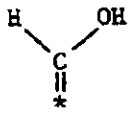
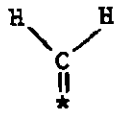
4. GENERAL DISCUSSION

One of the keys to understanding the Fischer-Tropsch synthesis is to comprehend the growth process by which hydrocarbon chains are formed on the catalyst surface. Controversy still exists as to whether growth takes place by surface condensation of an enolic intermediate[1] (43)



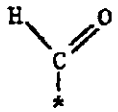
[1]

or polymerization of a methylene intermediate (82)



[2]

which may be formed via an oxygenated precursor (83, 84). A third alternative, first suggested by Zein El Deen (85) and modified by Henrici-Olivé and Olivé (49), consists of the insertion of adsorbed CO between a H—* bond to give an aldehydic surface complex



[3]

which, after hydrogen addition and elimination of oxygen as water, is converted to a surface methyl intermediate. Chain growth is then accomplished by alternate insertions of an adsorbed CO molecule into the C—* bond, hydrogen addition, and elimination of water.

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[1] * = catalytic site

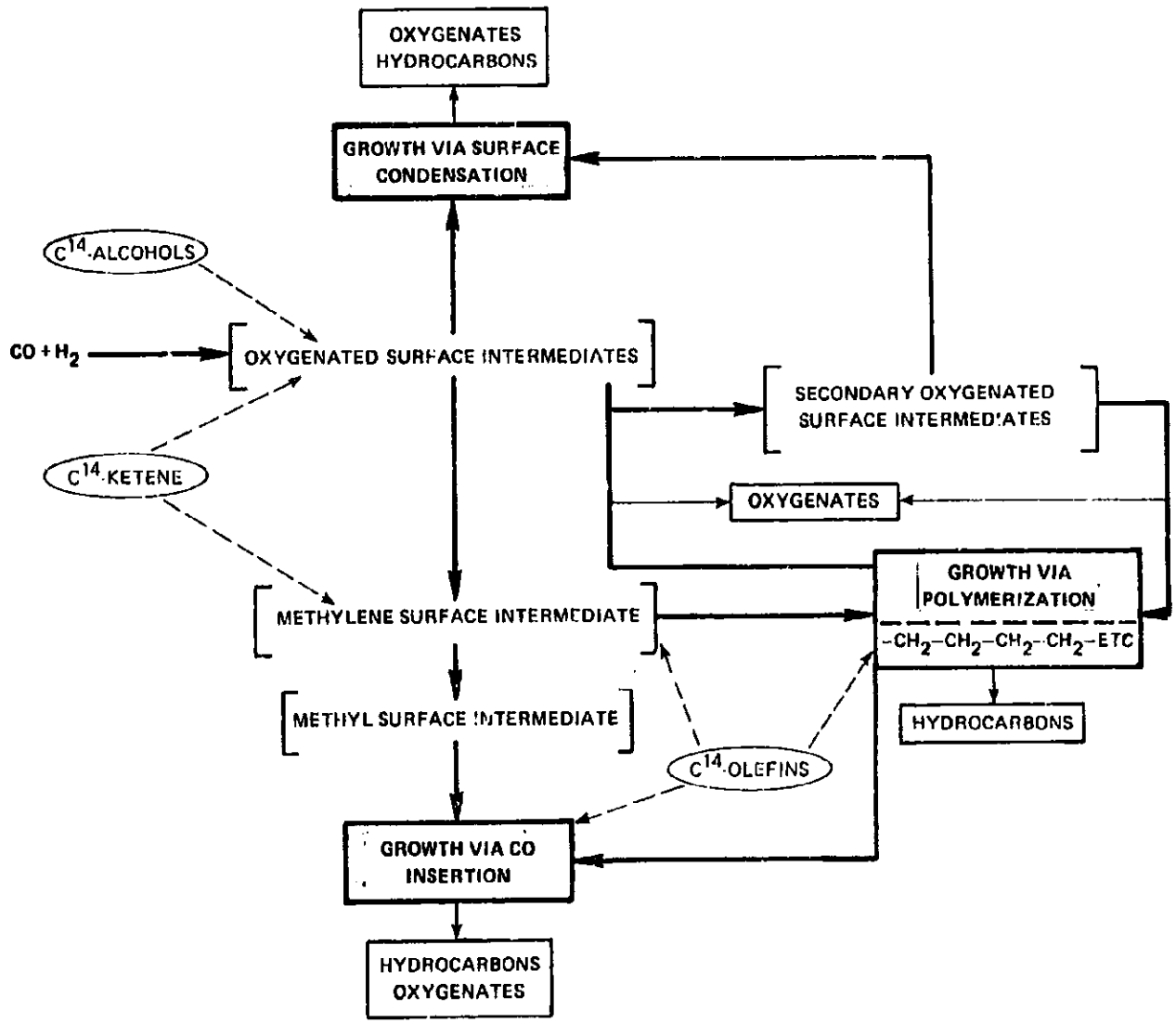
Initial radioactive tracer studies by Kummer et al. (86, 87) using C^{14}-tagged alcohols with synthesis gas on iron catalysts indicated that primary alcohols adsorbed on the catalyst to give oxygenated surface intermediates such as [1] which initiated the growth of hydrocarbon chains. Subsequent tracer studies showed a much smaller participation of labeled alcohols on Co (88, 89) than on Fe catalysts. Furthermore, labeled ethylene was shown to take part in the synthesis to a greater extent than ethanol on Co (89, 90), though the reverse was true for iron (91). Kokes et al. (88) concluded that oxygenated species such as [1] were probably active intermediates on Fe catalysts but not on Co catalysts, thus casting doubt on the general applicability of the condensation scheme (43) as the growth mechanism for the FT synthesis.

