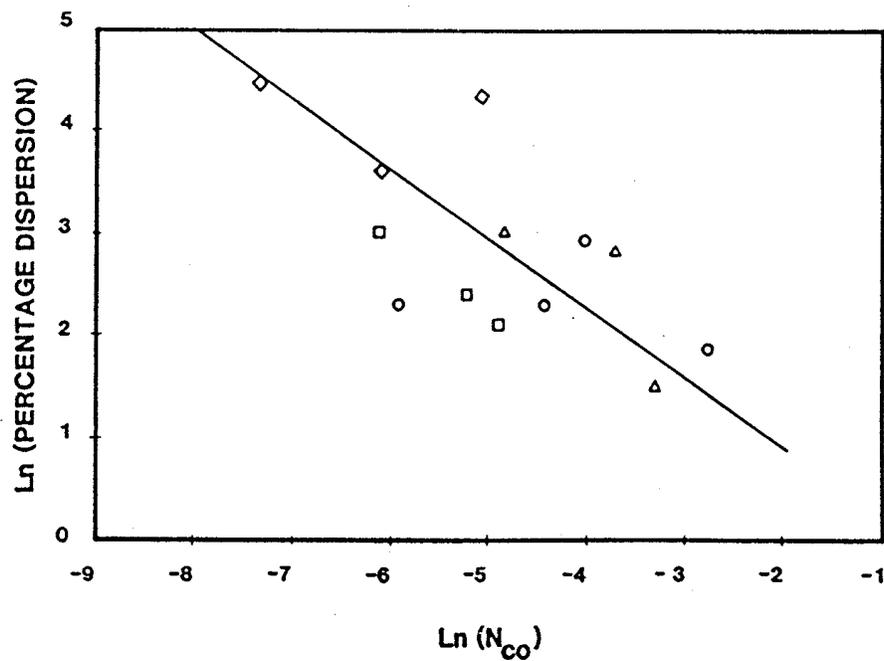


Figure III.14. Percentage dispersion vs CO turnover frequency at 225°C for impregnated, precipitated, and evaporatively deposited catalysts (□, Co/SiO₂; ○, Co/Al₂O₃; △, Co/TiO₂; ◇, Co/C) (from ref. III.34).

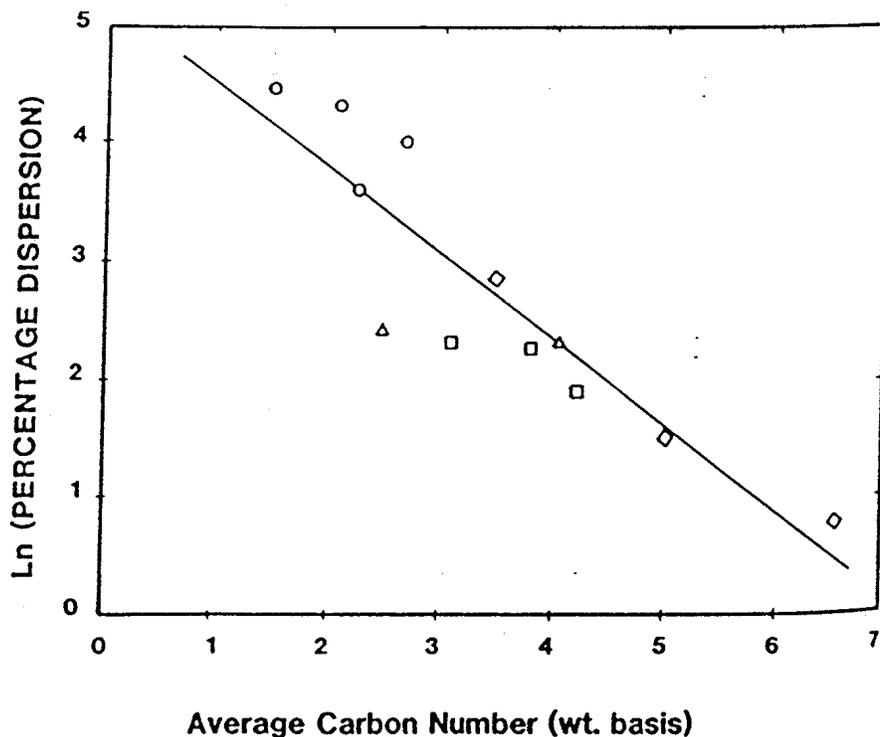


Figure III.15. Average carbon number of hydrocarbons produced at 225°C and 1 atm for 3 and 10 wt.% supported cobalt catalysts as a function of dispersion. (△, Co/SiO₂ (impregnated); □, Co/Al₂O₃ (impregnated); ◇, Co/TiO₂ (impregnated); ○, Co/C (evaporatively deposited) (from ref. III.34).

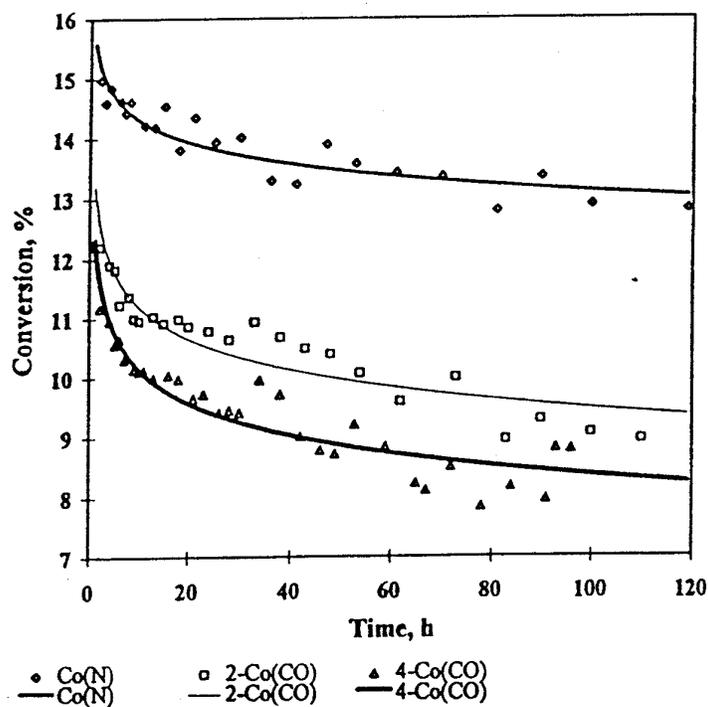


Figure III.16. The activity of Co/SiO₂ at 235°C for 120 h of reaction time (from ref. III.37).

