

## HISTORY OF COBALT CATALYST DESIGN FOR FTS

Calvin H. Bartholomew

BYU Catalysis Lab  
Department of Chemical Engineering  
Brigham Young University  
350 CB, Provo, UT 84602  
email: [bartc@byu.edu](mailto:bartc@byu.edu)

**Key words:** cobalt catalyst, catalyst design, Fischer-Tropsch reaction

Prepared for presentation at the National Spring Meeting of the American Institute  
of Chemical Engineers, New Orleans, March 30 – April 3, 2003

Copyright: Calvin H. Bartholomew, Brigham Young University, Provo, Utah  
January 26, 2003

AIChE shall not be responsible for statements or opinions contained in papers or  
printed in its publications

## **Abstract**

Cobalt catalysts for Fischer-Tropsch synthesis (FTS) of liquid and waxy paraffins from syngas were first discovered about 90 years ago. In the subsequent nine decades, catalyst technology has advanced from a simple cobalt oxide on asbestos to sophisticated, high-activity, highly-optimized cobalt catalysts supported on carefully-modified alumina, silica, or titania carriers and promoted with noble metals and basic oxides. Catalyst design has evolved from trial and error art based on experimental reactor tests of activity and selectivity to a scientific, nanoscale design founded on activity-structure relationships and computerized theoretical models. Documentation of the early work has been until recently somewhat sketchy; much of this work was forgotten or unavailable. Nevertheless, recently unearthed databases of Fischer-Tropsch literature, including early German patents and technical files of the Allied Technical Oil Mission (TOM) carried out just after World War II, provide new perspectives of the extensive work on FT catalysts carried out during the 1930's and 1940's in Germany. These documents provide evidence that a number of later developments, i.e., some of those resulting from an explosion of patents and processes during the last quarter of the 20<sup>th</sup> Century, are to some extent rediscoveries of the prior art. The importance of studying historical scientific and patent literatures is emphasized.

## Introduction

Production of liquid hydrocarbons over a cobalt catalyst was first reported in 1913 in a patent granted to BASF [1]. In the subsequent nine decades, catalyst technology has advanced from a simple cobalt oxide supported on asbestos to sophisticated, high-activity, highly-optimized cobalt catalysts supported on carefully-modified alumina, silica, or titania carriers and promoted with noble metals and basic oxides. Catalyst design has evolved from trial and error art based on experimental reactor tests of activity and selectivity to a scientific, nanoscale design founded on activity-structure relationships and computerized theoretical models.

Advances in cobalt catalyst design can be conveniently discussed in the context of five historical periods: (1) “discovery” (1902-1928), (2) “commercial development” of cobalt and iron catalysts (1929-1949), (3) the “iron age” (1950-1974), (4) “rediscovery” of cobalt (1975-1990), and (5) “GTL and the return to cobalt” (1991-present). During the first period, cobalt catalysts were established as the most active and selective for FT synthesis; during the second, commercial processes based on cobalt catalysts technology were developed in Germany and contributed significantly to their ability to produce gasoline and chemicals from coal. During the third period (iron age) iron catalysts were developed and commercialized, mainly in South Africa, while very little work focused on cobalt FT catalysts. In the fourth and fifth periods cobalt catalysts were rediscovered and developed to commercial application, mainly for conversion of natural gas to fuel liquids (GTL).

Documentation of the early work (Periods 1 and 2) has been until recently somewhat sketchy, and much of this work was either forgotten or not available in the public domain. Nevertheless, a recently developed web site containing large databases of Fischer-Tropsch literature [1], including early German patents and technical files of the Allied Technical Oil Mission (TOM files) carried out by U.S. Scientists immediately following World War II, was made available mainly through efforts of Professor Anthony Stranges of Texas A&M and Dr. Stephen LeViness of Syntroleum. This database provides new perspectives of the extensive work on FT catalysts carried out during the 1930’s and 1940’s in Germany. These documents provide evidence that some of the later developments, i.e., some papers, patents, and processes relevant to FTS during Periods 4 and 5, are to a significant extent a rediscovery of prior art. The importance of studying historical scientific and patent literatures is emphasized by con-

sidering the enormous investments in time and financial resources by governments, industries, and universities world-wide in rediscovering several aspects of FTS technologies from about 1975 to the present.