Another interesting series of experiments using ketene [CH_2=C=O], labeled with C^{14} in the methylene or carbonyl group were performed on an iron catalyst by Blyholder and Emmett (92, 93). The results showed that the ketene probably dissociated on the surface with the adsorbed CH_2 groups initiating chain growth. In contrast, Kölbel and co-workers (94-97) synthesized and characterized the surface complex HCOH and showed that other oxygen-containing surface species were probably also present during synthesis on iron. Using C^{14}-labeled ethylene and iron carbides, Kryukov et al. (98) established that chains could grow both by condensation of oxygen-containing surface intermediates and by polymerization of surface compounds containing or not containing oxygen. The authors postulated HCOH to be the primary surface intermediate and stated that the importance of the coexisting mechanisms depended on the relative rates of condensation and hydrogenation of the primary HCOH complex to form CH_3COH or CH_2 surface species. They further postulated that polymerization and condensation mechanisms not only coexisted but probably also interacted with each other. The authors also showed that the growth process took place not only by addition of individual C_1 groups to the growing chain but also to some extent by the addition of larger (C_2+) aggregates. Finally, the recent tracer work of Schulz et al. (51) on Co and Fe catalysts indicated that olefins could be incorporated in growing hydrocarbon chains and could also initiate or terminate the chain growth process. Moreover, they substantiated the arguments of Kryukov et al. (98) that structural units with more than one C atom could also take part in chain growth.

It is felt, from the above information, that no one particular intermediate or growth process can explain the FT synthesis on all catalysts. Nor is it necessary to assume that hydrocarbon production and the formation of oxygenated compounds take place via the same mechanism. In all cases, H_2 and CO probably interact to give some type of an oxygenated surface intermediate. Such an intermediate may itself be directly involved in the chain growth process, or it may be a precursor for the formation of adsorbed methylene radicals which participate via the polymerization or CO insertion mechanisms. Figure 4.1 summarizes the plausible pathways of the synthesis reaction and indicates where the results of past tracer studies would best fit. The figure also incorporates the hypothesis (98) that different growth mechanisms, while coexisting, may interact with each other. It may be argued that all schemes are generally probable, but with a particular catalyst

Figure 4.1

GROWTH SCHEMES FOR FISCHER-TROPSCH SYNTHESIS PRODUCTS



and/or process condition one of the schemes may be predominant. This may account for different FT product selectives on different catalysts and at different process conditions, and this also enables us to rationalize the tracer and other results discussed previously.

Our results, presented in Section 3, showed that the distribution of condensed products often varied with the type of catalyst used. For example, under certain conditions bi-modal distributions were obtained on the Co-based catalyst, skewed distributions on the Fe-Cu catalyst, but on Ru the distributions were neither bi-modal nor skewed. Such observations tend to substantiate the hypothesis that different growth schemes take place on different catalyst surfaces.

Though there is controversy regarding the actual mechanisms, it is generally agreed that growth takes place predominantly by a stepwise addition of units containing one carbon atom. This type of synthesis process is thus analogous to heterogeneously catalyzed polymerization or oligomerization reactions. Various computational analyses have been done in the past (40, 49, 99, 100) to fit the FT product distribution data in a polymerization-type of scheme. It has been shown that the data usually fit the schemes up to a carbon number of about 13 (49, 59). As the products become heavier, smaller amounts leave the reactor in the gas phase, and thus their residence time is increased. Such heavy products are most likely to be involved in secondary reactions. And these reactions may alter the product distribution that would have been obtained via the primary polymerization-type of growth process alone. Olefins perhaps play the most significant role in secondary reactions, and a discussion regarding this has already been given in Section 3.1.3. The bi-modal distributions observed by us on the Co-based catalyst cannot be explained by a polymerization-type of scheme alone, but such observations are feasible if the primary scheme is influenced by secondary reactions. Furthermore, these reactions may be more prevalent on some catalysts than on others. The occurrence of secondary reactions, therefore, complicates the problem of understanding which growth mechanism (Figure 4.1) is most probable for a particular catalyst.

So far we have discussed some plausible intermediates and growth schemes for FT products and alluded to the importance of secondary reactions which may influence product distribution. But a key question arises as to why growth, by whatever mechanism, takes place on some catalysts and not on others. An answer to this may be found by understanding the role of promoters, so many of which seem to be useful in FT catalysis (2). Though little is known as yet regarding the role of promoters, Dry et al. (25, 101) first suggested a possible function of alkali promoters. Their hypothesis, also discussed elsewhere (6) is based on the fact that alkali can donate electrons to a metal, and that this enhances CO adsorption, strengthens the C—* bond, and weakens the C—O bond which is hence more susceptible for reaction with hydrogen. The net result is an increase in the formation of heavy products. Sulfur compounds, on the other hand, on being adsorbed have been shown (102) to decrease the electron density of metals. Using the same hypothesis as that summarized above for alkali promoters, the presence of sulfur should decrease formation of heavy products. But the opposite effect

has been observed by us on Co and Ru (Sections 3.1.3 and 3.6.3) and by several other workers (see Ref. 6). Therefore in such cases the effect of sulfur compounds is not related to their propensity for electron extraction.

If the catalytic surface consists of different sites so that the more active ones produce lighter products, then S could preferentially adsorb on these more active sites, reducing the total conversion and shifting the overall selectivity to heavier products. Such an effect was observed for Ru (Section 3.6.3 and Ref. 80). However in the case of Co, it has been reported (38) that there is no large drop in activity, but that there is a significant improvement in selectivity to heavy hydrocarbons. Moreover, though we did not observe gross shifts in selectivity after adding S to our Co catalyst, we obtained definite variations of the distribution of heavy products and of gaseous olefin/paraffin ratios on using the catalysts with and without sulfur. Finally on our precipitated Fe-based catalyst we obtained no alteration in activity or selectivity due to the addition of sulfur; the only effect noted was that sulfided Fe consistently produced higher ethylene/ethane ratios. The results on precipitated Fe and Co catalysts obtained by us and by others (38, 60-62, 103) do not seem to fit the "site-blocking" argument given above and which seems to apply to Ru.

