



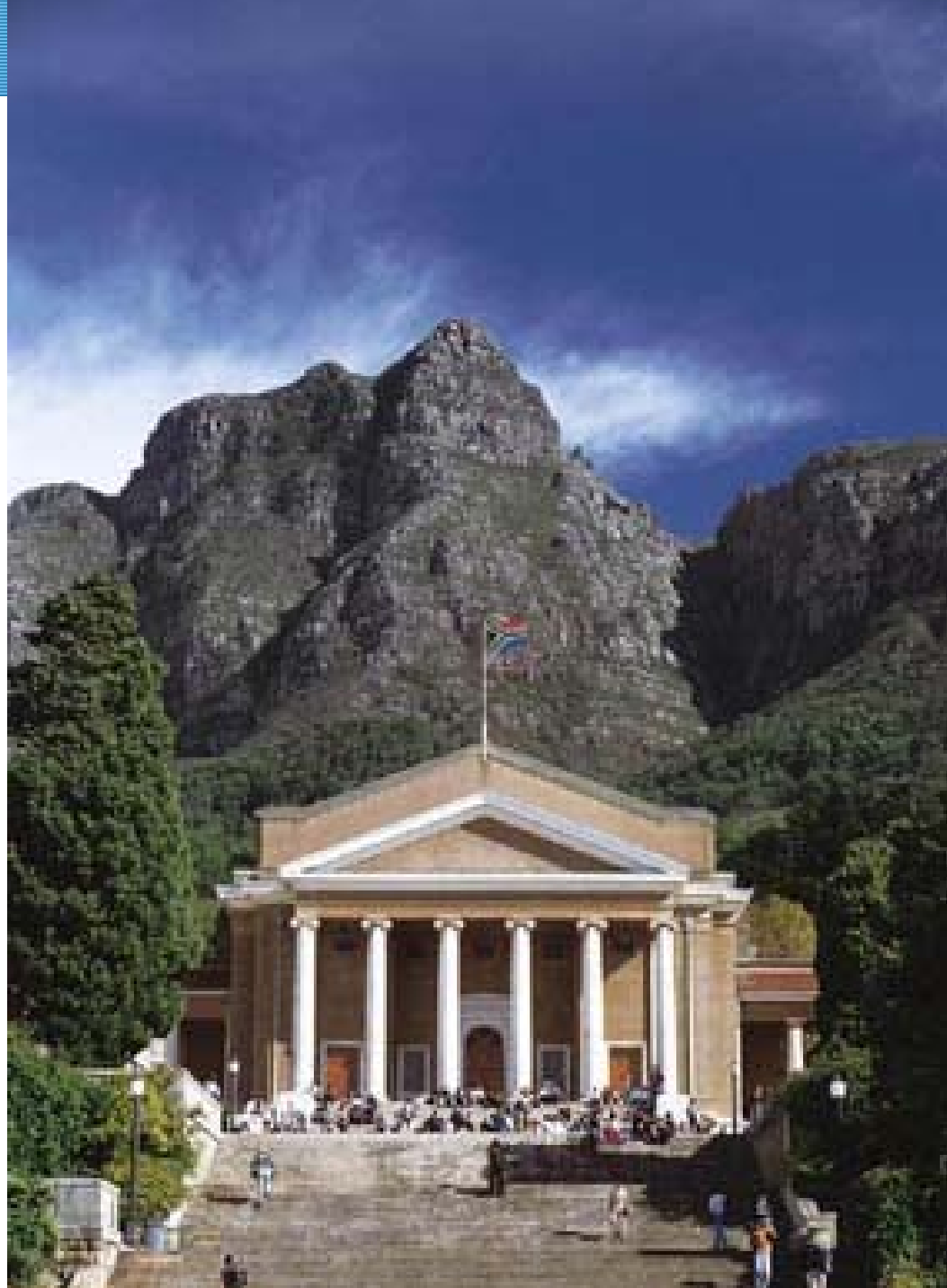
Centre for Catalysis Research

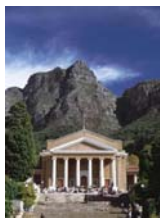
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Catalysts for Fischer-Tropsch synthesis

Eric van Steen

1. Fischer-Tropsch synthesis
2. Choice of catalytically active material
3. Cobalt-based catalysts
 - a. Intrinsic activity
 - b. Catalyst deactivation
4. Iron-based catalysts
 - a. Phases present
 - b. Intrinsic activity
 - c. Promoters/additives





Fischer-Tropsch synthesis

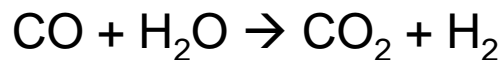
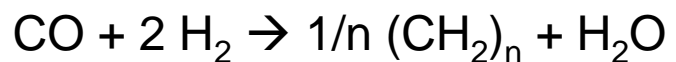


Synthesis gas

Mixture of
Hydrogen/
Carbon monoxide

Catalyst:

Fe, **Co** (Ru, Ni)



F. Fischer, H. Tropsch, *Brennstoff-Chem.* **7** (1926), 97



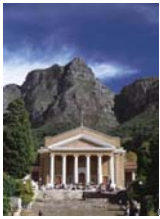
Choice of catalytically active metal

Molecular weight →
Relative price →
Required activity →

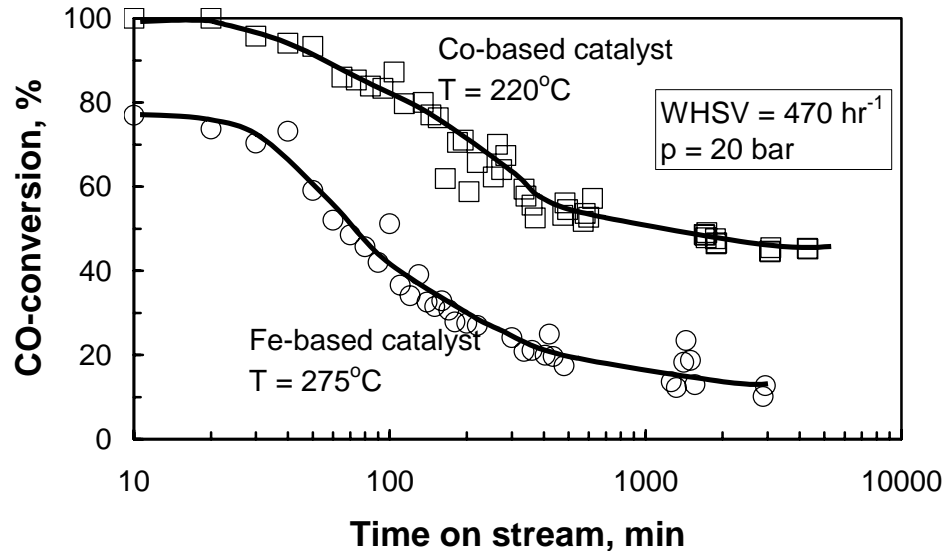
Fe M ¹ : 55.847 Rp²: 1 A ³ : 1	Co M ¹ : 58.9332 Rp²: 235 A ³ : 250	Ni M ¹ : 58.69 Rp²: 140 A ³ : 150	Cu M ¹ : 63.546 Rp ² : 32 A ³ : -
Ru M ¹ : 101.07 Rp²: 76 000 A ³ : 138 000	Rh M ¹ : 102.906 Rp ² : 824 000 A ³ : 1517 000	Pd M ¹ : 106.42 Rp ² : 49 000 A ³ : 94 000	Ag M ¹ : 107.868 Rp ² : 2 100 A ³ : -
Os M ¹ : 190.2 Rp ² : 408 000 A ³ : 1390 000	Ir M ¹ : 192.22 Rp ² : 59 000 A ³ : 203 000	Pt M ¹ : 195.08 Rp ² : 203 000 A ³ : 711 000	Au M ¹ : 196.967 Rp ² : 114 000 A ³ : -

