its final reduction. Kimpflin[38] reported yields of 124 cubic centimeters of liquid hydrocarbons per cubic meter of synthesis gas from a cobalt catalyst activated with 18 percent thoria, and yields of 166 cubic centimeters from a cobalt–nickel (1 : 1)–kieselguhr catalyst operated under the same conditions. The products contained, respectively, 12.6 and 9 percent olefins, 0.84 and 1 percent aromatic compounds, 18.8 and 24.6 percent naphthenes, and the remainder paraffinic hydrocarbons.

COBALT CATALYSTS

FISCHER'S COBALT CATALYSTS

Fischer and his coworkers and more recently other investigators[39] used a cobalt–copper–thoria–kieselguhr catalyst in many of their experiments. Fischer also carried out synthesis experiments with a cobalt–thoria–kieselguhr (100 : 18 : 100) catalyst, and several processes using this catalyst have since been reported.[40]

GERMAN COMMERCIAL NORMAL COBALT CATALYST

Magnesia was later substituted for part of the thoria so that the normal cobalt catalyst used in the commercial plants in Germany during World War II had the composition cobalt : thoria : magnesia : kieselguhr = 100 : 5 : 8 : 180–200. Hall and Smith[41] reported that this catalyst can be maintained in a high state of activity for 18 months by intermittent treatment with hydrogen under various conditions.

OTHER COBALT CATALYSTS

When operated under the same conditions of space velocity (150) and temperature (185° to 210° C.) as given above for nickel catalysts,[42] cobalt catalysts containing 5 to 10 percent of copper, 4 to 12 percent of manganese oxide, and 4 to 12 percent of thoria, alumina, or uranium oxide mixed with 1.25 times their weight of kieselguhr yield 120 to 170 cubic centimeters of liquid hydrocarbons per cubic meter of $2H_2 + 1CO$ gas per pass.

A cobalt–copper–thorium oxide–cerous oxide–chromium oxide–kieselguhr (34 : 4 : 2.3 : 0.24 : 4.6 : 54.86 parts by weight) was reported by Ghosh and Sastry[43] to yield 160 grams of liquid hydrocarbons per cubic meter, using 600 cubic centimeters of $1H_2 + 1CO$ per hour per cubic centimeter of catalyst, 205° C., and 5 atmospheres pressure.

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[38] Kimpflin, G. [The Work of the School of Louvain on Synthetic Motor Fuels]: Génie civil, vol. 119, 1942, pp. 279–281.

[39] Dreyfus, H., Hydrocarbon Synthesis from Carbon Monoxide and Hydrogen: U. S. Patent 2,338,805, Jan. 11, 1944.

Koch, H. [Synthesis of Benzine from Carbon Monoxide and Hydrogen Under Atmospheric Pressure by the Method of Franz Fischer and Tropsch]: Glückauf, vol. 71, 1935, pp. 85–90.

Pichler, H. [Synthesis of Gasoline]: Ztschr. Ver. deut. Ing., vol. 79, 1935, pp. 883–885. Coal Carbonisation, vol. 1, 1935, pp. 101–103.

[40] Feisst, W., Neweling, H., and Roelen, O., Converting Carbon Oxides into Higher Hydrocarbons: U. S. Patent 2,238,726, Apr. 15, 1941.

Herbert, W., Synthesis of Hydrocarbons from Carbon Monoxide and Hydrogen: U. S. Patent 2,271,259, Jan. 27, 1942. U. S. Patent 2,224,048, Dec. 3, 1940.

International Hydrogenation Patents Co., Ltd., Synthetic Hydrocarbons from Synthetic Gas Mixture of Carbon Monoxide and Hydrogen: British Patent 528,826, Nov. 7, 1940.

Roberts, G., Jr., Catalyst Adapted for Use in the Synthesis of Hydrocarbons from Carbon Monoxide and Hydrogen: U. S. Patent 2,244,573, June 3, 1941.

[41] Work cited in footnote 63, p. 11.

[42] Work cited in footnote 29, p. 9.

[43] Ghosh, J. C., and Sastry, S. L., Chromium Oxide as a Promoter in Catalysts for the Fischer-Tropsch Synthesis: Nature, vol. 156, 1945, p. 506.

PREPARATION OF COBALT CATALYSTS

Cobalt catalysts may be prepared by impregnating kieselguhr with the metal nitrates and subsequent decomposition by roasting; their activity when thus prepared is about the same as when they are produced by precipitation from aqueous solutions.[44] It appears, however, that the precipitation method is preferable for the preparation of nickel catalysts.[45]

Rubenshtein[46] and coworkers reported a yield of 160 cubic centimeters of gasoline per cubic meter of synthesis gas from a cobalt-copper-manganese catalyst produced by precipitation with potassium carbonate; but a similar catalyst prepared by igniting the nitrates was not as effective.

In the preparation of the normal cobalt catalyst used during World War II by the Germans, a solution containing 100 parts cobalt, 5 parts thoria, 10 parts magnesia, in the form of the metal nitrates or sulfates, and 200 parts kieselguhr in suspension was precipitated by sodium carbonate. The magnesium was present in greater quantity than that corresponding to the stoichiometric ratio of magnesium to cobalt in the catalyst. The precipitate was washed on the filter with water, and then with N/20 ammonium carbonate, and finally again with water.[47] [48] After filtration, the cake was placed in an extruding type press where the water content was reduced to 6–8 percent. The catalyst was dried at 120° C. for 2 hours in a steam-heated belt-conveyer drier. The dried catalyst was crushed to granules about 1–4 millimeters in diameter. The bulk density of the unreduced catalyst was 320 to 350 grams per liter.

The catalyst was reduced in a special unit in a block-shaped bed 2 by 1 square meters in area and 30 to 35 centimeters in depth, with top and bottom fittings in the form of truncated pyramids. A sheet-iron grill of 15-centimeter cubes for the purpose of breaking up the gas stream entering the reduction vessel was placed on top of the bed, sinking into it to a depth of about 10 centimeters. Each reduction vessel contained about 700 liters of catalyst. During reduction a stream of gas containing 75 percent hydrogen and 25 percent nitrogen heated to a temperature of 460° C. was passed down through the catalyst bed at a space velocity of 8800. The reduction period varied from 40 to 60 minutes. The effluent gas from the reducing zone was passed

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[44] Tsutsumi, S. [Catalysts for the Synthesis of Liquid Hydrocarbons from Carbon Monoxide and Hydrogen. III. Catalysts prepared by the Roasting Method]: Sci. Papers Inst. Phys. Chem. Research (Toyko), vol. 35, 1939, pp. 481–486. [Catalysts for the Synthesis of Liquid Hydrocarbons from Carbon Monoxide and Hydrogen. IV. Catalysts Prepared by the Roasting Method]: Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 36, 1939, pp. 47–52.

[45] Tsutsumi, S. [Catalysts for the Synthesis of Liquid Hydrocarbons from Carbon Monoxide and Hydrogen. VI. Selection of Catalysts for the Synthesis]: Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 36, 1939, pp. 251–256.

[46] Rubenshtein, A. M., Pribytkova, N. A., Kazanskii, B. A., and Zelinskii, N. D. [Catalysts for Benzine Synthesis from Carbon Monoxide and Hydrogen which do not Require High-Temperature Reduction]: Bull. Acad. Sci. U. S. S. R. Classe Sci. Chim., 1941, pp. 41–48. U. O. P. Surv. For. Petrol. Lit., Transl. 334.

[47] Work cited in footnote 96, p. 14.

[48] Heckel, H., and Roelen, O., Catalyst Containing Magnesium Oxide and Cobalt for the Catalytic Hydrogenation of Carbon Oxides: U. S. Patent 2,219,042, Oct. 22, 1940.

Ruhrchemie A. G., No title: German Appl. R–104,999, Apr. 15, 1939. Office of Publication Board Report 412, May 15, 1945. Catalysts for the Synthesis of Hydrocarbons: British Patent 518,334, Feb. 23, 1940. [Magnesium and Cobalt for the Conversion of Carbon Monoxide and Hydrogen Mixtures]: French Patent 843,305, June 30, 1939. Process for Production of Catalysts: British Appl. 26,276/1938.

through a methanization reactor where the carbon dioxide was hydrogenated to methane by passage over synthesis catalyst. The gas was then cooled and freed from water by refrigeration and passage through silica gel, returning to the hydrogen preheater for recirculation. In the reduction, if over 60 percent of the cobalt was reduced to metal,[49] a poor catalyst resulted. The extent of reduction was determined by measuring the volume of hydrogen evolved when a sample was treated with acid. Following reduction, the vessel was purged with nitrogen and then with carbon dioxide, either at room temperature or below,[50] so that the catalyst could be transported to the synthesis plant. The catalyst could also be protected from atmospheric oxidation by immersion in organic alcohols, aldehydes, or ketones.[51]

Another method of preparing active nickel and cobalt catalysts is that invented by Raney.[52] Alloys of nickel or cobalt or both with silicon or aluminum are prepared by fusion of the constituents in an induction furnace. The silicon or aluminum is subsequently dissolved by aqueous caustic soda solution, leaving a "skeleton" of nickel or cobalt, which is a highly porous, catalytically active material. Fischer and Meyer [53] found that the use of silicon yielded catalysts of higher activity than those obtained from aluminum alloys; that the optimum ratio of nickel to cobalt was 1 : 1; and that the presence of small amounts of copper or manganese was undesirable. The catalyst prepared from nickel, cobalt, and silicon in the ratio of 1 : 1 : 2 was very dense, with an apparent specific gravity of about 4.5, and yielded about 20 percent less liquid product in the hydrocarbon synthesis than was obtained from the same weight of nickel plus cobalt in the form of the precipitated catalysts described above.[54] [55] The precipitated catalysts deteriorated more slowly than the "skeleton" alloy catalysts, which, however, were better heat conductors. As the reaction is markedly exothermic (about one-fifth of the heat of complete combustion is evolved) the improved heat conductivity would result in a lower plant-installation cost with alloy catalysts.

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[49] Herbert, W. [Catalytic Conversion of Mixtures of CO and H]: German Patent 736,922, May 20, 1943. [Catalytic Synthesis of Hydrocarbons from CO and H]: German Patent 736,701, May 20, 1943.
Ruhrchemie A.-G., No title: German Appl. R-103,450, Oct. 1, 1938. Office of Publication Board Report 412, May 15, 1945. No title: German Appl. R-102,909, July 20, 1938. Office of Publication Board Report 412, May 15, 1945.

[50] Martin, F., and Johnswig, F. [Catalysts for Carbon Monoxide-Hydrogen Reaction Unaffected by Air]: German Patent 720,107, Apr. 2, 1942. Production and Use of Catalysts: U. S. APC SN 240,150, No date given.
Ruhrchemie A. G. [Protection of Catalysts from Air]: French Patent 845,301, Aug. 18, 1939.

[51] Myddleton, W. W., Treating Catalyst: British Patent 517,794, Feb. 8, 1940.

[52] Covert, L. W., and Atkins, H., Nickel by the Raney Process as Catalysts for Hydrogenation: Jour. Am. Chem. Soc., vol. 54, 1932, pp. 4116–4117.
Howk, B. W., Alloy-Skeleton Cobalt Catalyst Suitable for Use in Hydrogenation Reactions: U. S. Patent 2,257,800, Oct. 7, 1941.
Raney, M., Catalytic Nickel: U. S. Patent 1,563,587, Dec. 1, 1925. Finely Divided Nickel: U. S. Patent 1,628,190, May 10, 1927. Catalytic Material Suitable for Use in Hydrogenation of Oils, etc.: U. S. Patent 1,915,473, June 27, 1933.

[53] Fischer, F., and Meyer, K. [Alloy Skeletons as Catalysts for Synthesis of Benzine from Carbon Monoxide]: Brennstoff Chem., vol. 15, 1934, pp. 84–93.

