History of Cobalt Catalyst Design for Fischer-Tropsch Synthesis

Calvin H. Bartholomew
Brigham Young U.

History of Cobalt FT Catalyst Design

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III. LESSONS FROM HISTORY

- A. Observations from early work ignored/rediscovered
- B. Important advances and why they happened

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Introduction

- Cobalt Fischer-Tropsch catalysts - 90 years in development.
- Substantial improvements in materials/design:
  CoO/asbestos to 20% Co/0.3%PM/RE-Al_2O_3
- Catalyst design: trial & error to computer assisted nanoscale design.

History of Cobalt FTS
Historical timeline and periods

Period 1: Discovery, 1913-1928

1913	Hydrocarbons reportedly produced at BASF on cobalt oxide at 120 atm and 300-400°C
1925	Production of paraffins in measurable amounts at 1 atm and 220-250°C on unsupported CoCu and Co by Franz Fischer and Hans Tropsch

Pichler's Perspectives

Regarding Period 1

- Successful development of liquid fuel synthesis from syngas at the Kaiser Wilhelm Institute for Coal was result of cooperation among many scientists

- Fischer was "spiritual center of the work"

- First publication of Fischer and Tropsch in Spring of 1926
  - Generated great interest among catalyst researchers
  - They were surprised there would still be so much to learn about such a simple molecule as CO

Discovery of the First Cobalt FT Catalyst

PROFESSOR FRANZ FISCHER
19 March 1877–1 December 1947

DR. HANS TROPSCH

F. Fischer and H. Tropsch, *Ber. 59*, 830, 382, 923 (1926).

Pichler's Perspectives

Regarding Period 1 (cont.)

- **F&T's 1926 publication contained a "great many facts" important for later development:**
  - Fe, Co, Ni the most effective catalysts in hydrocarbon synthesis
  - Co most active for production of hydrocarbons, Ni for methane
  - Carriers, e.g. ZnO and Cr_2O_3, improves CO conversion while lowering sintering rates of metals
  - Addition of small amounts of alkali observed to favor selectivity to liquid hydrocarbons
  - Cu found to improve reduction of Fe at low temperatures
  - Syngas needs to be free of sulfur

Pichler's Perspectives

Regarding Period 1 (cont.)

- **Findings of 1928 paper of Fischer and Tropsch**
  - K_2CO_3 is the best promoter for iron
  - Best level 0.5-1.0%
  - Alkali poisons Co
  - Most effective catalysts are prepared by thermal decomposition of nitrates on porous carriers
  - Conversion of CO on iron favors formation of CO_2 and on cobalt H_2O

History of Cobalt FTS
Historical timeline and periods – cont.

Period 2: Commercial Development, 1928-1949

1932	100Co: 18 ThO_2: 100 kieselguhr catalyst with greatly improved activity and stability at 1 atm
1935-6	Optimal medium pressure (5-20 atm) synthesis on the Co-ThO_2/kieselguhr catalyst w/wo MgO

Pichler's Perspectives

(cont.)

- Fischer and Koch (1928 to 1934) developed precipitated Co-ThO_2/Kieselguhr
  - The standard cobalt catalyst for the next 40 years
  - Used in commercial plants during WWII to produce gasoline for the German war effort

- Fischer and Koch found
  - An optimum temperature for reduction of this catalyst of 365°C
  - 5-20 hour reduction produces most active catalyst
  - Thoria increases average molecular weight of hydrocarbon product
  - An optimum reaction temperature of 190°C

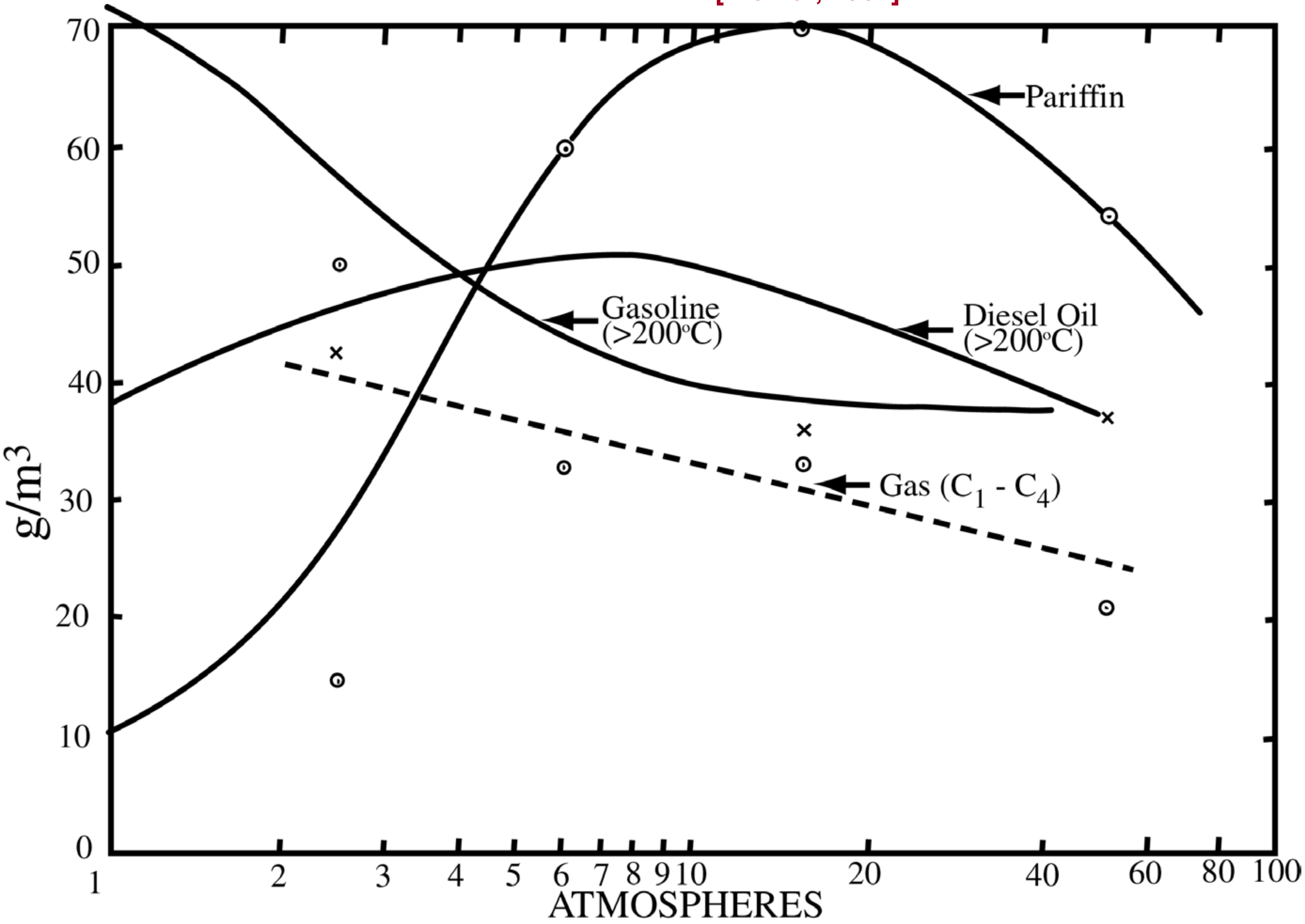
Pichler's Perspectives
(cont.)