Another tentative explanation of the sulfur effect may be associated with the hypothesis that more than one growth scheme (Figure 4.1) may be involved on the catalyst surface, with one particular scheme being more dominant than another. The addition of sulfur may alter this balance of mechanistic involvement and thus affect product selectivity. Furthermore, the addition of sulfur may also alter the amount of secondary reactions taking place at a certain condition on a catalyst and thus again lead to changes in selectivity.

On our Co-based and Fe-based catalysts the longitudinal sulfur gradients were very large, with most of the sulfur covering about 20% of the catalyst bed near the reactor entrance (Sections 3.1.1 and 3.2.1). Yet sulfur effects, as stated above, were observed. These observations indicate that the FT reactions taking part in one section of a fixed bed reactor may be dependent on reactions that have taken place in sections before it, and the extent of this dependence may be a strong function of catalyst type and process conditions. This would further complicate the elucidation of reaction mechanisms and the prediction of catalytic behavior concerning product selectivity.

Our discussion thus far has been involved with hydrocarbon chain growth and sulfur effects on traditional FT catalysts which are most probably active in the metallic state or possibly, in the case of Fe-based materials, as carbides. However, we have established that non-metallic catalysts and in particular oxidic and/or sulfidic forms of hydrotreating catalysts, such as Co-Mo/Al_2O_3, are active for CO hydrogenation, not only for producing CH_4 and light hydrocarbons but in several instances for producing heavy condensed products. If metallic sites are not present, questions arise as to where chemisoption occurs, what type of surface intermediate(s) is formed, and how

the reaction and chain growth take place. We proposed (Section 3.3.3) the hydrocarbon chain growing mechanism to be analgous to the Cossee-Arlman model (73) for polymerization on $TiCl_3$ where growth takes place with continuous interaction of the growing polymer chain and the adsorbed monomer on adjacent sites. One of these sites on $TiCl_3$ was initially a surface anionic vacancy and the other was one in which Cl^- was exchanged with a polymerization co-catalyst. In our case, we propose that two or more adjacent surface anionic vacancies are essential for catalytic action. First, chemisorption occurs at these vacancies. An active intermediate which can initiate chain growth is then formed. And finally, growth takes place probably via CO insertion and via a "flip-flop" mechanism akin to the Cossee-Arlman model. The extent of growth, however, may be dependent on the environment of the sites where the chain growth is taking place. And hence different catalyst pretreatments and/or addition of promoters could cause the selectivity to vary dramatically. In summary, the catalytic activity is related to the number of surface anion vacancies, whereas the selectivity depends on the environment of these vacancies. An important observation was made regarding the effect of alkali. The presence of alkali tends to decrease methane formation and increase the production of higher molecular weight hydrocarbons; the addition of sulfur to alkalized catalysts further enhances the formation of heavy products. It is therefore reasonable to assume that the growth mechanism is closely associated with the influence of the alkali-sulfur interaction.

5. RECOMMENDATIONS

Our work indicated that there were significant interactions of process conditions with different sulfided and unsulfided catalysts. Therefore for such a complex reaction as the FT synthesis, catalyst evaluation at a single set of experimental parameters would be inconclusive. Moreover, the FT reaction should be carried out under experimental conditions that allow the required product selectivity pattern to develop fully. If, as in our case, liquid products are required the reactor would have to be operated in the integral mode. As such operation often magnifies problems associated with transport phenomena, care should be taken to minimize the effects of such physical events on the complex FT kinetic studies.

Due to such problems, if integral operation is indeed necessary it seems fair to surmize that instead of using tubular plug-flow reactors it may be expedient to use laboratory recycle (or stirred) reactors in which though the conversion per pass s differential the overall conversion is integral, and thus integral data may be obtained with minimal influence of heat and mass transfer. A wide variety of such reactors, all of which are basically similar, are now available and have been discussed in a comprehensive review by Doraiswamy and Tajbl (104). But though fundamentally similar, these reactors due to their various different configurations may differ from each other with respect to gas flow patterns and residence time distributions. This is a crucial point for the FT synthesis where product selectivity is strongly dependent on the residence time distribution of the reacting components. Hence a reactor system with rapid recycling would probably give a selectivity pattern quite different than that from a one-pass plug-flow reactor. And, if the flow patterns and residence time distributions vary in the several different stirred reactors, then the product selectivity may be different in each reactor. It is also possible that as the recycle (or stirring) rate is changed in a reactor, the residence time distributions would be altered, and the selectivity would hence vary even in the same reactor system. Besides such complications, recycling of FT products, such as olefins, which, as discussed previously, participate in the reaction, would further complicate the study of FT catalyst activity and selectivity. Furthermore, Wei (105) has shown that for a complex system of first-order reactions all reactions are slowed down in a stirred or recycle reactor in comparison with those in a plug-flow reactor; more importantly, the faster reactions are slowed down much more than the slower ones. Such facts should be carefully heeded when contemplating a certain reactor system for studying the FT synthesis. It is true that certain required selectivities may be best obtained under certain stirred reactor conditions. But care must be taken to note the influence of the reactor system on such experimental results. Ideally, the study of the intrinsic performance of a catalyst for the FT synthesis should not be masked either by transport phenomena or by the effects of various residence time distributions and flow patterns inherent in the different types of recycle or stirred reactors.

Further kinetic studies with non-traditional, non-metallic catalysts should be carried out. Such studies could form the basis for developing sulfur resistant FT or methanation catalysts.