From an industrial view point:

iron/cobalt-based catalysts



Choice of catalytically active metal



Both iron and cobalt deactivate

	Iron		Cobalt
Activity	1	:	2-3
Cost	1	:	235
Susceptibility to promoters	yes		(no)
Potential for prod. of chemicals	high		low
% side products	high		low
HTFT possible ?	yes		no
Sulfur tolerance	< 1 ppm		<1 ppb
Kinetic inhibition by H ₂ O	yes		??



Choice of catalytically active metal

From an industrial view point: cobalt/iron-based catalysts

Required activity of cobalt over catalyst life time: 250

<u>Example</u>	catalyst life time iron-based catalyst	ca. 10 days
	activity of cobalt/iron	2-3 ¹

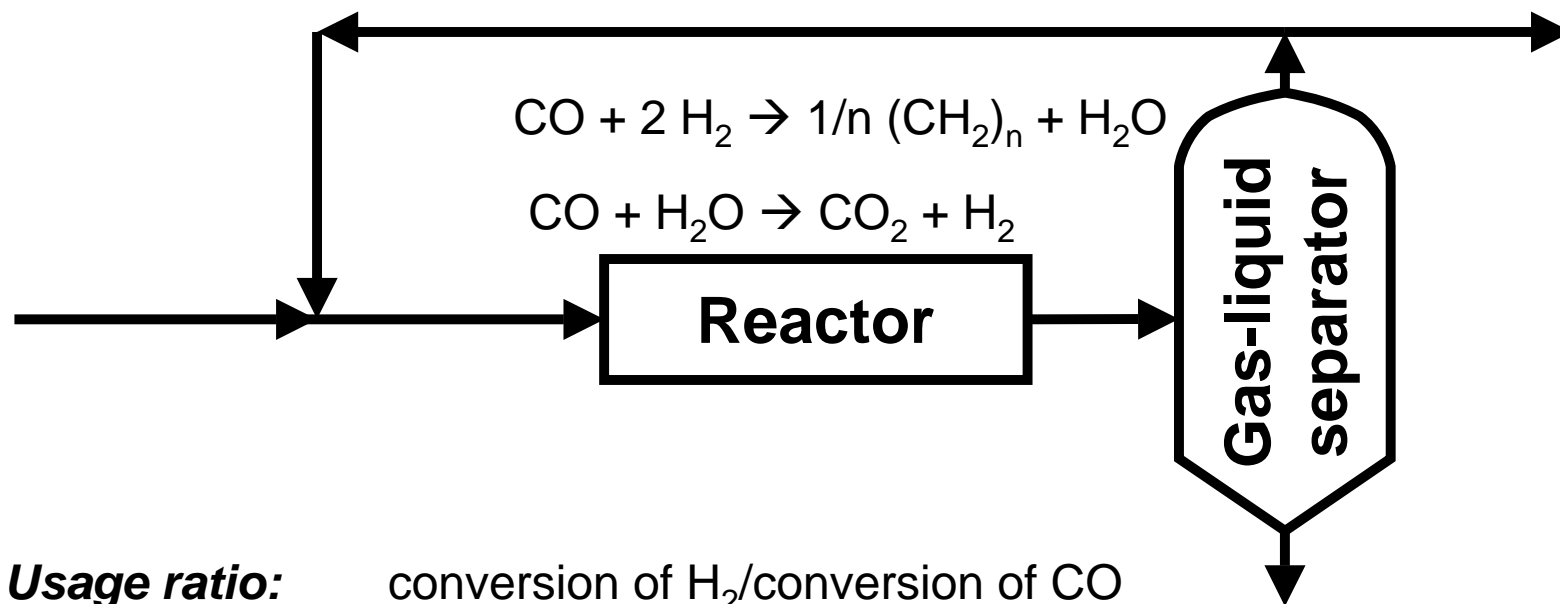
<u>Thus</u>,	required life time cobalt-based catalyst	at least 800 days
		2.2 years

(calculation assumes
identical utilisation, i.e. identical degree of reduction
identical selectivity for C₅₊-products)

¹S. Li, S. Krishnamoorthy, A. Li, G.D. Meitzner, E. Iglesia, *J. Catal.* **206** (2002), 202-217.



Cobalt or iron as catalytically active metal



Usage ratio: conversion of H_2 /conversion of CO

Optimal performance: $(\text{H}_2/\text{CO})_{\text{feed}} = \text{usage ratio}$

Usage ratio

cobalt ~ 2.05¹

iron ~ 1.3²

¹R.L. Espinoza, A.P. Raje, D. Jack, US 009 2609 (2004).

²N.S. Govender, M. Janse van Vuuren, M. Claeys, E. van Steen, *Ind. Eng. Chem. Res.* **45** (2006), 8629-8633.



Cobalt or iron as catalytically active metal

Cobalt-based catalysts:

Natural gas based synthesis gas

Any other synthesis gas with WGS-reactor before recycle loop

Iron-based catalysts:

Synthesis gas ex sources with reduced H-content (coal/oil residues)

For Fischer-Tropsch synthesis from **biomass** → depends on gasification^{1,2}

Air blown gasification $H_2/CO = 1.0-1.5$

O_2 -gasification $H_2/CO = 1.5-2.0$

(feed ratio H_2/CO less than usage ratio **cobalt**-based catalysts → **iron**-based systems should be explored)

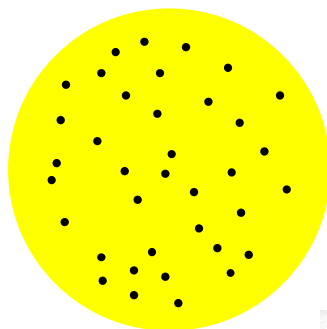
¹ C.N. Hamelinck, A.P.C. Faaij, H. den Uil, H. Boerrigter, *Energy* **29** (2004), 1743-1771.

² K.J. Ptasinski, M.J. Prins, A. Pierik, *Energy* **32** (2007), 568-574.