- In 1935 Fischer reported selectivity data for Co
    - reaction products are mainly straight chain alkanes
    - cetene number of 105, making it an excellent fuel for diesel engines

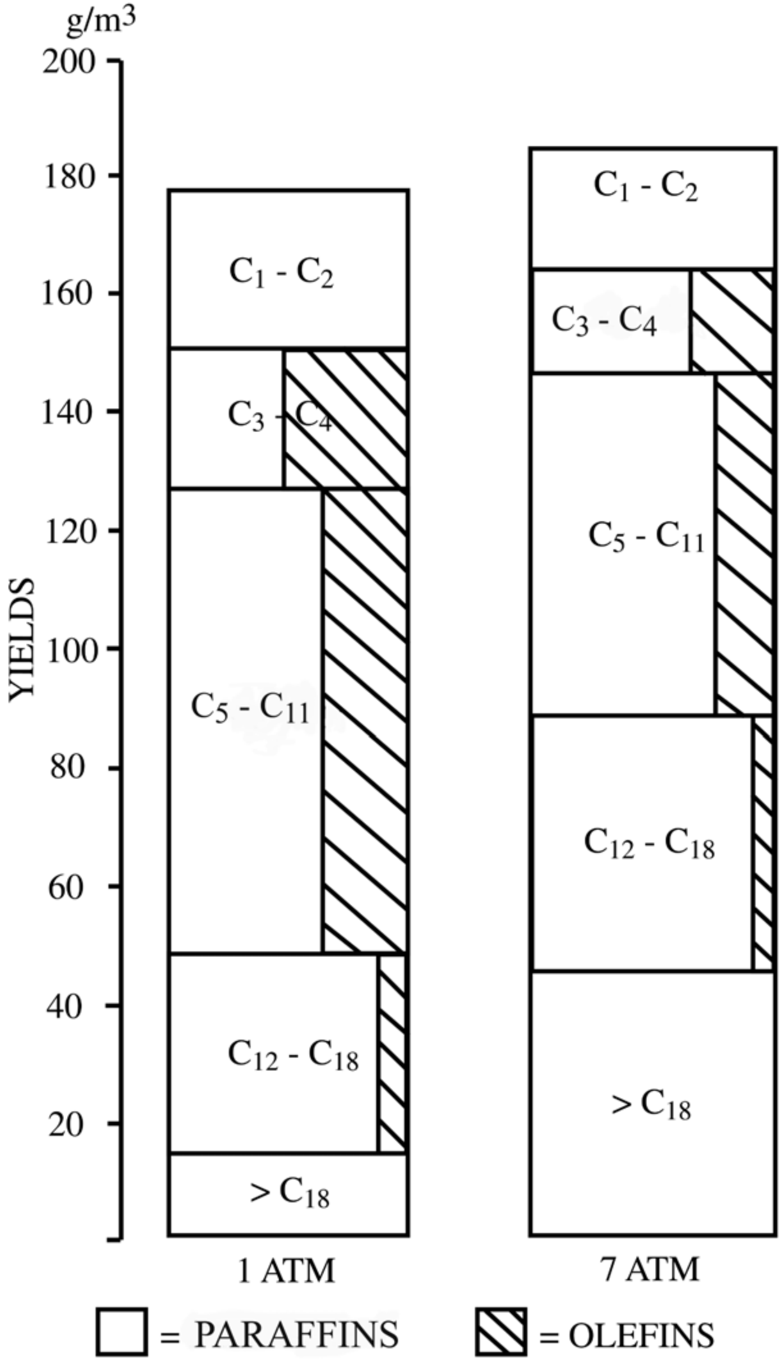
- Fischer and Pichler (1935-36) found the optimum operating pressure for the Co Catalyst to be 5-20 atm
    - Catalyst was much more stable than at 1 atm
    - Selectivity for saturated liquid hydrocarbons found to be much higher
    - Defined a route to paraffins and diesel oil

FT products for cobalt catalysts as a function of pressure.

[Pichler, 1952]



[Pichler, 1952]



The C_1 - C_2 and > C_{18} fractions include small amounts of olefins

1945 Report by Dr. Vladimir Haensel

Combined Intelligence Objectives Sub-Committee (CIOS)

Kaiser Wilhelm Institute for Coal Research

- The best cobalt catalyst is still Co-ThO_2/kieselghur
- Its optimum reduction temperature and time are 365°C and 4.5 hours
- Reduction is carried out at a gas flow rate as high as possible to keep water vapor above the catalyst to a minimum

History of FTS
Historical timeline and periods – cont.

Period 3: Age of Retreat and Sasol (i.e., iron age, 1950-1985)

1950	Sasol produces fuels and chemicals using coal-based FTS on iron catalysts (units are still in operation)
1954	Abundance of low-cost petroleum in the Middle East leads to shut-down of R&D in U.S. and elsewhere

History of FTS
Historical timeline and periods – cont.

Period 4: Rediscovery of Cobalt

1973-85 Measurement of specific activities for CO hydrogenation of supported metals including cobalt based on hydrogen chemisorption

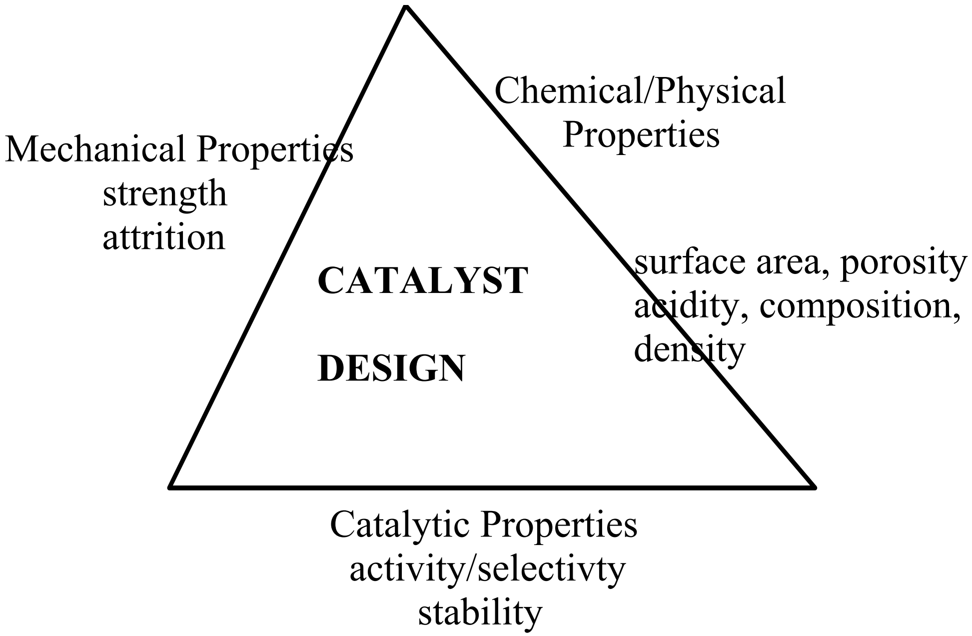
1976-88 Development of high-activity, high-metal-surface-area Co/Al_2O_3 catalysts promoted with Ru and basic oxides. Correlation of H_2 chemisorption with activity