[54] Work cited in footnote 29, p. 26.

[55] Work cited in footnote 30, p. 26.

Tsuneoka and his coworkers [56] and Lelchuk and his coworkers [57] made a detailed study of the behavior of alloy catalysts for the Fischer-Tropsch hydrocarbon synthesis. In addition to confirming the results of Fischer and his coworkers,[58] the Japanese investigators studied the effects of particle size, bulk density of catalyst, pretreatment with hydrogen, and the material used for the construction of the reaction tube. They found that the optimum particle size for a space velocity of about 100 with a nickel-cobalt (1 : 1) catalyst prepared from the alloy nickel–cobalt–silicon (1 : 1 : 2) was 1 to 4 millimeters. The yield of liquid hydrocarbons was about 130 cubic centimeters (93 grams) per cubic meter of synthesis gas. The efficiency of the catalysis at constant gas input for a given amount of catalyst diminished when the free space exceeded or fell below a certain optimum value, which varied with the diameter of the reaction tube. Thus, for 10 grams of nickel-cobalt (1 : 1) catalyst and 4 liters per hour of synthesis gas the optimum length for 13-millimeter tubing was about 30 centimeters; for 20-millimeter tubing it was 50 centimeters. If the length was shorter than the optimum, the average molecular weight of the liquid hydrocarbon product decreased and more gaseous hydrocarbons were produced. This effect may have been due to the existence of higher local temperatures when the catalyst was packed into a smaller space. If the free space exceeded the optimum value, a lower yield per pass was obtained owing to "channeling" of the gas.

At constant gas input, tube diameter, and bulk density (grams of catalyst per cubic centimeter) and with varying amounts of catalyst (that is, varying space velocities), a limiting quantity of catalyst was reached that depended on other reaction conditions. A further increase in quantity of catalyst (decrease in space velocity) did not influence the yield of liquid hydrocarbons but increased the yield of carbon dioxide and gaseous hydrocarbons. With less than the

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[56] Murata, Y., and Tsuneoka, S. [Benzine Synthesis from Carbon Monoxide and Hydrogen at Ordinary Pressure. XXXIII. Relation of Free Space in the Reaction Tube and the Reaction Rate of the Initial Gas, and Also the Influence of Materials Mixed with the Catalysts]: Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 33, 1937, pp. 313–332. [Benzine Synthesis from Carbon Monoxide and Hydrogen at Ordinary Pressure. XXX. The Influence of Catalyst Concentration]: Jour. Soc. Chem. Ind., vol. 39, 1936, Suppl. binding, pp. 294–298. Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 30, 1936, pp. 40–51.
Murata, Y., Ishikawa, S., and Tsuneoka, S. [Benzine Synthesis from Carbon Monoxide and Hydrogen at Ordinary Pressure. XXXI. The Influence of Current Velocity]: Jour. Soc. Chem. Ind., vol. 39, 1936, Suppl. binding, pp. 325–333. Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 30, 1936, pp. 52–59.
Tsuneoka, S. [Synthesis of Benzine]: Jour. Soc. Chem. Ind., Japan, vol. 37, 1934, Suppl. binding, pp. 738–744.
Tsuneoka, S., and Murata, Y., [Benzine Synthesis from Carbon Monoxide and Hydrogen at Ordinary Pressure. XXIII. The Extraction and Leaching Treatment of Alloy Catalysts]: Jour. Soc. Chem. Ind., Japan, vol. 38, 1935, Suppl. binding, pp. 199–206. [Benzine Synthesis from Carbon Monoxide and Hydrogen at Ordinary Pressure. XXIV. The Influence of the Particle Size and the Hydrogen Treatment or Oxidation Conditions of the Alloy Catalysts]: Jour. Soc. Chem. Ind., Japan, vol. 38, 1935, Suppl. binding, pp. 206–212. [Benzine Synthesis from Carbon Monoxide and Hydrogen at Ordinary Pressure. XXVII. Cobalt Alloy Catalysts]: Jour. Soc. Chem. Ind., Japan, vol. 39, 1936, Suppl. binding, pp. 267–273. Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 30, 1936, pp. 1–14. [Benzine Synthesis from Carbon Monoxide and Hydrogen at Ordinary Pressure. XXVIII. Nickel-Alloy Catalysts]: Jour. Soc. Chem. Ind., Japan, vol. 39, 1936, Suppl. binding, pp. 273–278. Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 30, 1936, pp. 1–14. [Benzine Synthesis from Carbon Monoxide and Hydrogen at Ordinary Pressure. XXXII. Studies on the Material of the Reaction Furnace]: Jour. Soc. Chem. Ind., Japan, vol. 40, No. 11, 1937, Suppl. binding, pp. 438–441. Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 33, 1937, pp. 305–312.
Tsuneoka, S., and Kuroda, R. [Benzine Synthesis from Carbon Monoxide and Hydrogen at Ordinary Pressure. XXXIV. Analytical Studies of Alloy Catalysts]: Jour. Soc. Chem. Ind., Japan, vol. 40, 1937, Suppl. binding, pp. 449–454. Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 33, 1937, pp. 333–338. [Benzine Synthesis from Carbon Monoxide and Hydrogen at Ordinary Pressure. XXXV. Microscopic Study of Alloy Catalysts]: Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 33, 1937, pp. 339–346.

[57] Lelchuk, S. L., Balandin, A. A., and Vaskevich, D. N., [Skeleton Catalysts and Their Application in Organic Chemistry]: Progress of Chemistry (Russia), vol. 14, No. 3, 1945, pp. 185–212. U. O. P. Surv. For. Petrol. Lit., Index April 26, May 3, 1946, 17 pp.

[58] Work cited in footnote 53, p. 30.

limiting amount of catalyst (that is, at higher space velocities) the liquid product was of lower molecular weight and also contained more olefins. With a tube diameter of 8 millimeters, a catalyst bulk density of 10 grams per 18 centimeters of tube length, and a gas input of 4 liters per hour, the best yield obtained with 22 grams of a nickel-cobalt catalyst at 180° C. was 127 cubic centimeters (91 grams) per cubic meter of synthesis gas.

Groombridge and Newns [59] have described a method for preparing cobalt or nickel catalysts by the following technique: The finely divided oxide of nickel or cobalt is sintered at 900° C. with thorium oxide, which upon reduction with water gas at 350° C. forms a porous, nonfriable structure of nickel or cobalt permeated with finely divided thorium oxide.

CONDITIONING OF NICKEL AND COBALT CATALYSTS

Pretreatment of nickel and cobalt with carbon monoxide, resulting in the formation of the carbides, was reported by Elian to increase the hydrocarbon yields by about 45 percent.[60] In one patented process[61] the carbide is produced by heating powdered nickel to 250°–450° C. in the presence of any suitable gas which can furnish carbon, and rapidly cooling the product to low temperatures of −190° C.; then the nickel carbide is mixed with cupric oxide and sintered. More recent information [62] indicates that in operation on a laboratory scale no pretreatment of cobalt catalysts is necessary and that the freshly reduced catalyst may be taken immediately into operation at 190° C. In a commercial plant several procedures have been recommended for preventing an uncontrollable temperature rise in the top layers of catalyst when starting the synthesis. The following techniques have been suggested: (1) Starting the synthesis at a low space velocity;[63] (2) impregnating with liquid synthesis product the catalyst layers which first come in contact with synthesis gas;[64] (3) introducing over the fresh catalyst synthesis gas which is diluted with 40 to 70 percent inerts or consists of "tail" gas from a previous operation;[65] (4) adding steam or ammonia to the synthesis gas during initial operations;[66] (5) carefully oxidizing the carbon dioxide-treated catalyst with air at room temperature, so that the temperature rise does not exceed 7° C.[67]

Pretreatment with hydrogen is not essential for the nickel-cobalt alloy catalyst but appears to be desirable for the nickel catalyst obtained from a nickel–aluminum alloy. The latter catalyst, as well as those obtained from alloys of nickel with silicon, with manganese and silicon, and with iron and aluminum, are markedly inferior to the nickel–cobalt catalyst prepared from a nickel–cobalt–silicon alloy. The catalyst obtained from a nickel–cobalt–magnesium alloy is a very poor one; examination [68] of polished and etched sections under the microscope indicate a much coarser crystal structure for it than for the nickel–cobalt–silicon alloy. Some data on the activity of nickel and cobalt catalysts obtained from nickel–aluminum, cobalt–aluminum, and cobalt–silicon alloys have been presented by Rapoport and Polozhintseva.[69]

REACTIVATION OF COBALT CATALYSTS

Procedures for reactivating the catalyst by removing paraffin have been patented. Among others,[70] periodically increasing the proportion of hydrogen in the synthesis gas from a ratio of $2H_2 + 1CO$ to $2.5H_2 + 1CO$;[71] or flushing with a suitable paraffin-wax solvent such as hydrocarbon oil, at a temperature higher than reaction temperature [72] is recommended. The solvent treatment may be followed by passing hydrogen over the catalyst for about 6 hours at 400°–450° C. at 1,000 cubic meters per hour per square meter cross section of the catalyst chamber.[73]

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[59] Groombridge, W. H., and Newns, J. E., Catalysts: British Patent 507,419, June 9, 1939.

[60] Elian, J. [The Synthesis of Liquid Hydrocarbons by the Induschimie (Carsyn Process)]: Brussels, Aug. 2, 1941. Synthetic Process for Preparing Hydrocarbons, Particularly Gasoline: U. S. Patent 2,369,548, Feb. 13, 1945.

[61] Elian, J. [Synthesis of Hydrocarbons, Particularly Those Corresponding to Gasoline]: Belgian Patent 440,751, Apr. 30, 1941.

Hsiung, S. Y., and Kung, K. M. [A Study on the Synthesis of Liquid Fuels from Carbon Monoxide and Hydrogen]: Jour. Chinese Chem. Soc., vol. 8, 1941, pp. 112–122.

[62] Work cited in footnote 2, p. 20.

[63] Myddleton, W. W., Temperature Control in Effecting Exothermic Catalytic Reactions such as Hydrocarbon Production from Hydrogen and Carbon Monoxide: U. S. Patent 2,255,126, Sept. 9, 1941.

[64] Brabag, No title: German Appl. B–182,388, Mar. 15, 1938. Office of Publication Board Report 412, May 15, 1945.

Sauter, E., [Starting of Contact Catalysts]: German Patent 728,766, Nov. 5, 1942. [Alkalizing Molded Catalysts]: German Patent 738,368, July 8, 1943.

[65] Currie, W. E., Forming Hydrocarbons by Hydrogenation of Carbon Oxides: U. S. Patent 2,209,190, July 23, 1940.

Metallgesellschaft A. G. [Synthesis of Hydrocarbons from Carbon Monoxide and Hydrogen]: French Patent 885,784, Sept. 24, 1943. Hydrocarbons: British Patent 510,513, Aug. 2, 1939. British Patent 510,514, Aug. 2, 1939.

Wagner, A. [Fischer-Tropsch Synthesis]: German Patent 739,569, Aug. 12, 1943.

[66] Brabag, No title: German Appl. B–182,409, Mar. 16, 1938. Office of Publication Board Report 412, May 15, 1945. No title: German Appl. B–182,020, Feb. 19, 1938. Office of Publication Board Report 412, May 15, 1945.

Braune, W., and Schaefer, H. [Synthesizing Hydrocarbons from Carbon Monoxide]: German Patent 710,963, Aug. 21, 1941.

Braunkohle-Benzin A. G. [Improving the Effect of Cobalt Catalyst in Hydrocarbon Synthesis]: German Patent Abridgments, vol. 64, 1943, p. 726.

Schaefer, H., and Lorenz, W. [Raising the Efficiency of Cobalt Catalysts]: German Patent 732,684, Feb. 11, 1943.

[67] Mann, A., and Lorenz, W., [Catalytic Synthesis of Hydrocarbons from Carbon Monoxide and Hydrogen]: German Patent 710,128, July 24, 1941.