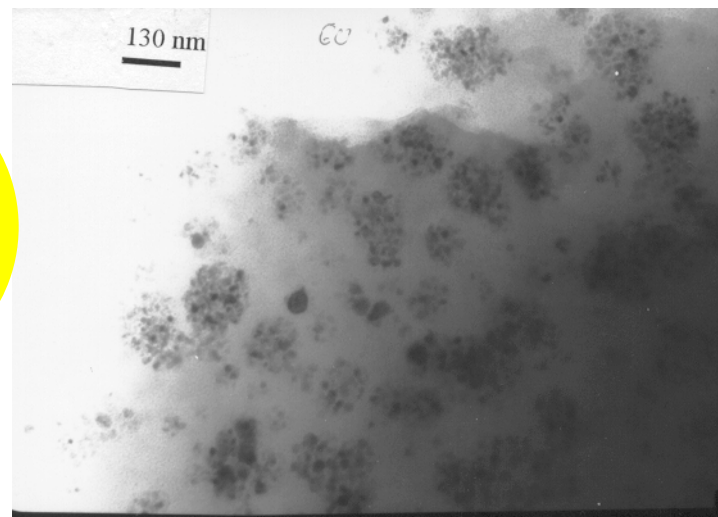
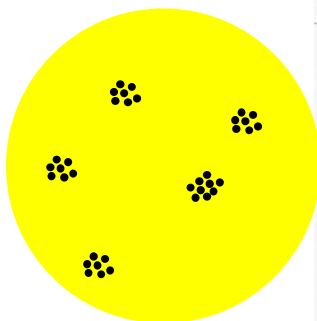
Cobalt-based Fischer-Tropsch catalysts

Supported catalysts



Low pressure drop
Mechanical stability
Thermal stability

Prepared by impregnation

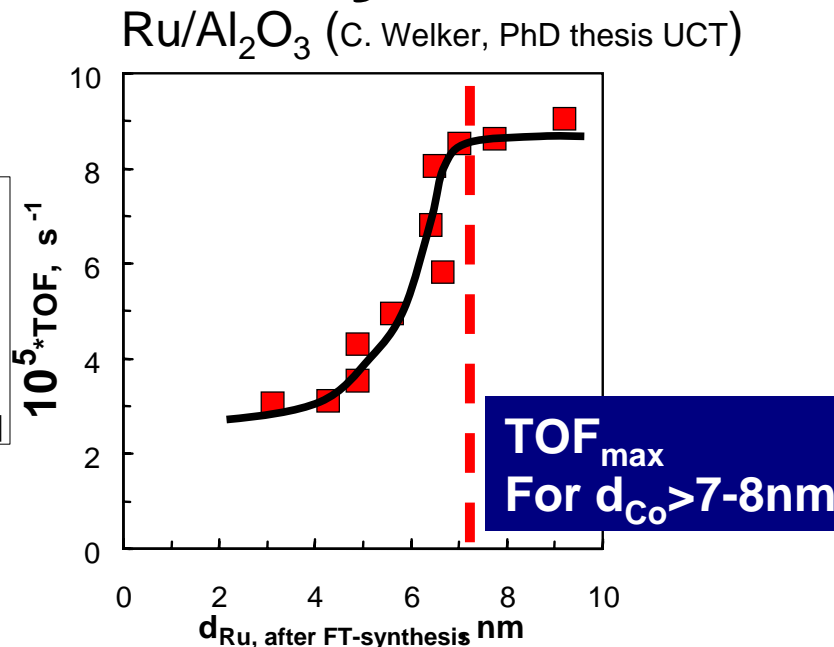
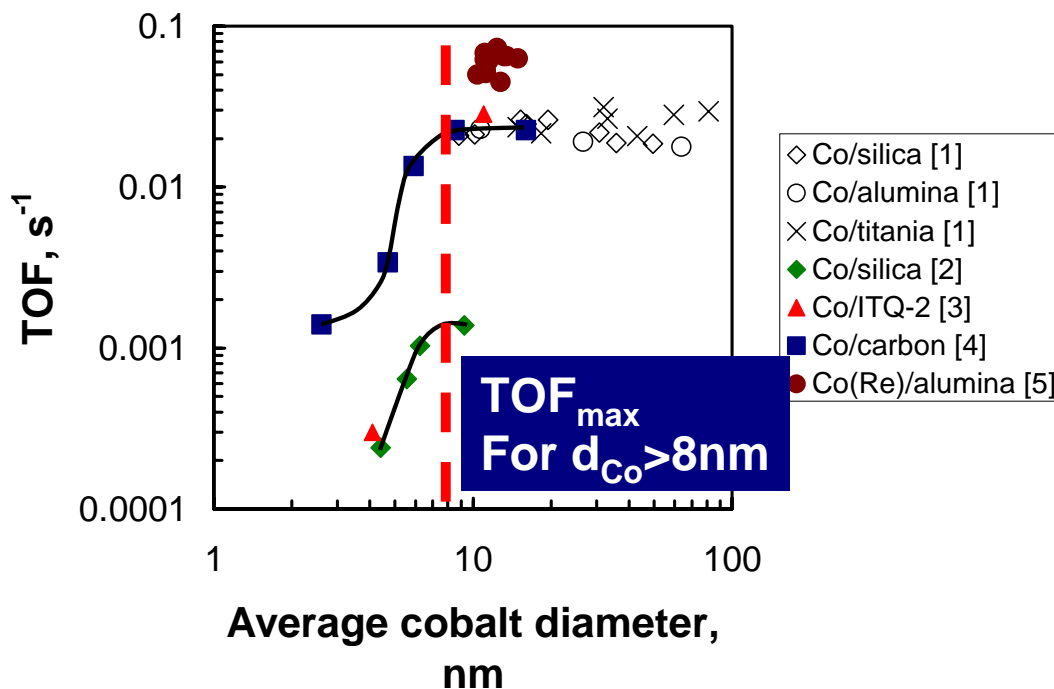


A. Feller,, M. Claeys, E. van Steen, *J. Catal.* **185** (1999), 120-130.
A.M. Saib, M. Claeys, E. van Steen, *Catal. Today* **71** (2002), 395-402

Typical cobalt-loading ca. 20 wt. -%



Intrinsic activity of **Cobalt**-based Fischer-Tropsch catalysts



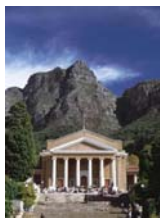
¹ E. Iglesia, *Appl. Catal. A: General* **161** (1997), 59-78.

² A. Barbier, A. Tuel, I. Arcon, A. Kodre, G.A. Martin, *J. Catal.* **200** (2001), 106-116.

³ A. Martínez, G. Prieto, *J. Catal.* **245** (2007), 470-476.

⁴ G.L. Bezemer, J.H. Bitter, H.P.C.E. Kuipers, H. Oosterbeek, J.E. Holewijn, Z. Xu, F. Kapteijn, A.J. van Dillen, K.P. de Jong, *J. Am. Chem. Soc.* **128** (2006), 3956-3964.

⁵ Ø. Borg, S. Eri, E.A. Blekkan, S. Storsæter, H. Wigum, E. Rytter, A. Holmen, *J. Catal.* **248** (2007), 89-100



Origin of size dependent intrinsic activity

Bezemer et al.¹ (Co/CNT):
domains which catalyse the FT-synthesis (geometric effect)

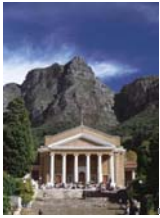
Ojeda et al. (Rh/Al₂O₃):
increase in defect sites with increasing crystallite size

Kellner and Bell (Ru/Al₂O₃):
unspecified electronic effect with increasing crystallite size

¹ G.L. Bezemer, J.H. Bitter, H.P.C.E. Kuipers, H. Oosterbeek, J.E. Holewijn, Z. Xu, F. Kapteijn, A.J. van Dillen, K.P. de Jong, *J. Am. Chem. Soc.* **128** (2006), 3956-3964.