Period 4: Rediscovery of Cobalt (1975-1989)

- Vannice reports TOF data for CO hydrogn. on metals (1973)
- Substantial support by DOE of university and company research for synfuels research (1975-1989)
- FT research intense at oil companies, esp. Gulf, Exxon, Mobil and Shell
- FTS is a hot topic at catalysis and syngas conversion meetings, e.g., syngas conversion meeting in Kingston.
- Elucidation of support, promoter, dispersion and surface structure effects at Gulf, Exxon, BYU, and other labs using sophisticated methods/tools
- Development of activity/structure and design concepts for FT

Period 4: Catalyst Design Concepts

General Catalyst Design Principles



Chemical/Physical
Properties

Mechanical Properties
strength
attrition

CATALYST

DESIGN

surface area, porosity
acidity, composition,
density

Catalytic Properties
activity/selectivty
stability

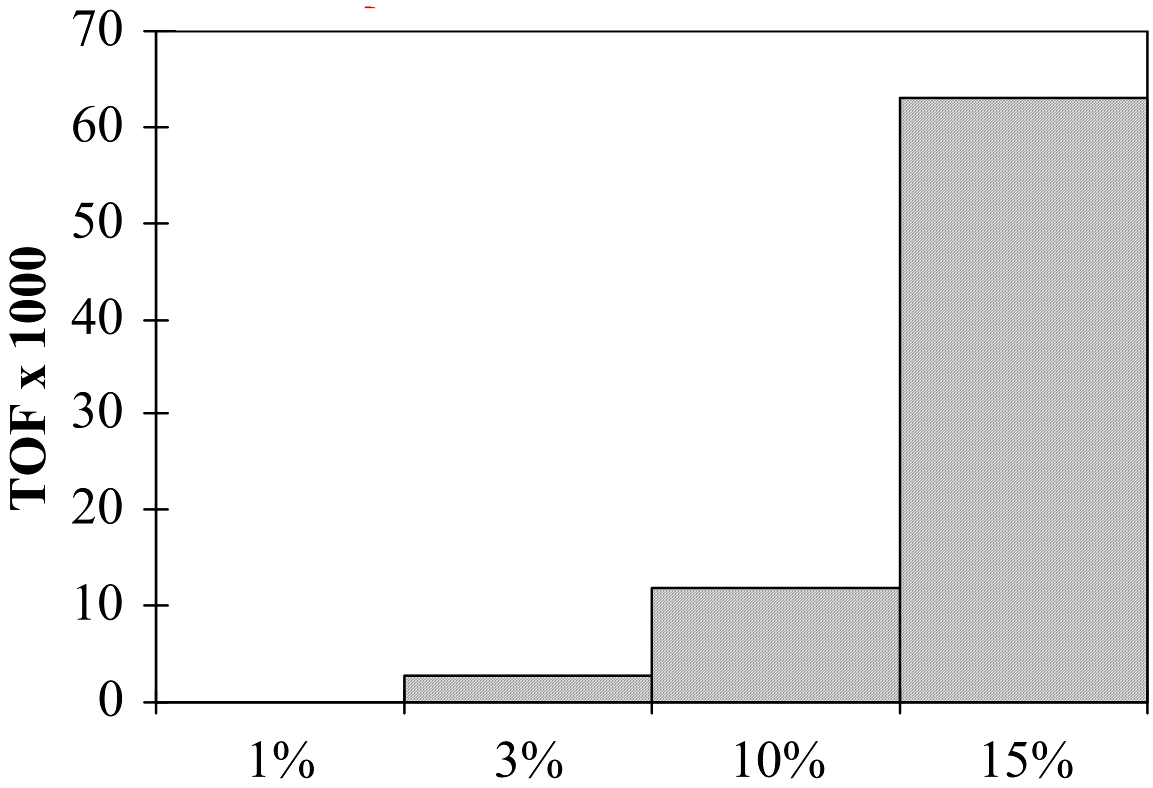
Triangular concept for catalyst design: catalyst design is an optimized combination o
interdependent mechanical, chemical/physical, and catalytic properties [adapted from
Richardson, 1989].

Period 4: Important Developments

- **Gulf Research: Kobylinski, Kibby, and Pannell**
  - Focus on preparation of high-SA, high-activity Co/Al_2O_3 promoted with Ru and basic oxides (e.g. ThO_2).
  - Fundamental understanding of design principles, e.g.
    - high-purity, low-acidity, high-SA supports
    - low heating ramp during reduction
    - use of basic oxides to lower support acidity
    - correlation of high activity with high H_2 uptake
    - optimal reduction temperature of 350°C

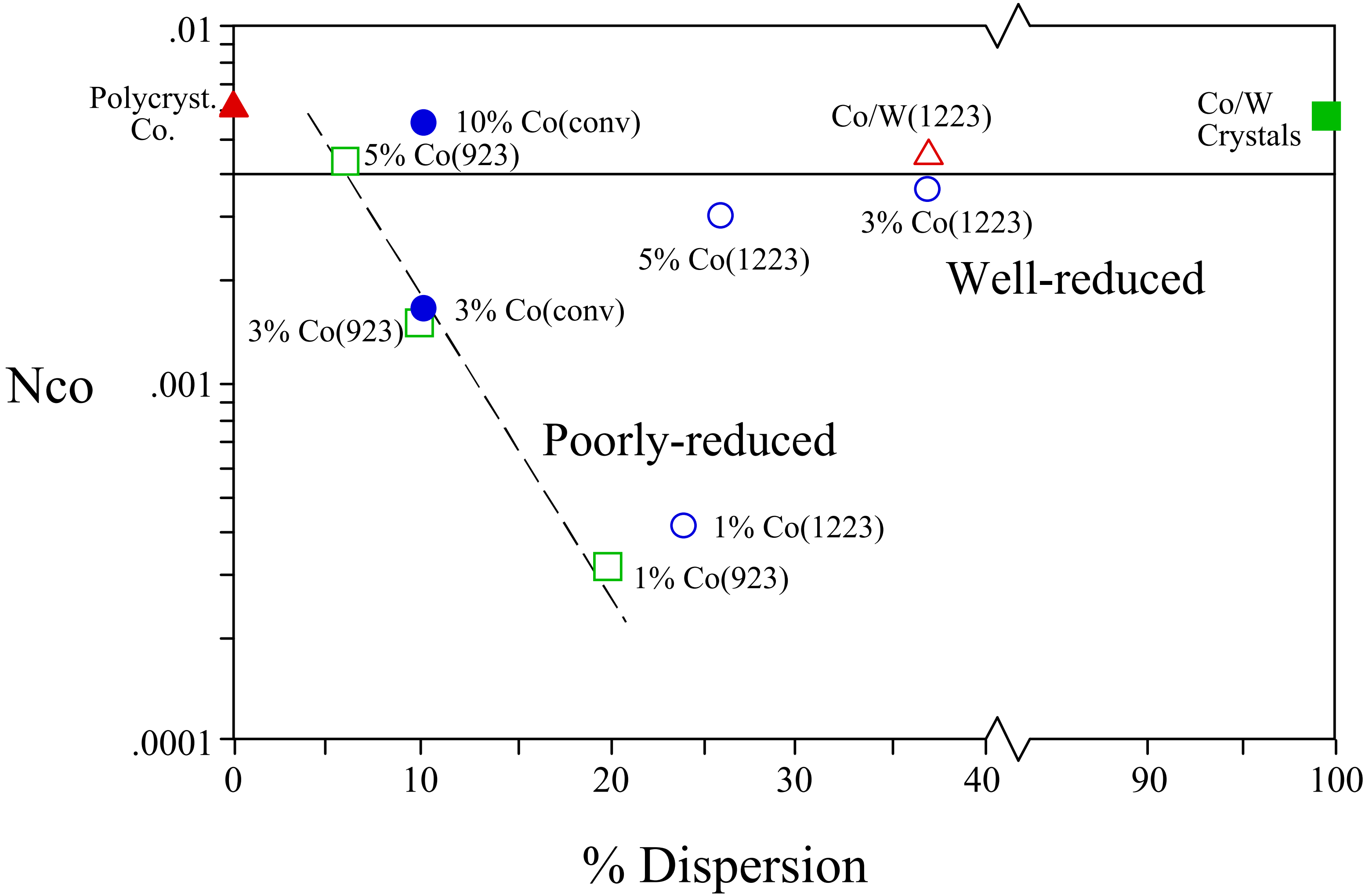
Period 4: Important Developments (continued)