[68] Rapoport, I. B., and Polozhintseva, E. [Synthesis of Hydrocarbons from Carbon Monoxide and Hydrogen. II]: Khim. Tverdogo Topliva, vol. 9, 1938, pp. 64–70.

[69] Work cited in footnote 68.

[70] Dreyfus, H., Catalytic Production of Hydrocarbons from Hydrogen and Carbon Monoxide: U. S. Patent 2,231,990, Feb. 18, 1941.

[71] International Hydrocarbon Synthesis Co. [Converting Carbon Monoxide into Hydrocarbons]: French Patent 853,302, Mar. 15, 1940.

Potts, H. E., Conversion of Carbon Monoxide into Hydrocarbons: British Patent 526,465, Sept. 18, 1940.

Sabel, F., Laudenklos, H., Wenzel, W., and Keilig, F., Liquid Hydrocarbons from Carbon Monoxide and Hydrogen: U. S. Patent 2,251,554, Aug. 5, 1941.

[72] Myddleton, W. W., Dewaxing Catalysts Used for Hydrocarbon Synthesis: U. S. Patent 2,259,961, Oct. 21, 1941.

I. G. Farbenindustrie A. G., Converting Carbon Monoxide and Hydrogen into Hydrocarbons: British Patent 516,160, Dec. 22, 1939.

Roelen, O., and Hanisch, F. [Reviving Cobalt Catalysts Used for Synthesizing Benzine]: German Patent 717,693, Feb. 5, 1942.

Brabag, No title: German Appl. B–182,389, Mar. 15, 1938. Office of Publication Board Report 412, May 15, 1945.

Roelen, O., Heckel, H., and Hanisch, F., Reactivation of Catalysts for Hydrogenation of Carbon Monoxide: U. S. Patent 2,289,731, July 14, 1942.

[73] Feisst, W., Roelen, O., and Schuff, W., Synthesis of Multilink Hydrocarbons from Hydrogen and Carbon Monoxide: U. S. 2,369,956, Feb. 20, 1945.

International Hydrocarbon Synthesis Co., Regeneration of Catalysts for the Hydrogenation of Carbon Monoxide: British Patent 533,459, Feb. 13, 1941.

Roelen, O., Heckel, H., and Hanisch, F. [Regenerating Catalysts Used for Synthesizing Benzine]: German Patent 722,706, June 4, 1942.

Roelen, O., and Feisst, W. [Catalytic Conversion of Carbon Monoxide into Higher Hydrocarbons]: German Patent 701,846, Dec. 24, 1940.

Ruhrchemie, A. G., No title: German Appl. R–103,712, Nov. 7, 1938. Office of Publication Board Report 412, May 15, 1945. No title: German Appl. R–103,713. Office of Publication Board Report 412, May 15, 1945. No title: German Appl. R–103,714, Nov. 7, 1938. Office of Publication Board Report 412, May 15, 1945.

RECOVERY OF SPENT COBALT CATALYSTS

One cubic meter per second of steam may be blown over spent catalyst at 300° C., before its removal from the reactor.[74] A process is reported for emptying catalyst tubes by suddenly applying a gas pressure of 5–20 atmospheres after wetting the pressure side of the catalyst bed with a liquid.[75] In recovery of the spent catalyst containing principally cobalt, cobalt oxide, magnesium oxide, thorium oxide, and kieselguhr, all the constituents but the kieselguhr are dissolved by 3 to 5 percent nitric acid. After filtration, the kieselguhr residue is discarded. The filtrate is neutralized with sodium carbonate to a *p*H of 4.2. This precipitates thorium and magnesium carbonates, which are separated from the cobalt nitrate and the calcium nitrate impurity by filtration. The filtrate is treated with sodium fluoride, precipitating calcium fluoride which is separated from the cobalt nitrate mother liquor by filtration. The latter is then ready for the catalyst-preparation plant.

The thorium, magnesium carbonate precipitate is dissolved in sulfuric acid, and upon the addition of a controlled quantity of sodium hydroxide, magnesium and ferric hydroxides are precipitated. These are separated from the thorium solution by filtration. The thorium solution contains a double salt, thorium-sodium sulfate, which upon heating to 80° C. is hydrolyzed, precipitating thorium hydroxide. Alternatively, the addition of potassium sulfate precipitates the double salt, thorium-potassium sulfate, which upon boiling with a concentrated solution of sodium carbonate is converted to thorium bicarbonate. The thorium salt after washing is dissolved in nitric acid and the solution sent to the catalyst preparation plant.[76] [77] [78]

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[74] Baumann, W. [Removing the Catalysts Used for Synthesizing Benzine from the Contact Oven]: German Patent 715,759, Dec. 4, 1941.

Kroepelin, H. [Procedure for Emptying Granular Masses from Reaction Tubes]: German Patent 711,422, Aug. 28, 1941.

Ruhrchemie, A. G., No title: German Appl. R 101,215, Jan. 6, 1938. Office of Publication Board Report 412, May 15, 1945.

[75] Brabag, No title: German Appl. B-184,450, Aug. 27, 1938. Office of Publication Board Report 412, May 15, 1945.

[76] Aldrich, R. C., Manufacture, Regeneration of Fischer-Tropsch Catalyst: Technical Industrial Intelligence Committee Report 30. Nat. Petrol. News, vol. 37, No. 45, R922–924, 1945.

Ruhrchemie A. G., Catalytic Recovery from Spent Catalysts: British Appl. 37,085, 1938. No title: German Appl. R-101,354, Jan. 21, 1938. Offices of Publication Board Report 412, May 15, 1945.

[77] Feisst, W., Roelen, O., and Schuff, W., Synthesis of Multilink Hydrocarbons from Hydrogen and Carbon Monoxide: U. S. APC 414,926, Oct. 14, 1941.

Roelen, O., and Hanisch, F., Cobalt, Recovery from Spent Catalysts: U. S. Patent 2,215,885, Sept. 24, 1940.

Roelen, O., and Feisst, W. [Regenerating Contact Catalysts]: German Patent 705,311, Mar. 20, 1941.

Ruhrchemie A. G., Process for Treatment of Spent Cobalt Catalysts: British Appl. 26,275, 1938. [Metallic Catalysts]: French Patent 842,278, June 8, 1939. No title: German Appl. R-103,371, Sept. 20, 1938. Office of Publication Board Report 412, May 15, 1945.

[78] Braunkohle Benzin A. G., Klein, O., and Meyer, K. [Regeneration of Catalysts]: German Patent 722,533, July 14, 1942.

Buchner, K. [Reclaiming Thorium from Spent Hydrogenation Catalysts]: German Patent 729,059, Nov. 12, 1942. Regeneration of Catalysts Containing Thorium: U. S. Patent 2,278,644, Apr. 7, 1942.

International Hydrocarbon Synthesis Co. [Regneration of Thorium Catalysts]: French Patent 856,933, Aug. 16, 1940.

N. V. Internationale Koolwaterstoffen Synthese Maatschappij, Regeneration of Spent Catalysts in the Synthesis of Hydrocarbons: British Patent 530,036, Dec. 3, 1940.

Ruhrchemie A. G., No title: German Appl. R-102,874, July 1, 1938. Office of Publication Board Report 412, May 15, 1945. No title: German Appl. R 103,507, Oct. 8, 1938. Office of Publication Board Report 412, May 15, 1945. No title: German Appl. R-103,605, Oct. 24, 1938.

ANALYSIS OF COBALT CATALYSTS

Hale[79] has described analytical methods for determination of cobalt and thoria in unreduced Fischer-Tropsch catalysts. The procedure for cobalt involves titration in an ammoniacal solution with potassium ferricyanide. Thorium is precipitated as the iodate which is dissolved and reacted with iodide; the liberated iodine is titrated with sodium thiosulfate.

IRON CATALYSTS

The relatively high cost of cobalt and nickel has prompted continuous research on the development of iron catalysts for the hydrocarbon synthesis.

IRON-COPPER CATALYSTS

Decarriere and Autheaume[80] stated that the Fischer-Tropsch[81] iron–copper catalyst could be improved by using less copper. However, Kodama and Fujimura,[82] who studied iron–copper catalysts with the ratios 1 : 2, 1 : 1, 3 : 1, and 5 : 1, could find little, if any, difference in the catalytic activity of these four mixtures. They found also that an iron–copper (1 : 1) catalyst containing 0.5 percent of alkali was active for a considerably longer time than those containing more alkali.

Fischer and Pichler in a later investigation prepared an iron–copper (4 : 1) catalyst precipitated with sodium carbonate and impregnated with 0.125 percent potassium carbonate. Passing 0.4 liter of $2H_2 + 3CO$ gas over each gram of catalyst at 260° C. and 15 atmospheres pressure, after conditioning for 3 days at 240° C. with $2H_2 + 1CO$ gas at 1 atmosphere pressure, yielded 130 to 150 grams of hydrocarbons per cubic meter of $2H + 3CO$ gas.[83] Active iron catalysts of productivity in the medium-pressure synthesis equal to that of cobalt catalysts resulted from research at the Kaiser Wilhelm Institute. Several reviews have been published[84] on this subject.

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[79] Hale, C. H., Rapid Analysis of Fischer Synthesis Catalyst: Petrol. Refiner, vol. 25, No. 6, 1946, pp. 117–120.

[80] Decarriere, E., and Autheaume, I. [An Iron Catalyst for Hydrogenation of Carbon Dioxide at Ordinary Pressure]: Compt. rend., vol. 196, 1933, pp. 1889–1891.

[81] Work cited in footnote 17, p. 4.

[82] Kodama, S., and Fujimura, K. [The Catalytic Reduction of Carbon Monoxide at Ordinary Pressure VII. The Influence of the Alkali Content on an Iron–Copper Catalyst]: Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 29, 1936, pp. 272–279.

Fujimura, K. [The Catalytic Reduction of Carbon Monoxide at Ordinary Pressure. VIII. The Effect of the Ratio of the Two Metals in Iron–Copper Catalyst]: Sci. Papers Inst. Phys. Chem. Research (Tokyo) vol. 29, 1936, pp. 280–284.

[83] Fischer, F., and Pichler, H. [Process for the Production of Solid Liquid and Easily Liquefied Aliphatic Hydrocarbons from CO and H_2]: German Appl. St. 56,470, July 30, 1937.

[84] Chemical and Engineering News, Fischer Summarizes Wartime Progress in Synthetic Oil Research: Vol. 22, 1944, p. 391.

Dewey, D. R. [Hydrocarbon Syntheses. Wartime Work of the Kaiser Wilhelm Institutut für Kohlenforschung]: Ind. Chemist, vol. 21, 1945, pp. 681–683. Office of Publication Board Report 289, June 1945, 6 pp.

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Hirschkind, W., and Lowdermilk, F. R., Fischer-Tropsch and Allied Processes: Combined Intelligence Objectives Subcommittee Reports 22 and 30, 27/82, July 1945, 24 pp.

The Industrial Chemist and Chemical Manufacturer, Thirty Years of Franz Fischer's Work: Vol. 20, 1944, pp. 257–259.

Petroleum Times, New Synthetic Oil Processes in Germany: Vol. 48, 1944, p. 28.

Tahara and his coworkers [85] have also reported higher liquid-hydrocarbon yields at medium pressure (10 atmospheres) than at atmospheric pressure.

According to several Metallgesellschaft patents [86] the life of iron catalysts for the medium-pressure synthesis was increased by adding 2 to 30 percent of water glass (calculated as alkali carbonate based on the weight of iron) to the iron solution during precipitation. The catalyst also contained up to 25 percent of copper, with kieselguhr as carrier. Passage over the reduced catalyst of less than 100 liters of synthesis gas ($1H_2 + 1CO$) per liter of catalyst per hour at 200°-250° C. yielded up to 155 grams of hydrocarbons per cubic meter of synthesis gas, 64 percent of which was paraffin wax.