Besides conducting necessary kinetic studies, more fundamental information should be obtained regarding catalyst-sulfur interactions in order to understand why favorable changes in selectivities may result from the addition of catalyst poisons to FT catalysts. Besides helping to improve catalytic selectivities, such information could also be useful for developing sulfur resistant catalysts and for learning how to reactivate sulfur poisoned catalysts. The active material, support, promoters, and sulfur are all important components of a FT catalyst. And therefore besides speculating on mechanisms via which synergistic interactions with these components may occur, we feel that it is essential to study the catalyst topography before and after exposure to reactants in order to ascertain the location and oxidation state of each component. Recently, physical tools such as Auger electron spectroscopy (106), x-ray photoelectron spectroscopy (64, 75), electron probe microanalysis (107, 108), and electron paramagnetic resonance spectroscopy (109) have been used to study multicomponent commercial catalysts. Such investigations could enhance our understanding of the interactions between catalyst components, and could also possibly help in explaining the kinetic results that are obtained with such catalysts. The concept that a parasitic agent can favor symbiosis in the presence of a particular catalyst component is certainly worth pursuing.

REFERENCES

1. Taylor, W. F., and Hall, H. J., "Future Synthetic Fuels", Final Report, Contract No. DAAD05-73-C-0559, Office of the Chief of Research, Development and Acquisition, Washington, D.C., 1975.

2. Anderson, R. B., "Catalysis", Vol. IV, ed. P. H. Emmett, Reinhold Publ. Corp., New York, 1956.

3. Fischer, F., and Tropsch, H., Brennstoff Chem. 7, 97 (1926).

4. Fischer, F., and Dilthey, P., Gest. Abh. Kennt. Kohle 9, 512 (1928).

5. Fischer, F., Brennstoff Chem. 16, 1 (1935).

6. Madon, R. J., and Shaw, H., Catal. Rev. — Sci. Eng. 15, 69 (1977).

7. Grant, E. L., "Statistical Quality Control", McGraw-Hill, New York 1952.

8. Carberry, J. J., Ind. Eng. Chem. 58, 40 (1966).

9. Satterfield, C. N., "Mass Transfer in Heterogeneous Catalysis", MIT Press, Cambridge, Mass., 1970.

10. Hall, C. C., Gall, D., and Smith, S. L., J. Inst. Petroleum 38, 845 (1952).

11. Mears, D. E., J. Catal., 20, 127 (1971).

12. Mears, D. E., J. Catal., 30, 283 (1973).

13. Harriott, P., Chem. Eng. Sci. 29, 1309 (1974).

14. Shultz, J. F., Abelson, M., Stein, K. C., Anderson, R. B., J. Phys. Chem. 63, 496 (1959).

15. Taylor, W. F., Kuenzly, J. D., Webber, W. T., "External Catalyst Breakup Phenomena", Final Report No. AFRPL-TR-76-47, Air Force Rocket Propulsion Lab., Edwards A.F.B., California, 1976.

16. Anderson, R. B., Karn, F. S., and Shultz, J. F., U.S. Bur. Mines Bull. 614 (1964).

17. Weisz, P. B., and Prater, C. D., Advan. Catal. 6, 143 (1954).

18. Hudgins, R. R., Can. J. Chem. Eng. 50, 427 (1972).

19. Anderson, J. B., Chem. Eng. Sci. 18, 147 (1963).

20. Mears, D. E., Ind. Eng. Chem. Proc. Des. Develop. 10, 541 (1971).

21. Young, L. C., and Finlayson, B. A., Ind. Eng. Chem. Fundam. 12, 412 (1973).

22. Kölbel, H., Ackerman, P., and Engelhardt, F., Erdöl Kohle 9, 153 (1956).

23. Anderson, R. B., and Hofer, L. J. E., J. Chem. Eng. Data 5, 511 (1960).

24. Wilke, C. R., and Chang, P., Am. Inst. Chem. Eng. J. 1, 264 (1955).

25. Dry, M. E., Shingles, T., and Boshoff, L. J., J. Catal. 25, 99 (1972).

26. Eidus, Ya. T., Bulanova, T. F., and Sergeeva, N. S., Dokl. Akad. Nauk. SSSR. 147, 1095 (1962).

27. Miyauchi, T., Kikuchi, T., and Hsu, K., Chem. Eng. Sci. 31, 493 (1976).

28. Nelson, P. A., and Galloway, T. R., Ibid. 30, 1 (1975).

29. Kunii, D., and Suzuki, M., Int. J. Heat Mass Transfer 10, 845 (1967).

30. Gilliland, E. R., Ind. Eng. Chem. 26, 681 (1934).

31. Gunn, D. J., and De Souza, J. F. C., Chem. Eng. Sci. 29, 1363 (1974).

32. Wakao, N., Ibid. 31, 1115 (1976).

33. Denbigh, K. G., "Chemical Reactor Theory", Cambridge Univ. Press, Cambridge, England, 1966.

34. Carberry, J. J., and Butt, J. B., Catal. Rev.— Sci. Eng. 10, 221 (1974).

35. Agnew, J. B. and Potter, O. E., Trans. Inst. Chem. Eng. (London) 48, T15 (1970).

36. Yagi, S., and Kunii, D., Am. Inst. Chem. Eng. J. 6, 97 (1960).

37. Karn, F. S., Shultz, J. F., Kelly, R. E., and Anderson, R. B., Ind. Eng. Chem. Prod. Res. Develop. 2, 43 (1963).

38. Herington, E. F. G., and Woodward, L. A., Trans. Faraday Soc. 35, 958 (1939).

39. Pichler, H., Schulz, H., and Hojabri, F., Brennstoff Chem. 45, 215 (1964).

40. Friedel, R. A., and Anderson, R. B., J. Am. Chem. Soc. 72, 1212, 2307 (1950).

41. Roelen, O., See Ref. 2.

42. Anderson, R. B., Hall, W. K., Krieg, A., and Seligman, B. J., J. Am. Chem. Soc. 71, 183 (1949).

43. Storch, H. H., Golumbic, N., and Anderson, R. B., "The Fischer-Tropsch and Related Synthesis", John Wiley and Sons, New York, 1951.