- **BYU: Bartholomew et al. (20+ papers)**
  - Methods for measuring Co dispersion
    - H_2 chemisorption to measure active site density
    - Oxygen titration to determine extent of reduction
  - Fundamental understanding of
    - Effects of support and metal loading on act/sel
    - Effects of dispersion and surface structure
    - Metal support interactions
    - Role of support surface hydroxyl concentration
    - Hydrothermal breakdown of supports

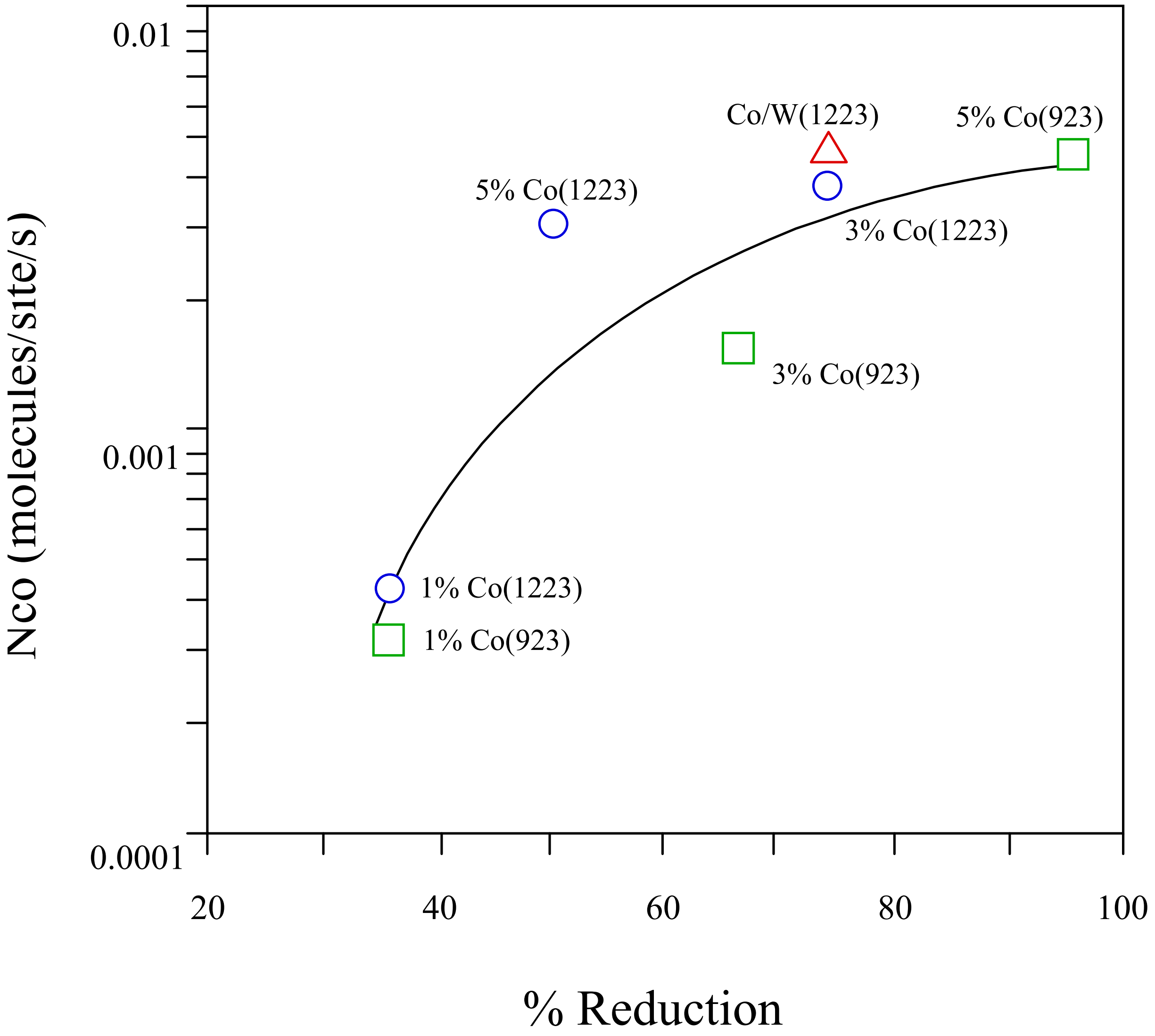


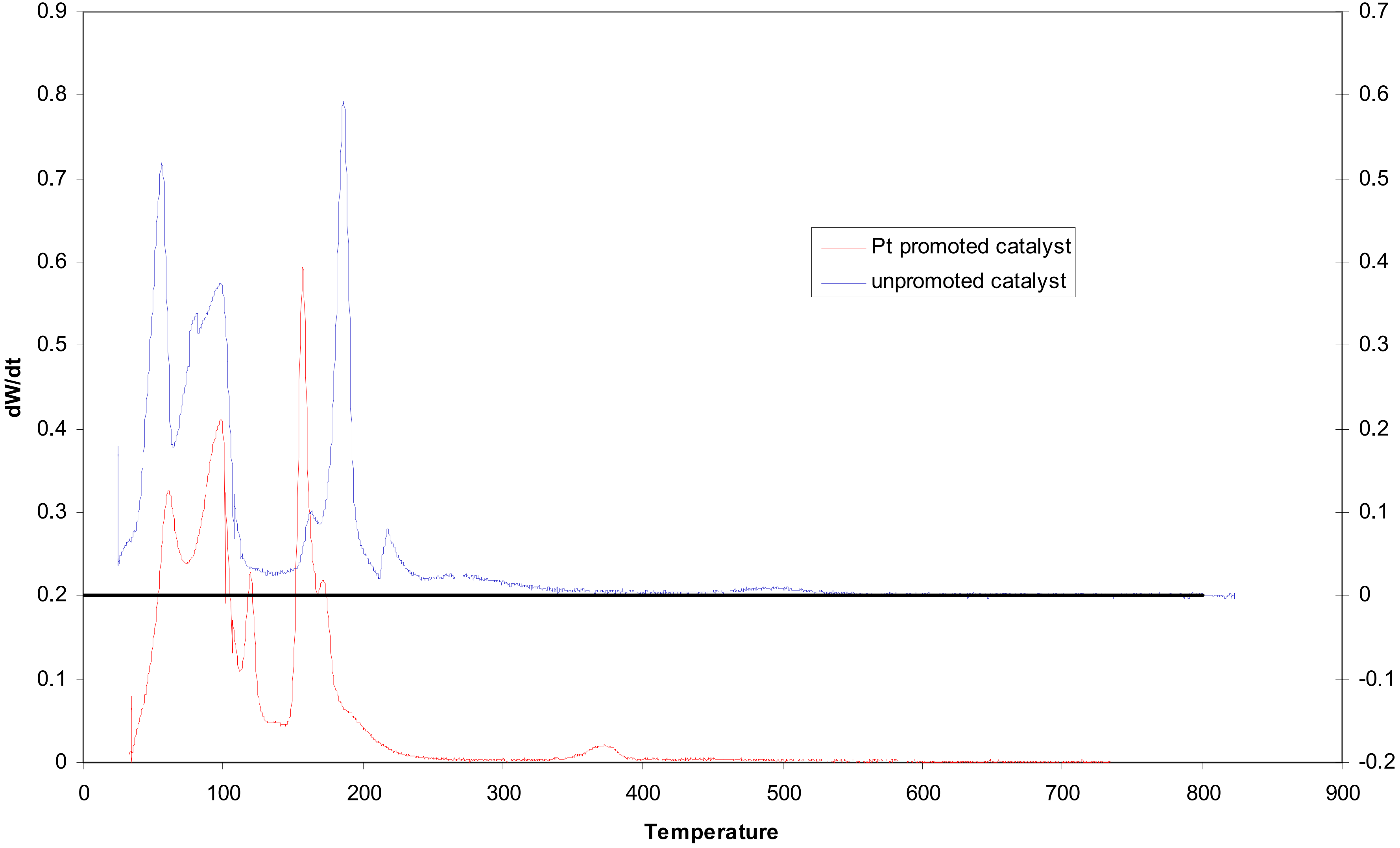
Effects of metal loading of Co/alumina on specific activity [Reuel and Bartholomew, 1985].

CO TOF (485k) vs. Dispersion, Cobalt.
Johnson et al. [1991]



CO TOF vs. Extent of Reduction for Co/Alumina. Johnson et al. [1991]





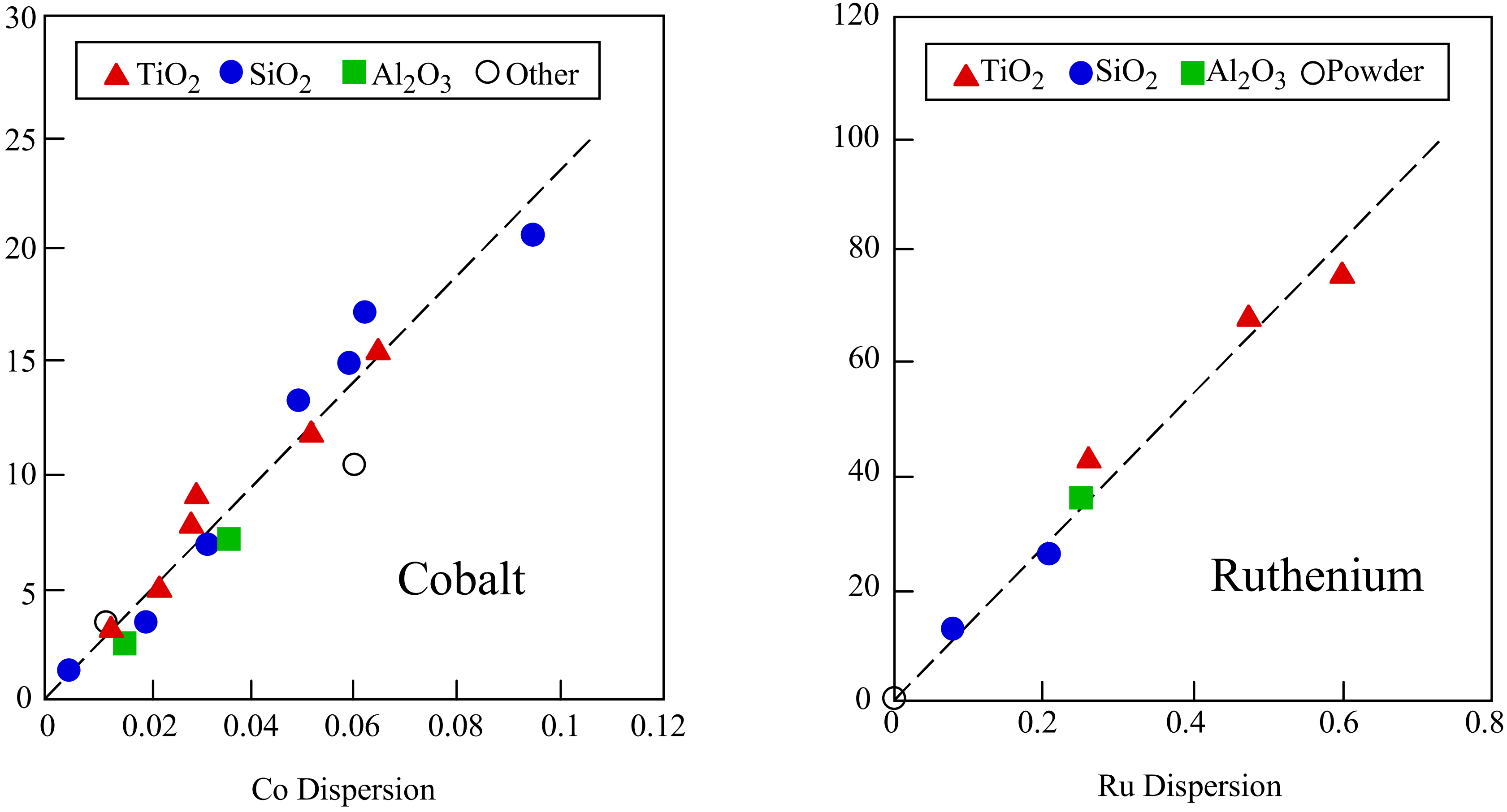
TPR Comparison of Pt promoted catalyst vs. unpromoted Co/Davisil

10 % H2 in AR Ramp 1 C/min to 800 C

Period 4: Important Developments (continued)

- **Exxon: Iglesia, Fiato, Soled, Reyes (10+ papers; 20+ patents)**
  - Fundamental understanding
    - Correlation of activity and Co dispersion for suite of catalysts
    - Effect of PM promoters in enhancing reduction of Co and minimizing carbon deposits
    - Effects of support and PM promoters on in situ regenerability
  - Development of quantitative models describing effects of
    - reaction, readsorption and pore diffusional transport on product selectivity
    - particle size and/or impregnation depth on selectivity

Rate (metal-time yield; moles CO converted per second per gram atom metal) Proportional to Active Sites Iglesia et al. [1992]



Conclusion: TOF or site-time yield is independent of dispersion.