Careful examination of these early developments will continue to be of technical and economic importance, e.g., in more cost-effectively developing efficient catalyst and reactor technologies and in sorting out intellectual property issues, as nascent GTL developments expand to a burgeoning, world-wide industry during the coming two to three decades. Indeed, since the first modern large-scale GTL plant based on cobalt catalyst technology was constructed by Shell in Malaysia about 10 years ago, approximately 8-10 additional plants are in either in construction or planning and by 2008-2010 could be producing two million barrels per day of premium sulfur-free diesel.

This paper summarizes significant milestones in the evolution of cobalt catalyst technology from its humble beginning to its present day and ever-increasing sophistication. It focuses on developments in catalyst chemical/physical design, preparation, and application of promoters, while emphasizing fundamental principles of catalyst design learned along the way.

### **History of Cobalt Catalyst Design**

Important advances in cobalt catalyst design are summarized in Table 1 for the first two and last two periods of development. A lapse in the development of cobalt catalyst technology is evident from about 1950 to 1972 coinciding with the third period or “iron age.” It should be emphasized that list of important advances in Table 1 is meant to be representative rather than complete but is admittedly to some extent unavoidably biased by the author’s experience. The list of publications in Table 1 [1, 3-44] is also only representative rather than exhaustive, since there are literally hundreds of papers and patents addressing cobalt FT catalyst design. Caveats and disclaimers acknowledged, let us move to a brief discussion of these advances with the objective of trying to provide some perspective.

There is apparently some controversy surrounding the claims of the 1913 BASF patent. Examination of the original patent (2 pages in length) reveals two examples, both of which describe in only qualitative terms that hydrocarbons were produced; no specific data regarding production rates, selectivities or amounts are provided. Pichler [4] indicates that Fischer was of

**Table 1. Important Advances in Cobalt Catalyst Design.**

Period	Advance	Contributor(s)	Ref.
	<i>Period 1: Discovery, 1913-1928</i>		
1913	Hydrocarbons reportedly produced on cobalt oxide at 120 atm and 300-400°C.	BASF	1
1925	Production of paraffins in measurable amounts at 1 atm and 220-250°C on unsupported CoCu and Co.	Fischer and Tropsch	3
	<i>Period 2: Commercial Development, 1928-1949</i>		
1932	100Co: 18ThO <sub>2</sub> : 100 kieselguhr catalyst with greatly improved activity and stability at 1 atm.	Fischer, Koch	4
1935-6	Optimal medium pressure (5-20 atm) synthesis on the same Co-ThO <sub>2</sub> /kieselguhr catalyst.	Fischer, Pichler	4
	<i>Periods 4 &amp; 5: Rediscovery of Cobalt; GTL, 1975-Present</i>		
1972-85	Measurement of specific activities for CO hydrogenation of supported metals including cobalt based on hydrogen chemisorption.	Vannice	5
1976-1988	Development of high-activity, high-metal-surface-area Co/Al <sub>2</sub> O <sub>3</sub> catalysts promoted with Ru and basic oxides. Correlation of H <sub>2</sub> chemisorption with activity.	Kobylinski, Kibby, and Pannell (Gulf, Chevron, and Shell)	6-9
1978-2003	Preparation, characterization, and activity testing of cobalt on different supports; proven methods of measuring hydrogen uptake, extent of reduction and dispersion of cobalt catalysts; elucidation of effects of support, dispersion, and surface structure. Effects of Pt promotion.	Bartholomew, Reuel, Fu, Johnson, Huber (BYU), Goodman (TAMU)	10-18
1982-1995	Preparation, characterization, and activity testing at commercial conditions of cobalt on different supports with Re, Ru promoters; design of catalysts of optimal activity and selectivity based on activity-structure relationships, e.g. activity vs. H <sub>2</sub> uptake and chi; development of commercial catalysts of high activity and selectivity.	Fiato, Soled, Mauldin, Iglesia, Reyes (Exxon)	19-27
1983-1990	Development of commercially viable Co/SiO <sub>2</sub> catalysts promoted with Zr and rare earth metals; wax-crack concept.	Minderhoud, Post, Sie, De Jong (Shell)	28-34
1987-1999	Study of effects of La, Zr, and Ru promoters on chemical, physical, and catalytic properties; development of commercial cobalt catalysts of high activity and selectivity promoted with Re, Ru, Pt, Pd; design for attrition resistance.	Goodwin, Eri, Riis, Marcelin, Oukaci, Singleton (U.Pitt., EIC, Statsoil)	35-41
1995-2002	Basic studies of active sites on cobalt and effects of precious metal promoters.	Holman et al. (U. Trondheim, Norway)	42-44