² M. Ojeda, S. Rojas, M. Boutonnet, F.J. Pérez-Alonso, G.J. Garcia-Garcia, J.L.G. Fierro, *Appl. Catal. A: General* **274** (2004), 33-41.

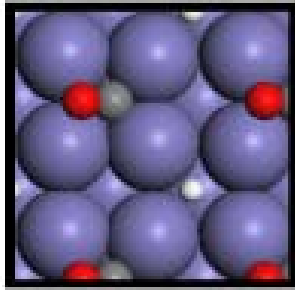
³ C.S. Kellner, A.T. Bell, *J. Catal.* **75** (1982), 251-261.



Origin of size dependent intrinsic activity

Co-adsorption of H and CO on Fe(100)-surfaces

(P. van Helden, E. van Steen, *J. Phys. Chem. C* (accepted))



-2.34

Charge on CO: -0.89

(charge on C -0.43; charge on O: -0.46)

Charge on H: - 0.29

Charge transfer during adsorption leads to negatively charged surface species

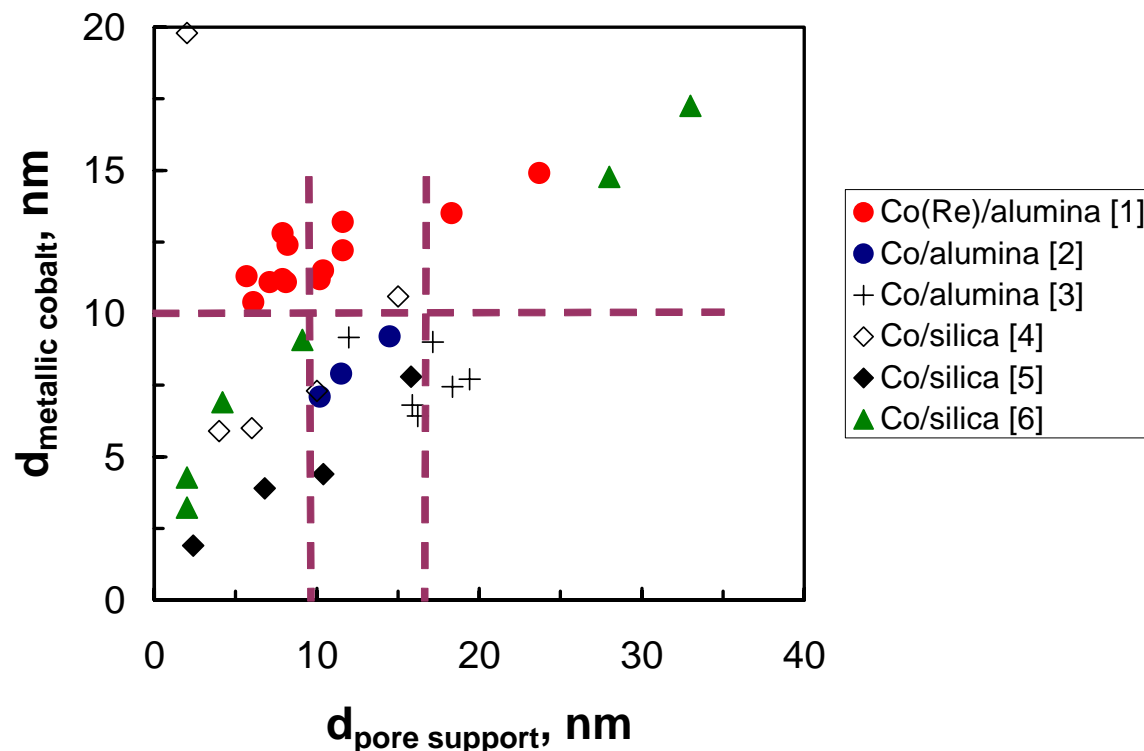
Surface species repel each other (coverage dependent heat of adsorption)

Repulsion through long-range Coulombic interaction

Reduced repulsion through limited surface on nano-sized materials → enhancement of strength of adsorption



How to obtain supported **cobalt** catalyst with maximum TOF?



Incipient wetness impregnation (ex cobalt nitrate) on support material with a pore diameter between 10 and 16 nm results in metallic cobalt crystallites with a size of ca. 10 nm

¹ Ø. Borg, S. Eri, E.A. Blekkan, S. Storsæter, H. Wigum, E. Rytter, A. Holmen, *J. Catal.* **248** (2007), 89-100

² H. Xiong, Y. Zhang, S. Wang, J. Lim, *Catal. Comm.* **6** (2005), 512-516.

³ J. Zhang, J. Chen, J. Ren, Y. Sun, *Appl. Catal. A: General* **243** (2003), 121-133.

⁴ A.M. Saib, M. Claeys, E. van Steen, *Catal. Today* **71** (2002), 395-402.

⁵ D. Song, J. Li, *J. Mol. Catal. A: Chemical* **247** (2006), 206-212.

⁶ A.Y. Khodakov, A. Griboval-Constant, R. Bechara, V.L. Zholobenko, *J. Catal.* **206** (2002), 230-241.



Deactivation of cobalt catalyst

Deactivation mechanisms¹:

1. Poisoning

Cobalt catalysts → highly susceptible to poisons

Poisons → competitive adsorption (**reversible deactivation** – H_2S , NH_3)
→ inducing sintering (chlorine compounds, water, **CO**)
carbon deposition
Fe-deposition²
phase transformations

2. Sintering (seems to level off with time on stream)

3. Phase transformation

4. Carbon deposition

¹ C.H. Bartholomew, *Appl. Catal A: General* **212** (2001), 17-60.

² K.P. de Jong, M.F.M. Post, A. Knoetser, *Stud. Surf. Sci. Catal.* **119** (1998), 119-124.



Deactivation of **cobalt** catalyst

Oxidation of cobalt

Oxidation of small cobalt crystallites with product water^{1,2,3}



(for bulk metallic cobalt oxidation at 493K will occur if $p_{\text{H}_2\text{O}}/p_{\text{H}_2} > 100$

Thus, oxidation of bulk metallic cobalt will not occur under realistic Fischer-Tropsch conditions))

Model developed to predict oxidation of nano-sized cobalt⁴:

$$\mu_{\text{CoO(s)}}^0 + \mu_{\text{H}_2\text{(g)}}^0 - \mu_{\text{Co(s)}}^0 - \mu_{\text{H}_2\text{O(g)}}^0 + RT \cdot \ln\left(\frac{p_{\text{H}_2}}{p_{\text{H}_2\text{O}}}\right) + \frac{6 \cdot \gamma_{\text{Co}}}{\rho_{\text{Co}} \cdot d_{\text{Co}}} \cdot \left(\frac{\gamma_{\text{CoO}}}{\gamma_{\text{Co}}} \cdot \left(\frac{\rho_{\text{Co}}}{\rho_{\text{CoO}}} \right)^{2/3} - 1 \right) > 0$$

Bulk oxidation of Co with H_2O

Reaction conditions

Change in surface energy

¹ D. Schanke, A.M. Hilmen, E. Bergene, K. Kinnari, E. Rytter, E. Ådhanes, A. Holmen, *Catal. Lett.* **34** (1995), 269-284.