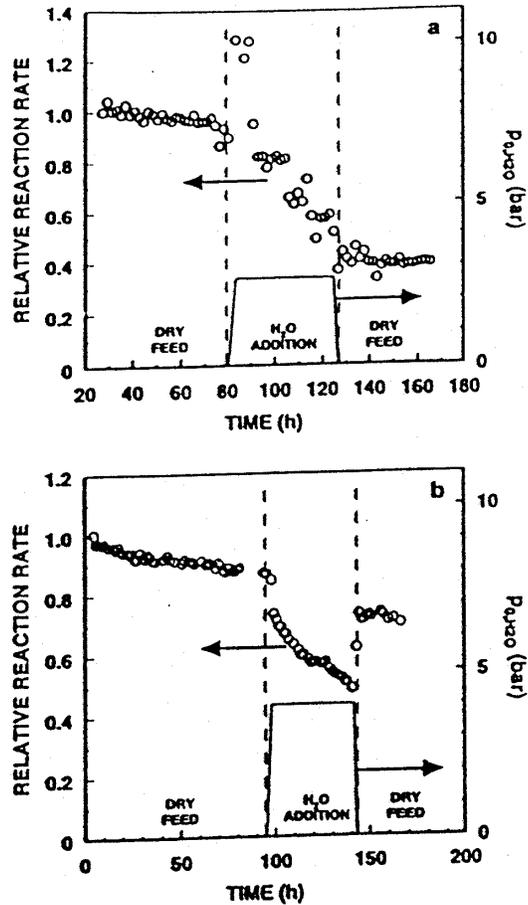


Figure III.17. Observed reaction rate relative to the initial rate for hydrocarbon formation as a function of time during simulated high conversion conditions. p_{o,H_2O} = partial pressure of water at reactor inlet. Feed composition: 50 mole% H_2 + CO, $H_2/CO=2$, balance N_2+He or $N_2 + He + H_2O$. CO conversion before addition of water: 20-28%. (a) Catalyst: 21%Co-1%Re/ $\gamma-Al_2O_3$ (Puralox). $T=483K$, $P=13bar$. (b) Catalyst: 20%Co/ $\gamma-Al_2O_3$ (Vista-B). $T=493 K$, $P = 8 bar$. (from ref. III.38).

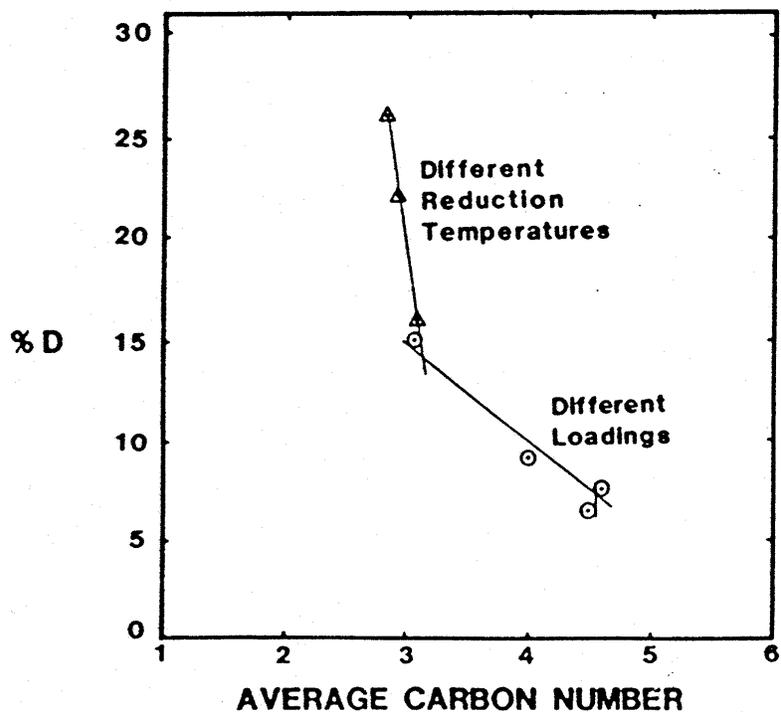


Figure III.18. Correlations of dispersion with average carbon number for $\text{Co}/\text{Al}_2\text{O}_3$ catalysts of different loading and reduction temperature. (Δ , different reduction temperatures; \circ , different loadings) (from ref. III.61).

ATTACHMENT IV

Fischer Tropsch - Examples of Activation

EX-SITU

1. Oukaci et al. [R. Oukaci, J. G. Goodwin, Jr., G. Marcelin and A. Singleton, ACS Fuel Chem Preprint, 39, (1994) 1118] reported that the catalyst is first reduced ex-situ in a fluidized bed assembly and then transferred into a glove box for weighing and subsequent transfer into the slurry bubble column reactor.
2. Beuther et al. reported a procedure known as ROR [H. Beuther, T. P. Kobylinski, C. E. Kibby and R. B. Pannell, South Africa Patent Application No. 855317, July 15, 1985.] in which a reduction in hydrogen, oxidation, and rereduction (ROR) procedure was utilized. The rereduction was conducted the same as the first reduction. The reduction procedure was conducted so that the water vapor pressure did not exceed 1% of the exit gas. The catalyst particles were then suspended in a liquid medium but details of catalyst transfer not given nor were the details of any in-situ treatment prior to the synthesis.
3. Iglesia et al. [E. Iglesia, S. Soled, R. Fiato; Cobalt-ruthenium catalysts for FT synthesis and process for their preparation; patent 4,738,948 (Apr. 1988).] claim a hydrocarbon synthesis catalyst prepared by a process that comprises an impregnation of a refractory support comprising titania with solutions of catalytically active amounts of cobalt and ruthenium salts, drying the impregnated support, reducing the cobalt and ruthenium, treating the reduced metals with an oxygen containing stream at conditions sufficient to form oxides of cobalt and oxides of ruthenium and reducing the cobalt and ruthenium oxides. It

appears that this procedure is either the same as or very similar to the ROR procedure utilized by Beuther et al. (IV.1).

