Literature

1. Hoog, H., Energie Spectrum, October 1977
2. van Krevelen, D.W., Coal - typology, chemistry, physics, constitution, Elsevier Publishing Company, Gouda, 1961
3. Donath, E.E., Advances in Catalysis, Vol. VIII, ed. by W.G. Frankenburg, V.I. Komarewsky, E.K. Rideal, Academic Press, Inc., New York, 1956, 239-292
4. Oblad, A.G., Catal. Rev. - Sci. Eng. 14, 83-95 (1976)
5. Coal Conversion Technology, ed. by I. Howard-Smith and G.J. Werner, Noyes Data Corporation, U.S.A., 1976
6. Wender, I., Catal. Rev. - Sci. Eng. 14, 97-129 (1976)
7. Shora, F.C., Jr., Symposium Clean Fuels from Coal, ed. by J.W. White and M. Larson, Institute of Gas Technology, U.S.A., 1973
8. Mills, G.A., Catal. Rev. - Sci. Eng. 14, 69-82 (1976)
9. Handbook of Chemistry and Physics, 55th ed., ed. by R.C. Weast, CRC Press, Inc., Cleveland, 1974
10. Pichler, H., Hector, A., Kirk-Othmer Encyclopedia of Chemical Technology, Vol. 4, John Wiley & Sons, U.S.A., 1964, 446-489
11. Dry, M.E., Energie Spectrum, October 1977
12. Chem. Week Jan. 22, 36 (1975)
13. Chem. Week March 7, 23 (1979)
14. Storch, H.H., Golumbic, H., Anderson, R.B., The Fischer-Tropsch and Related Synthesis, John Wiley & Sons, New York, 1951
15. Pichler, H., Advances in Catalysis, Vol. IV, ed. by W.G. Frankenburg, V.I. Komarewsky, E.K. Rideal, Academic Press, Inc., New York, 1952, 271-341
16. Anderson, R.B., Catalysis, Vol. IV, ed. by P.H. Emmett, Reinhold Publishing Corporation, Baltimore, 1956, 1-371
17. Kölbel, H., Chemische Technologie, Band 3, ed. by K. Winnacker and L. Küchler, Carl Hanser Verlag, München, 1959, 439-520
18. Vlasenko, V.M., Yuzefovich, G.E., Russ. Chem. Rev. (Engl. Transl.) 38, 728-739 (1969)
19. Pichler, H., Schulz, H., Chem.-Ing.-Tech. 42, 1162-1174 (1970)
20. Mills, G.A., Steffgen, F.W., Catal. Rev. 8, 159-210 (1973)

21. Shah, Y.T., Perrotta, A.J., Ind. Eng. Chem., Prod. Res. Dev. 15, 123-131 (1976)
22. Dry, M.E., Ind. Eng. Chem., Prod. Res. Dev. 15, 282-286 (1976)
23. Vannice, M.A., Catal. Rev. - Sci. Eng. 14, 153-191 (1976)
24. Fischer, F., Tropsch, H., Ber. Dtsch. Chem. Ges. 59, 830-836 (1926)
25. Craxford, S.R., Rideal, E.K., J. Chem. Soc. 1939, 1604-1614
26. Pichler, H., Chem. Tech. 18, 392-396 (1966)
27. Joyner, R.W., Roberts, M.W., J. Chem. Soc., Faraday Trans. 1 70, 1819-1824 (1974)
28. Kishi, K., Roberts, M.W., ibid 71, 1715-1720 (1975)
29. Moyes, R.B., Roberts, M.W., J. Catal. 49, 216-224 (1977)
30. Wentrcek, P.R., Wood, B.J., Wise, H., J. Catal. 43, 363-366 (1976)
31. Araki, M., Ponec, V., J. Catal. 44, 439-448 (1976)
32. Sexton, B.A., Somorjai, G.A., J. Catal. 46, 167-187 (1977)
33. Rabo, J.A., Risch, A.P., Poutsma, M.L., J. Catal. 53, 295-311 (1978)
34. Kitzelmann, D., Dissertation, Bonn (1978)
35. Sachtler, J.W.A., Kool, J.M., Ponec, V., J. Catal. 56, 284-286 (1979)
36. van Barneveld, W.A.A., Ponec, V., J. Catal. 51, 426-430 (1978)
37. Biloen, P., Helle, J.M., Sachtler, W.M.H., J. Catal. 58, 95-107 (1979)
38. Frohning, C.D., Cornils, B., Hydrocarbon Process. 53 (11) 143-146 (1974)
39. The Stage and Development Possibilities of the Fischer-Tropsch Synthesis for the Production of Primary Chemicals and Feedstocks, Final Report, Bundesministerium für Forschung und Technologie, 1977
40. Asboth, K., Austrian 171 701 (1952)
41. Nonnenmacher, H., Oettinger, W., Göhre, O., Ger. Offen. 896 338 (1953)
42. Davies, H.G., Wilson, T.P., US 2 717 259 (1955)
43. Wilson, T.P., US 2 824 116 (1958)
44. Tsutsumi, S., Ger. Offen. 1 271 098 (1955)
45. Nonnenmacher, H., Oettinger, W., Ger. Offen. 922 883 (1955)
46. Peters, K., Austrian 204 018 (1959)