Ghosh and Sen [87] prepared some iron-copper catalysts containing 0.5 percent potassium carbonate and small amounts of nickel and rare-earth oxides by impregnation of such quantities of asbestos with the metal nitrates that 50 percent of asbestos was present in the final catalyst. Passing 0.65 liter of synthesis gas per hour over 5 grams of each catalyst yielded 30 grams of liquid hydrocarbons per cubic meter for Fe-Cu-Ni, 4 : 1 : 0.01; 45 grams for Fe-Cu-Ni, 4 : 1 : 0.02; and 80 grams for Fe-Cu-Ni-CeO_2-ThO_2, 4 : 1 : 0.05 : 0.001 : 0.006.

More recently Chao and coworkers [88] have reported satisfactory yields from an iron-copper (5 : 1) -kieselguhr-potassium carbonate catalyst operated at 240° C. Tsuneoka and his coworkers [89] and Kita[90] have also studied the preparation of iron-copper catalysts. Two catalysts, the one containing iron, copper, kieselguhr, and potassium carbonate in the ratio 4 : 1 : 5 : 0.08, and the other 0.08 part of manganese in addition to the same constituents as in the former catalyst, were prepared by Tsuneoka by mixing solutions of the nitrates with unpurified kieselguhr and precipitating with a solution of an equivalent amount of alkali carbonate. The precipitate, after filtration and washing, was impregnated with a small amount of potassium carbonate, air-dried at 100° C., and pulverized. The yields were 83 and 88 cubic centimeters of liquid hydrocarbons, respectively, per cubic meter of a gas containing equal parts of hydrogen and carbon monoxide when 3.8 liters per hour per 4 grams of iron was employed at 250° C.

A catalyst similar to the second one but containing 0.08 part rubidium carbonate instead of potassium carbonate resulted in a yield of 90 cubic centimeters per cubic meter. When 3 percent aluminum oxide was added to the iron-copper-kieselguhr-manganese-potassium hydroxide catalyst after precipitation, the hydrocarbon yield was increased to 94 cubic centimeters per cubic meter. The oxygen appeared entirely as carbon dioxide rather than as water, which is the main oxygen-containing product of cobalt and nickel catalysts. Kita's catalyst contained iron, copper, kieselguhr, manganese, and boric acid in the ratio 4 : 1 : 5 : 0.08 : 0.08 and an indeterminate quantity of alkali as potassium carbonate and hydroxide. The optimum amounts of copper and potassium carbonate for this catalyst were found to be 20 to 40 percent and 2 to 3 percent, respectively. The addition of 5 percent of nickel or cobalt enhanced the activity for $2H_2 + 1CO$ synthesis but was undesirable for gas containing equal parts of hydrogen and carbon monoxide. Formation of water was observed when the catalyst contained more than 2.5 percent of nickel. The addition of thoria, urania, etc., to an iron catalyst containing 10 percent of nickel did not appreciably affect its activity.

Eidus and coworkers [91] [92] studied a series of catalysts containing iron, copper, thorium dioxide, potassium carbonate, and kieselguhr in the ratio 4 : 1 : 0.08 : 0.08 : 5. The reactor, a glass tube 10 millimeters in diameter, fitted with three-way stopcocks at both ends so that the tube could be closed to the system but open to a connected manometer, was charged with a layer of catalyst 2 centimeters long in some experiments and 40 centimeters long in others. During the experiments with synthesis gas containing $1H_2 + 1CO$ or $3H_2 + 1CO_2$ at 258° C., measurements could be taken under static or dynamic conditions. It was found that no catalytic hydrogenation of carbon dioxide took place under the conditions of the experiments. Further, only those catalysts were active in the hydrogenation of carbon monoxide that contained both iron and copper and either thorium

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[85] Tahara, H., Sawade, Y., and Komiyama, D. [The Catalytic Reaction of Carbon Monoxide and Hydrogen Under High Pressure. II. The Influence of High Pressure on the Iron Catalyst Employed in the Synthesis of Benzine]: Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 38, 1941, pp. 184-195. Jour. Soc. Chem. Ind., Japan, vol. 44, 1941, Suppl. binding, pp. 77-82B.

[86] Herbert W., Schall, A., and Gross, H. W. [Catalyst for Hydrogenation of CO]: German Patent 736, 977, May 27, 1943.

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[87] Ghosh, J. C., and Sen, S. [Synthesis of Higher Paraffins from Water Gas.Use of Promoters for Activating Iron-Copper Catalyst.]: Jour. Indian Chem. Soc., vol. 12, 1935, pp. 53-62.

[88] Chao, T. Y., Hsu, W. W., and Wen, C. [A Study of Iron Catalysts for the Synthesis of Liquid Fuels from Carbon Monoxide and Hydrogen]: Jour. Chinese Chem. Soc., vol. 12, 1945, pp. 1-14.

[89] Makino, S., Koide, H., and Murata, Y. [The Benzine Synthesis from Carbon Monoxide and Hydrogen, LIII. Influence of Aluminum Oxide, Silver and Other Addition Agents Upon the Iron Catalysts]: Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 37, 1940, pp. 350-365. Jour. Soc. Chem. Ind., Japan, vol. 43, 1940, Suppl. binding, pp. 235-241.

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Tsuneoka, S., Murata, Y., and Makino, S. [Production of Synthetic Gasoline from Carbon Monoxide and Hydrogen at Ordinary Pressure. XLVI. Preparation of New Iron Catalysts and Their Superior properties]: Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 35, 1939, pp. 330-336. Jour. Soc. Chem. Ind., Japan, vol. 42, 1939, Suppl. binding, pp. 107-114. [Production of Synthetic Gasoline from Carbon Monoxide and Hydrogen at Ordinary Pressure. XLVII. Composition of Starting Gases with New Iron Catalyst]: Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 35, 1939, pp. 337-347.

[90] Kita, G., Method of Preparing an Iron Catalyst in Synthesizing Gasoline: U. S. APC SN272,175, May 6, 1939. Iron Catalyst for Synthesizing Gasoline and Method of Preparing Same. U. S. APC SN301,-721, May 4, 1941. Catalyst for the Production of Gasoline: British Patent 529,390, Nov. 20, 1940.

The Chemical Trade Journal and Chemical Engineer, Iron Catalyst: Vol. 108, 1941, p. 8.

[91] Eidus, Y. T. [Catalysts for Hydrogenation of CO by Joint Application of the Dynamic and Static Methods. I. Activity of the Complex Fe-Cu-ThO_2-K_2CO_3 Kieselguhr Catalyst]: Bull. Acad. Sci. U. R. S. S., Classe Sci. Chim., 1944, pp. 255-262. Universal Oil Products Company Surv. For. Petrol. Lit., Transl. 492A.

Eidus, Y. T., and Altshuller, S. B. [Investigation of Catalysts for Hydrogenation of CO by Simultaneous Use of the Dynamic and Static Methods. II. Activity of Catalysts Containing Various Components of the Catalyst Iron-Copper-Thorium Dioxide-Potassium Carbonate-Kieselguhr]: Bull. Acad. Sci. U. R. S. S., Classe Sci. Chim., 1944, pp. 349-357. Universal Oil Products Company Surv. For. Petrol. Lit., Transl. 507, May 1945.

[92] Eidus, Y. T., and Elagina, N. V. [Activity and Stability of Fe-Cu-ThO_2-K_2CO_3 Catalyst in the Synthesis of Liquid Hydrocarbons from CO-H Mixtures as Influenced by Composition of the Catalyst and the Nature of the Carrier]: Bull. Acad. Sci. U. R. S. S., Classe Sci. Chim., 1943, pp. 305-311.

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Eidus, Y. T., et al. [The Activating Effect of Oxides of Some Metals on the Iron-Copper Contacts Used for Synthesis of Gasoline from Water Gas]: Bull. Acad. Sci. U. R. S. S., Classe Sci. Chim., 1943, pp. 145-151. Universal Oil Products Company Surv. For. Petrol. Lit., Transl. 441.

dioxide or potassium carbonate, addition of the second promotor producing a sharp rise in activity. Catalysts containing manganese oxide in addition to the constituents mentioned above were the most active of those tested, yielding 80 cubic centimeters of liquid plus solid hydro-carbons per cubic meter of starting gas.

SINTERED-IRON CATALYSTS

It has been reported that partial sintering of precipitated iron and iron–alumina catalysts by reduction at 850° C. enhances their activity for the synthesis of olefinic liquid hydrocarbons.[93][94]

Avdeeva and Troitskii [95] recommended fusion of metallic iron or magnetic ore with potash or alumina or other activators in a stream of oxygen. Just before the melt solidified, a powder of the same composition, made under the same conditions, was added. Similarly prepared cobalt or nickel catalysts also were recommended. The production of catalysts of the iron group by decomposition of a carbonyl compound of the metal at a temperature above 500° C. but below the melting point of the metal, and for such a length of time as produces at least partial sintering of the metal[96] has been recommended. Thus, for example, iron powder obtained by thermal decomposition of iron carbonyl was then treated with 1 to 1.5 percent sodium borate, compressed into pills, and heated at 850° C. in the presence of hydrogen for 4 hours, whereby the pills became partly sintered. With $1.2H_2 + 1CO$ gas at 330° C. and 15 atmospheres pressure, a yield of 130 grams of liquid and solid hydrocarbons per cubic meter was obtained, with only minor amounts of oxygenated compounds.[97]

EFFECT OF ALKALI ADDITION IN PRECIPITATED-IRON CATALYSTS

Addition of small amounts of alkali to precipitated-iron catalysts has no important effect on the total yield of product; but it does influence the distribution, resulting in an increase in paraffins and oxygen-containing products and a decrease in the liquid and gasol hydrocarbons with increasing alkali content. A low alkali content, less than 1 percent of potassium carbonate, enhances the durability of the catalyst.[98][99][1] Alkalization of cobalt–thoria–kieselguhr catalyst with 0.25 to 2 percent of sodium carbonate and 0.5 to 1 percent potassium carbonate increased the yield of solid paraffins in the fraction boiling above 300° C. by 50 percent. Synthesis gas was passed over the catalyst at the rate of 0.4 liter per hour per gram at atmospheric pressure and temperatures of 190° to 200° C.[2]

CONDITIONING OF IRON CATALYSTS

Pretreatment of iron catalysts with carbon monoxide increases their longevity and productivity considerably. Four-tenths liter of carbon monoxide or carbon monoxide-rich mixtures per hour per gram of iron is passed at 1/10 atmosphere and 325° C. for 25 hours over a catalyst precipitated from ferric nitrate solution by sodium carbonate and containing 0.125 percent of potassium carbonate. Synthesis with $1H_2+1.8CO$ mixture at the same space velocity, 15 atmospheres pressure, and a temperature of 235° C. resulted in yields of solid, liquid, and gasol (C_3+C_4) hydrocarbons of 150 grams (40 grams of this constituted gasol hydrocarbons) per normal cubic meter of synthesis gas without any decrease in catalyst activity in 3 months of operation.[3][4]

RUTHENIUM CATALYSTS

Ruthenium powder itself and a mixture thereof with 2 percent potassium carbonate has been tested as catalyst for the Fischer-Tropsch hydrocarbon synthesis. Liquid hydrocarbons were obtained at atmospheric pressure,[5] and at about 90 atmospheres the product was mainly solid paraffins.[6] At atmospheric pressure the yield of hydrocarbons was very low, but at the higher pressure 120 grams of 80–90 percent solid paraffin plus 10–20 percent oil were obtained. The use of ruthenium catalysts at pressures up to 1,000 atmospheres will be described in a later section of this chapter.

EFFECT OF CARRIER ON CATALYSTS

Some attention has been given to the selection of suitable refractory supports for precipitated catalysts and for catalysts prepared by

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[93] Work cited in footnote 8, p. 22.