Iglesia, 1997

Effects of dispersion and metal loading on selectivity of Co

- At low metal loadings and relatively high dispersions, C_{5+} selectivity increases with decreasing dispersion and/or increasing metal loading (this is due to a decreasing metal-support interaction with decreasing dispersion resulting in less methane formation and to an increasing extent of olefin readsorption).

- At high metal loadings (> 10%) and low dispersions ($D < 0.05$), C_{5+} selectivity increases with increasing dispersion and/or increasing metal loading (this is due to an increasing extent of olefin readsorption).

- A structural parameter χ which reflects the extent of olefin readsorption can be used to correlate C_{5+} selectivity with catalyst structure [Iglesia, 1997]:

$$\chi = R_o^2 \varepsilon \theta_{Co} / r_{pore}$$

where R_o = the radius of the catalyst pellet

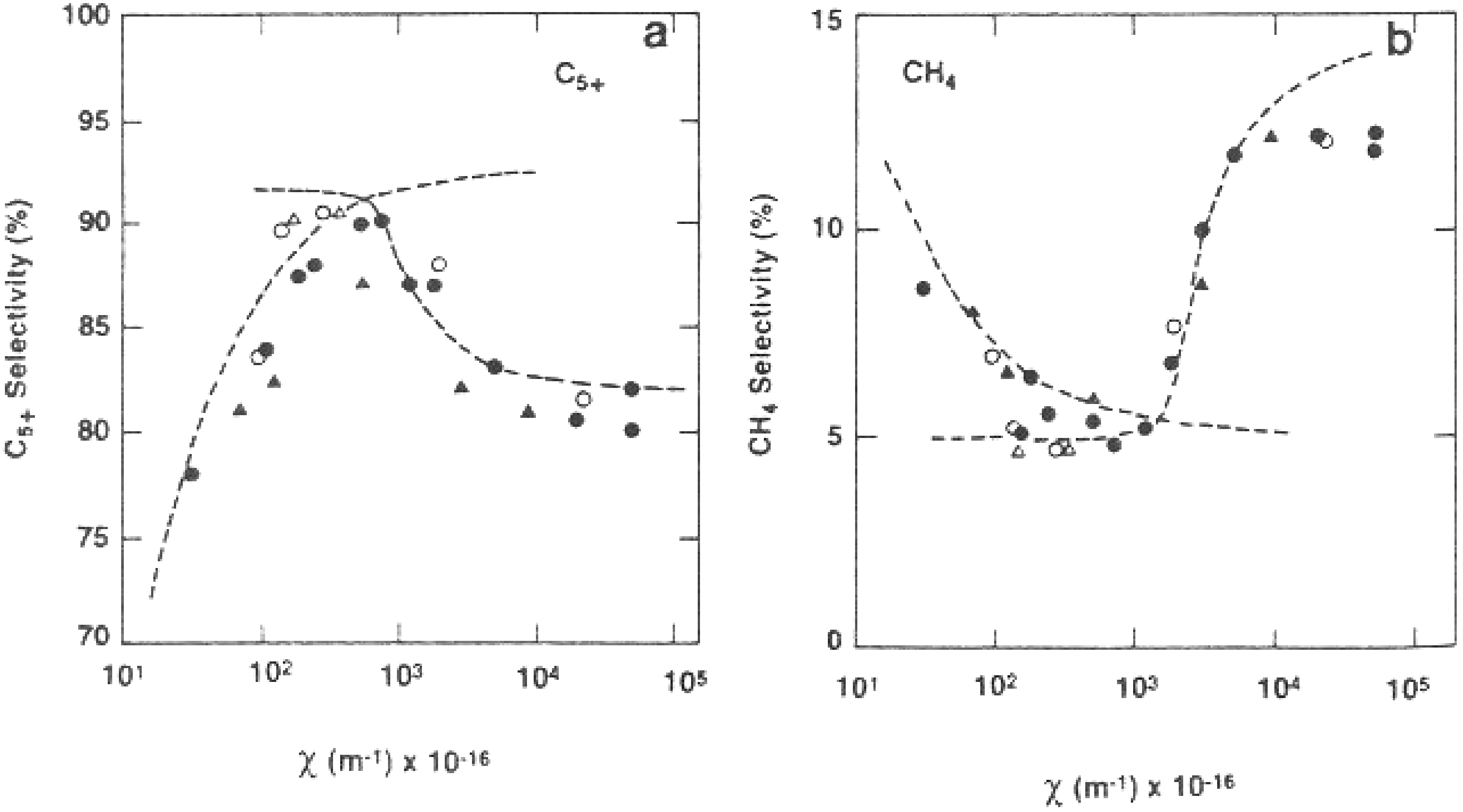
ε = void fraction

θ_{Co} = density of Co sites per unit area

r_{pore} = pore radius

χ and hence olefin readsorption and C_{5+} selectivity increase with increasing Co site density either due to increasing Co loading (θ_{Co}) or dispersion. At the same time, the probability of chain termination to methane decreases with increasing θ_{Co} because termination is more likely to be reversed by a high local concentration of olefins in the pores leading to a high surface concentration of C_n* that can react with adsorbed monomer species that would otherwise desorb as methane.

An increase in C_{5+} selectivity accompanied by a decrease in methane selectivity with increasing χ is indeed observed experimentally up to values of about 200 x 10^{16} m^{-1} (see attached Fig. 12 from Iglesia, 1997). At higher values of χ, diffusion-limited arrival of CO decreases chain growth rates.