44. Sakharov, M. M., and Dokukina, E. S., Kinet. Katal. 2, 639 (1961).

45. Vannice, M. A., J. Catal. 37, 449 (1975).

46. Schlatter, J. C., and Boudart, M., Ibid. 24, 482 (1972).

47. Eidus, Ya. T., Russ. Chem. Revs. 36, 338 (1967).

48. Pichler, H., and Schulz, H., Chem. Ing. Tech. 42, 1162 (1970).

49. Henrici-Olivé, G., and Olivé, S., Angew. Chem. Int. Ed. Engl. 15, 136 (1976).

50. Pichler, H., Schulz, H., and Elstner, M., Brennstoff Chem. 48, 78 (1967).

51. Schulz, E., Rao, B. R., and Elstner, M., Erdöl Kohle 23, 651 (1970).

52. Eidus, Ya.T., Zelinskii, N. D., and Puzitski, K. V., Bull. Acad. Sci. U.S.S.R., Classe Sci. Chim. 110, (1949).

53. Eidus, Ya.T., Ershov, N. I., Batuev, M. I., and Zelinskii, N. D., Ibid. 722 (1951).

54. Kölbel, H., and Ruschenburg, E., Brennstoff Chem. 35, 161 (1954).

55. Anderson, R. B., Seligman, B., Shultz, J. F., Kelly, R., and Elliott, M. A., Ind. Eng. Chem. 44, 391 (1952).

56. Kölbel, H., Ackermann, P., Ruschenburg, E., Langheim, R., and Engelhardt, P., Chem. Ing. Tech. 23, 153 (1951).

57. Tramm, H., Brennstoff Chem. 33, 21 (1952).

58. Anderson, R. B., Karn, F. S., Shultz, J. F., J. Catal. 4, 56 (1965).

59. Anderson, R. B., Shultz, J. F., Hofer, L. J. E., and Storch, H. H., U.S. Bur. Mines Bull. 580 (1959).

60. Rapoport, I. B., and Muzovskaya, O. A., Khim. Tekhnol. Topl. Masel No. 2, 18 (1957).

61. Rapoport, I. B., and Muzovskaya, O. A., Ibid. No. 5, 19 (1957).

62. Muzovskaya, O. A., and Rapoport, I. B., Ibid. 6 (5), 5 (1961).

63. Ratnasamy, P., Ramaswamy, A. V., Banerjee, K., Sharma, D. K., and Ray, N., J. Catal. 38, 19 (1975).

64. Patterson, T. A., Carver, J. C., Leyden, D. E., and Hercules, D. M., J. Phys. Chem. 80, 1700 (1976).

65. Hagenbach, G., Courty, Ph., and Delmon, B., J. Catal. 31, 264 (1973).

66. Canesson, P., Delmon, B., Delvaux, G., Grange, P., and Zabala, J. M., Proc. Int. Congr. Catal. 6th, (1976).

67. Mitchell, P. C. H., and Trifirò, F., J. Catal. 33, 350 (1974).

68. Massoth, F. E., Ibid. 36, 164 (1975).

69. De Beer, V. H. J., Bevelander, C., van Sint Fiet, T. H. M., Werter, P. G. A. J., and Amberg, C. H., Ibid. 43, 68 (1976).