² M. Rothaemel, K.F. Hanssen, E.A. Blekkan, D. Schanke, A. Holmen, *Catal. Today* **38** (1997), 79-84.

³ E. Iglesia, *Appl. Catal. A: General* **161** (1997), 59-78.

⁴ E van Steen, M Claeys, ME Dry, J van de Loosdrecht, EL Viljoen, JL Visagie, *J. Phys. Chem. B* **109** (2005), 3575-3577



Deactivation of **cobalt** catalyst

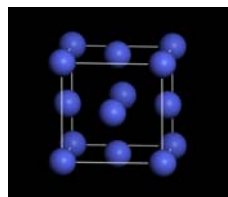
Oxidation of cobalt

Critical parameter in model:

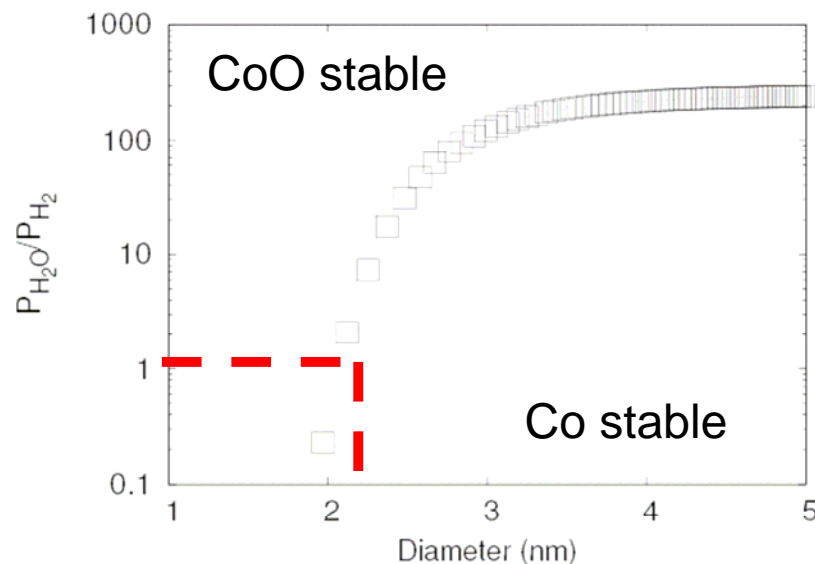
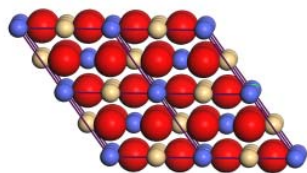
$$\gamma_{\text{Co}}, \gamma_{\text{CoO}}/\gamma_{\text{Co}}$$

Further estimation of surface energies using DFT

$$\gamma_{\text{Co}(111)}^1 = 2.75 \text{ J/m}^2$$



$$\gamma_{\text{CoO}(100)}^2 = 1.55 \text{ J/m}^2$$



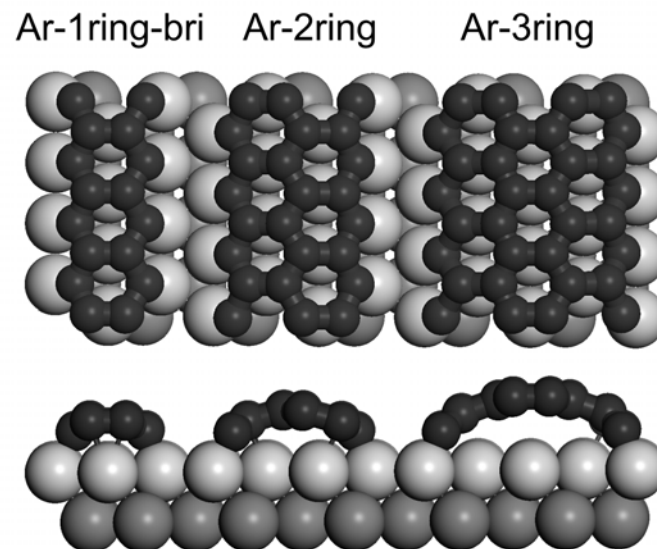
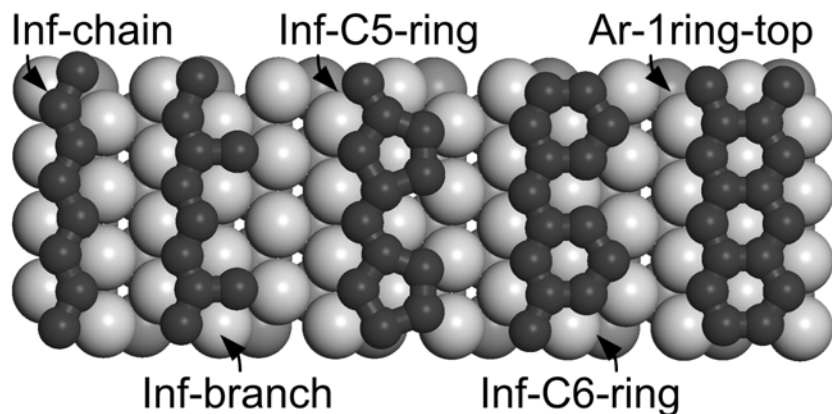
¹ J.C.W. Swart, P. van Helden, E. van Steen, *J. Phys. Chem. C* **111** (2007), 4998-5005.

² J.C.W. Swart, E. van Steen, in preparation



Deactivation of **cobalt** catalyst

Carbon formation on cobalt



Carbon overlayers formed through¹

1. Combination of C1-units adsorbed
2. Yielding linear chains
3. Branching may occur on longer chains
4. Connecting branched chains result in formation of aromatic structures

¹ J.C.W. Swart, I. Ciobica, R.A. van Santen, E. van Steen, *J. Phys. Chem. C* (in press)

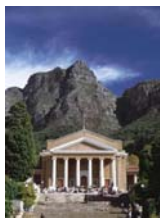


Iron-based Fischer-Tropsch catalysts

Iron-based Fischer-Tropsch synthesis:

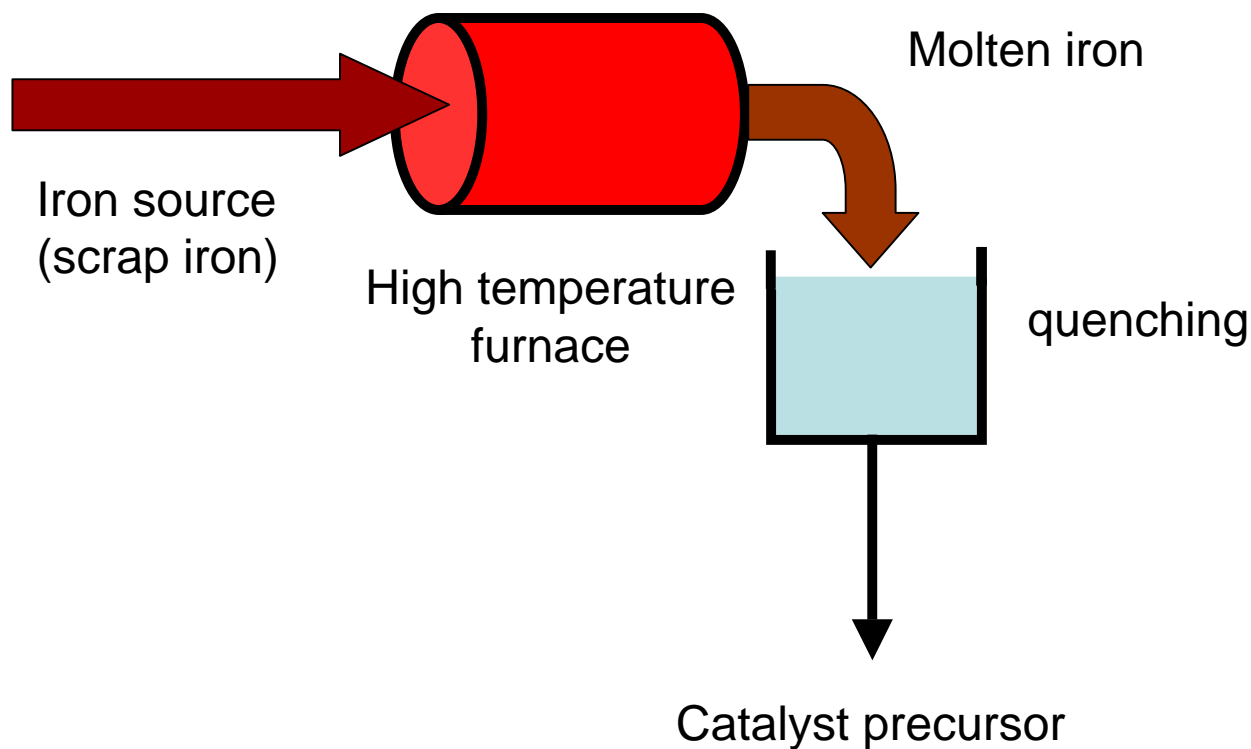
High temperature Fischer-Tropsch synthesis (300-350°C)
→ fused iron catalyst
aim: production of petrol/light olefins

Low temperature Fischer-Tropsch (ca. 250°C)
→ precipitated Fe-catalyst
aim: production of wax/liquid products