4. Nay et al. [B. Nay, M. R. Smith and C. D. Telford, "Catalyst treatment;" U.S. Patent 5,585,316, December 17, 1996.] claimed a process for reducing a catalyst containing cobalt, suitable for use in a Fischer Tropsch process for converting synthesis gas into hydrocarbons, which comprises pretreating said cobalt catalyst at 200-600°C with a gas containing molecular oxygen to produce an oxidized cobalt catalyst, a majority of said cobalt being in an oxide form, and then contacting said oxidized cobalt catalyst at elevated temperatures with a gas containing carbon monoxide substantially free of hydrogen, to produce a reduced cobalt containing catalyst. In one example, a 10% Co on ZnO and one portion treated at 500°C in air for 6 hr and then hydrogen for 9 hr at 320°C. The other portion was treated with air for 50 hr and then with CO for 3 hr at 250°C.

Conversion was obtained in fixed bed at 30 bar, GHSV 1250 h⁻¹.

Catalyst Treatment	Hr. on Stream	Mean Bed Temp (°C)	CO Conv %	% CH ₄	CO ₂	C ₅ +
Air/H ₂	214	214	87	7.5	2.5	76.8
Air/CO	213	212	87	4.6	1.9	91.0

During the early work at Air Products, catalysts were activated in syngas. To accomplish this the catalyst precursor was heated to 180°C in a nitrogen flow at atmospheric pressure. At 180°C, the flow was switched to the synthesis gas (CO/H₂ = 1) and then heated to the reaction temperature. At the reaction temperature, the pressure was increased to the one used for the synthesis. Later in their work, they compared the impact of activation in pure H₂ or syngas (CO/H₂ = 1). For a 4%Co-

zirconia promoted alumina catalyst, they found that the sample activated in hydrogen had a significantly higher activity and higher yield of liquid fuels (Figure VI.1; Table VI.1).

IN-SITU

The reduction procedure used by the U.S. Bureau of Mines [6. H. E. Benson, J. H. Field, D. Bienstock, R. R. Nagel, L. W. Brunn, C. O. Hawk, J. H. Crowell and H. H. Storch, "Development of the Fischer-Tropsch oil-recycle process," Bureau of Mines Bulletin 568, 1957.] was conducted at atmospheric pressure. To begin the reduction the temperature was raised to 360°C as rapidly as possible, maintaining a flow of about 40 GHSV. At 360°C the hydrogen flow was increased to 500 to 1,000 GHSV, and was maintained for four hours. The flow was then reduced to 20 GHSV and the temperature reduced to 150°C. Process oil was then added to the reactor, nitrogen replaced the hydrogen flow and the pressure was increased to about 40 psig. When the reflux and readdition of process oil stabilized, the nitrogen flow was replaced by synthesis gas. The pressure was slowly increased which in turn slowly increased the temperature inside the reactor. During 48 h. the temperature remained below 175°C and the gas contraction held to a maximum of 50%. The temperature was increased to 180°C during 24 h. after which the induction period had been completed and the temperature was adjusted to obtain maximum productivity.

Mitchell [W. N. Mitchell, "Activation of hydrocarbon synthesis catalyst;" U.S. patent 5,292,705 (Mar. 1994).] claimed a method for activating an essentially fresh, reduced cobalt containing FT catalyst which comprises treating the catalyst with hydrogen or a hydrogen containing gas in the presence of hydrocarbon liquids for a period sufficient to increase substantially the initial catalyst productivity.

REFERENCES

- IV.1. H. Beuther, C. L. Kibby, T. P. Kobylinski and R. B. Pannell, U.S. patent 4,605,680, Aug. 12, 1986.

Table VI.1

**Effect of syngas vs. hydrogenation activation on the hydrocarbon selectivity
using a 4% Co on Zr/Al₂O₃ catalyst utilized in a slurry CSTR.**

	Syngas	H ₂
Space velocity, NL/gcat/hr	1.6	2.0
CO/H ₂	1.6	1.5
Pressure, psig	300	300
Temperature, °C	250	258
Hydrocarbon, wt. %		
C ₁	11.5	7.2
C ₂₋₄	10.4	10.8
C ₅₋₁₁	29.2	34.1
C ₁₂₋₁₈	15.3	27.9
C ₁₉₋₂₃	12.5	8.6
C ₂₄₊	21.1	11.4
C ₅₋₂₃	57.0	70.6