70. Voorhoeve, R. J. H., Ibid. 23, 236 (1971).

71. Farragher, A. L., and Cossee, P., Proc. Int. Congr. Catal. 5th, 1301 (1972).

72. Schuit, G. C. A., and Gates, B. C., Am. Inst. Chem. Eng. J. 19, 417 (1973).

73. Arlman, E. J., and Cossee, P., J. Catal. 3, 99 (1964).

74. Stewart, S. G., U.S. Patent 2,490,488 (1949).

75. Ng, K. T., and Hercules, D. M., J. Phys. Chem. 80, 2094 (1976).

76. Lo Jacono, M., Schiavello, M., and Cimino, A., Ibid. 75, 1044 (1971).

77. Karn, F. S., Shultz, J. F., and Anderson, R. B., Ind. Eng. Chem. Prod. Res. Develop. 4, 265 (1965).

78. Pichler, H. Advan. Catal. 4, 289 (1952).

79. Pichler, H., Burgert, W., Gabler, W., and Kioussis, D., Brennstoff Chem. 49, 36 (1968).

80. Dalla Betta, R. A., Piken, A. G., and Shelef, M., J. Catal. 40, 173 (1975).

81. Bond, G. C., and Turnham, B. D., Ibid. 45, 128 (1976).

82. Eidus, Ya T., Uspekhi Khim. 20, 54 (1951).

83. Hamai, S., J. Chem. Soc. Japan 62, 576 (1941); Bull. Chem. Soc. Japan 16, 213 (1941).

84. Eidus, Ya T., Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 65 (1943).

85. Zein El Deen, A., Dissertation, Univ. of Karlsruhe, 1970. Also see Ref. 48.

86. Kummer, J. T., Podgurski, H. H., Spencer, W. B., and Emmett, P. H., J. Am. Chem. Soc. 73, 564 (1951).

87. Kummer, J. T., and Emmett, P. H., Ibid. 75, 5177 (1953).

88. Kokes, R. J., Hall, W. K., and Emmett, P. H., Ibid. 79, 2989 (1957).

89. Golovina, O. A., Roginskii, S. Z., Sakharov, M. M.. and Eidus, Ya T., Dokl. Akad. Nauk SSSR 108, 253 (1956).

90. Golovina, O. A., Dokukina, E. S., Roginskii, S. Z., Sakharov, M. M., and Eidus, Ya T., Ibid. 112, 864 (1957).

91. Hall, W. K., Kokes, R. J., and Emmett, P. H., J. Am. Chem. Soc. 82, 1027 (1960).

92. Blyholder, G., and Emmett, P. H., J. Phys. Chem. 63, 962 (1959).

93. Blyholder, G., and Emmett, P. H., Ibid. 64, 470 (1960).

94. Kölbel, H., Patzschke, G., and Hammer, H., Brennstoff Chem. 47, 4 (1965).

95. Kölbel, H., and Hanus, D., Chem. Ing. Tech. 46, 1042 (1974).

96. Kölbel, H., Ralek, M., and Jiru, P., Erdöl Kohle 23, 580 (1970).

97. Kölbel, H., and Roberg, H., Ber Bunsen. 75, 1100 (1971).

98. Kryukov, Yu. B., Bashkirov, A. N., Liberov, L. G., Butyugin, V. K., and Stepanova, N. D., Kinet. Katal. 2, 702 (1961).

99. Herington, E. F. G., Chemistry and Industry 347 (1946).

100. Anderson, R. B., Friedel, R. A., and Storch, H. H., J. Chem. Phys. 19, 313 (1951).

101. Dry, M. E., Shingles, T., Boshoff, L. G., and Oosthuizen, G. J., J. Catal. 15, 190 (1969).

102. Enikeev, E. Kh., and Krylova, A. V., Kinet. Katal. 3, 116 (1962).

103. Myddleton, W. W., British Patent 509,325 (1939).

104. Doraiswamy, L. K., and Tajbl, D. G., Catal. Rev. — Sci. Eng. 10, 177 (1974).

105. Wei, J., Can. J. Chem. Eng. 44, 31 (1966).

106. Silverman, D., Ph.D. Dissertation, Stanford University, (1975).

107. Chen, H. C., and Anderson, R. B., J. Colloid Interf. Sci. 38, 535 (1972).

108. Chen, H. C., and Anderson, R. B., J. Catal. 28, 161 (1973).

109. Lo Jacono, M., Verbeek, J. L., and Schuit, G. C. A., Proc. Int. Congr. Catal. 5th, 1409 (1973).

APPENDIX A

SUMMARY OF PAST RESEARCH ON SULFUR EFFECTS ON FISCHER-TROPSCH CATALYSTS

Researchers	Catalyst	Sulfur Addition	Important Observations
	NICKEL BASED		
Fujimura et al. [J. Soc. Chem. Ind. Japan 37, 395 (1934).]	Ni-Mn-ThO_2 (3%) kieselguhr	CS_2 or H_2S in synthesis gas	Catalytic activity and gasoline yields are both decreased.
	Ni-Mn-Fuller's Earth (25%)	CS_2 or H_2S in synthesis gas	Initially active remains constant, whereas the gasoline yield increases.
Dalla Betta et al. [J. Catal. 40, 173 (1975).]	Raney Ni, Ni/ZrO_2 and Ni/Al_2O_3	H_2S in synthesis gas	The activity declined at both the reaction temperatures used, 400°C and 250°C. The selectivity to C_2+ hydrocarbons improved at 400°C, but at 250°C there was little change. In fact, at 250°C when using Ni/Al_2O_3 the selectivity was worse after sulfur addition.
	COBALT BASED		
Myddleton [British Patent 509,325 (1939).]	Co : ThO_2 : kieselguhr + K_2CO_3	H_2S or organic S in synthesis gas	The proportion of olefins and the oil forming capacity of the catalyst is enhanced.
Herington and Woodward [Trans. Faraday Soc. 35, 958 (1939).]	100 Co : 18 ThO_2 : 100 kieselguhr	H_2S or CS_2 added in regulated discontinuous amounts to the synthesis gas	The addition of up to approximately 0.7 wt% S on the catalyst the liquid hydrocarbon production increased, and the formation of gaseous hydrocarbon decreased.
King [J. Inst. Fuel 11, 484 (1938).]	100 Co : 18 ThO_2 : 100 kieselguhr	CS_2 in synthesis gas	Active for production of liquid hydrocarbons.

APPENDIX A (Continued)

SUMMARY OF PAST RESEARCH ON SULFUR EFFECTS ON FISCHER-TROPSCH CATALYSTS

Researchers	Catalyst	Sulfur Addition	Important Observations
	COBALT BASED (Continued)		
Mulford and Russell [J. Am. Chem. Soc. 74, 1969 (1952).]	Co promoted with Cu, Ce, and alkali salts	As alkali sulfide, sulfate, and thio-sulfate	Distribution between liquid and gaseous hydrocarbons was altered, oil yields increased, and the temperature range required to obtain maximum oil yields shifted.
	IRON BASED		
I. G. Farbenindustrie [British Patent 322,284 (1929).]	100 (Fe + Co) : 0.5 K : 0.2 S, Fe/Co = 41 100 Fe : 0.4 K : 0.32 S (Both precipitated Fe)	As alkali sulfide or as H_2S in synthesis gas	The catalyst life is lengthened, the proportion of light hydrocarbons is reduced, and the formation of unsaturated hydrocarbons is increased.
Layng [U.S. Patent 2,446,426 (1948).]	Fused Fe + Al_2O_3 + K_2O (Fluidized bed reactor used)	H_2S in synthesis gas	Drastic reduction in CO_2 formation. Activity did not decrease, but the yield of liquid hydrocarbons and the olefinic content of the products increased.
Davis et al. [British Patent 727,833 (1955).]	Precipitated iron based catalyst treated with a halogen	Either as an iron sulfate during catalyst preparation, or as H_2S or organic S in synthesis gas	Substantially increased the formation of ethylene, propylene and butenes, and reduced formation of C_5+ hydrocarbons.