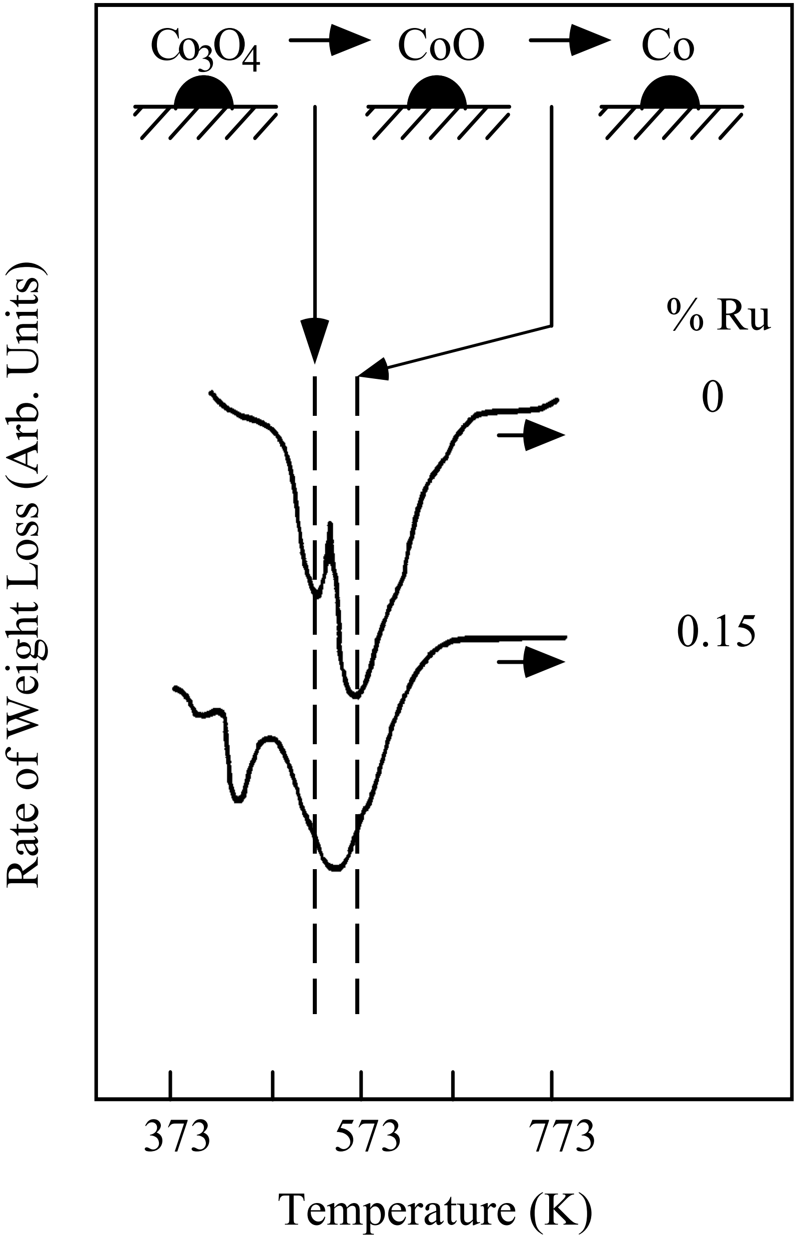
$$\chi = \frac{R^2 \varepsilon \theta_{CO}}{r_p}$$

Where R = radius of catalyst pellet

ε = void fraction

θ_{Co} = density of Co surface atoms

r_p = mean pore radius



Iglesia et al., 1993

Period 5: GTL and Return to Cobalt (1985-2003+)

- Large number of patents in 1980s and 1990s claiming active, selective, stable cobalt FT catalysts based on new catalyst compositions, PM and RE promoters, and stabilized supports by Shell, Exxon, and Statoil.
  - PM promoters include Pd, Pt, Re, and Ru
  - RE promoters include oxides of Zr, La, Gd, Ti, etc.
  - SiO_2 stabilized with ZrO_2, TiO_2 with SiO_2
- Third generation Co catalysts used in commercial Shell middle distillate plant in Malasia and in Exxon demo plant; Conoco develops new Co catalyst after testing 5,000 candidates.
- Goodwin et al. study effects of (1) Zr, La, and Ru promoters; (2) effects of pretreatment; and (3) attrition resistance.
- Some 20+ studies in a dozen labs of effects of preparation and pretreatment on the activity, selectivity and EOR of Co/silica.
- Holmen et al. study effects of ZrO_2 and PM promoters on specific activity—use SSITKA to estimate active site conc.

Optimizing Co FT Catalyst Design Present State of Knowledge Regarding the Design of Cobalt FT Wax/Crack Catalysts from Patents/Papers.

Desired Catalytic Functions	Proven Catalyst Components/Structural Features	Critical Aspects of Preparation and Pretreatment
High activity	high cobalt surface area high extent of reduction to metal high cobalt site density (>10 wt.%) moderate dispersion (10-15%) optimum value of χ	high SA support low-temp. drying; inert support slow reduction at high SV high metal loading addition of Re or Ru (0.1 wt.%) optimum particle size and catalyst distribution
High C_{5+} selectivity	high extent of redn. of Co to metal optimum value of χ	high metal loading moderate dispersion addition of Pd, Pt, Re or Ru (0.1 wt.%) optimum particle size and catalyst distribution
Low methane selectivity	high extent of redn. of Co to metal low acidity support & basic additives optimum value of χ	low acidity support, e.g. TiO_2 basic additives, e.g. ZrO_2, ThO_2 optimum particle size and catalyst distribution
Resistance to oxidation	addition of Pt, Pd, or Ru	intimate mixing of Co and Ru
Resistance to deactivation by carbon	additives such as Ru which gasify carbon	intimate mixing of Co and Ru
Regenerability	additives which increase reducibility of cobalt oxide and reactivity of carbon deposited	intimate mixing of Co and Ru
High surface area and mechanical integrity	alumina, silica and titania	support pretreatment, forming methods, binders, and stabilizers; drying temp.; alumina is favored

State of the Art Cobalt FT Catalyst

- 15-25% cobalt and 0.1-0.5% of Pd, Pt, Re or Ru
- 1-3% rare-earth oxides, e.g. ZrO_2, La_2O_3, ThO_2.
- extent of reduction of cobalt to the metal of about 80-90%
- cobalt metal dispersion of 8-10%
- stabilized alumina, silica or titania support with BET area of 150-250 m^2/g
- productivity at 200-210°C, 20 atm of 1-2 gHC/gcat-h
- methane selectivity of 5 mole%

Characteristics of Co Catalysts based on Patent Literature [24°C, 32 bar, slurry, Oukaci et al., 1999]

Catalyst	BET area m^2/g	H_2 uptake (μmol/g)	%Dispersion	Prod $gCH_2/gcat\text{-}h$	$\%CH_4$
20% Co/ 0.43% Ru/ 1% La_2O_3/Al_2O_3	149	155	9.1	1.4	12
20% Co/1% Re/ 1% La_2O_3/Al_2O_3	191	168	9.9	1.4	12
12% Co/ 0.75% Re/TiO_2	16	32	4.3	0.13	8.3
12% Co/ 0.5% Ru/TiO_2	15	38	3.7	0.40	6.1

LESSONS FROM HISTORY

“Nothing is new under the sun.”

- History repeats itself; rediscovery of some aspects of science and technology occurs in 30-40 year cycles (but it’s always better the next time around—better tools).
- We can learn something of worth from the old literature. Too many don’t make the effort and reinvent the wheel.
- FTS falls in and out of fashion on 10-15 year cycles; it was popular and well supported in 1975-85, then fell out of favor. Just wait, it will become fashionable again.

LESSONS FROM HISTORY
(Cont.)

- Some aspects of technology practiced by the Germans and Americans in the 1940-1950s have been re-patented. Thus, some of these patents may be based on prior art.

- Cyclic prices of oil and gas, as well as new discoveries, continue to threaten the development of FTS and GTL technologies; however the need for their development is inevitable. The hardy, tenacious, hard-working and patient will probably survive and do well.