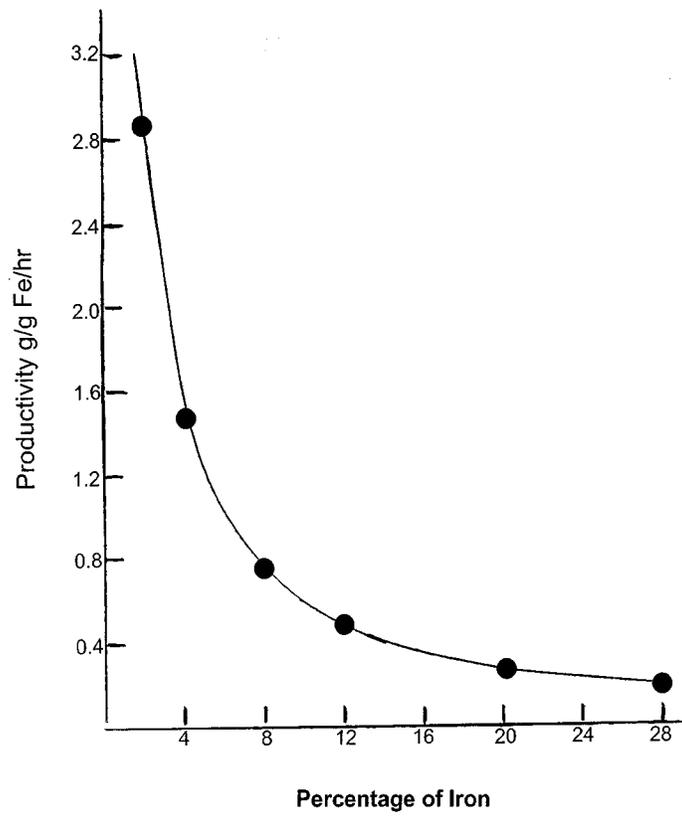


Figure IV.1. Productivity, based upon 2,500 bbl/day and assumed reactor filling, of the Sasol slurry reactor versus percentage of iron in the slurry.

ATTACHMENT V

Productivity - Slurry Phase

I. Iron Catalyst

H. Kölbel, "Chemische Technologie. Band 3: Organische Technologie I, Carl Hansen Verlag, München, 1959, p. 439.

Kg Product/m³ Reactor/day = 1,000 to 2,000 in the large pilot plant [60 m³].

0.47 - 0.94 g/g catalyst/hr

Experimental was 0.44 g/g catalyst/hr

Sasol

The reactor is 5 m diameter and 22 m tall. Assuming that only 2/3rd of the total volume is available for synthesis, the reactor volume is about 288 m³. The productivity is 2,500 bbl/d which is 16,561 L/hr and, assuming a density of 1 g/cm³ for the product, this corresponds to 16,561 kg/hr. The productivity/reactor volume is then 57.8 kg/hr/m³. Assuming various iron content per reactor volume produces a productivity of 2.89 g/gFe/hr for 0.02 fraction of iron whereas a loading of 0.2 iron gives a productivity of 0.289 g/gFe/hr (Figure V.1).

II. Cobalt Catalyst

La Porte

Run design for LaPorte Run 3-4

Slurry concentration 24-25 wt.% catalyst, reactor temperature 250-260°C;

reactor pressure = 710 psig (48.3 atm), reactor productivity = 150g hc/L/hr.

Assume density of slurry is 1.25 kg/L

0.5 g hc/g catalyst/hr

Exxon

R. M. Koros, "Bubble column, tube slurry process and apparatus," U.S. Patent 5,384,336, January 24, 1995.

At 65% CO conversion with $H_2/CO = 2.1$, 5 cm/s, reaction temperature of 183°C or higher, space velocities of 2800 to 3600 hr^{-1} , the productivities ranged from 450 to 750.

This gives a productivity of 0.28 to 0.47 g hc/cm³/hr. If the bulk density is 2.7g/cm³ as given [W.C. Behrmann et al, U.S. Patent 5,545,674, August 13, 1996] this corresponds to a productivity of **0.104 to 0.174 g/g catalyst/hr.**

ATTACHMENT VI

Early Slurry Reactors

A unique slurry reactor involved an arrangement of trays, each containing catalysts, that were contained in a cylindrical vertical reactor that was fitted at the top with a reflux condenser and an arrangement for removal of liquid at the bottom of the reactor (figure VI.1) (VI.1,VI.2) Experiments were conducted in a 7-tray reactor, 4.5 cm diameter and 60 cm tall, with up flow of gas.

A tube containing cells, a bundle of tubes, is employed to effect the conversion wherein the catalyst bed is completely submersed in a liquid. An example of one version of this reactor is shown in figure VI.2 (VI.3). Preheated oil is pumped into the outer shell and allowed to descend to the bottom where it is carried, together with the reactant gas, through the reactor tube containing the catalyst. Unconverted gases, the cooling oil and products pass overhead, are cooled and pass to a separator to produce gaseous and liquid product streams as well as recycle cooling oil.

Another reactor is constructed along the lines of a modern multi-tray bubble cap distillation tower. Thus, a reactor is fitted with a number of trays that contain the catalyst with bubble caps arranged to allow vapors, unconverted feed gases and vapor phase products, to be distributed to keep the catalyst in suspension (figures VI.3 and VI.4) (VI.4) Some bubble caps are fitted with downcomers that allow nonvolatile liquid to descent to the bottom of the reactor. In an example, 0.75 lb of catalyst was suspended in one gallon of oil (about 10 % slurry) and charged to a reaction chamber containing 50 bubble trays.

Another variation was provided (figure VI.5 and VI.6) (VI.5). In this version the cooling liquid could be added at several levels in the reactor so as to maintain a better control of the temperature during startup and synthesis.

Benson et al. (VI.6) report that after the preliminary work by F. Duftschmid, E. Linckh and F. Winkler as described above, a pilot plant with a reactor of 0.2 m diameter and 6 m height (about 200 L) was constructed during 1936 and 1937 at pressures of 100 atm and then at 15 to 20 atm. In 1938, a larger plant with a 0.5 m diameter and 6 m tall (1,500 L) was operated.