the opinion that the 1913 patent was based on thermodynamic calculations rather than real data. He emphasizes the Fischer and Tropsch were the first to produce hydrocarbons in measurable amounts under well-defined, mild (hence catalytically relevant) conditions (1 atm, 220-250°C).

Pichler [4] provides some interesting perspectives regarding this period of discovery:

1. The successful development of liquid fuel synthesis from syngas at the Kaiser Wilhelm Institute for Coal was the result of cooperation among many scientists, although Fischer was the “spiritual center of the work.” This observation, in fact, can be generalized to all of the advances described in Table 1, i.e., each was accomplished by a group of scientists and engineers but would not have happened without the leadership, inspiration, and/or genius of one or two key members of each group.
2. The first publication of Fischer and Tropsch in Spring of 1926 generated great interest among catalyst researchers; there was surprise that there would still be so much to learn about such a simple molecule as CO after all the work that had been done to that point with carbon chemistry.
3. The 1926 publication contained a “great many facts” important for the later development: (a) iron, cobalt and nickel were reported to be the most effective catalysts for hydrogenation of carbon monoxide to hydrocarbons; cobalt was the most active for production of hydrocarbons and nickel favored formation of methane; (b) irreducible oxides (e.g. ZnO and Cr<sub>2</sub>O<sub>3</sub>) improved CO conversion while lowering sintering rates of the metals, (c) addition of small amounts of alkali were observed to favor selectivity to liquid hydrocarbons, (d) copper was found to improve the reduction of Fe at low temperatures, and (e) the syngas needed to be free of sulfur.
4. Following the 1926 publication and before Tropsch left Mülheim in 1928 (to become director of another institute) Fischer and Tropsch undertook basic research which they summarized in a 1928 paper. The following were among their findings: (a) K<sub>2</sub>CO<sub>3</sub> is the best promoter for iron and the optimization of its content at a level of 0.5-1.0%, (b) alkali poisons Co, (c) the most effective catalysts could be prepared by thermal decomposition of nitrates on porous carriers, and (d) the conversion of CO on iron favors formation of CO<sub>2</sub> and on cobalt H<sub>2</sub>O.

5. From 1928 to 1934 Fischer and Koch developed a precipitated Co-ThO<sub>2</sub>/kieselguhr catalyst (composition shown in Table 1) which was to become the standard cobalt catalyst for the next 40 years. It was the one used on a commercial scale in several plants during WWII to produce gasoline for the German war effort. Fischer and Koch found (a) an optimum temperature for reduction of this catalyst of 365°C above which sintering was observed, (b) that reduction could be ended after about 5 hours, although 20 hour reduction produced a more active catalyst, (c) that thoria increased the average molecular weight of the hydrocarbon product, and (d) an optimum reaction temperature of 190°C.
6. In 1935 Fischer published data regarding the selectivity of the standard cobalt catalyst for different hydrocarbon products, finding that the reaction products are mainly straight chain hydrocarbons with a cetene number of 105, making it an excellent fuel for diesel engines.
7. During experiments in 1935-36 Fischer and Pichler found the optimum operating pressure for the cobalt catalyst to be 5-20 atm; in this pressure range, the catalyst was much more stable than at 1 atm, while the selectivity for saturated liquid hydrocarbons was found to be much higher—i.e., the catalysts defined a route to paraffins and diesel oil.