Examples of early developments that have since been rediscovered, re-invented or re-patented

Year	**Source**	**Catalyst**	**Key Concept**
1928	Fischer and Tropsch paper	Co	most effective catalysts prepared by thermal decomposition of nitrates on porous carriers
1928-1934	Fischer and Koch (Pichler)	Co/ThO_2/kieselguhr	optimum reduction temperature of 365ºC; reduction time of 5-20 h
1928-1934	Fischer and Koch (Pichler)	Co/ThO_2/kieselguhr	thoria increases molecular weight of product
1934	Ger 597,515	Group VIII metal	rare earth halide promoters
1935-1936	Fischer and Pichler	Co/ThO_2/kieselguhr	optimum operating pressure of 5-20 atm; product is ideal for diesel—cetane no of 105
1935-1936	Fischer and Pichler	Co/ThO_2/kieselguhr	reduction carried out at high gas flow rate to minimize water vapor above catalyst
1951	Ger 973,965	Fluid bed	preparation of hydrogel silica with abrasion resistance

FUTURE OF Co CATALYST DESIGN

- More sophisticated preparations,e.g., colloidal methods, could lead to more uniformly dispersed, active, selective, stable catalysts.
- The role of PM promotion needs to be better understood; this understanding could lead to more efficient use of the PM.
- Development of a microkinetics model for FTS on cobalt with greater mechanistic understanding could enable fine tuning of active sites, promoters and supports.
- Theoretical calculations (e.g. DFT) could be used to understand the role of promoters in affecting the reaction mechanism. This insight could lead to more effective catalyst design (as in development of SR catalyst).

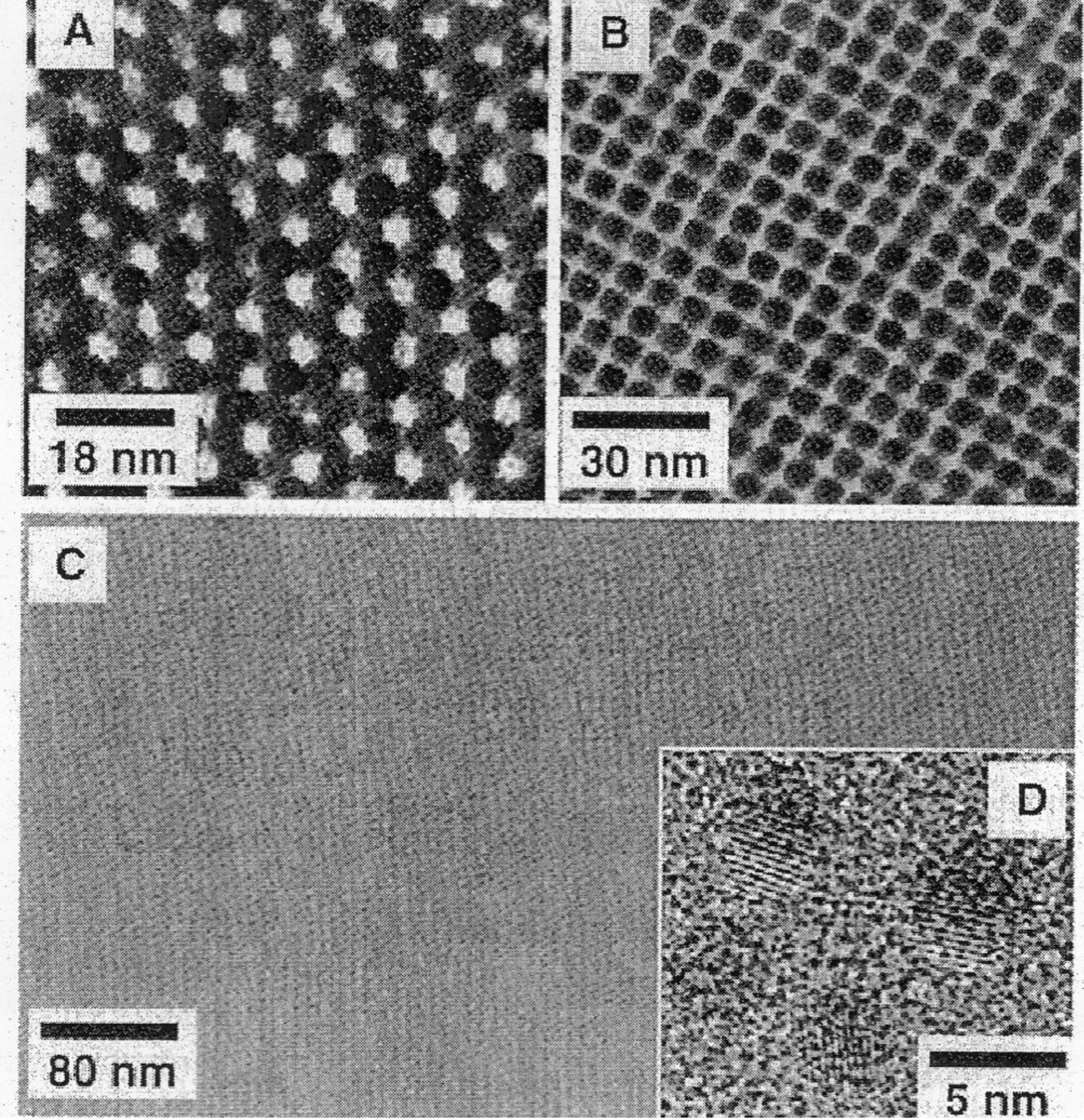
Example of new colloidal preparation

Nano-scale design of PtFe alloy magnetic storage devices [S. Sun et al., Science 287 (2000) 1989]. New synthesis of FePt nano-clusters of finely-controlled diameters (±5%) in the range of 3-10 nm. Thermal annealing converts the disordered clusters to ordered ferromagnetic assemblies which are chemically and mechanically robust and which can support high-density (terabyte) magnetization reversal transitions—i.e., these are terabyte storage devices!

PtFe clusters

A & B

6 nm



C & D

4 nm

Summary

- Each of several important advances in FT catalysts design was accomplished by a group of scientists and/or engineers but would not have happened without the leadership, inspiration and/or genius of one or two key members of each group.
- A number of important observations relevant to catalyst design emerge from the study of early literature, e.g., regarding preparation, pretreatment, active components, etc.
- A number of these observations were apparently rediscovered and patented in the last 25 years.
- Three generations of cobalt catalyst have been developed in the past 90 years. A fourth may emerge in the next decade.

Important Advances in Cobalt Catalyst Design

- F&T development of Co-ThO_2/kieselguhr—best for 4 decades.
- Measurement of TOFs based on H_2 uptake.
- Development of methods for measuring dispersion and EOR.
- Development of activity-structure relationships, e.g. effects of preparation, pretreatment, dispersion, supports, etc.
- Development of selectivity-transport model providing a quantitative relationship between selectivity and chemico-physical properties
- Development of stable, high-activity cobalt catalysts with high selectivities for liquid/wax products based on activity-structure relationships.
- Optimization of catalyst performance based on the selectivity-transport model

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