[94] I. G. Farbenindustrie A. G., Hydrocarbons, etc.: British Patent 473,932, Oct. 22, 1937. Hydrocarbons and Their Oxygen-Containing Derivatives: British Patent 474,448, Oct. 26, 1937. Hydrocarbons and Oxygen-Containing Derivatives Thereof: British Patent 496,880, Dec. 5, 1938. [Catalytic Synthesis of Hydrocarbons]: French Patent 841,030, May 9, 1939.
Linckh, E., Hydrocarbons from Hydrogen and Carbon Monoxide: U. S. Patent 2,287,891, June 30, 1942.
Michael, W., Hydrocarbons from Carbon Monoxide and Hydrogen: U. S. Patent 2,254,806, Sept. 2, 1941.
Michael, W., and Jaeckh, W., Hydrogenating Carbon Monoxide: U. S. Patent 2,211,022, Aug. 13, 1940. Hydrocarbons from Carbon Monoxide and Hydrogen: U. S. Patent 2,254,748, Sept. 2, 1941. U. S. Patent 2,183,145, Dec. 12, 1939.

[95] Avdeeva, A. V. [Methane]: Russian Patent 53,249, May 31, 1938.
I. G. Farbenindustrie A. G. [Hydrocarbons and Their Oxygen-Containing Derivatives from Carbon Monoxide and Hydrogen]: German Patent 708,512, June 12, 1941.
Troitskii, K. W. [Catalyst for CO–H_2 Synthesis]: Russian Patent 54,392, Jan. 31, 1939. Oel u. Kohle, vol. 36, 1940, p. 73.

[96] I. G. Farbenindustrie A. G., Catalyst: British Patent 490,090, Aug. 9, 1938.
Linckh, E., Hydrocarbons from Carbon Monoxide and Hydrogen: U. S. Patent 2,234,568, Mar. 11, 1941.
Michael, W., and Jaeckh, W., Hydrocarbons from Carbon Monoxide and Hydrogen: U. S. Patent 2,183,146, Dec. 12, 1939.

[97] International Hydrocarbon Synthesis Co. [Hydrocarbons from Water Gas]: Italian Patent 370,250, Dec. 14, 1939.
No inventor given, Catalyst for Synthesis of Hydrocarbons from Water Gas: U. S. APC TC 1,190, OZ 11,220, Dec. 18, 1938. German Appl. I–63,257.

[98] Work cited in footnote 83, p. 35.

[99] Leva, M., Translation of German Documents on the Development of Iron Catalysts for the Fischer-Tropsch Synthesis, Part I. (Technical Oil Mission Reel 101, Document PG–21574–NID, Iron Catalysts for the Middle-Pressure Synthesis by Dr. H. Pichler, Sept. 9, 1940): Office of Synthetic Liquid Fuels Report, Pittsburgh, 1947, pp. 49–67.

[1] Fischer, F., and Pichler, H. [Process for Producing Iron Catalysts]: German Appl. St. 60,795, May 23, 1941. Technical Oil Mission Reel 100, Item 20,581.

[2] Koch, H., and Billig, R. [Investigation of the Solid Paraffin Hydrocarbons Produced in the Benzine Synthesis of Franz Fischer and Tropsch (Atmospheric Pressure Synthesis)]: Brennstoff Chem., vol. 21, 1940, pp. 157–167, 169–177.

[3] Work cited in footnote 99, p. 39.

[4] Fischer, F., and Pichler, H. [Process for the Production of Higher Hydrocarbons from Carbon Monoxide and Hydrogen Under Increased Pressure]: German Patent 738,091, July 1, 1943. Technical Oil Mission Reel 100, Item 20,578. [Process for the Production of Solid, Liquid, and Easily Liquefiable Aliphatic Hydrocarbons from Carbon Monoxide and Hydrogen]: German Appl. ST–61,859, May 5, 1942. Technical Oil Mission Reel 100, Item 20,581. [Process for the Production of Hydrocarbons from Carbon Monoxide and Hydrogen]: German Appl. ST–56,856, Nov. 25, 1937. Technical Oil Mission Reel 100, Item 20,579. Hydrocarbons from Gases Containing Carbon Monoxide and Hydrogen: U. S. Patent 2,257,457, Sept. 30, 1941. [Process for the Production of Hydrocarbons from Carbon Monoxide and Hydrogen]: German Appl. ST–60,409, Jan. 22, 1941. Technical Oil Mission Reel 100, Item 20,577.

[5] Fischer, F., Bahr, T., and Meusel, A. [Catalytic Reduction of Carbon Dioxide to Methane and Higher Hydrocarbons at Ordinary Pressure. Preliminary Communication]: Brennstoff Chem., vol. 16, 1935, pp. 466–469.

[6] Fischer, F., Pichler, H., and Lohmar, W. [Synthesis of Kogasin and Paraffins in the Aqueous Phase]: Brennstoff Chem., vol. 20, 1939, pp. 247–250.

impregnation of the support with a solution of nitrates and subsequent roasting.[7]

The Fuel Research Station [8] has studied the effect of the carrier on carbon deposition on nickel-thorium dioxide-magnesium oxide-kieselguhr catalysts and has concluded that a kieselguhr with low specific surface area promotes the most rapid carbon deposition.

In addition to kieselguhr and asbestos mentioned above, magnesium carbonate[9] and several other compounds, namely, barium sulfate, silicon carbide, chromium oxide, aluminum oxide, and silicates,[10] have been recommended.

A catalyst containing 1 part cobalt, 1 to 2 parts aluminum oxide, and 0.1 to 0.15 part zinc oxide is reported to yield 135 grams of oil (70 percent of which boils above 320° C.) per cubic meter of synthesis gas, when the aluminum oxide has previously been heated for 6 hours at 850° to 1,000° C. If untreated aluminum oxide is used, the yield is 30 grams of oil, of which 50 percent boils above 320° C.[11] Ruhrchemie suggested purification of kieselguhr by leaching with hydrochloric or nitric acid to remove inorganic impurities and subsequently calcining below the sintering temperature to remove organic matter and reduce the solubility of the carrier during precipitation of the catalyst.[12] Ruhrchemie also suggested heating certain carrier materials to incandescence so as to reduce their solubility in any acid reagents that might be employed for catalyst regeneration.[13] A silica gel obtained by allowing a homogeneous solution at a pH of 3 to 4.5 to solidify and drying at 200° to 300° C. was impregnated with cobalt and aluminum nitrates and potassium carbonate in solution.[14] Passing 1.3 liters of synthesis gas per hour per gram of cobalt over the catalyst yielded 100 grams per cubic meter.

EFFECT OF SULFUR COMPOUNDS ON CATALYST ACTIVITY

All catalysts used in the synthesis of higher hydrocarbons from hydrogen and carbon monoxide are very readily poisoned by sulfur compounds. Thus, the activity of nickel–manganese–thoria and nickel–manganese–kieselguhr catalysts was reduced 50 percent by 17 and 35 milligrams, respectively, of hydrogen sulfide per gram of nickel. The reported tolerance for carbon bisulfide of the same catalysts is much larger than that for hydrogen sulfide.[15] A similar report of a large tolerance for organic sulfur as compared with hydrogen sulfide was given by King [16] for cobalt–thoria kieselguhr (100:18:100) catalyst.

King stated:

> In our experiments, carbon disulfide was added to the process gas over a period of four days to an extent corresponding to 33 milligrams of sulfur per cubic centimeter of catalyst. The catalyst continued to synthesize oil at a high degree of conversion, but in order to maintain the efficiency it was necessary to raise the temperature progressively from 185° to 210° C. With the space velocity used (190 volumes per volume per hour) the degree of fouling corresponds to about 10 years' working at the concentration of sulfur (0.2 grams per cubic meter) usually accepted as the highest permissible.

Fujimura and his coworkers [17] reported also that the initial effect of small amounts of hydrogen sulfide was to increase the catalyst (nickel–manganese) activity. This was confirmed by Herington and Woodward [18] for cobalt–thoria–kieselguhr (100 : 18 : 100) catalysts. Hydrogen sulfide was mixed with the synthesis gas in small measured batches. No hydrogen sulfide was eliminated in the off-gas during the course of the sulfur-poisoning experiments. The results are given in table 3.

TABLE 3.—*Effect of hydrogen sulfide on yield*

Amount of sulfur added, milligrams per gram of catalyst	Catalyst temperature, ° C.	Ratio of hydrocarbon yield to corresponding yield before addition of sulfur	
		Condensed oil	Hydrocarbons in off-gas, $C_{1.7}H_{5.7}$
0.00	183	1.0	1.0
0.67	183	2.3	1.0
3.50	183	2.1	.8
7.94	183		.5
7.94	195	2.0	1.3
13.4	195	1.5	
33.5	207	1.2	2.1

The first additions of sulfur caused a marked increase in the yield of liquid hydrocarbons at constant reaction temperature. There was, however, an immediate falling off in the yield of gaseous hydrocarbons. The total hydrocarbon yield increased until more than 8.0 milligrams of sulfur had been added to each gram of catalyst. Further additions of hydrogen sulfide caused a drop in total hydrocarbon yield; but, as shown in table 3, this could be offset by raising the reaction temperature rather more rapidly than would normally be necessary in the absence of hydrogen sulfide. The higher temperatures favor the production of lighter hydrocarbons; but even so, after the addition of as much as 33.5 milligrams of sulfur per gram of catalyst, the yield of liquid hydrocarbons was still 20 percent greater

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[7] Eidus, Y. T., Kazanskii, B. A., and Zelinskii, N. D. [The Influence of the Type of Carrier on the Synthesis of Liquid Hydrocarbons over Ni-MnO-Al_2O_3 Catalysts at Atmospheric Pressure]: Bull. Acad. Sci. U. R. S. S. Classe Sci. Chim., 1941, pp. 27-33. Universal Oil Products Co. Survey For. Petrol. Lit., Transl. 325-B.

[8] Great Britain Gas Research Board, Synthesis of Methane: 6th Ann. Rept., 1944–45, pp. 18–32.

[9] Ruhrchemie A. G., Catalysts for Benzine Synthesis: British Patent 498,007, Dec. 28, 1938. Process for Producing Catalysts for the Synthesis of Hydrocarbons: British Patent 518,334, Feb. 23, 1940. Catalysts for Benzine Synthesis: British Appl. 31,293, 1938.

[10] Ruhrchemie A. G. [Synthesis of Gasoline]: French Patent 819,701, Oct. 26, 1937. No inventor given [Process for Making Salt-Containing Colloidal Solutions of Metal Hydroxides]: U. S. APC TC 1,204, OZ 11,158, German Appl. I-62,993.

[11] No inventor given [Preferred Form of Alumina as Carrier for Fischer-Tropsch Catalysts]: U. S. APC TC 1,188, OZ 12,177, May 30, 1940, German Appl. I-67,099.

[12] International Hydrocarbon Synthesis Co., Hydrocarbons Containing More Than 1 Carbon Atom: British Patent 536,767, May 27, 1941. [Hydrocarbons by Conversion of Carbon Monoxide with Hydrogen in the Presence of Catalysts]: Netherlands Patent 50,858, Sept. 15, 1941. Ruhrchemie A. G., No title: German Appl. R-103,980, Dec. 6, 1938. Office of Publication Board Report 412, May 15, 1945. Roelen, O., and Feisst, W., Synthesizing Hydrocarbons from Carbon Monoxide and Hydrogen: U. S. Patent 2,261,184, Nov. 4, 1941.

[13] Ruhrchemie A. G., Catalyst: British Patent 500,182, Feb. 1, 1939.

[14] Stoewener, F., Kaunecke, E., and Becke, F., Catalytic Reactions with Carbonaceous Materials: U. S. Patent APC 389,039, Apr. 17, 1941.