47. Kölbel, H., Tillmetz, K.D., Ger. Offen. 2 507 647 (1976)
48. Büssemeier, B., Frohning, C.D., Horn, G., Kluy, W., Ger. Offen. 2 518 964 (1976)
49. Büssemeier, B., Frohning, C.D., Horn, G., Kluy, W., Ger. Offen. 2 536 488 (1976)
50. Rottig, W., Ger. Offen. 2 518 982 (1976)
51. Kitzelmann, D., Vielstich, W., Dittrich, T., Chem.-Ing.-Tech. 49, 463-468 (1977)
52. Kölbel, H., Ralek, M., Tillmetz, K.D., Proc. 13th Intersociety Energy Conversion Engineering Conference, San Diego, 1978, p. 482
53. Chem. Week March 15, 25 (1978)
54. Chem. Eng. News Jan. 30, 26-28 (1978)
55. Chang, C.D., Lang, W.H., Silvestri, A.J., J. Catal. 56, 268-273 (1979)
56. Caesar, P.D., Brennan, J.A., Garwood, W.E., Ciric, J., J. Catal. 56, 274-278 (1979)
57. Thomas, M.G., Beier, B.F., Muetterties, E.L., J. Am. Chem. Soc. 98, 1296-1297 (1976)
58. Demitras, G.C., Muetterties, E.L., J. Am. Chem. Soc. 99, 2796-2797 (1977)
59. Cawse, J.N., US 3 948 965 (1976)
60. Walker, W.E., Bryant, D.R., Brown, E.S., Jr., US 3 952 039 (1976)
61. Pruett, R.L., Walker, W.E., US 3 957 857 (1976)
62. Walker, W.E., Brown, E.S., Jr., US 3 968 136 (1976)
63. Ponec, V., Catal. Rev. - Sci. Eng. 18, 151-171 (1978)
64. Vannice, M.A., J. Catal. 37, 462-473 (1975)
65. Poutsma, M.L., Elek, L.F., Ibarbia, P.A., Risch, A.P., Rabo, J.A., J. Catal. 52, 157-168 (1978)
66. Atkinson, S.J., Brundle, C.R., Roberts, M.W., Chem. Phys. Lett. 24, 175-178 (1974)
67. Bradshaw, A.M., Menzel, D., Steinkilberg, M., Chem. Phys. Lett. 28, 516-519 (1974)
68. Jones, A., McNicol, B.D., J. Catal. 47, 384-388 (1977)
69. Kelley, R.D., Madey, T.E., Yates, J.T., Jr., J. Catal. 50, 301-305 (1977)

70. German, A.L., Heynen, H.W.G., J. Sci. Instrum. 5, 413-414 (1972)
71. Kaiser, R., Chromatographie in der Gasphase, Bibliographisches Institut, Mannheim, 1966, p. 133
72. Anderson, R.B., Experimental Methods in Catalytic Research, Academic Press, Inc., New York, 1968, p. 8
73. Satterfield, C.N., Sherwood, T.K., The Role of Diffusion in Catalysis, Addison-Wesley Publishing Company, Inc., Reading, 1963
74. Hougen, O.A., Ind. Eng. Chem. 53, 509-528 (1961)
75. Yoshida, F., Ramaswami, D., Hougen, O.A., A.I.Ch.E.J. 8, 5-11 (1962)
76. Henrici-Olive, G., Olive, S., Angew. Chem. 88, 144-150 (1976)
77. Dixon, G.M., Nicholls, D., Steiner, H., Proc. Third Intern. Congr. on Catalysis, Vol. II, North Holland Publishing Company, Amsterdam, p. 815
78. Klug, H.P., Alexander, L.E., X-ray Diffraction Procedures, 2nd ed., John Wiley & Sons, Inc., New York, 1974, p. 687
79. Pope, D., Walker, D.S., Whalley, L., Moss, R.L., J. Catal. 31, 335-345 (1973)
80. Nowotny, J., Nowotny, J.T., Rekas, M., Sadowski, A., Twardosz, M., Z. Phys. Chem. (Frankfurt am Main) 104, 155-164 (1977)
81. Schuit, G.C.A., Gates, B.C., A.I.Ch.E.J. 19, 417-438 (1973)
82. Tomlison, J.R., Keeling, R.O., Rymer, G.T., Bridges, J.M., Actes du Deuxieme International de Catalyse, Technip, Paris, 1961, p. 1831
83. Richardson, J.T., Vernon, L.W., J. Phys. Chem. 62, 1153-1157 (1958)
84. Ashley, J.H., Mitchell, P.C.H., J. Chem. Soc. A 1969, 2730-2735
85. Lojacono, M., Verbeek, J.L., Schuit, G.C.A., J. Catal. 29, 463-474 (1973)
86. Grimblot, J., Bonnelle, J-P., J. Microsc. Spectrosc. Electron. 1, 311-316 (1976)
87. Keeling, R.O., Jr., J. Chem. Phys. 31, 279-280 (1959)
88. Rao, C.N.R., Subba Rao, G.V., Transition Metal Oxides, U.S. Government Printing Office, 1974
89. Belova, I.D., Shalaginov, V.V., Galyamov, B.Sh., Roginskaya, Yu.E., Shub, D.M., Kinet. Catal. (Engl. Transl.) 23, 161-163 (1978)

90. Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. XIV, ed. by J.W. Meller, Longmans, Green and Co., London, 1957
91. Kohl, K.K., Marincek, B., Helv. Chim. Acta 49, 1229-1237 (1966)
92. Pospisil, M., Collect. Czech. Chem. Commun. 42, 1278-1284 (1977)
93. Pospisil, M., Taras, P., Collect. Czech. Chem. Commun. 42, 1266-1277 (1977)
94. Prout, E.G., Tompkins, F.C., Trans. Faraday Soc. 40, 488-498 (1944)
95. Bond, W.D., J. Am. Chem. Soc. 66, 1573-1577 (1962)
96. Voge, H.H., Atkins, L.T., J. Catal. 1, 171-179 (1962)
97. Bracconi, P., Dufour, L.C., C.R. Hebd. Seances Acad. Sci., Ser. C 270, 1152-1155 (1970)
98. Batley, G.E., Ekstrom, A., Johnson, D.A., J. Catal. 34, 368-375 (1974)
99. Ratnasamy, P., Ramaswamy, A.V., Banerjee, K., Sharma, D.K., Ray, N., J. Catal. 38, 19-32 (1975)
100. Dollimore, D., Rickett, G., Thermal Analysis, Vol. 2, Proc. Third ICTA, Davos, 1971, p. 43
101. Holm, V.C.F., Clark, A., J. Catal. 11, 305-316 (1968)
102. Büssemeier, B., Frohning, C.D., Cornils, B., Hydrocarbon Process. 55 (11) 105-112 (1976)
103. Yang, C-H., Massoth, F.E., Oblad, A.G., Am. Chem. Soc., Anaheim Meeting, 1978, Preprints, p. 538
104. Achtsnit, H.D., Dissertation, Karlsruhe (1973)
105. Boudart, M., Advances in Catalysis, Vol. XX, ed. by D.D. Eley, H. Pines, P.B. Weisz, Academic Press, Inc., New York, 1969, 153-166
106. Bridge, M.E., Comrie, C.M., Lambert, R.M., Surf. Sci. 67, 393-404 (1977)
107. Prior, K.A., Schwaha, K., Lambert, R.M., Surf. Sci. 77, 193-208 (1978)
108. Vannice, M.A., J. Catal. 44, 152-162 (1976)
109. King, A.L., J. Catal. 51, 386-397 (1978)
110. Blyholder, G., Allen, M.C., J. Am. Chem. Soc. 91, 3158-3162 (1969)

111. Bradshaw, A.M., Pritchard, J., Proc. R. Soc. London, Ser. A 316, 169-183 (1970)
112. Baker, F.S., Bradshaw, A.M., Pritchard, J., Sykes, K.W., Surf. Sci. 12, 426-436 (1968)
113. Heal, M.J., Leisegang, E.C., Torrington, R.G., J. Catal. 51, 314-325 (1978)
114. Hooker, M.P., Grant, J.T., Surf. Sci. 62, 21-30 (1977)
115. Kehrer, V.J., Jr., Leidheiser, H., Jr., J. Phys. Chem. 58, 550-555 (1954)
116. Renshaw, G.D., Roscoe, C., Walker, P.L., Jr., J. Catal. 22, 394-410 (1971)
117. Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. V, ed. by J.W. Meller, Longmans, Green and Co., London, 1956
118. Bond, G.C., Catalysis by Metals, Academic Press, Inc., Ipswich, 1962
119. Dry, M.E., Shingles, T., Boshoff, L.J., J. Catal. 25, 99-104 (1972)
120. Randhava, S.S., Rehmat, A., Camara, E.H., Ind. Eng. Chem., Proc. Des. Dev. 8, 482-486 (1969)
121. Randhava, S.S., Rehmat, A., Camara, E.H., Ind. Eng. Chem., Prod. Res. Dev. 8, 347-352 (1969)
122. Vannice, M.A., J. Catal. 37, 449-461 (1975)
123. Zein el Deen, A., Jacobs, J., Baerns, M., Chemical Reaction Engineering - Houston, ACS Symposium Series 65, Am. Chem. Soc., Washington, D.C., 1978, p. 26
124. Anderson, R.B., Krieg, A., Friedel, R.A., Ind. Eng. Chem. 41, 2189-2197 (1949)
125. Dalla Betta, R.A., Piken, A.G., Shelef, M., J. Catal. 40, 173-183 (1975)
126. Palmer, R.L., Vroom, D.A., J. Catal. 50, 244-251 (1977)
127. Dalla Betta, R.A., Piken, A.G., Shelef, M., J. Catal. 35, 54-60 (1974)
128. Schonbye, P., J. Catal. 14, 238-246 (1969)
129. Vlasenko, V.M., Kukhar, L.A., Rusov, M.T., Sachenko, N.P., Kinet. Catal. (Engl. Transl.) 5, 301-306 (1964)
130. van Herwijnen, T., van Doesburg, H., de Jong, W.A., J. Catal. 28, 391-402 (1973)

131. Bond, G.C., Turnham, B.D., J. Catal. 45, 128-136 (1976)
132. Boudart, M., Burwell, R.L., Jr., Investigation of Rates and Mechanisms of Reactions, Part I, 3rd ed., ed. by E.S. Lewis, John Wiley & Sons, Inc., New York, 1974, p. 708
133. van Driel, C.P., Report, Eindhoven University of Technology, 1978
134. Dautzenberg, F.M., Helle, J.N., van Santen, R.A., Verbeek, H., J. Catal. 50, 8-14 (1977)
135. Blyholder, G., Neff, L.D., J. Phys. Chem. 66, 1664-1667 (1962)
136. Blyholder, G., Shihabi, D., Wyatt, W.V., Bartlett, R., J. Catal. 43, 122-130 (1976)
137. Blyholder, G., Neff, L.D., J. Catal. 2, 138-144 (1963)
138. Balaji Gupta, R., Viswanathan, B., Sastri, M.V.C., J. Catal. 26, 212-217 (1972)
139. Sastri, M.C.V., Balaji Gupta, R., Viswanathan, B., J. Catal. 32, 325-332 (1974)
140. Kölbel, H., Patzschke, G., Hammer, H., Z. Phys. Chem. (Frankfurt am Main) 48, 145-150 (1966)
141. Kölbel, H., Tillmetz, K.D., Ber. Bunsenges. Phys. Chem. 76, 1156-1160 (1972)
142. Kölbel, H., Tillmetz, K.D., J. Catal. 34, 307-316 (1974)
143. Goddard, W.A., III, Walch, S.P., Rappe, A.K., Upton, T.H., Melius, C.F., J. Vac. Sci. Technol. 14, 416-418 (1977)
144. Singh, K.J., Grenga, H.E., J. Catal. 47, 328-332 (1977)
145. Goodman, D.W., Madey, T.E., Ono, M., Yates, J.T., Jr., J. Catal. 50, 279-290 (1977)
146. Dalla Betta, R.A., Shelef, M., J. Catal. 49, 383-385 (1977)
147. Blyholder, G., Emmett, P.H., J. Phys. Chem. 63, 962-965 (1959)
148. Blyholder, G., Emmett, P.H., J. Phys. Chem. 64, 470-472 (1960)
149. Toyoshima, I., U.S. Atomic Energy Report, unpublished report
150. Kemball, C., Catal. Rev. 5, 33-54 (1971)
151. Thompson, S.O., Turkevich, J., Irsa, A.P., J. Am. Chem. Soc. 73, 5213-5215 (1951)
152. Doering, W. von E., Buttery, R.G., Laughlin, R.G., Chaudhuri, N., J. Am. Chem. Soc. 78, 3224 (1956)
153. Yamamoto, T., J. Chem. Soc., Chem. Commun. 1978, 1003-1004
154. Young, G.B., Whitesides, G.M., J. Am. Chem. Soc. 100, 5808-5815 (1978)