Iron-based Fischer-Tropsch catalysts

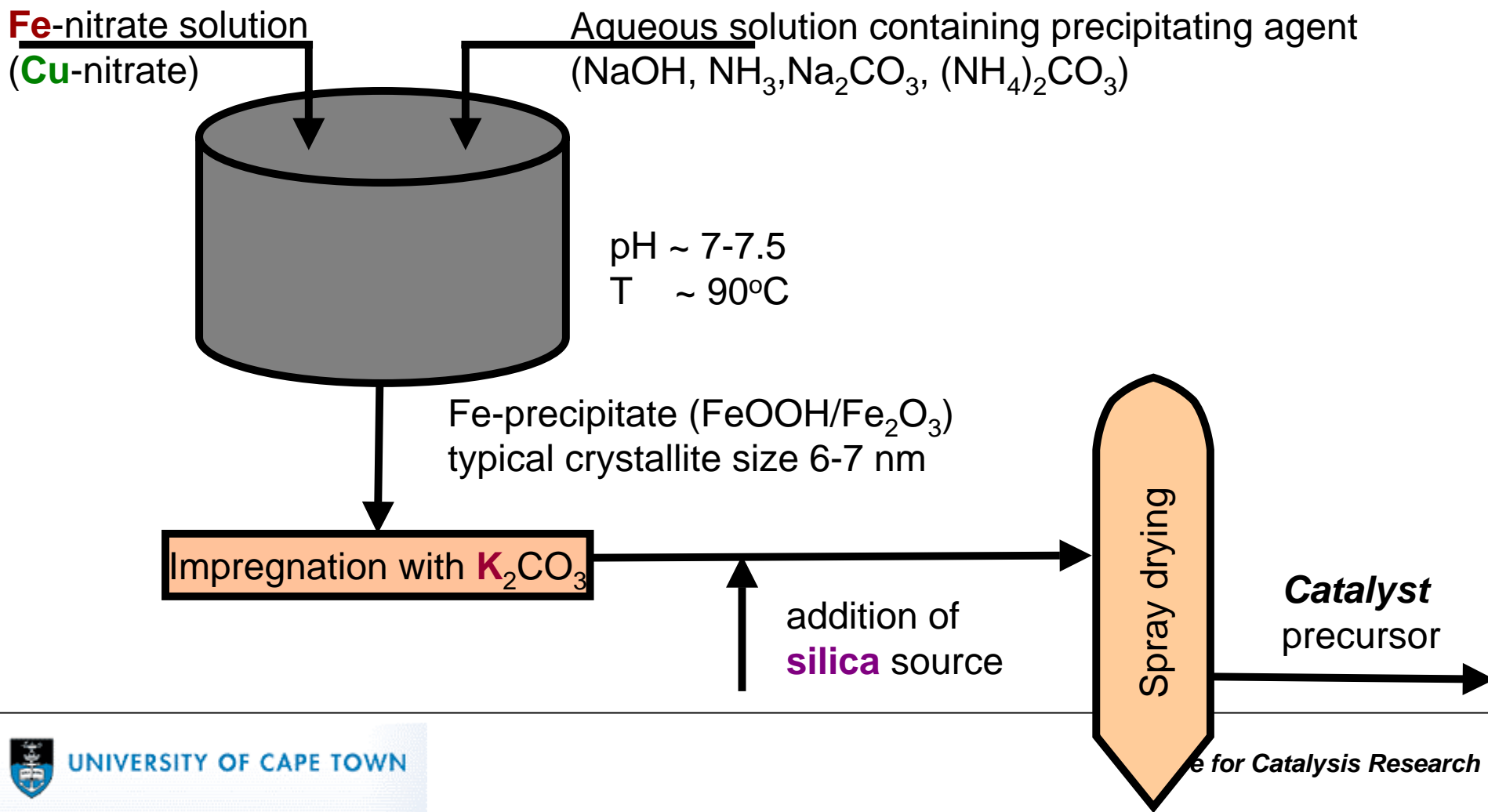
Fused Fe-catalyst





Iron-based Fischer-Tropsch catalysts

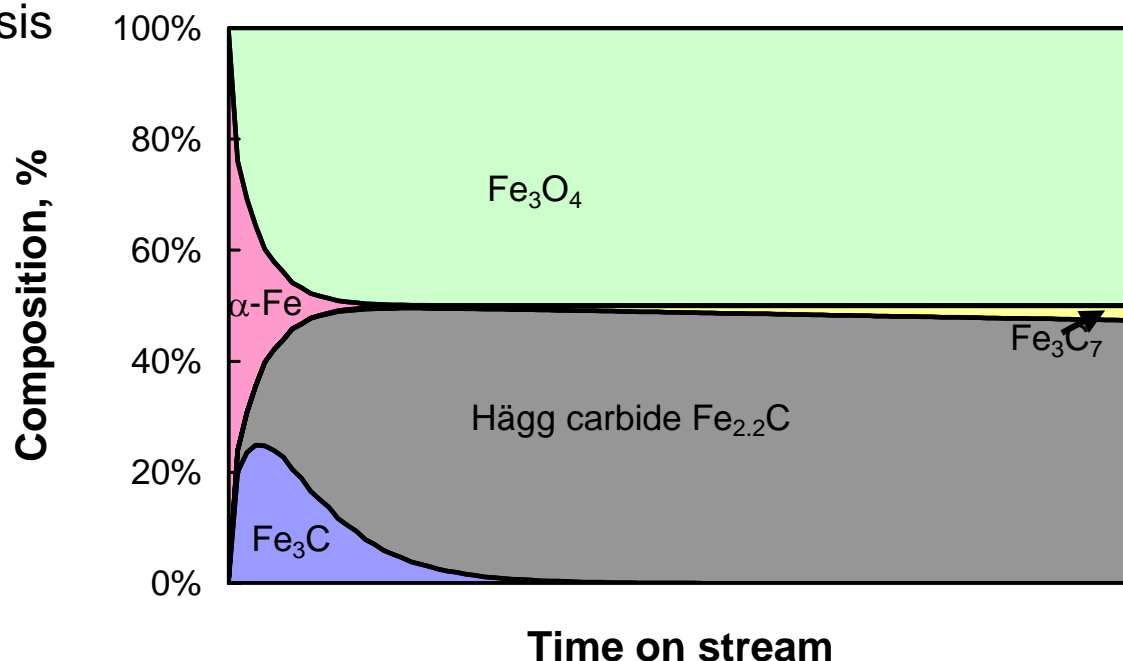
Precipitated Fe-catalyst





Active phase in **iron**-based Fischer-Tropsch catalysts

Typical phase compositions of an iron-based catalyst in the Fischer-Tropsch synthesis



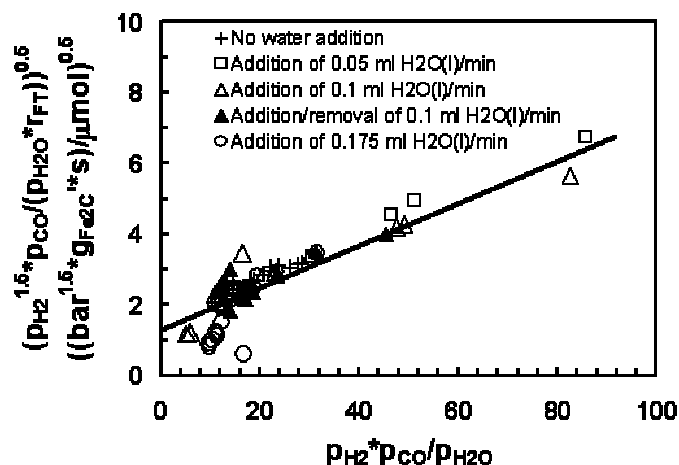
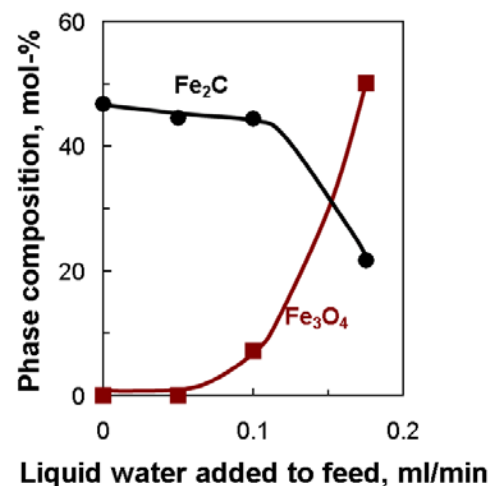
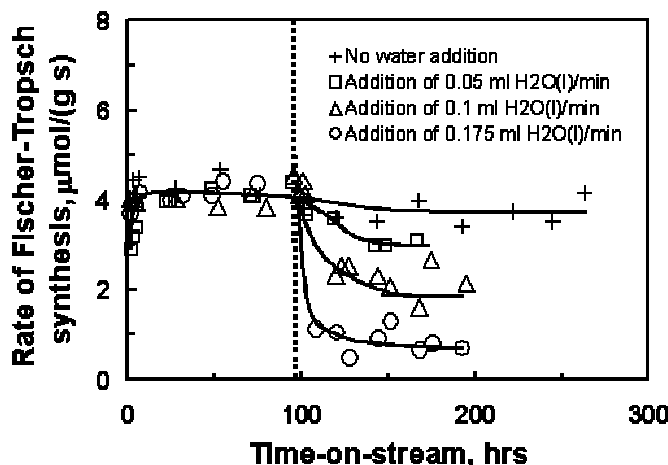
Redrawn from: O. Malan, J. Louw, L. Ferreira, *Brennstoff-Chem.* **42** (1961), 209

Iron carbide (Fe_xC) is usually seen as the catalytically active phase

Catalyst however typically contains magnetite as well (inefficient usage of Fe)



Active phase in **iron**-based Fischer-Tropsch catalysts

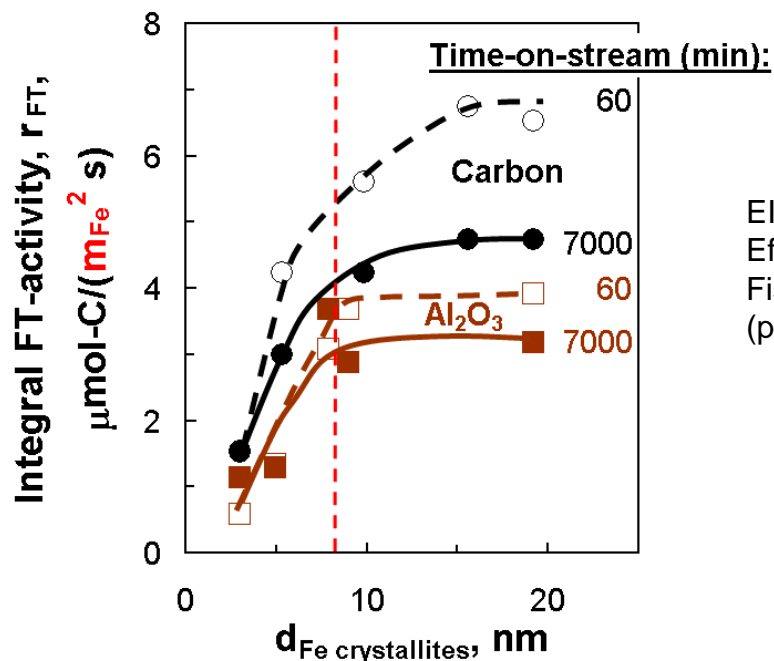


Presence of Fe_3O_4 seems to reduce activity \rightarrow Iron carbide seems to be the catalytically active phase