APPENDIX A (Continued)

SUMMARY OF PAST RESEARCH ON SULFUR EFFECTS ON FISCHER-TROPSCH CATALYSTS

Researchers	Catalyst	Sulfur Addition	Important Observations
	IRON BASED (Continued)		
Fuel Research Board, U.K. [Report p. 20 (1955); p. 22 (1956).]	Mill-scale	(a) H_2S admitted to an evacuated glass bulb containing the reduced catalyst	Activity was reduced very rapidly and methane formation was favored. The liquid phase contained more alcohols and less olefins.
		(b) H_2S in synthesis gas	Activity was reduced gradually. Data regarding selectivity was not given.
Rapoport and Muzovskaya [Khim. i Tekhnol. Topliv. i Masel No. 2, 18 (1957); No. 5, 19 (1957); 6 (5), 5 (1961).]	Precipitated Fe-Cu catalyst promoted with alkali	50 to 100 ppm S as COS or CS_2 in synthesis gas	The catalyst was reduced under mild conditions (H_2 at about 200°C) so that iron was present predominantly as FeO. The catalyst worked almost identically in synthesis gas containing 50 to 100 ppm sulfur as in pure synthesis gas for long periods of time. Selectivity changes were minimal.
Anderson and coworkers, USBM [J. Phys. Chem. 66, 501 (1962); Ind. Eng. Chem. Prod. Res. Develop. 2, 43 (1963); 3, 33 (1964); J. Catal. 4, 56 (1965).]	Fused iron catalyst promoted with MgO, Cr_2O_3, and alkali	(a) Uniform sulfiding by immersing reduced catalysts in a solution of a S compound in heptane	Activity decreased, CH_4 to C_4 hydrocarbon formation increased, and heavy hydrocarbon formation decreased.
	Above catalyst used in 3 forms (a) reduced (b) carbided (c) nitrided	(b) H_2S (different concentrations) in synthesis gas	Activity for the same amount of sulfur addition decreased in the following order: reduced>carbided>nitrided. The latter two forms slightly enhanced C_5+ hydrocarbon production. Alkali compounds were essential to improve resistance to poisoning. Decreasing catalyst size from 6-8 mesh to 23-32 mesh increased activity and resistance to poisoning by a factor of 3. Small catalyst particles enhanced wax formation.

APPENDIX A (continued)

SUMMARY OF PAST RESEARCH ON SULFUR EFFECTS ON FISCHER-TROPSCH CATALYSTS

Researchers	Catalyst	Sulfur Addition	Important Observations
	MOLYBDENUM BASED		
Sebastian [Carnegie Inst. Tech., Coal Res. Lab. 35, 1 (1936).]	MoS_2		Active for methanation, and resistant to sulfur poisoning.
Stewart [U.S. Patent 2,490,488 (1949).]	MoS_2-unpromoted or promoted with (a) ThO_2 (b) Cr_2O_3 (c) Al_2O_3 (d) KOH		All catalysts were active for methanation. MoS_2 containing KOH was the only catalyst that gave compounds other than methane: 30% of C_3+ hydrocarbons and oxygenated organic compounds.
Wencke [Freiberger Forschung A-151 (1960).]	High Mo loading (60 to 70%) on Al_2O_3	H_2S in synthesis gas	Drop in activity for methanation was counterbalanced by raising the pressure. Maximum pressure used was 4 MPa.
Anderson and co-workers, USBM [USBM RI 6974 (1967).]	$MoS-Al_2O_3$	H_2S in synthesis gas	Primarily methane was produced. As more H_2S was added formation of C_3+ hydrocarbons was increased.
	RUTHENIUM BASED		
Dalla Betta et al. [J. Catal. 40, 173 (1975).]	Ru/Al_2O_3	H_2S in synthesis gas	The activity declined at both the reaction temperatures used, 400°C and 250°C. The selectivity to C_2+ hydrocarbons improved, but unlike the Ni catalysts the selectivity improvement was more significant at 250°C than at 450°C.

APPENDIX B

MEASUREMENT OF GAS FLOW INTO THE REACTORS

Figure A1 shows a portion of the test unit which is used to set and check that the flow rates of reactants going into the reactors are as identical as possible. The procedure outlined below has been necessitated by the unreliability of the small rotameters, r_1-r_7. P, P_0-P_8 are back-pressure regulators; the settings of P_0-P_8 are identical. The control valves are designated as V_{sub}, on-off valves by either A_{sub}, B_{sub}, or C_{sub}, reactors by Rx_{sub}, and M_{sub} are points where the gas flows can be measured either by a wet-test meter or a soap-bubble meter.

- A calibrated amount of gas enters the manifold, all valves except V_8 and B_8 are kept shut. The total flow of gas is measured at M_8, say X cc/min.

- The total gas flow is divided by 7 to obtain the flow required to go through each reactor. Valves C_1 and A_1 are opened, B_1 is kept closed. Valves V_1 and V_8 are adjusted till the flow through V_1 measured at M_0 is equal to X/7 cc/min. The pressure reading on gauge G is noted. Valve V_0 has been installed so that the pressure drop across it can approximate the pressure drop across a reactor. (It must be noted that valves V_1 to V_7 have the lowest C_V values hence the largest pressure drop across them.)

- Valves C_1 and A_1 are shut and C_2 and A_2 opened. Valve V_2 is adjusted without touching V_8 or V_0 until the pressure gauge reading is identical to that obtained before and the flow through V_2 measured at M_0 is X/7 cc/min.

- All seven valves, V_1-V_7 are thus adjusted so that the flow through each is X/7 cc/min.