155. Kummer, J.T., Emmett, P.H., J. Am. Chem. Soc. 75, 5177-5182 (1953)
156. Hall, W.K., Kokes, R.J., Emmett, P.H., J. Am. Chem. Soc. 79, 2983-2989 (1957)
157. Kokes, R.J., Hall, W.K., Emmett, P.H., J. Am. Chem. Soc. 79, 2989-2996 (1957)
158. Hall, W.K., Kokes, R.J., Emmett, P.H., J. Am. Chem. Soc. 82, 1027-1037 (1960)
159. Henrici-Olive, G., Olive, S., J. Mol. Catal. 4, 379-383 (1978)
160. Kieffer, E.Ph., private communication

APPENDIX

Equations Used in Model Calculations

The following simplified scheme is used to describe the Fischer-Tropsch reactions kinetically:

$$H_2 + CO \xrightarrow{k_o} [C_1^*] \xrightarrow{k_p} [C_2^*] \xrightarrow{k_p} [C_3^*] \rightarrow \qquad (1)$$

$$\downarrow k_1 \qquad \downarrow k_t \qquad \downarrow k_t$$

$$C_1 \qquad C_2 \qquad C_3$$

The surface coverages are calculated using the Langmuir adsorption model:
for hydrogen

$$\theta_H = \frac{\sqrt{K_{H_2} p_{H_2}}}{1 + \sqrt{K_{H_2} p_{H_2}} + K_{CO} p_{CO} + 2\sqrt{K_C p_{CO}}} \qquad (2)$$

for the molecularly adsorbed carbon monoxide

$$\theta_{CO} = \frac{K_{CO} p_{CO}}{1 + \sqrt{K_{H_2} p_{H_2}} + K_{CO} p_{CO} + 2\sqrt{K_C p_{CO}}} \qquad (3)$$

and for the dissociatively adsorbed carbon monoxide

$$\theta_C = \frac{\sqrt{K_C p_{CO}}}{1 + \sqrt{K_{H_2} p_{H_2}} + K_{CO} p_{CO} + 2\sqrt{K_C p_{CO}}} \qquad (4)$$

where K_{H_2}, K_{CO} and K_C are the equilibrium constants for the adsorption of hydrogen and the molecular and dissociative adsorption of carbon monoxide, respectively.

p_{H_2} and p_{CO} are the partial pressures of H_2 and CO, respectively.

The equations (2) to (4) are applicable both for the model of the chain growth via CO insertion and for the model of the chain growth via C_1 insertion.

CHAIN GROWTH VIA CO INSERTION

The steady-state surface coverage of a C_1-complex, $[C_1^*]$, is

$$[C_1^*] = \frac{k_o\ \theta_C\ \theta_H^{x_o}}{k_1\ \theta_H^{z} + k_p\ \theta_H^{x_2}\ \theta_{CO}} \tag{5}$$

and generally for a C_i-complex, $[C_i^*]$

$$[C_i^*] = \frac{k_p\ [C_{i-1}^*]\ \theta_{CO}\ \theta_H^{x_2}}{k_t\ \theta_H^{x_1} + k_p\ \theta_H^{x_2}\ \theta_{CO}} \tag{6}$$

$$= [C_1^*]\ \alpha^{i-1} \tag{7}$$

x_o, x_1, x_2 and z represent the numbers of hydrogen atoms involved in initiation, termination, chain growth and C_1-termination, respectively.

CHAIN GROWTH VIA C_1 INSERTION

The steady-state surface coverage of a C_1-complex is a root of equation (8)

$$\frac{d\ [C_1^*]}{dt} = 0 = k_o\ \theta_C\ \theta_H^{x_o} - k_t\ [C_1^*]\ \theta_H^{x} - \sum_{i=1}^{n-1} k_p\ [C_i^*]\ [C_1^*] \tag{8}$$

which can be transformed into the following form:

$$[C_1^*]^3 + \frac{k_t}{k_p}\theta_H^{\,x}\,[C_1^*]^2 + \left(\frac{k_t\,\theta_H^{\,x}}{k_p}\right)^2 [C_1^*] - \frac{k_o\,k_t}{k_p^{\,2}}\,\theta_C\,\theta_H^{\,x_o+x} = 0 \qquad (9)$$

x_o and x represent the numbers of hydrogen atoms involved in initiation and termination respectively.
Independent of the values of the various constants equation (9) has only one real root.

The steady-state surface coverage of a C_i-complex is

$$[C_i^*] = \frac{k_p\,[C_1^*]\,[C_{i-1}^*]}{k_p\,[C_1^*] + k_t\,\theta_H^{\,x}} \qquad (10)$$

$$= [C_1^*]\,\alpha^{i-1} \qquad (11)$$

In tables 1-4 the reaction orders calculated with the equations described above are given. The set of constants which gave the best fit to the experimentally found orders is used.