H. Biel, MSc thesis, University of Cape Town (2004)



Effect of crystallite size in **iron**-based Fischer-Tropsch catalysts



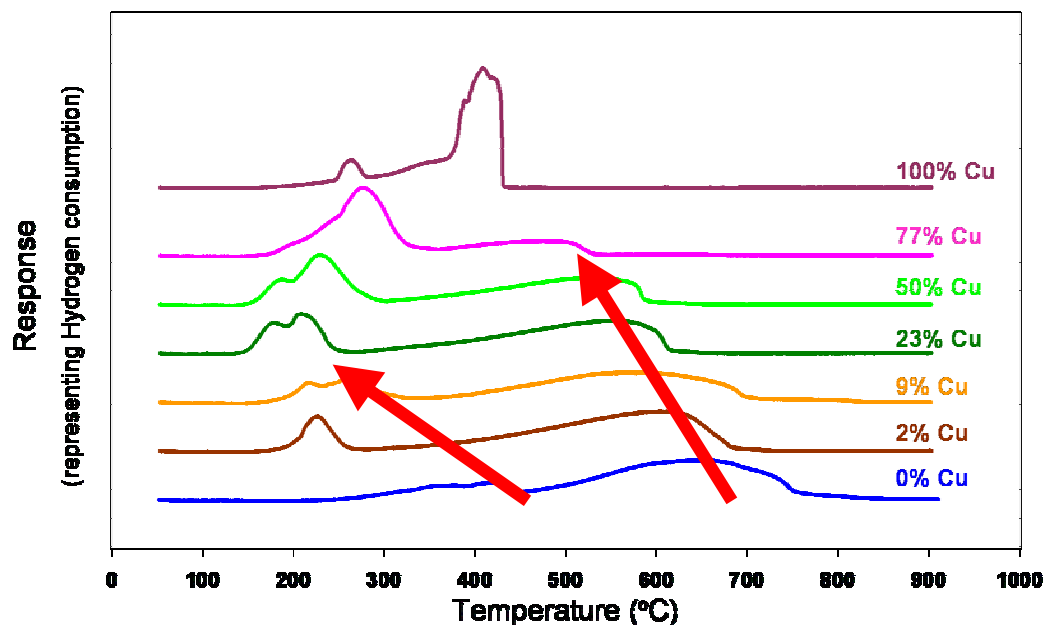
EI Mabaso, E van Steen, M Claeys
Effect of metal crystallite size in supported iron based Fischer-Tropsch catalysts
(presented at NACS05; full manuscript in preparation)

***TOF difficult to determine
Phase transformations may
obscure size effect***



Cu-promotion of iron-based Fischer-Tropsch catalysts

Temperature programmed reduction (TPR) of copper promoted iron-catalysts



Copper enhances reduction (in particular $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$)

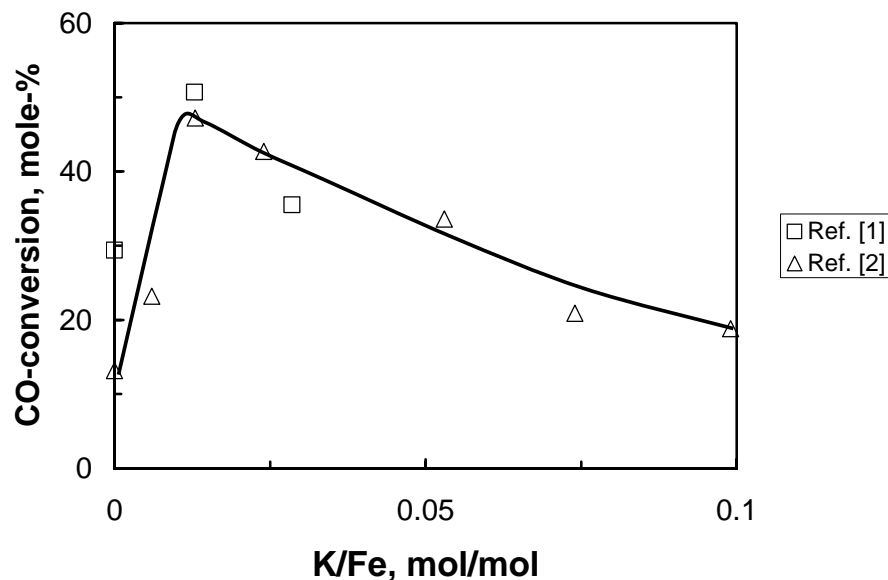
Copper may also act as chemical promoter^{1,2}, if activated in CO-containing gas

¹S. Li, A. Li, S. Krishnamoorthy, E. Iglesia, *Catal. Lett.* **77** (2001), 197-205.

²R.J. O'Brien, B.H. Davis, *Catal. Lett.* **94** (2004), 1-6



K-promotion of iron-based Fischer-Tropsch catalysts



Optimum K-loading enhances activity with factor 2-3

Inhibition at high K-loadings → surface effect

K is most likely present as surface K-O-surface species or carbonate species, but metallic potassium

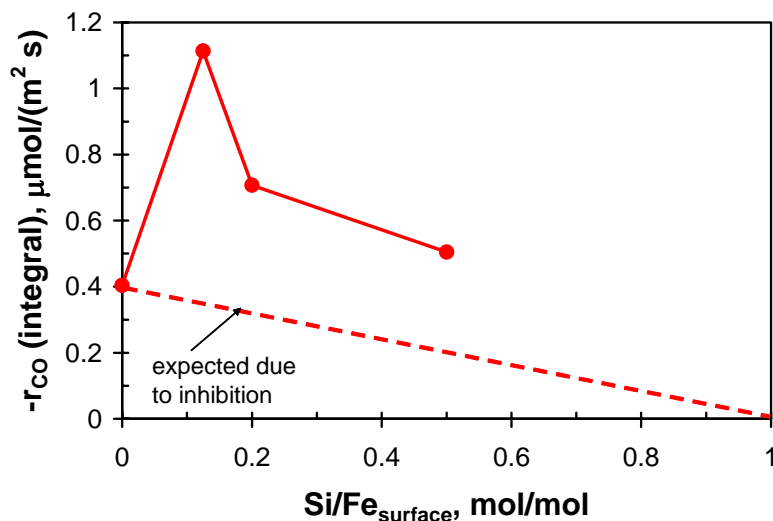
¹ W. Ma, E.L. Kugler, D.B. Dadyburjor, *Energy&Fuels* **21** (2007), 1832-1842.

²A. Blignaut, MSc-thesis University of Cape Town (2007).



Silica addition to iron-based Fischer-Tropsch catalysts

Silica is typically added as a binder and thought to be inert



E.I. Mabaso, R.P. Mogorosi, M.J. Malagas, M. Claeys, E. van Steen, Proc. 2007 Pittsburg Coal Conference



Concluding remarks

Catalytic active metal decided on the basis
available synthesis gas
life time of the catalyst

Larger crystallites in the range of ca. 10 nm seems to be the preferred size of the catalytically active phase (rather than sizes in the 1-2 nm range)

Catalysts have been developed empirically.
The role of the various additives needs to be re-evaluated.