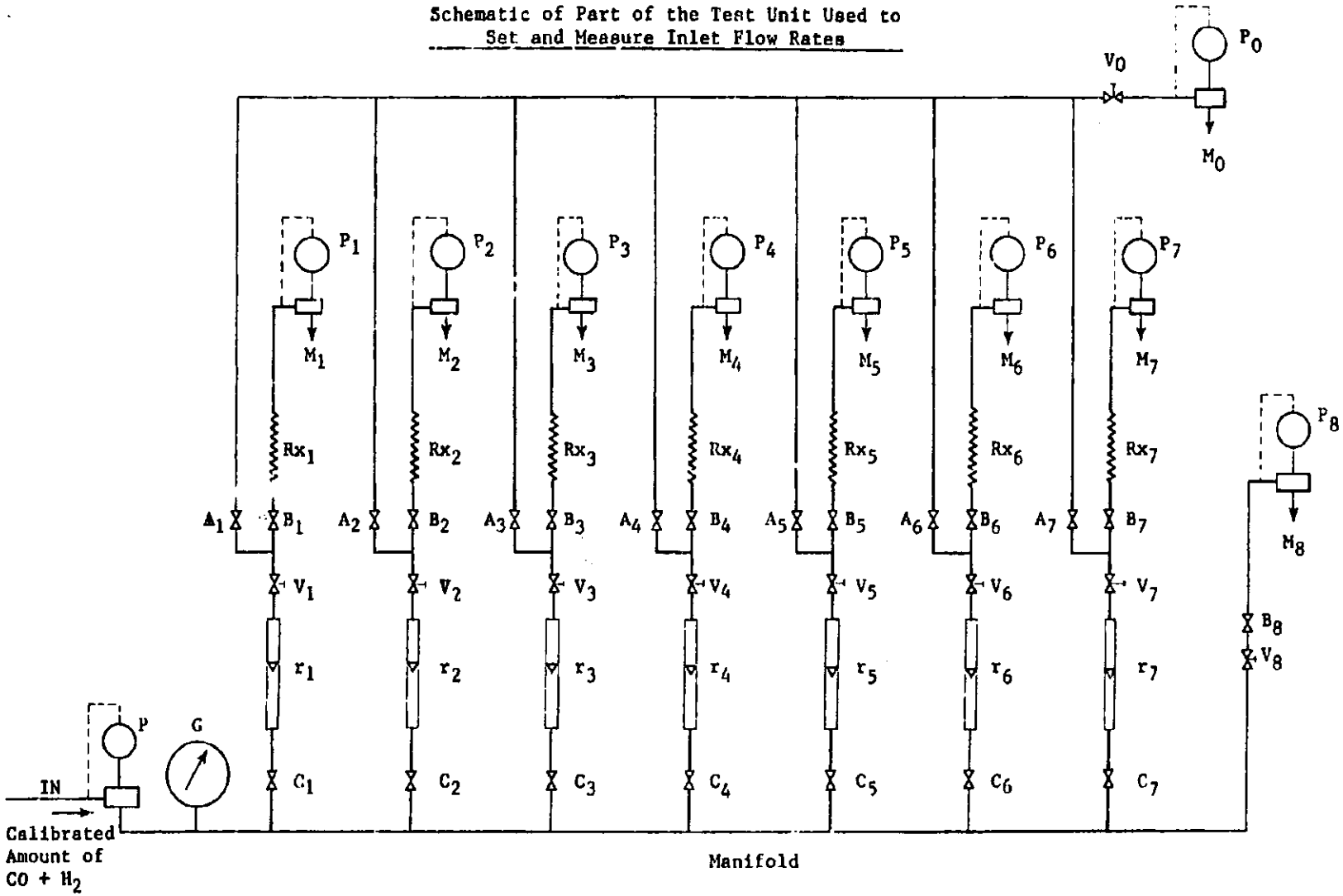
- After the above adjustments valve B_8 is closed, valves C_1-C_7 and B_1-B_7 are opened and the gas flows through the reactors. Outlet gas flows, after reaction, are measured at points M_1-M_7.

- During or after a run, the flow into any reactor is checked by shutting off the B valve, opening the A valve and measuring the flow at M_0.

- This technique assures the flows through the reactor to be close, usually the difference is less than 10%. If the flows are different, the values are known, and hence can be used in the calculations. This degree of confidence was not available when the rotameters were used.

Figure A1

Schematic of Part of the Test Unit Used to Set and Measure Inlet Flow Rates



APPENDIX C

SAMPLE CALCULATION FOR THE REPRODUCIBILITY OF RESULTS

The reproducibility of results was discussed in Section 2.4, and the average range ($\bar{R}$) for the normalized difference between replicate measurements and standard deviations of the measured (or calculated) values (σ') were given in Table 2.2. The following example will demonstrate the calculation of $\bar{R}$ and σ' for one set of results.

Table A1

Sample Calculation of $\bar{R}$ and σ'

Run 5 -- precipitated Fe catalyst

CO_2-free contraction, %:

Experiment	Reactors 5	Reactors 7	Normalized Range %
5-1	76.56	75.72	1.1[1]
5-2	72.57	71.81	1.0
5-3	84.35	82.90	1.7
5-4	73.21	73.65	0.6
5-5	72.90	72.74	0.2
5-6	60.02	58.86	1.9
5-7	47.76	46.53	2.6
5-8	64.54	65.60	1.6
5-9	68.82	68.86	0.1
5-10	69.13	66.82	3.3
5-11	70.97	68.55	3.4
5-12	48.58	47.81	1.6
			19.1

$$\bar{R} = \frac{19.1}{12} = 1.59\%$$

$$\sigma' = \frac{1.59}{1.128} = 1.4\%$$

The standard deviation σ' is obtained by dividing $\bar{R}$ by a factor which is dependent on the number of observations in a subgroup. In our case the number of observations in a subgroup was 2, and the factor is 1.128 (Grant, E. L., "Statistical Quality Control," McGraw-Hill, N.Y., 1952).

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[1] Normalized Range % = $\frac{76.56 - 75.72}{76.56} \times 100 = 1.1\%$