Table 1. Orders calculated from the model of the chain growth via CO insertion. Catalyst: Co/Al_2O_3.
K_{H_2} = 0.01, K_{CO} = 0.1, K_C = 0.1, k_o = 1.0, k_p = 100, k_1 = 25, k_t = 1.2.

	order in hydrogen				order in carbon monoxide		
p_{CO} (kPa)	10	20	40	p_{H_2} (kPa)	10	20	40
C_T	0.93	0.94	0.94	C_T	-0.09	-0.06	-0.06
C_1	1.12	1.24	1.30	C_1	-0.82	-0.63	-0.69
C_2	0.63	0.75	0.81	C_2	-0.39	-0.31	-0.26
C_3	0.62	0.74	0.80	C_3	-0.12	-0.03	~ 0

Table 2. Orders calculated from the model of the chain growth via C_1 insertion. Catalyst: Co/Al_2O_3.
K_{H_2} = 0.005, K_C = 0.2, k_o = 1.0, k_p = 1.0, k_1 = 10.0, k_t = 0.4.

	order in hydrogen				order in carbon monoxide		
P_{CO} (kPa)	10	20	40	P_{H_2} (kPa)	10	20	40
C_T	1.06	1.06	1.05	C_T	-0.20	-0.20	-0.20
C_1	1.36	1.38	1.40	C_1	-0.42	-0.40	-0.38
C_2	0.83	0.85	0.88	C_2	-0.18	-0.16	-0.14
C_3	0.77	0.81	0.84	C_3	-0.12	-0.10	-0.07

Table 3. Orders calculated from the model of the chain growth via CO insertion. Catalyst: Co.
K_{H_2} = 0.08, K_{CO} = 0.05, K_C = 1.0, k_o = 1.0, k_p = 10, k_1 = 0.2, k_t = 0.05.

	order in hydrogen				order in carbon monoxide		
P_{CO} (kPa)	10	20	40	P_{H_2} (kPa)	10	20	40
C_T	1.34	1.36	1.38	C_T	-0.62	-0.61	-0.59
C_1	1.35	1.37	1.39	C_1	-0.82	-0.80	-0.78
C_2	1.32	1.35	1.38	C_2	-0.54	-0.52	-0.50
C_3	1.29	1.34	1.37	C_3	-0.27	-0.24	-0.22

Table 4. Orders calculated from the model of the chain growth via C_1 insertion. Catalyst: Co.
K_{H_2} = 0.01, K_C = 1.0, k_o = 1.0, k_p = 1.0, k_1 = 60.0, k_t = 10.0.

	order in hydrogen				order in carbon monoxide		
P_{CO} (kPa)	10	20	40	P_{H_2} (kPa)	10	20	40
C_T	1.52	1.42	1.37	C_T	-0.62	-0.60	-0.63
C_1	1.56	1.48	1.43	C_1	-0.70	-0.67	-0.68
C_2	1.32	1.22	1.16	C_2	-0.56	-0.48	-0.46
C_3	1.09	0.98	0.89	C_3	-0.42	-0.30	-0.25

List of Symbols

Latin symbols

		unit
A, a	constants	
B	constant	
C, c	constants	
c	concentration	mol i^{-1}
C_i	rate of formation of hydrocarbons with i carbon atoms or hydrocarbons with i carbon atoms	mol $(g\ cat\ s)^{-1}$
C_i^-	rate of formation of paraffin with i carbon atoms or paraffin with i carbon atoms	mol $(g\ cat\ s)^{-1}$
$C_i^=$	rate of formation of olefin with i carbon atoms or olefin with i carbon atoms	mol $(g\ cat\ s)^{-1}$
$[C_i^*]$	surface complex with i carbon atoms	
ΔCO	overall rate	mol $(g\ cat\ s)^{-1}$ mol $(g\ Co\ s)^{-1}$
E	(apparent) activation energy	kJ mol^{-1}
f	degree of reduction	
i	carbon number	
K	equilibrium constant	
k	reaction rate constant or constant	depends on kinetics
m	weight fraction	
n	number of nuclei	
O	oxygen concentration in oxide	at g^{-1}
p	partial pressure	Pa
r	reaction rate	mol $(g\ cat\ s)^{-1}$ mol $(g\ Co\ s)^{-1}$
r	radius of a nucleus	m
T	temperature	K

		unit
t	time	s
TOF	turnover frequency	s^{-1}
w	weight change	g (g cat)$^{-1}$
		g (g Co)$^{-1}$
w_i	weight of the product fraction with i carbon atoms	g (g cat s)$^{-1}$
		g (g Co s)$^{-1}$
X	reaction order in hydrogen	
x	mole fraction	
x, x_i	number of hydrogen atoms	
Y	reaction order in carbon monoxide	
y	number of hydrogen atoms	
z	number of hydrogen atoms	

Greek symbols

α	Flory constant, probability of chain growth	
η	effectiveness factor	
θ	surface fraction	
τ	residence time	g cat ks Nl^{-1}
Φ_1	selectivity of methane	

Subscripts

C	surface carbon	o	initiation or initial
e	empty sites	ol(ef)	olefin
f	flushed	p	chain growth
H	dissociatively adsorbed hydrogen	par(af)	paraffin
		T	total
i	number of carbon atoms	t	termination or time
m	maximum value	α	connected to α

Symbols, which are not explained in this list, are used only locally and are explained in the text.

Summary

Since the energy crisis of 1973 interest in coal as a possible source of energy and as a raw material increased quickly. In spite of numerous investigations on coal conversion processes none of the processes is developed so far that it could compete with the processes based on oil. The main aim of this thesis is to study the mechanism and kinetics of one indirect method for the conversion of coal to hydrocarbons, viz. the hydrogenation of carbon monoxide or the Fischer-Tropsch synthesis on cobalt catalysts.