A report summarizing the mid-June 1945 visit of members of the Combined Intelligence Objectives Sub-Committee (CIOS) to the Kaiser Wilhelm Institute for Coal Research [45] addresses the state of FT catalyst and reactor technologies just after the end of WWII. The author of the report, Dr. Vladimir Haensel of the U.S., indicates that the best cobalt catalyst was still the Co-ThO<sub>2</sub>/kieselguhr catalyst having the composition shown in Table 1 and confirms that its optimum reduction temperature and time were 365°C and 4.5 hours. Moreover, it was noted that the reduction was carried out at a gas flow rate as high as possible to keep water vapor above the catalyst to a minimum (a concept that is claimed in some recent patents treating cobalt catalyst activation).

Following WWII FT research conducted from about 1945 to 1954 in the U.S., Great Britain, and Germany focused mainly on processes based on relatively inexpensive Fe catalysts. However, the discovery of cheap oil in the Mid-East brought a sharp end to FT research and development activities in these countries.

Interest in synthetic fuels development in the U.S. received a great boost in 1973 as a result of the oil embargo by the Arab oil cartel. Government support of synfuel R&D including FT was substantial in the mid and late 1970s and continued at a high level through the mid 1980s.

Interest in FTS was stimulated in 1975 in part by the publication of a paper authored by Vannice (then at Exxon) reporting the results of his study of the intrinsic turnover frequencies for CO hydrogenation on supported Group VIII metals. His work demonstrated that cobalt and iron are among the most active metals. Quite a number of university and company laboratories in the U.S. undertook research on cobalt, iron and ruthenium catalysts for FTS; DOE provided substantial support for such research at roughly a dozen U.S. universities. Research on FT catalysts during this period of time was a “hot” topic and the subject of intense discussion at catalysis and fossil energy meetings. A 2-3 day syngas conversion meeting for researchers in U.S. and Canada held annually in either Kingston, Ontario or Pittsburgh was typically religiously attended by 40-50 researchers in syngas conversion during the period from about 1978 to 1985. The annual two-day Rocky Mountain Fuel Society meeting in Salt Lake City drew 80-120 attendees during this same period, and the annual coal conference in Pittsburgh was a huge affair.

FT research at oil companies during the late 70's and through most of the 80's was well funded; it was especially intense at Gulf, Exxon, Mobil, and Shell. Gulf Oil led out in mid and late 1970's with some major advances in FT catalyst development. Work begun by Kobylinski and joined by Kibby and Pannell focused on the preparation of high-activity Co/alumina catalysts promoted with Ru and basic oxides such as ThO<sub>2</sub>; the Gulf group made use of the latest methods and instrumentation, using for example, hydrogen chemisorption to determine metal surface area and GC/MS to determine product distributions.

The Gulf patents [6-9] reflect a reasonably high level of fundamental understanding of catalyst design principles. For example, Kobylinski [6] was the first to discover that a small amount of Ru promoter substantially increase cobalt catalyst activity. In several patents, Kibby, Pannell, and coworkers [8,9] reveal (1) the ideal properties for the alumina support, i.e., high purity, low acidity, and relatively high surface area (e.g. 150-250 m<sup>2</sup>/g), (2) importance of reducing the catalyst with a low heating ramp to prevent sintering, (3) the use of basic oxides such as ThO<sub>2</sub>, La<sub>2</sub>O<sub>3</sub>, ZrO and rare-earth oxides to lower the acidity of the support which otherwise causes cracking of olefin intermediates, (4) the importance of high metal surface area



corresponding to a hydrogen adsorption uptake of 150-300 micromoles/g, (5) the application of non-aqueous solvents during the preparation to obtain a uniform thin layer of catalyst on the support and (6) an optimal reduction temperature of about 350°C for decomposing cobalt nitrate.