[15] Fujimura, K., Tsuneoka, S., and Kawamichi, K. [Synthesis of Benzine from Carbon Monoxide and Hydrogen Under Ordinary Pressure]: Jour. Soc. Chem. Ind., Japan, vol. 37, 1934, Suppl. binding, pp. 395-400.

[16] Work cited in footnote 86, p. 16.

[17] Work cited in footnote 15, p. 41.

[18] Herington, E. F. G., and Woodward, L. A., Experiments in the Fischer-Tropsch Synthesis of Hydrocarbons from Carbon Monoxide and Hydrogen: Trans. Faraday Soc., vol. 35, 1939, pp. 958–966.

than before the addition of sulfur. Further additions of sulfur resulted in a continuous decrease in activity until complete poisoning was reached.

PRESSURE, DILUENTS, HYDROGEN: CARBON MONOXIDE RATIO, THROUGHPUT, TEMPERATURE, ADSORPTION, AND PROBABLE REACTION MECHANISM

EFFECT OF PRESSURE

The earlier work of Fischer and his coworkers showed that high pressure favors the formation of "Synthol" and of high-molecular-weight hydrocarbons and reduces the yield of liquid hydrocarbons per cubic meter of synthesis gas.[19]

A detailed study of the effect of pressures above atmospheric was made by Fischer and Pichler[20] in 1939. As the pressure was increased above atmospheric, the yield at first increased and then (above 5 atmospheres) decreased. Table 4 shows the results with a Co-ThO_2–kieselguhr catalyst when 1 liter per hour of synthesis gas was used per gram of cobalt. The data are averages for 4 weeks' operation. Only a single pass of the gas through the catalyst was made, and no catalyst regenerating was done.

TABLE 4.—*Effect of pressures above atmospheric*

[Yield data in grams per cubic meter of synthesis gas]

Pressure, atmospheres	Total yield of solid and liquid hydrocarbons	Paraffin wax	Oil boiling above 200° C.	Gasoline boiling below 200° C.	Gaseous hydrocarbons, including C_3 and C_4
1.0	117	10	38	69	38
1.5	131	15	43	73	50
5.0	150	60	51	39	33
15.0	145	70	36	39	33
50.0	138	54	37	47	21
150.0	104	27	34	43	31

Martin[21] presented similar data on the effect of pressure on the total and fractional yields when two-stage operation is employed. In Fischer and Pichler's data[22] the total yield of solid plus liquid hydrocarbons showed a minimum drop with time for reaction pressures of 5 to 15 atmospheres. At these pressures the initial yield was more than 150 grams per cubic meter and was still more than 100 grams per cubic meter after 26 weeks of operation. At atmospheric pressure the yield dropped from 130 grams to 100 grams per cubic meter in only 4 weeks of operation. At 150 atmospheres the drop in yield with time was very rapid. At such pressures there was a noticeable formation of cobalt carbonyl and consequent loss of activity of the catalyst; nickel catalysts deteriorated even more rapidly.

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[19] Fischer, F., and Kuster, H. [The Influence of Pressure and Temperature Upon the Synthesis of Benzine and Synthol in Liquid Medium]: Brennstoff Chem., vol. 14, 1933, pp. 3-8.

[20] Fischer, F., and Pichler, H. [The Synthesis of Paraffin from Carbon Monoxide and Hydrogen Upon Cobalt Catalysts (Medium-Pressure Synthesis)]: Brennstoff Chem., vol. 20, 1939, pp. 41-48.

[21] Martin, F. [The Development of the Synthesis of Hydrocarbons from Water Gas]: Chem. Fabrik, vol. 12, 1939, pp. 233-240.

[22] Work cited in footnote 20, p. 42.

The slower drop in activity of the catalyst at medium pressures was shown also by the smaller temperature increase required to maintain maximum activity. Increasing time of operation was associated with a gradual drop in catalytic activity, presumably owing to the accumulation of solid hydrocarbons on the catalyst. This reduction could be partly compensated by raising the temperature at which the reaction was carried out. In the experiments at 5 to 15 atmospheres the initial temperatures of 175° to 180° C. were not raised to 195° C., even after 6 months' operation. At 1 atmosphere the temperature had to be raised from the initial value of 180° C. to 195° C. after 5 weeks. The rate of temperature increase necessary to maintain activity was less if the paraffin was periodically removed from the catalyst by solvent extraction or by destructive distillation in a stream of hydrogen.[23] [24] [25] [26] The advantages of intermediate pressures for the hydrocarbon synthesis are claimed in several patents.[23] [27]

The effect of pressures up to 100 atmospheres on the synthesis of hydrocarbons on a ruthenium catalyst was studied by Fischer and Pichler,[28] [29] and by Pichler,[30] and up to 1,000 atmospheres by Pichler and Buffleb.[30] The results obtained in experiments at pressures from 15 to 1,000 atmospheres and at a temperature of 180° C. are shown in figure 3. Three grams of ruthenium catalyst were used, and a flow of synthesis gas was so adjusted that 1 liter of effluent gas was obtained per hour. Under these conditions the conversion to hydrocarbons increased rapidly with increasing pressure up to about 300 atmospheres and more slowly above this pressure. At all pressures, solid paraffinic hydrocarbons constituted about 60 percent of the total yield of liquid plus solid hydrocarbons. The fraction of gaseous hydrocarbons in the products was approximately 25 percent for all pressures. Yields remained constant over 200 days' operation at 195° C. and 100 atmospheres and thereafter slowly diminished. After 560 days, when the temperature had been raised to 215° C., the yield was 140 grams per cubic meter, only 10 percent below the initial value.

A French patent[31] claims that, of the 120-gram yield obtained from a cobalt-manganese catalyst operated at 165° to 180° C. and 5 to 50 atmospheres pressure, 80 percent was solid paraffin. The Ruhrchemie claimed[32] that production of high-molecular-weight hydrocarbons could be increased by passing through the reactor 0.4 liter of synthesis gas per hour per gram of catalyst, at 160° to 180° C.

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[23] Work cited in footnote 65, p. 32.

[24] Work cited in footnote 66, p. 32.

[25] Work cited in footnote 67, p. 33.

[26] Work cited in footnote 68, p. 33.

[27] Metallgesellschaft A. G., Hydrocarbons: British Patent 510,350, July 31, 1939.

[28] Work cited in footnote 6, p. 39.

[29] Fischer, F., and Pichler, H. [Process for the Production of Solid Aliphatic Hydrocarbons]: German Patent 705,528, Mar. 27, 1941, Technical Oil Mission Reel 100, Item 20,582.

Pichler, H. [The Discovery and Synthesis of New Paraffins of Very High Molecular Weight]: Brennstoff Chem., vol. 19, 1938, pp. 226–230.

Pichler, H., and Buffleb, H. [Synthesis of Paraffin Wax on Ruthenium Catalysts at Pressures Up to 100 Atmospheres]: Brennstoff Chem., vol. 21, 1940, pp. 257–264. [Behavior of Ruthenium Catalysts in Synthesis of Paraffin Hydrocarbons of High Molecular Weight]: Brennstoff Chem., vol. 21, 1940, pp. 273-280.

[30] Work cited in footnote 29, this page.

[31] International Hydrocarbon Synthesis Co. [Synthesis of Hydrocarbons from CO and H_2]: French Patent 871,909, May 22, 1942.

[32] Ruhrchemie A. G., No title: German Appl. R–105,297, May 24, 1939. Office of Publication Board Report 412, May 15, 1945.

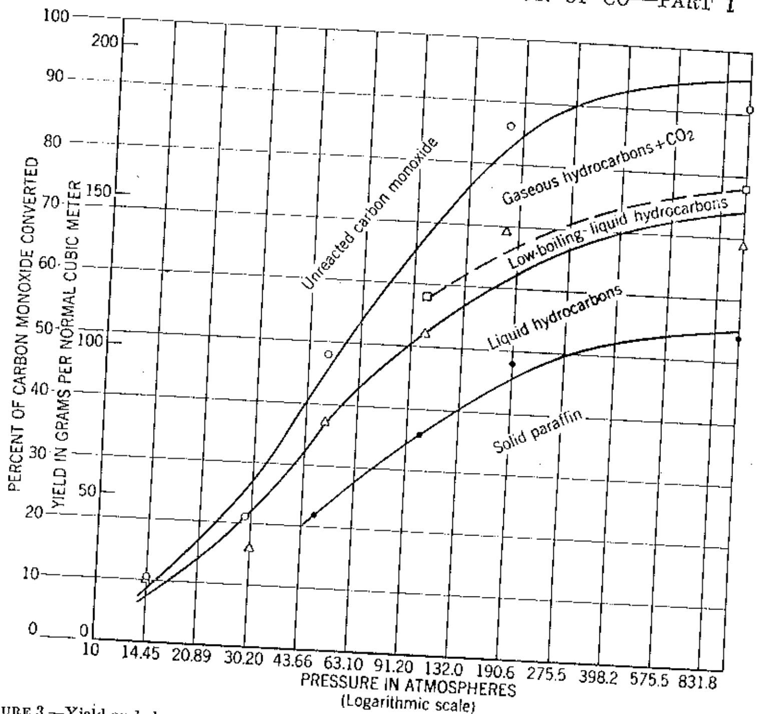

FIGURE 3.—Yield and character of products at 180° C. and various pressures, with ruthenium catalyst.

and 10 to 20 atmospheres pressure. A preparation containing 100 grams of cobalt per liter of catalyst and uncalcined magnesia or low-density kieselguhr as the carrier is recommended.

Pressures lower than atmospheric necessitated proportionately greater amounts of catalyst for equal conversion to hydrocarbons, although the average molecular weight and chemical composition of the product were unaffected by the reduced pressure.[33] This effect of pressures below 1 atmosphere is somewhat difficult to understand, as subsequent experiments with nickel–manganese–aluminum catalysts by Myddleton and Walker[34] showed that dilution of a mixture of $1H_2 + 1CO$ with inert gases such as nitrogen somewhat increased the yield per cubic meter of synthesis gas. It is possible that the slow step in the reaction is the desorption of the products and that the rate of such desorption is directly proportional to the total gas pressure; this would be true if desorption due to molecular bombardment from the gas phase was very much more rapid than that due to energy transfer from the catalyst. Weller[35] reported that in the range 300 to 700 millimeters of mercury the reaction rate of $2H_2 + 1CO$ on a cobalt–thoria–magnesia–kieselguhr catalyst is proportional to the 0.45 power of the pressure.

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[33] Fischer, F., and Pichler, H. [The Influence of Pressure Upon Several Conversions of Water Gas]: Brennstoff Chem., vol. 12, 1931, pp. 365–372.

[34] Myddleton, W. W., and Walker, J., The Production of Hydrocarbon Oils from Industrial Gases. II.: Jour. Soc. Chem. Ind., vol. 55, 1936, pp. 121–124T.

[35] Weller, S. [Kinetics of Carbiding and Hydrocarbon Synthesis with Cobalt Fischer-Tropsch Catalysts]: Jour. Am. Chem. Soc., vol. 69, 1947, pp. 2432–2436.

EFFECT OF DILUENTS

Tsuneoka and Fujimura[36] obtained data on the effect of diluents, particularly nitrogen, methane, and carbon dioxide, using a nickel–manganese–thoria catalyst. They found that gaseous mixtures containing less than 20 percent of these gases had no deleterious effect on the reaction. Lower yields, however, were obtained with 40 percent of nitrogen. Carbon dioxide was more effective than either nitrogen or methane in reducing the yield. With gradual dilution of the initial gas containing 2 parts of hydrogen and 1 part of carbon monoxide, the molecular weight of the liquid hydrocarbon product decreased.