The experiments are carried out in a plug flow reactor under differential conditions in order to minimize mass and heat transfer limitations, to decrease the side reactions and to maintain isothermal conditions.

The preparation of the two catalysts, pure cobalt and cobalt on alumina, via the reduction of the corresponding oxides is studied in a thermobalance. The reduction of the unsupported cobalt oxides by hydrogen can be described by a model according to which during the reaction three stages can be distinguished: i) induction, ii) acceleration and iii) decay. Whereas the unsupported cobalt oxides can be reduced completely, the maximum degree of reduction of the cobalt oxide on alumina is limited to about 90% in hydrogen reduction at 673 K.

The product distribution for the Fischer-Tropsch reaction can be described by the Flory-Schulz equation i.e. the ratio of the rates of chain growth and of termination is constant for every carbon fraction. The whole product distribution is determined by two parameters: initiation rate (the ordinate intercept of the Flory-lines) and the Flory constant (the slope of the lines) mentioned above. Both parameters are discussed in this thesis.

The decrease in the intercept of the Flory-lines without variation in the slope is ascribed to the formation of continuous areas of carbonaceous species which inhibit a part of the initiation sites but do not influence the product distribution. This is what happens during the deactivation in the first hours of an experiment. A strong deactivation causes also changes in the product distribution. If the probability of the chain growth is diminished while the rate of

initiation remains constant, we interpret that as the formation of randomly distributed carbonaceous species which do not influence the initiation but inhibit the mobility of intermediates and thus hinder the chain growth. This indicates that a bigger aggregate of active sites is needed for the chain growth than for the initiation.

The rate of formation of carbonaceous species from carbon monoxide is much faster on the supported than on the unsupported catalyst. We suggest that this is due to the fact that the mobility of carbonaceous species is easier on the former catalyst. This can also explain why more higher hydrocarbons are formed on the supported catalyst than on the unsupported catalyst.

The calculated turnover frequencies are much lower than found in most other heterogeneous catalytic processes. From the flushing experiments during which adsorbed intermediates and products are desorbed from the catalyst by flushing with helium or hydrogen, it is concluded that the whole catalyst surface is covered with carbon containing species which can desorb as such or are converted to hydrocarbons with the aid of hydrogen. These experiments further suggest that under synthesis conditions the number of at least some of the active ensembles is low and thus causes the low turnover frequencies.

Mechanisms of the three steps of the Fischer-Tropsch reaction (initiation, chain growth and termination) are studied as well. We conclude that initiation proceeds via dissociatively adsorbed carbon monoxide followed by the hydrogenation of surface carbon to a CH_x-group. Based on the kinetic data a model is proposed according to which the rate determining step is the hydrogenation of surface carbon. Oxygen is primarily converted to water. A subsequent water-gas shift reaction may cause the formation of small quantities of carbon dioxide.

Chain growth proceeds via addition of a complex with one carbon atom to a growing chain. The most probable building unit is a methylene group.

In the product both olefins and paraffins are found. The kinetic results indicate that paraffins are mainly formed in a consecutive reaction from olefins. But some formation of paraffins parallel with the olefin formation is not excluded and is somewhat more likely for ethane than for propane.

Yhteenveto

Summary in Finnish

Vuoden 1973 energiakriisin jälkeen kiinnostus hiilen mahdollisuuksiin energian ja raaka-aineiden lähteenä lisääntyi nopeasti. Huolimatta lukuisista tutkimuksista hiilen konversioprosessit eivät kykene tällä hetkellä kilpailemaan prosessien kanssa, joiden raaka-aineena on öljy.

Tässä väitöskirjassa on tutkittu erään hiilen epäsuoran konversioprosessin mekanismia ja kinetiikkaa, so. hiilimonoksidin hydrausta hiilivedyiksi kobolttikatalyyteillä eli Fischer-Tropsch-synteesiä.

Kokeet on suoritettu differentiaalireaktorissa, jotta aineen- ja lämmönsiirrosta aiheutuvat vastukset minimoitaisiin ja jotta reaktiot voitaisiin suorittaa isotermisissä olosuhteissa.

Katalyyttien, kobolttioksidi alumiinioksidikantajalla ja kobolttioksidi, pelkistystä on tutkittu termovaa'assa. Kobolttioksidin (ilman kantajaa) pelkistys vedyllä voidaan kuvata kineettisellä mallilla, jonka mukaan reaktio käsittää kolme vaihetta: i) induktio-, ii) kiihdytys- ja iii) hidastusvaihe. Ilman kantajaa olevat kobolttioksidit voidaan pelkistää vedyllä täydellisesti, mutta alumiinioksidikantajalla olevan kobolttioksidin maksimipelkistysaste on noin 90% 673 K:ssa.

Fischer-Tropsch reaktion tuotejakautuma voidaan esittää Flory-Schulz-mallin avulla, so. ketjun kasvun nopeuden suhde terminaation nopeuteen on vakio. Tällöin tuotejakautuma voidaan määrittää kokonaisuudessaan kahden tekijän, initiaationopeuden ja yllä mainitun vakion avulla, joita on erikseen tarkasteltu.

Kokeiden alussa todettiin, että katalyytin aktiivisuus pienenee, mutta tuotejakautuma pysyy samana. Deaktivoituminen aiheutuu sellaisia alueita muodostavista hiiltä sisältävistä yhdisteistä, joilla initiaatio ei ole mahdollinen. Voimakas deaktivoituminen aiheuttaa muutoksia myös tuotejakautumassa. Tällöin ketjun kasvun todennäköisyys

pienenee, mutta initiaationopeus pysyy vakiona. Tämän on tulkittu aiheutuvan hiiliyhdisteistä, jotka ovat satunnaisesti jakautuneet katalyytin pinnalla eivätkä siten vaikuta initiaationopeuteen, vaan estävät reaktion välimuotojen liikkuvuuden ja täten ketjun kasvun. Tämä osoittaa, että ketjun kasvuun tarvitaan suurempi kokonaisuus aktiivisia kohtia kuin initiaatioon.