Bartholomew et al. [10-18] utilized a basic regimen of characterization methods to further understanding of activity-structure relationships for cobalt on different supports. Reuel and Bartholomew [10-11] develop the foundation for measuring metal dispersion of cobalt catalysts using hydrogen chemisorption at 100°C (for most catalysts) to determine metal site density and oxygen titration the extent of reduction of cobalt to the metallic state, methods that are presently used widely [14]. Their work with cobalt on different supports at different metal loadings demonstrated that (1) activity of cobalt catalysts can vary over 3-4 orders of magnitude depending upon support and metal loading (higher loadings favor higher activity), (2) product molecular weight decreases with increasing dispersion at low metal loadings and (3) activity increases with increasing extent of reduction. Fu and Bartholomew (12) demonstrated how to determine the optimum combination of dispersion, extent of reduction and cobalt surface area for a given loading of cobalt on alumina.

The work of Johnson et al. [13, 15] focused on the effects of support chemistry, metal loading, and dispersion on activity selectivity properties of cobalt/alumina catalysts. It demonstrated that (1) partial dehydroxylation of the support is critical in maximizing extent of reduction, (2) maximum activity is observed for catalysts having extents of reduction higher than 70-80%, and (3) the specific activity per site is independent of dispersion from 0 to 100%. These are three important consideration in the design of commercially viable cobalt catalysts. The work of Huber et al. [18] addresses an important problem in commercial operation, namely the breakdown of untreated silica (probably also untreated alumina) supports in the presence of high pressure steam produced in substantial amounts by reaction at high conversions.

FT research and development activities at Exxon have been substantial over the past 25 years, resulting in several hundred patents and a number of important journal articles addressing important fundamental principles, for example, those treating catalyst design; representative examples of these publications are included in References 19-27. Exxon has developed and demonstrated a commercial GTL process. However, the most important advances have come from fundamental studies in corporate research by Iglesia, Soled, Fiato,

and Reyes [23-27] leading to a better understanding of (1) activity-site density relationships, e.g. a linear correlation between activity and cobalt metal dispersion for a suite of well-characterized cobalt catalysts supported on alumina, silica, and titania, based on activity tests under commercially-relevant conditions; (2) studies showing the effects of precious metal promoters in enhancing reduction of cobalt at lower temperatures while minimizing the accumulation of inactive carbonaceous deposits on the metal surface; and (3) the development of quantitative models describing effects of reaction, readsorption and pore diffusional transport on product selectivity and how these phenomena are affected by fundamental structural properties of the catalyst through a parameter  $\chi$ . This latter development is one of the most important recent advances in cobalt catalyst design, because it enables optimization of product selectivity (maximizing  $C_{5+}$  hydrocarbons while minimizing methane) through appropriate choice of basic catalyst structural properties such as catalyst particle diameter, pore diameter, and active site density. This model predicts that an eggshell distribution is favored for sizable catalyst pellets.

Work at Shell over the past 20 years has also been quite significant in terms of patents [28-34] and the development of the first large-scale GTL plant in Bintulu, Malaysia. Catalyst development has focused on design of cobalt supported on a  $ZrO_2$ -modified silica (silica may be modified with other closely related oxides Group IIIA,B or IVA,B and rare earth oxides. Shell has developed a method (similar to that developed by Exxon) for preparing an eggshell catalyst distribution for pellets used in its fixed bed process.

Goodwin and coworkers [35-41] have contributed in significant ways to a better understanding of (1) catalyst activity-structure relationships, (2) effects of Zr, La, and Ru promoters, (3) effects of pretreatments, and (4) tests for attrition of slurry bed catalysts and relative attrition resistances of different supports. They have also developed commercially viable cobalt FT catalysts containing Re, Ru, Pt, or Pd promoters described in patents [35] and compared the activities, selectivities, and productivities of cobalt catalysts prepared according to descriptions in selected patents [41].