The U.S. Bureau of Mines constructed and operated a pilot plant that utilized oil-recycle in a reactor with a 3 inch (7.6 cm) and 8 ft. (2.44 m) tall (VI.6). After several runs during 1946-47 with co-current downflow of gas and liquid over cobalt catalysts, a run was made with the cobalt catalyst completely submerged in liquid and co-current upflow of gas and liquid. After it had been demonstrated that the unit could be operated with the cobalt catalyst, the later runs were made with an iron catalyst. The composition of the cobalt catalyst was Co:ThO₂:MgO:kieselguhr = 100:7:12:200. The cobalt catalyst was reduced at atmospheric pressure in the reactor. The temperature was raised to 360°C as rapidly as possible using a hydrogen flow of 10 ft³/h and then the hydrogen flow was increased to 200 to 400 ft³/h and the reduction continued for 4 h. Since the catalyst bed occupied about 0.25 ft³, the GHSV was about 800 to 1600 h⁻¹ during the reduction at 360°C. Following reduction, the hydrogen flow was reduced to 5 ft³/h and the temperature reduced to 150°C. Nitrogen replaced hydrogen at this point and the pressure was increased to 40 psig. Oil was then admitted to the reactor. After the oil was added, syngas flow of GHSV = 100 was started. The temperature was slowly increased from 150°C by increasing the pressure in small increments, which

decreased the rate of evaporation of the cooling oil. The temperature was maintained below 175°C, maintaining a gas contraction of less than 50%, during 48 hours. The temperature was increased to 180°C during the next 24 h., after which the induction was considered complete. The conditions were then adjusted as required to obtain maximum productivity.

Kölbel and Ackermann (VI.7, VI.8). obtained patents for an apparatus for carrying out gaseous catalytic reactions in liquid medium. The reactions included Fischer-Tropsch synthesis.

It is stated that the "[Fischer-Tropsch] synthesis according to known processes is feasible without trouble in a reaction space of up to 20 cm [7.9 in] diameter. With increasing horizontal diameter of the reaction space the amount of gas conversion decreases and it is always more difficult to maintain a constant gas conversion. The larger the horizontal diameter of the reaction space, the more the liquid substance leans toward changing from stationary state to a state of vertical rotation. The liquid flows downwardly along the surface of the wall and flows along the bottom to the middle of the reaction space, whereby it is drawn out by the gas bubbles leaving at the middle of the bottom. The compressed central gas stream flows along with the liquid toward the top whereby the firmly compressed gas bubbles combine to form large elongated gas bubbles. Only at the upper reversal point of the liquid, in the vicinity of the surface of the column of liquid, the gas spreads out horizontally across the transverse section and the large gas particles are partially decomposed (Figure VI.7)."

Kölbel and Ackermann illustrated the problem with figure VI.7. As shown, the liquid flows upwardly in the interior of the reactor tube and flows downward along the

wall side of the reactor. They indicated several disadvantages accrue from this situation, including:

1. decreased gas conversion,
2. occurrence of secondary reactions,
3. increased catalyst damage, and
4. increased catalyst aging.

These authors state that, for reactions like Fischer-Tropsch synthesis where the gas composition changes with conversion and where the products admix with the unconverted gas, "...the gas conversion should be complete as possible on passing the gas through once..." The authors indicate that, prior to their patent, none of the available operations permit "...maintaining the liquid medium and the suspended catalyst stationary and nevertheless permitting the gas bubbles in uniform size and distribution to pass vertically through the liquid medium at equalized velocity..." The authors indicate that the disadvantages of the liquid and catalyst circulation, as shown in figure VI.7, can be overcome in a cylindrical reactor with a horizontal diameter of more than 30 cm (11.8 in) and up to 3 m or more (9.8 ft or more) and more than 1.5 m (4.9 ft) in height, and a gas headspace above the liquid at least as large as the reactor diameter. To provide within the reaction zone a stationary catalyst and liquid condition, the large reactor shell is subdivided into similar, vertical shafts which are open at top and bottom that have liquid-tight casings and a diameter of at least 5 cm (2 in) (figure VI.8). The shafts should terminate above the expanded liquid level; i.e., in the free gas space. Because of the flows in the bottom of the reactor, it is stated that each of the shafts, in the center as well as at the wall region, receive the same amount gas. While there is circulation of the liquid in the sump (bottom of reactor in figure VI.8), "...there

are formed in the shafts extremely stationary liquid columns whose expansion depends on the amount of gas."

The authors indicate that in certain cases, as in the Fischer-Tropsch reaction, it may be an advantage to allow the temperature to rise toward the top of the reactor, and provisions are described which would allow for this to occur. Thus, as the partial pressure of the reactants decrease, the higher temperature will be able to compensate, completely or partially, for the partial pressure decrease.

References

- VI.1 F. Duftschmid, E. Linckh and F, Winkler, "Production of valuable hydrocarbons and their derivatives containing oxygen," U.S. Patent 2,159,077, May 23, 1939.
- VI.2 F. Duftschmid, E. Linckh and F, Winkler, "Preparation of products containing valuable hydrocarbons or their derivatives, U.S. Patent 2,207,581, July 9, 1940.
- VI.3 F. Duftschmid, E. Linckh and F, Winkler, "Synthesis of hydrocarbons," U.S. Patent 2,287,092, June 23, 1942.
- VI.4 E. B. Peck, "Method of controlling exothermic reactions, U.S. Patent 2,161,974, June 13, 1939.
- VI.5 F. Duftschmid, E. Linckh and F, Winkler, "Synthesis of hydrocarbons," U.S. Patent 2,318,602, May 11, 1943.
- VI.6 H. E. Benson, J. H. Field, D. Bienstock, R. R. Nagel, L. W. Brunn, C. O. Hawk, H. H. Crowell and H. H. Storch, "Development of the Fischer-Tropsch Oil-Recycle Process," Bureau of Mines Bulletin 568, 1957.
- VI.7 H. Kölbel and P. Ackermann, U.S. Patent 2,853,369, Sept. 23, 1958.
- VI.8 H. Kölbel and P. Ackermann, U.S. Patent 2,868,627, Jan. 13, 1959.