Hiiliyhdisteitä muodostuu hiilimonoksidista nopeammin katalyyteillä, joissa on kantaja, kuin ilman sitä olevilla. Tämä osoittaa jälleen, että ensiksi mainittujen katalyyttien hiiliyhdisteiden liikkuvuus on helpompaa kuin jäljempänä mainittujen. Tämä selittää myös, miksi kantajallisilla katalyyteillä muodostuu enemmän korkeampia hiilivetyjä kuin ilman kantajaa olevilla.

Lasketut reaktiofrekvenssit ovat paljon alhaisempia kuin useimmissa muissa heterogeenisissä katalyyttisissä reaktioissa. Kokeissa, joissa katalyytti on synteesin jälkeen käsitelty vedyllä tai heliumilla, on todettu, että katalyytin pinta on täysin hiiltä sisältävien yhdisteiden tai niiden välimuotojen peittämä. Nämä voivat joko desorboitua sellaisenaan, tai ne voidaan hydrata vedyn avulla hiilivedyiksi. Kokeet osoittavat edelleen, että synteesin aikana vain pieni osa katalyytin pinnasta on aktiivinen, mikä on syynä alhaisiin reaktiofrekvensseihin.

Fischer-Tropsch reaktio voidaan jakaa kolmeen vaiheeseen: initiaatio, ketjun kasvu ja terminaatio. Jokaisen vaiheen mekanismia on tutkittu. On todettu, että initiaatiossa dissosioitunut hiilimonoksidi reagoi adsorboituneen vedyn kanssa muodostaen CH_x-ryhmän. Kineettiset tulokset voidaan tulkita reaktiomallin avulla, jossa hiilen hydraus on nopeutta määräävä askel. Happi konvertoituu ensisijaisesti vedeksi. Mahdollinen vesikaasureaktio aiheuttaa hiilidioksidin muodostumisen.

Ketjun kasvu tapahtuu reaktion välityksellä, jossa yhden hiiliatomin sisältävä kompleksi liittyy kasvavaan hiiliketjuun. Todennäköisin kompleksi on metyleeniryhmä.

Tuote sisältää sekä olefiinejä että parafiinejä. Kineettiset tulokset osoittavat, että suurin osa parafiineistä on muodostunut olefiineistä hydrausreaktion kautta. Täysin mahdotonta ei ole, että osa parafiineista on muodostunut rinnakkain olefiinien muodostumisen kanssa. Rinnakkaisreaktio on todennäköisempi etaanin kuin propaanin muodostumisessa.

Samenvatting

Summary in Dutch

Sinds de energiecrisis van 1973 is de belangstelling voor steenkool als mogelijke energiebron en als grondstof in de chemische industrie snel gestegen. Ondanks het uitgebreide onderzoek naar processen voor de conversie van koolstof is nog geen van deze processen zover ontwikkeld dat het op dit moment kan concurreren met de processen gebaseerd op olie. Het voornaamste doel van dit proefschrift is de bestudering van het mechanisme en de kinetiek van een indirecte methode voor de conversie van koolstof naar koolwaterstoffen, nl. de hydrogenering van koolmonoxyde ofwel de Fischer-Tropsch-synthese met kobalt katalysatoren.

De experimenten zijn uitgevoerd in een propstroom-reactor onder differentiële condities om belemmeringen van warmte- en massatransport te minimaliseren, om nevenreacties te verminderen en om isotherme condities te handhaven.

De bereiding van de twee katalysatoren, zuiver kobalt en kobalt op alumina-drager, door de reductie van de overeenkomstige oxyden is bestudeerd in de thermobalans. De reductie van het ongedragen kobaltoxyde met waterstof kan worden beschreven met een model, dat in de reactie drie stappen onderscheidt: i) inductie, ii) versnelling en iii) verval. In tegenstelling tot ongedragen kobaltoxyden, die totaal gereduceerd kunnen worden, is de maximale reductiegraad van kobaltoxyde op alumina beperkt tot ca. 90% voor reductie met waterstof bij 673 K.

De produktverdeling van de Fischer-Tropsch-reactie kan worden beschreven met de Flory-Schulz-vergelijking, die voor iedere koolstoffractie een constante verhouding tussen de snelheden van ketengroei en van terminatie veronderstelt. De hele produktverdeling wordt bepaald door twee parameters: de initiatiesnelheid (hoogte van de Flory-lijnen) en de Flory-constante (helling van de lijnen). Beide parameters worden in dit proefschrift besproken.

De daling van het niveau van de Flory-lijnen zonder verandering van de helling wordt toegeschreven aan de vorming van continue gebieden van koolstofhoudende deeltjes, die een deel van de reactieplaatsen voor de initiatie blokkeren maar de produktverdeling niet beïnvloeden. Dit gebeurt tijdens de activiteitsdaling in de eerste uren van een experiment. Een sterke deactivering heeft ook veranderingen in de produktverdeling tot gevolg. Als de kans op ketengroei verminderd wordt terwijl de initiatiesnelheid constant blijft, interpreteren we dat als de vorming van statistisch over het oppervlak verdeelde koolstofhoudende deeltjes, die de initiatie niet beïnvloeden maar de mobiliteit van de intermediairen remmen en zo de ketengroei belemmeren. Dit wijst erop dat voor de ketengroei een groter aggregaat van actieve reactieplaatsen nodig is dan voor de initiatie.

De vormingssnelheid van koolstofhoudende deeltjes uit koolmonoxyde is veel groter op de gedragen dan op de ongedragen katalysator. We veronderstellen dat dit te wijten is aan het feit dat de beweeglijkheid van de koolstofhoudende deeltjes op eerstgenoemde katalysator het grootst is. Dit kan ook verklaren waarom op de gedragen katalysator meer hogere koolwaterstoffen gevormd worden dan op de ongedragen katalysator.