Holman et al. [42-44] have contributed new insights into the nature of active sites on cobalt catalysts and the effects of  $ZrO_2$  and noble metal promoters on specific activity. One of their most significant contributions has been the use of steady-state isotopic transient kinetic analysis (SSITKA) to estimate active site concentrations during reaction and how these active site

concentrations vary with promoter and temperature. These data show, for example, that active sites in ZrO<sub>2</sub>-promoted cobalt are less covered with carbon and hydrogen atoms than unpromoted cobalt at higher reaction temperatures.

## Conclusions

1. Each of several advances in FT catalyst design was accomplished by a group of scientists and engineers but probably would not have happened without the leadership, inspiration, and/or genius of one or two key members of each group.
2. A number of important observations emerge from a study of the early literature/work, for example: (a) iron, cobalt and nickel are the most effective catalysts for hydrogenation of carbon monoxide to hydrocarbons; cobalt was the most active for production of hydrocarbons and nickel favored formation of methane; (b) The most active cobalt catalysts can be prepared by impregnation of carriers with nitrates, (c) addition of small amounts of alkali favors selectivity to liquid hydrocarbons, (d) copper improves the reduction of Fe at low temperatures, (e) the syngas needs to be free of sulfur; (f) K<sub>2</sub>CO<sub>3</sub> is the most effective promoter for iron catalysts but poisons cobalt, (g) reduction of cobalt catalysts should be carried out at a gas flow rate as high as possible to keep water vapor above the catalyst to a minimum.
3. A number of the observations in No. 2 above were rediscovered and patented in the last 25 years.
4. Important advances in cobalt catalyst design include:
  - a. The work of Fischer and Tropsch resulting in the discovery of a Co-ThO<sub>2</sub>/kieselguhr that was the best cobalt FT catalyst for about four decades.
  - b. Measurement of specific activities per site (turnover frequencies) based on H<sub>2</sub> uptake.
  - c. Development of methods for measuring metal dispersion, extent of reduction
  - d. Development of activity-structure relationships, e.g. effects of preparation, pretreatment, dispersion, support properties, metal-support interactions, extent of reduction and promoters on catalyst activity and selectivity.

- e. Development of a selectivity-transport model providing a quantitative relationship between selectivity and catalyst chemical and physical properties.
- f. Development of stable, high-activity cobalt catalysts with high selectivities for liquid/wax products based on these activity-structure relationships.
- g. Optimization of catalyst performance based on the selectivity-transport model.

## Acknowledgments

The author gratefully acknowledges financial support of this project by the Syntroleum Corporation, encouragement from Dr. Steve LeViness, and technical assistance by Nick Cieslak, Cody Nelson, and Tom Valdez.

## References

1. German Patent 293,787, "Process for Production of Hydrocarbons and their Derivatives," assigned to BASF, granted March 8, 1913.
2. <http://www.fischer-tropsch.org>; website sponsored by Syntroleum, Inc.
3. F. Fischer and H. Tropsch, German Patent 484,337, "Process for Production of Paraffin Hydrocarbons from Carbon Monoxide and Hydrogen by Catalytic Paths," granted to the inventors July 22, 1925, made public on October 3, 1929.
4. H. Pichler, "Twenty-five Years of Synthesis of Gasoline by Catalytic Conversion of Carbon Monoxide and Hydrogen," *Advances in Catalysis*, 4 (1952) 271.
5. M.A. Vannice, "The Catalytic Synthesis of Hydrocarbons from H<sub>2</sub>/CO Mixtures over the Group VIII Metals," *J. Catal.* 37 (1975) 449-461.
6. T.B. Kobylinski, U.S. Patent, 4,088,671 (1978).
7. C.L. Kibby, T.P. Kobylinski, U.S. Patents 4,492,774 (1985); 4,497,903 (1985).
8. H. Beuther, C.L. Kibby, T. P. Kobylinski, R. B. Pannell, U.S. Patents 4,413,064 (1983); 4,493,905 (1985); 4,585,798 (1986); 4,605,680 (1986); 4,613,624 (1986).
9. T.P. Kobylinski, C.L. Kibby, R.B. Pannell, E.G. Eddy, U.S. Patents, 4,605,676 (1986); 4,605,679 (1986).
10. R.C. Reuel and C.H. Bartholomew, "The Stoichiometries of H<sub>2</sub> and CO Adsorptions on Cobalt: Effects of Support and Preparation," *J. Catal.*, 85 (1984) 63.
11. R.C. Reuel and C.H. Bartholomew, "Effects of Support and Dispersion on the CO Hydrogenation Activity/Selectivity Properties of Cobalt," *J. Catal.*, 85 (1984) 78.