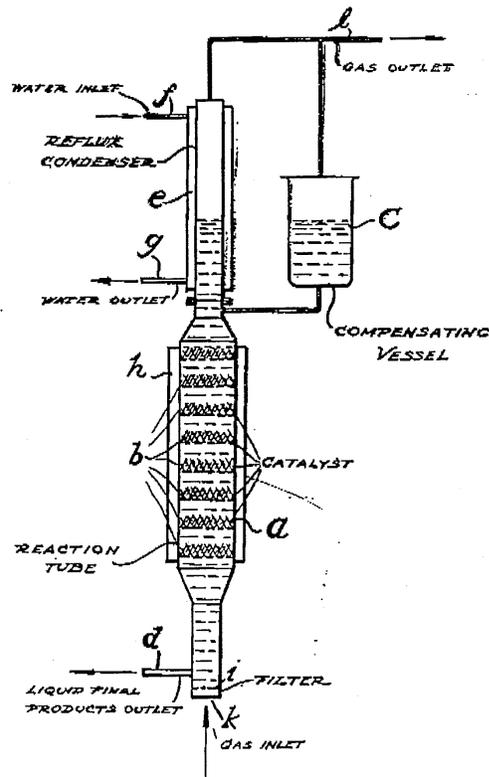


Figure VI.1. Schematic reactor fitted with catalyst trays for the preparation of hydrocarbons from synthesis gas in slurry reactor (from ref. VI.1.).

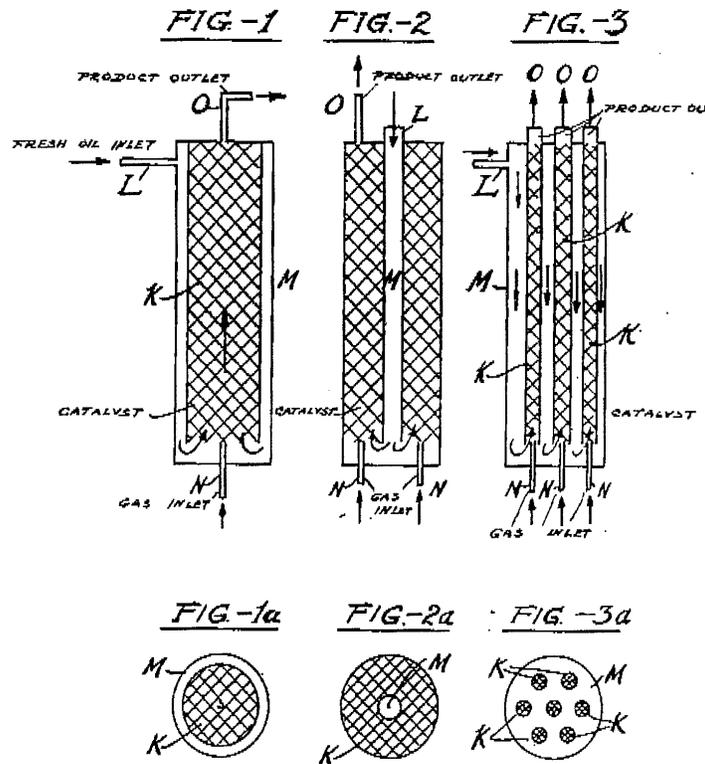


Figure VI.2. Schematic of slurry reactor tube subdivided into cells to modify liquid flow patterns (from ref. VI.3.).

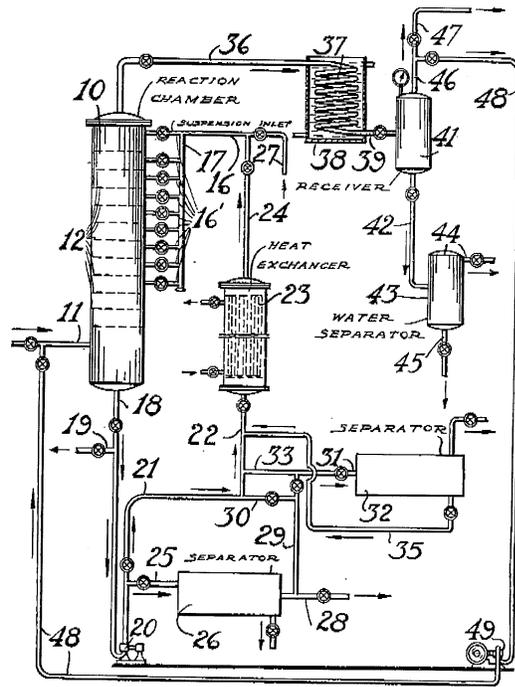


Figure VI.3. Reactor fitted with catalyst trays, each containing bottle caps, to effect slurry phase synthesis of hydrocarbons (from ref. VI.4).

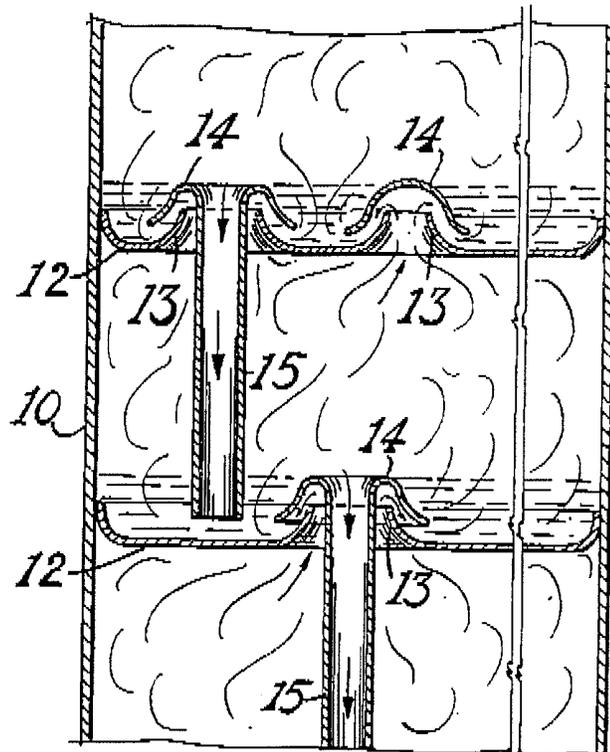


Figure VI.4. Schematic of bubble caps and gas transport columns for trays in reactor shown in figure VI.3 (from ref. VI.4).