Murata and Yamada[37] studied the effect of diluents in the initial gas on an iron–copper–kieselguhr catalyst. Their data confirmed those of Tsuneoka and Fujimura and should be compared with the results obtained by Fischer and Pichler,[38] Appleyard,[39] and Eidus[40] with various nickel, cobalt, and iron catalysts. They reported that, whereas the presence of carbon monoxide in a H_2–CO_2 mixture retarded the catalytic hydrogenation, the presence of carbon dioxide in a H_2–CO mixture exerted no influence on the yield of liquid hydrocarbons. It should be noted however, that in the former instance no liquid plus solid hydrocarbons were formed. No explanation of these conflicting reports concerning the effect of dilution with carbon dioxide is apparent.

HYDROGEN : CARBON MONOXIDE RATIO

The effect of decreasing the hydrogen : carbon monoxide ratio is to produce more olefins and more carbon dioxide[41] and to favor carbon deposition.[42] Herbert[43] claims that CO-rich synthesis gas produces high yields of antiknock gasoline. A large excess of hydrogen produces a saturated product and favors methane formation. The percentage of olefins decreases in the order iron, cobalt, nickel (60, 40, and 5 percent, respectively, of olefins in the product) when these are used as catalysts and increases with very short layers of catalyst (high space velocities). The yield of olefins is inversely proportional to the hydrogen content of the synthesis gas.[44] A $2H_2 + 1CO$ gas

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[36] Tsuneoka, S., and Fujimura, K. [Effect of Nitrogen, Methane, or Carbon Dioxide on the Benzine Synthesis. XX]: Jour. Soc. Chem. Ind., Japan, vol. 37, 1934, Suppl. binding, pp. 704–711.

[37] Murata, Y., and Yamada, T. [The Benzine Synthesis from Carbon Monoxide and Hydrogen Under Ordinary Pressure. LIV. Influence of Carbon Dioxide in the Initial Gas Upon the Iron Catalyst]: Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 38, 1940, pp. 118–131. Jour. Soc. Chem. Ind., Japan, vol. 44, 1941, Suppl. binding, pp. 33–38. [The Benzine Synthesis from Carbon Monoxide and Hydrogen Under Ordinary Pressure. LV. Influence of Nitrogen, Methane, Oxygen, and Ammonia in the Initial Gas Upon the Iron Catalyst]: Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 38, 1941, pp. 218–229. Brennstoff Chem., vol. 24, 1943, p. 10.

[38] Fischer, F., and Pichler, H. [The Simultaneous Effect of Carbon Monoxide and Carbon Dioxide During Hydrogenation, with Particular Regard to Benzine Synthesis]: Brennstoff Chem., vol. 14, 1933, pp. 306–310.
Pichler, H. [The Reaction of Carbon Dioxide During Hydrogenation]: Brennstoff Chem., vol. 24, 1943, pp. 39–40.

[39] Appleyard, K. C., Chemistry of Fischer-Tropsch Oil Production: South African Min. Eng. Jour., vol. 50, 1940, pp. 585–587, 615–617.

[40] Work cited in footnote 91, p. 37.

[41] Watanabe S., Morikawa, K., and Igawa, S. [The Synthesis of Benzine from Carbon Monoxide by Means of Catalytic Reduction at Atmospheric Pressure. IV. The Influence of the Mixing Ratio of CO and H_2]: Jour. Soc. Chem. Ind., Japan, vol. 38, 1935, Suppl. binding, pp. 328–331.

[42] Meller, A., Catalytic Hydrogenation of CO–CH_4 Synthesis from Water Gas: Australian Chem. Inst. Jour. and Proc., vol. 10, 1943, pp. 100–114, 123–129.

[43] Herbert, W. [Production of Hydrocarbons by Carbon Monoxide Hydrogenation]: German Patent 744,078, Jan. 8, 1944.

[44] Murata, Y., and Tsuneoka, S., No title: Jour. Soc. Chem. Ind., Japan, vol. 41, 1938, Suppl. binding, pp. 16–22. Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 34, 1937, pp. 99–115.

mixture was stated by Tsuneoka and Fujimura[45] to be the optimum for the maximum yield of hydrocarbons, using cobalt catalysts. However, with iron catalysts the optimum gas mixture is $1H_2 + 1.7CO$.[46]

THROUGHPUT

Operating at 10 atmospheres pressure with a $Co\text{–}ThO_2$–kieselguhr (100 : 18 : 100) catalyst and using two-stage operation, Fischer and Pichler[47] studied the influence of contact time on the amount and nature of the hydrocarbons produced. The results are given in tables 5 and 6 and are presented graphically in figure 4. Four grams of cobalt were contained in the second stage and 8 grams in the first stage. The apparatus consisted of two thermostated (with water-steam under pressure), 1-centimeter tubes, with a trap for liquid hydrocarbons at the exit of each tube. For the first stage two tubes were connected in series and contained in the same thermostat and the depth of catalyst in each was about 50 centimeters. The temperature was adjusted in each test for optimum yield of liquid plus solid hydrocarbons.

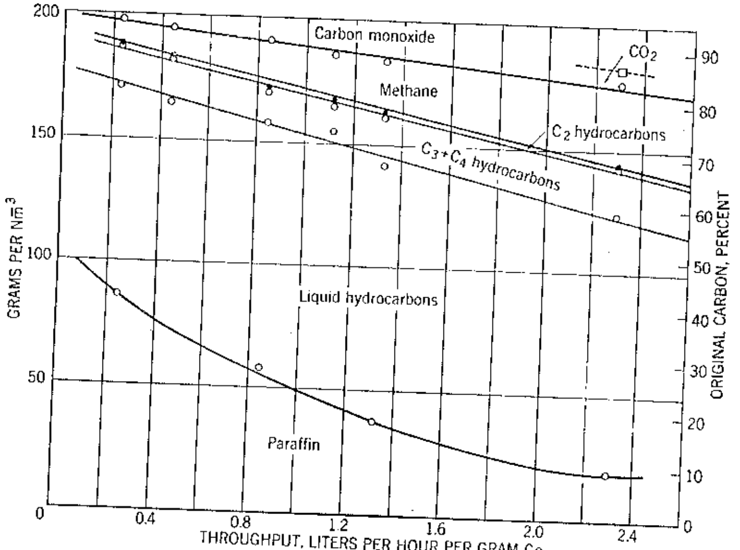

FIGURE 4.—Intermediate-pressure synthesis yields and carbon balance vs. throughput.

One of the outstanding facts shown by table 5 and figure 4 is the extraordinarily small amounts of C_2 hydrocarbon produced. This marked discontinuity in the composition of the product should be correlated with Smith, Hawk, and Golden's[48] observations that ethylene, when added to the reactants, enters into the synthesis, although little or no reaction to form higher hydrocarbons occurs with ethylene alone or with ethylene plus either hydrogen or carbon monoxide alone. Craxford[49] confirmed the results obtained by these experimenters.

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[45] Tsuneoka, S., and Fujimura, K. [Benzine Synthesis from Carbon Monoxide and Hydrogen at Ordinary Pressure. XIX. The Ratio of $CO:H_2$ in the Initial Gas Mixture]: Jour. Soc. Chem. Ind., Japan, vol. 37, 1931, Suppl. binding, pp. 463–467.

[46] Work cited in footnote 99, p. 39.

[47] Fischer, F., Pichler, H., and Dienst, W. [Approach to Theoretically Possible Yields in the Fischer-Pichler Intermediate-Pressure Synthesis]: Brennstoff Chem., vol. 20, 1939, pp. 221–228.

[48] Work cited in footnote 24, p. 5.

The yield of solid paraffin decreased with increasing throughput, as did also the total yield of higher hydrocarbons. Per cubic meter of synthesis gas, yields approaching 190 grams of solid, liquid, and gaseous ($C_3 + C_4$ only) hydrocarbons were obtained with a throughput of 0.2 liter per hour per gram of cobalt. This yield, consisting of 48 percent solid paraffin, 44 percent liquid hydrocarbons, and 8 percent gasol ($C_3 + C_4$), formed about 90 percent of the theoretical (208 grams per cubic meter). At a throughput of 2.0 liters per hour, 145 grams of hydrocarbons (excluding $C_1 + C_2$) were obtained, of which 14 percent was solid paraffin, 73 percent liquid hydrocarbons, and 13 percent gasol. The increased methane formation with increasing throughput, shown in figure 4, is due to the increasing optimum temperature (see table 5). If the temperature is kept constant, the yield of solid plus liquid hydrocarbons per cubic meter of synthesis gas drops rapidly with increased throughput. However, the space-time yield, grams per gram of cobalt per hour, increased to a maximum with increasing throughput (table 7). Table 7 contains some data obtained by Fischer and Pichler[50] at 200° C. and 15 atmospheres using a $Co\text{–}ThO_2$–kieselguhr catalyst. Similar data were obtained by Tsuneoka and Fujimura[51] and by Aicher, Myddleton, and Walker.[52] Data obtained by Tsuneoka and Nishio[53] at lower throughputs than given in table 7 show that the space-time yield rises to a maximum with increasing throughput before decreasing. This observation was confirmed by Jerosejev and coworkers[54] who found that the space-time yield (grams per cubic centimeter of catalyst per hour) rises with increasing throughput at space velocities ranging from 0.45 to 1.02 liters of cobalt per hour ($100Co\text{–}15ThO_2\text{–}100SiO_2$ catalyst). Their experimental data satisfy the equations, (1) $A = a + (b/u_o)$, (2) $u_k = cu_o$, and (3) $\pi = Au_o = au_o + b$, where u_o and u_k = original and final throughput, A = contraction, π = yield, and a, b, and c are constants.

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[49] Craxford, S. R., Reactions of the Fischer-Tropsch Process. Fischler-Tropsch Synthesis of Hydrocarbons and Some Related Reactions: Trans. Faraday Soc., vol. 35, 1939, pp. 946–958, 966–967.

[50] Work cited in footnote 20, p. 42.

[51] Work cited in footnote 45, p. 46.

[52] Aicher, A., Myddleton, W. W., and Walker, J., The Production of Hydrocarbon Oils from Industrial Gases: Jour. Soc. Chem. Ind., vol. 54, 1935, pp. 313–320T.

[53] Tsuneoka, S., and Nishio, A. [Gasoline Synthesis from Carbon Monoxide and Hydrogen at Ordinary Pressure. XXXVII. Volume Velocity of the Gas]: Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 34, 1937, pp. 83–98. Jour. Soc. Chem. Ind., Japan, vol. 41, 1938, Suppl. binding, pp. 11–16.

Murata, Y., and Tsuneoka, S. [Gasoline Synthesis from Carbon Monoxide and Hydrogen at Ordinary Pressure. XXXVIII. Relation Between Conditions of Synthesis and the Unsaturation of the Gasoline Produced]: Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 34, 1937, pp. 99–115. Jour. Soc. Chem. Ind., Japan, vol. 41, 1938, Suppl. binding, pp. 16–22.

[54] Jerosejev, B. W., Runtso, A. P., and Volkova, A. A. [Kinetics of the Catalytic Reduction to Hydrocarbons of Carbon Monoxide by Hydrogen on a Cobalt-Thorium Catalyst]: Acta Physiochim. U. R. S. S., vol. 13, 1940, pp. 111–122.