12. L. Fu and C.H. Bartholomew, "Structure Sensitivity and Its Effects on Product Distribution in CO Hydrogenation on Cobalt/Alumina," *J. Catal.* 92 (1985) 376.
13. B.G. Johnson, M. Rameswaran, M.D. Patil, G. Muralidhar, and C.H. Bartholomew, "Physical Properties and Fischer-Tropsch Activities of Co/Al<sub>2</sub>O<sub>3</sub> Catalysts Prepared from the Decomposition of Co<sub>4</sub>(CO)<sub>12</sub>," *Catalysis Today* 6 (1989) 81-88.
14. C.H. Bartholomew, "Hydrogen Adsorption on Supported Cobalt, Iron, and Nickel," *Catal. Letters* 7 (1990) 27-52.
15. B. G. Johnson, C. H. Bartholomew, and D. W. Goodman, "The Role of Surface Structure and Dispersion in CO Hydrogenation on Cobalt," *J. Catal.* 128 (1991) 231.
16. G. W. Huber, S.J.M. Butala, M.L. Lee and C.H. Bartholomew, "Gd Promotion of Co/SiO<sub>2</sub> Fischer-Tropsch Synthesis Catalysts," *Catal. Lett.* 74 (2001) 45-48.
17. G.W. Huber, C.H. Bartholomew, "Pt-Promotion of Co/SiO<sub>2</sub> Fischer-Tropsch Synthesis Catalysts," *Stud. Surf. Sci. & Catal.*, 136 (2001) 283-288.
18. G.W. Huber, C.G. Guymon, T.L. Conrad, B.C. Stephenson, C.H. Bartholomew, "Hydrothermal Stability of Co/SiO<sub>2</sub> Fischer-Tropsch Synthesis Catalysts," *Stud. Surf. Sci. & Catal.*, 139 (2001) 423-430.
19. C.H. Mauldin and V.L. Payne, U.S. Patents, 4,542,122 (1985); 4,568,663 (1986); 4,579,995 (1986); 4,670,476 (1987).
20. E. Iglesia, S. Soled, R.A. Fiato, U.S. Patents, 4,794,099 (1988); 4,822,824 (1988); 4,738,948 (1988); 4,960,801 (1990).
21. W.C. Behrman, C. H. Mauldin, K.B. Arcuri, U.S. Patent 4,962,078 (1990).
22. C. Mauldin, K.L. Riley, U.S. Patents, 4,977,126 (1990); 4,992,406 (1991); 5,140,050 (1992).
23. E. Iglesia, S.L. Soled, R.A. Fiato, "Fischer-Tropsch Synthesis on Cobalt and Ruthenium. Metal Dispersion and Support Effects on Reaction Rate and Selectivity," *Journal of Catalysis* 137 (1992) 212-224.
24. E. Iglesia, S.L. Soled, R.A. Fiato, G.H. Via, "Bimetallic Synergy in Cobalt-Ruthenium Fischer-Tropsch Synthesis Catalysts," *Journal of Catalysis* 143 (1993) 345-368.
25. E. Iglesia, S.C. Reyes, and S.L. Soled, "Reaction-Transport Selectivity Models and the Design of Fischer-Tropsch Catalysts," in *Computer-Aided Design of Catalysts*, eds. E.R. Becker, and C.J. Pereira, Marcel Dekker, 1993.
26. E. Iglesia, S.L. Soled, J. Baumgartner, "Synthesis and catalytic properties of eggshell cobalt catalysts for the Fischer-Tropsch synthesis," *Journal of Catalysis* 153 (1995) 108-122.
27. E. Iglesia, "Design, Synthesis, and Use of Cobalt-Based Fischer-Tropsch Synthesis Catalysts," *Applied Catalysis*, 161 (1997) 59-78.
28. J.K. Minderhoud, M.F.M. Post, S.T. Sie, European Pat. Appl. 0 109 702 A1 (1983).
29. J.K. Minderhoud, M.F.M. Post European Pat. Appl. 0 127 220 A2 (1984).