De berekende reactiefrequenties zijn veel lager dan die welke voor de meeste andere heterogene katalytische processen worden gevonden. Uit experimenten waarbij geadsorbeerde intermediairen en produkten van het katalysatoroppervlak desorberen door spoelen met helium of waterstof, wordt geconcludeerd dat het katalysatoroppervlak bedekt is met koolstofhoudende deeltjes die of als zodanig kunnen desorberen of met behulp van waterstof omgezet worden in koolwaterstoffen en dan desorberen. Deze experimenten suggereren verder dat onder synthesecondities het aantal van bepaalde reactie-clusters klein is en dat daardoor de berekende reactiefrequenties laag zijn.

De mechanismen van de drie stappen van de Fischer-Tropsch-reactie (initiatie, ketengroei en terminatie) zijn eveneens bestudeerd. Wij concluderen dat initiatie plaatsvindt door hydrogenering van oppervlakte-koolstof tot een CH_x-groep uit dissociatief geadsorbeerde koolmonoxyde. Op basis van de kinetische gegevens wordt een model voorgesteld waarin de hydrogenering van oppervlakte-koolstof de snelheidsbepalende stap is. Zuurstof wordt voornamelijk in water omgezet. Een daarop volgende 'water-gas shift'-reactie kan de oorzaak zijn van de vorming van kleine hoeveelheden kooldioxyde.

Ketengroei vindt plaats door additie van een complex met één koolstofatoom aan een groeiende keten. De meest waarschijnlijke bouwsteen is een methyleen-groep.

In het produkt worden zowel olefinen als paraffinen gevonden. De kinetische resultaten wijzen erop dat paraffinen voornamelijk gevormd worden uit olefinen in een volgreactie. Maar enige vorming van paraffinen parallel aan die van olefinen wordt niet uitgesloten en is voor ethaan iets waarschijnlijker dan voor propaan.

Curriculum Vitae

The author of this thesis was born May 20th 1948 in Laukaa, Finland. After her graduation from the Secondary School of Laukaa in 1967 she started her studies in the Department of Chemistry at the Helsinki University of Technology. In 1972 she obtained the degree of Master of Science (Chem. Eng.) with honours. In August of the same year she joined the scientific staff of Professor O. Harva in the laboratory of Industrial Chemistry of the University, where she acquired the degree of Licentiate in Technology with a thesis titled "The Decarbonylation of Aldehydes on Platinum Catalysts", in June 1975.

In September of that year she obtained a scholarship from the Neste Oy Foundation for a period of three years. With this scholarship she started to study with Professor H.S. van der Baan of the laboratory of Chemical Technology of the Eindhoven University of Technology. In 1978 that University granted her a research fellowship to finalize the work presented in this thesis.

In October 1979 she will join the research staff of Neste Oy, Kulloo, Finland.

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Last but by no means least my deep gratitude goes out to our Heavenly Father who has given me the strength and wisdom to study.

Statements

1. The mass spectrometric data obtained by Tillmetz during the Fischer-Tropsch synthesis under low pressure conditions can also be explained without assuming aldehydes as products.

   Tillmetz, K.D., Dissertation, Berlin (1976)

2. Goto et al, assert that in a trickle-bed reactor the reaction rate is zero order in the liquid reactant, if the concentration of this liquid reactant is much higher than that of the gaseous reactant in the liquid phase. This assertion, however, is only valid in very specific cases.

   Goto, S., Levec, J., Smith, J.M., Catal. Rev. - Sci. Eng. 15, 187-247 (1977)

3. The absence of the kinetic isotope effect need not imply that hydrogen is not involved in the rate determining step of a heterogeneous catalytic reaction.

   Dalla Betta, R.A., Shelef, M., J. Catal. 49, 383-385 (1977)
   van Meerten, R.Z.C., Morales, A., Barbier, J., Maurel, R., J. Catal. 58, 43-51 (1979)

4. Serious objections can be raised against the kinetic model given by Kosugi and Yoshizawa for the desulphurization of oil fractions over a $Co/Mo/Al_2O_3$ catalyst.

   Kosugi, M., Yoshizawa, T., J. Jpn Pet. Inst. 21, 199-206 (1978)

5. The description of the hydration of sugars with the aid of a Langmuir adsorption isotherm /1/ cannot explain the results of Harvey and Symons /2/.

   1. Shiio, H., J. Am. Chem. Soc. 80, 70-73 (1958)
   2. Harvey, J.H., Symons, M.C.R., Nature (London) 261, 435-436 (1976)

6. Application of the relation given by Olbrich and Potter for mass transport to the wall of a packed bed to chemical reactions taking place at the wall of a packed tubular wall reactor may lead to erroneous results.

   Olbrich, W.E., Potter, O.E., Chem. Eng. Sci. 27, 1733-1743 (1972)

7. In the recent mechanism for the Fischer-Tropsch synthesis proposed by Biloen et al. /1/ features of the original suggestion by Fischer and Tropsch can be found back /2/.

   1. Biloen, P., Helle, J.M., Sachtler, W.M.H., J. Catal. 58, 95-107 (1979)
   2. Fischer, F., Tropsch, H., Ber. Dtsch. Chem. Ges. 59, 830-836 (1926)

8. If the European Community reduced its oil imports this year by 5% it would save $ 4 billion. If the European Community spent a fraction of this amount to the know-how of catalytic conversion of coal it could save several times more in imports.

9. One way to judge the reliability of patents is to look at the publications of the authors.

10. A good promotor of the catalyst for the preparation of a thesis is criticism.

Eindhoven, 7th September 1979 A.O.I. Rautavuoma