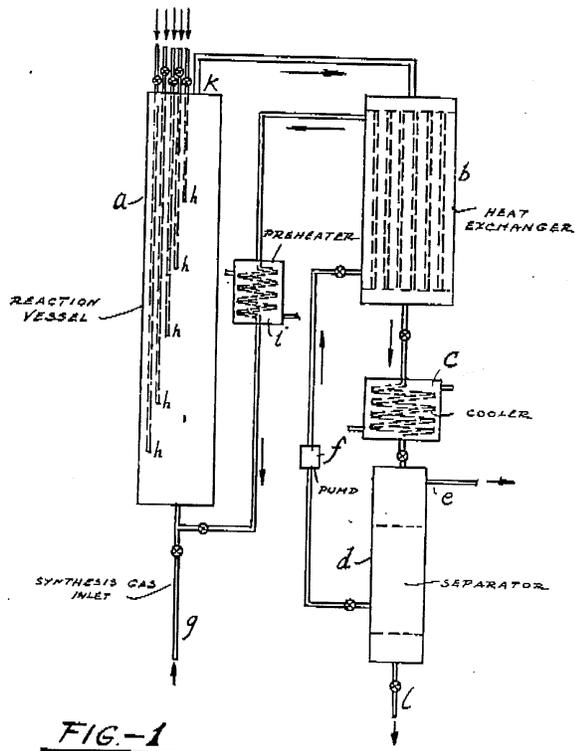


Figure VI.5. Schematic of slurry reactor with capability of adding preheated liquid as several levels within the reactor (from ref. VI.5).

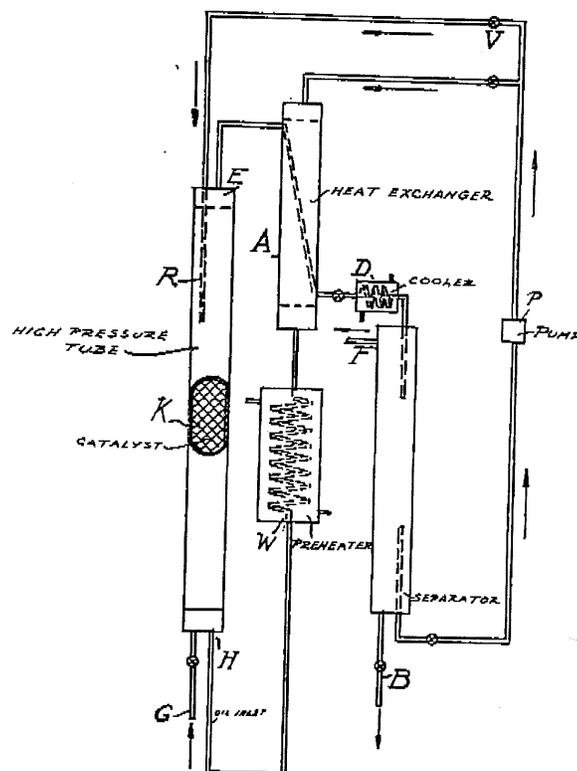


Figure VI.6. Schematic of slurry reactor with recycle of oil to the reactor (from ref. VI.5).

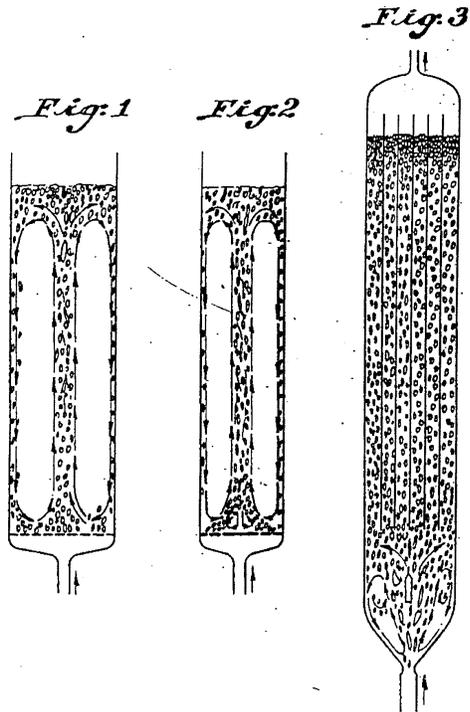


Figure VI.7. Schematic of oil recirculation within slurry reactor (figures VI.1 and VI.2) and the elimination of recirculation by adding shafts (tubes) (figure VI.3) (from ref. VI.7).

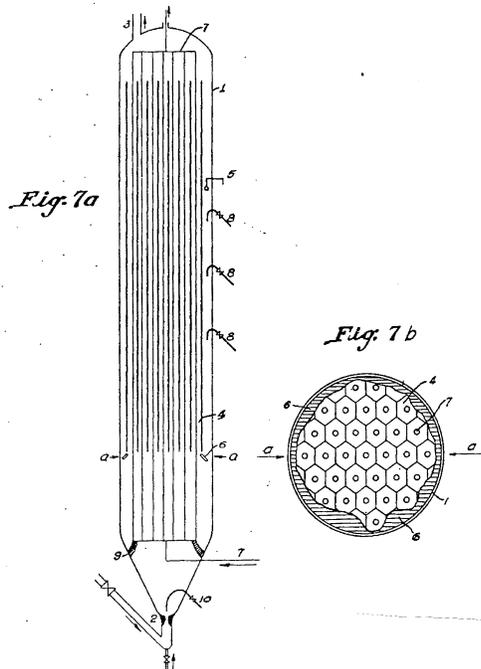


Figure VI.8. Schematic of slurry reactor with shafts (open at top and bottom) to subdivide reactor shell to establish reactor zone with stationary catalyst and liquid condition (from ref. VI.8).