30. J.K. Minderhoud, M.F.M. Post, S.T. Sie, E.J.R. Sudholter, European Pat. Appls. 0 142 887 A2 (1984); 0 142 888 A2 (1984).
31. M.F.M. Post, S.T. Sie, European Pat. Appls., 0 153 781 A2 (1985); 0 167 215 A2 (1986).
32. D. Bode, S.T. Sie, European Pat. Appl. 0 188 304 A1 (1986).
33. K.P de Jong, J.E. Glezer, M.F.M. Post, European Pat. Appl 0 221 598 A2 (1986).
34. M.F.M. Post, W.A. van Erp, European Pat. Appl. 0 398 420 A2 (1990).
35. S. Eri, J.G. Goodwin Jr, G. Marcelin, T. Riis, U.S. Patents 4,880,763 (1989); 4,801,573 (1989); 4,857,599 (1989); 5,102,851 (1992); 5,116,879 (1992).
36. S. Vada, B. Chen, and J.G. Goodwin, "Isotopic transient study of La promotion of Co/Al<sub>2</sub>O<sub>3</sub> for CO hydrogenation," *Journal of Catalysis* 153 (1995) 224-231.
37. S. Ali, B. Chen, J.G. Goodwin, "Zr promotion of Co/SiO<sub>2</sub> for Fischer-Tropsch synthesis," *Journal of Catalysis* 157 (1995) 35-41.
38. G.J. Haddad, B. Chen, J.G. Goodwin, "Characterization of La<sup>3+</sup>-promoted Co/SiO<sub>2</sub> Catalysts," *Journal of Catalysis* 160 (1996) 43-51.
39. A. Kogelbauer, J.G. Goodwin, R. Oukaci, "Ruthenium promotion of Co/Al<sub>2</sub>O<sub>3</sub> Fischer-Tropsch catalysts," *Journal of Catalysis* 160 (1996) 125-133.
40. A.R. Belambe, R. Oukaci, J.G. Goodwin, "Effect of pretreatment on the activity of a Ru-promoted Co/Al<sub>2</sub>O<sub>3</sub> Fischer-Tropsch catalyst," *Journal of Catalysis* 166 (1997) 8-15.
41. R. Oukaci, A.H. Singleton, J.G. Goodwin Jr., "Comparison of patented Co F-T catalysts using fixed-bed and slurry bubble column reactors," *Applied Catal. A: General* 186 (1999) 129-144.
42. D. Schanke, S.Vada, E.A. Blekkan, A.M. Hilmen, A. Hoff, A. Holmen, "Study of Pt-Promoted Cobalt CO Hydrogenation Catalysts," *Journal of Catalysis* 156 (1995) 85-95.
43. S.Vada, A. Hoff, E. Ådnanes, D. Schanke, A. Holmen, "Fischer-Tropsch synthesis on supported cobalt catalysts promoted by platinum and rhenium," *Topics in Catalysis* 2 (1995) 155-162.
44. E.A. Blekkan, F. Rohr, and A. Holmen, "SSITKA Study of Fischer-Tropsch Synthesis over Supported Catalysts," Preprints of the Petroleum Division of the ACS, 217<sup>th</sup> National Meeting, Anaheim, March 21-25, 1999.
45. V. Haensel, CIOS File No. 30, Item XXX-1, Kaiser Wilhelm Institut für Kohlenforschung,, Mulheim, CIOS Target No. 30/6.01, Fuels and Lubricants, June 15, 1945 (accessible on the site in Ref. 2 under government reports).