Attachment VII

Tube-in-Shell Fischer-Tropsch Reactor

1. W. C. Behrmann, C. H. Mauldin and L. E. Pedrick, **Exxon**, U.S. Patent 5,382,748. The reactor consists of 2-4 inch tubes that are 39.8 ft tall [5.08-10.2 cm x 12.1 m]
2. R. M. Koros, **Exxon**, U.S. Patent 5,384,336; January 24, 1995; filed November 30, 1993. The reactor uses of plurality of reactor tubes (L/D at least 10) in a shell. [Example used 6inch x 50 foot (15.2 cm x 15.2 m) single tube].
3. T. M. Stark, **Exxon**, U.S. 5,409,960; April 25, 1995; filed June 15, 1994. The patent covers the use of pentane rather than steam for heat removal.
4. G. B. Lorentzen, A. Westvik and T. Myrstad; **Statoil**, U.S. Patent 5,520,890; May 28, 1996; filed August 18, 1994. This patent is based on data in U.S. Patent 4,801,573 and presents calculations with no experimental data. The optimum tube diameter is stated to be one which exactly matches heat exchange surface to the synthesis.

ATTACHMENT VIII

Cooling Coils in or outside the Fischer-Tropsch Reactor Shell

1. H. Kölbel, P. Ackermann and Fr. Engelhardt, Erdöl Kohle, 9 (1956) 225; **Rheinpreussen-Koppers**. This report is based on extensive work at Rheinpreussen-Koppers that started in the 1930s. It utilized an iron catalyst and a reactor with dimensions of 1.55 m diameter and 8.6 m height. It used external wax/slurry separation, including filtration, gravity settling and distillation. It also included ex-situ catalyst regeneration.
2. B. Jager and R. Espinoza, Catal. Today, 23 (1995) 17; **Sasol**. The work at Sasol has been scaled from early laboratory work to a 5 m x 22 m reactor that produces 2,500 bbl/day using iron catalyst. Smaller scale work with a 3m diameter pilot plant using a cobalt catalyst has been reported. The commercial plant uses internal separation of wax/slurry.
3. H. Beuther, T. P. Kobylinski, E. E. Kibby and R. B. Pannel, South Africa Patent 855317, July 15, 1985; **Gulf Oil, now Shell**. The work utilized a reactor with external wax-catalyst slurry separation and ex-situ catalyst regeneration. Reactor diameter was not specified - one could reasonably make the assumption that this patent covers **all** reactor diameters. Patent demonstrated the higher productivity of the slurry reactor because of (1) smaller catalyst particle and (2) better temperature control and a lower methane make. The patent also contains data showing the impact of diffusion on the activity, methane selectivity and the C₅+ selectivity when the catalyst is utilized in a fixed-bed reactor.
4. S. J. Hsia, U.S. Patent 5,260,239; November 9, 1993; filed December 18, 1992.

No examples with experimental data. Utilizes downcomer-conduit means of catalyst mixing/transport in reactor and/or ex-situ rejuvenation vessel as means of catalyst rejuvenation on a continuous basis.

5. W. C. Behrmann, C. H. Mauldin and L. E. Pedrick, U.S. Patent 5,382,748; January 17, 1995; filed December 18, 1992.

Utilizes downcomer(s) to effect liquid recirculation to effect uniform distribution of catalyst in the suspension; a single 3 inch pipe can provide an upward liquid velocity of 2-3 cm/sec in a 4 foot diameter reactor.

6. M. Chang, U.S. Patent 5,332,552; July 26, 1994; filed December 18, 1992.

A means of catalyst/slurry recirculation that utilizes concentric shells to provide means for recirculation transport of slurry from the top to bottom of reactor with the additional provision of catalyst rejuvenation on a continuous or at interval basis.

7. C. D. Ackerman, U.S. Patent 5,527,473, June 18, 1996; filed January 9, 1995;

Not Assigned to Company.

A slurry reactor with means of internal wax/catalyst slurry separation.

8. E. Rytter, P. Lian, T. Myrstad, P. T. Roterud and A. Solbakken, U.S. Patent 5,422,375; June 6, 1995; February 24, 1993.

Experimental data using a 4.8 cm x 2 m tube filled with cobalt-alumina catalyst slurry and liquid withdrawn through internal filter during 400 hours of operation.

They claim a process using multiphase Fischer-Tropsch synthesis.

9. M. Chang, U.S. Patent 5,242,613; October 12, 1993; filed December 18, 1992.

An improvement of the mixing to improve catalyst distribution by introducing a secondary-suspending liquid, e.g. pentane, above the gas distributor but in the bottom 20% of the column. This is a variation, and may be the same, as used by the Bureau of Mines operation in the 1950s.

10. E. Herbolzheimer and E. Iglesia, U.S. Patent 5,348,982, September 20, 1994; filed May 20, 1993.

This patent claims a method for optimally operating a large diameter (greater than 15 cm) for Fischer-Tropsch synthesis over a **supported cobalt catalyst** in which particles are fluidized in the liquid phase by bubbles of the gas phase. Derivations are made to define the flows that balance catalyst settling by gravity to catalyst uplift due to the gas bubble velocity. To many, this is a patent based on earlier textbook examples of bubble column operation. It would appear that the region in figure 7 that is considered for optimal performance falls completely, or mostly, within the flows used or described by Kölbel and Ralek.

11. L. E. Pedrick, C. H. Mauldin and W. C. Behrmann, U.S. Patent 5,268,344, December 7, 1993; filed December 18, 1992; **Exxon**.

One or more vertical draft tubes that are fully immersed in the liquid are used for catalyst mixing and for rejuvenation using pure, or nearly pure, gaseous hydrogen and injecting the rejuvenate catalyst into the top of the reactor.

12. M. W. McEwan and M. B. Teekens, U.S. Patent 4,139,352, February 13, 1979; filed March 14, 1978; **Shell Oil Company**.

An improved process and apparatus is described for the slurry phase Fischer-Tropsch synthesis. The process utilizes a catalyst but the catalyst is not specified. The slurry reactor separates unconverted gas and gaseous products

from the catalyst slurry at the top of the reactor. The catalyst slurry passes through a downcomer fitted with coolers and is returned to the bottom of the reactor. Excess liquid can be removed at the top of the downcomer as can catalyst which requires regeneration.