TABLE 5.—*Intermediate-pressure syntesis in 2 stages at various throughputs*[1]

Experiment No.	Time of test, days	Throughput, liters per hour per gram of cobalt	Temperature, ° C.		Contraction, percent		Conversion of CO, percent		Yield, grams per cubic meter					Yield of C_3 and higher hydrocarbons	
			First stage	Second stage	First stage	Second stage	First stage	Second stage	Condensed hydrocarbons	Gasoline	C_1+C_4	C_2	C_4	Grams per cubic meter	Percent of theoretical
1	22	1.12	189	189	56.5	81.5	62	89	141	15	10	2	16	166	80
2	23	1.11	190	190	55.5	81.1	60	88	140	15	10	2	17	165	80
3	23	1.15	192	192	59.0	82.0	64	89	134						
4	24	.87	190	192	60.0	84.4	65	92	144	15	12	2	19	171	82
5	26	.87	189	192	55.0	84.4	61	92	142	15	12	2	21	169	81
6	28	.43	190	192	69.5	84.5	78	98	133						
7	29	.83	191	192	65.8	84.1	74	94	144	16	13	1.4	19	173	83
8	30	.46	186	187	69.0	85.3	78	96	148						
9	31	.48	184	185		85.2		95	150	14	15	2	13	179	86
10	33	.43	184	184	66.0	85.1	72	94	151	14	15	2	12	180	86
11	34	.43	185	185	64.0	84.7	72	95	150	14	15	2	12	179	86
12	35	.27	178	177	69.0	86.1	75	96	157	11	16	1	12	184	88
13	36	.24	175	177		85.1		94	158	11	16	1	7	185	89
14	37	.25	177	177.5	69.0	86.1	76	98	159	11	16	1	11	186	89
15	40	1.02	195	195	48.5	75.0	54	82	114	24	20	2	12	158	76
16	41	1.09	198	198	51.0	77.1	57	84	114	24	20	2	14	158	76
17	42	2.13	212	212.5	61.0	77.0	70	88	98	26	19	1	35	143	69
18	43	2.16	213.5	214	59.0	76.5	66	87	96	26	19	1	33	141	68
19	44	1.3	202.5	202.5	59.0	79.7	65	88	118	24	20	2	20	162	78
20	45	1.26	204.5	204.5	60.0	79.4	68	90	115	24	20	2	21	159	76
21	47	1.28	205	205	62.0	79.8	69	90	116	24	20	2	23	160	77

[1] Work cited in footnote 47, p. 46.

TABLE 6.—*Estimates of paraffin yield*[1]

Experiment No.	Throughput per hour per gram of cobalt	Temperature, ° C.	Paraffin yield		
			Percent of condensed hydrocarbons		Grams per cubic meter of synthesis gas
			First stage	Second stage	
13–14	0.24–0.27	175–178	52.8–54.6	54.5–56.0	86
4–5	0.87	189–192	40.4–40.7	40.2–40.8	58
15–16	1.02–1.09	195–198	33.0	31.4–32.9	37
17–18	2.13–2.16	212–214	20.4–20.8	19.2–21.6	20

[1] Work cited in footnote 47, p. 46.

TABLE 7.—*Effect of increased throughput at constant temperature*[1]

Throughput, liters per hour per gram of cobalt	1.15	2.25	3.6	10.0
Yield, grams per cubic meter	101	85	60	16.5
Yield, grams per hour per gram of cobalt	.116	.191	.216	.165

[1] Work cited in footnote 20, p. 42.

The effect of increased throughput of synthesis gas with a ruthenium catalyst maintained at 230° C. and under 100 atmospheres pressure is shown in table 8. The total reaction (third column, table 8) continually increases, while the yield of solid plus liquid hydrocarbons (fourth, fifth, and sixth columns, table 8) reaches a maximum at about 9 liters of gas per hour per gram of ruthenium.[55] The condensed hydrocarbons contained 65 to 68 percent of solid paraffinic hydrocarbons.

TABLE 8.—*Effect of increased throughput with ruthenium catalyst at 230° C.*

Throughput, liters per hour per gram of Ru	Contraction, percent	Gas reacted per gram of Ru per hour, liters	Yield, grams of liquid+solid hydrocarbons per—			Conversion of CO to condensed hydrocarbons, percent—	
			Cubic meter of gas	Gram of Ru per hour	Liter of catalyst space per hour	CO used	Reacted
1.8	81	1.46	136	0.24	108	78	87
3.2	79	2.53	125	.40	180	72	83
4.3	69	2.97	98	.43	194	56	74
7.0	62	4.34	84	.59	265	48	70
9.1	56	5.10	79	.72	324	45	--------
10.7	50	5.35	65	.70	310	37	68
16.7	36	6.01	37	.62	270	21	54

TEMPERATURE

The temperature range over which the synthesis of hydrocarbons from hydrogen and carbon monoxide occurs is quite narrow. Even for the most active catalysts the reaction is very slow below 175° C., and above 225° C. the rate of production of liquid hydrocarbon falls

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[55] Pichler, H., and Buffleb, H. [Behavior of Ruthenium Catalysts in Synthesis of Paraffin Hydrocarbons of High Molecular Weight]: Brennstoff Chem., vol. 21, 1940, pp. 273–280.

off sharply, and methane formation predominates.[56] The methane synthesis proceeds at a rapid rate at higher temperatures, such as 300° to 350° C. At such temperatures the main oxygenated compound formed is carbon dioxide rather than water, which is the chief oxygen-containing product at low temperatures.

Data given by Aicher and his coworkers[57] make it possible to calculate the temperature coefficient of the over-all reaction on a nickel-manganese-aluminum catalyst at short contact times. For the temperature intervals 197° to 207° C. and 191° to 270° C. the coefficients per 10° C. are 1.40 and 1.67. These coefficients are sufficiently larger than that of a diffusion process to suggest that the slow step is not the diffusion of reactants to, or of the products from, the catalyst surface through a "blanket" of high-boiling paraffin. Aicher and his associates[57] plotted the yield of oil per unit time per volume of catalyst against the ratio of the concentration of the reactants to that of the products and obtained an almost straight line. This indicates that the reaction rate is directly proportional to the partial pressure of the reactants and inversely proportional to the concentration of the products. It is probable, therefore, that the slow step in the reaction is the desorption of the products from the catalyst surface.

ADSORPTION

Matsumura and his coworkers[58] studied the adsorption of hydrogen, carbon monoxide, carbon dioxide, and water on cobalt and iron catalysts which were active in the hydrocarbon synthesis. The adsorptions are of importance in any discussion of the reaction mechanism. Rumford[59] has postulated a positive correlation between adsorption of hydrogen and carbon monoxide on zinc chromium catalyst (for the decomposition of methyl alcohol) and activity. Van Itterbeek,[60] and Van Itterbeek and Van Dingenen[61] have demonstrated a similar correlation, using nickel and copper–thoria catalysts. The following adsorption data are, therefore, outlined briefly. The activated adsorption of hydrogen on the cobalt catalyst starts at 60° C. and reaches a maximum at 160° C. On the iron catalyst the corresponding temperatures are 60° and 190° C. Carbon monoxide is chemisorbed by the cobalt catalyst to form cobalt carbide at temperatures above 60° C., whereas the minimum temperature for carbide formation on the iron catalyst is 190° C. The activated adsorption of water on the cobalt catalyst begins at 30° C. and reaches a maximum at 100° C., and at about 200° C. (optimum temperature for hydrocarbon synthesis) very little adsorption occurs. On the iron catalyst, activated adsorption of water starts at 200° C. and increases slowly with increasing temperature. The activated adsorption of carbon dioxide on the cobalt catalyst begins at 100° C. and reaches a maximum at 150° C. and then decreases slowly with rising temperature. On the iron catalyst there is evidence for activated adsorption of carbon dioxide to only a slight extent at 200° to 250° C.

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[56] Tsuneoka, S. [Benzine Synthesis from Carbon Monoxide and Hydrogen at Ordinary Pressure. XXI. Relations of the Gas Composition to the Working Temperature and to the Degree of Saturation of the Benzine, Respectively]: Jour. Soc. Chem. Ind., Japan, vol. 37, 1933, Suppl. binding, pp. 711–716. Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 25, 1934, pp. 137–143, 144–151.

Tsuneoka, S., and Murata, Y. [Synthesis of Benzine from Carbon Monoxide and Hydrogen at Ordinary Pressure. XXXVI. The Relation of the Activity of the Catalyst to the Synthesis Requirements at Too High a Temperature]: Jour. Soc. Chem. Ind., Japan, vol. 40, 1937, Suppl. binding, pp. 478–484. Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 34, 1937, pp. 68–82.

[57] Work cited in footnote 52, p. 47.

[58] Matsumura, S., Tarama, K., and Kodama, S. [Benzine Synthesis and Activated Adsorption of Hydrogen, Carbon Monoxide, Carbon Dioxide, and Water on Cobalt and Iron]: Jour. Soc. Chem. Ind., Japan, vol. 43, 1940, Suppl. binding, pp. 175–184. Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 37, 1940, pp. 302–322.

[59] Rumford, F., Correlation of Adsorption and Catalytic Activity. II. Carbon Monoxide and Hydrogen Adsorption on Zinc–Chromium Catalysts: Jour. Roy. Technol. Coll. (Glasgow), vol. 4, 1940, pp. 643–649.

[60] Van Itterbeek, A. [The Relation Between Adsorption and the Catalytic Activity of Metals]: Meded. Kon. Vlaamsche Acad. Wetensch., Letteren Schoone Kunsten Belgie, Klasse Wetensch., vol. 3, No. 10, 1941, pp. 3–20.

[61] Van Itterbeek, A., and Van Dingenen, W. [Catalytic Action of Nickel and Copper–Thorium in the Formation of Methane and Heavy Gases]: Ztschr. physik. Chem., vol. B50, 1941, pp. 341–360.

DISCUSSION OF REACTION MECHANISM

From a study by Craxford[62] and Craxford and Rideal[63] of the kinetics of the hydrocarbon synthesis the following results and postulates may be summarized:

(1) At the temperature of the synthesis carbon monoxide reacts slowly with a cobalt catalyst to give cobalt carbide, according to the equation $2Co + 2CO = Co_2C + CO_2$ but this reaction is always slower than the reduction of the carbide by hydrogen at the same temperature.

(2) At this temperature the catalyst reacts with carbon monoxide and hydrogen to give carbide; that is, $2Co + CO + H_2 = Co_2C + H_2O$, and this reaction is faster than the reduction of the carbide by hydrogen under the synthesis conditions.

(3) Reduction of cobalt carbide may lead to methane or to higher hydrocarbons, according to the conditions, and the experiments showed that, when normally liquid hydrocarbons are being produced, the ortho-para-hydrogen conversion is somewhat inhibited; that is, decreased from 95 to 70 percent or less.

(4) Whenever methane is the main product of the hydrocarbon synthesis, the ortho-para-hydrogen conversion occurs freely to the extent of over 95 percent, showing that chemisorbed hydrogen then covers a very large proportion of the catalyst surface.

(5) The water-gas shift reaction; that is, $CO + H_2O = CO_2 + H_2$, runs parallel to the ortho-para-hydrogen conversion; it occurs when methane is being formed but is inhibited when normally liquid hydrocarbons are being produced.

(6) The hydrogenation cracking of paraffin hydrocarbons on catalysts active for hydrocarbon synthesis is similarly inhibited when liquid hydrocarbons are being produced and also by the presence of carbide on the catalyst surface, but otherwise it occurs freely at similar temperatures.

(7) Craxford[62] verified Smith and his coworkers'[64] results concerning the effect of ethylene on the synthesis which gives an increased yield of liquid hydrocarbons and appreciable amounts of oxygenated organic compounds.

Before discussing the probable mechanism of the reaction, mention should be made of the fact, disclosed by several experimenters,[65] [66] that during the first few hours after a freshly reduced catalyst is exposed to synthesis gas only methane, and carbon dioxide or water as byproduct are produced, depending upon the synthesis conditions. Some of those experimenters found it desirable to use the following procedure[66] to start the synthesis:

The temperature should be well over 150° C. when synthesis gas is first admitted to replace hydrogen. The temperature should then be raised very slowly, a satisfactory procedure being to hold the temper-

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[62] Work cited in footnote 49, p. 47.

[63] Craxford, S. R., and Rideal, E. K., The Mechanism of the Synthesis of Hydrocarbons from Water Gas: Jour. Chem. Soc., 1939, pp. 1604–1614.

Rideal, E. K., The Mechanism of Catalytic Hydrogenation: Chemistry and Industry, 1943, pp. 335–338.

[64] Work cited in footnote 24, p. 5.

[65] Work cited in footnote 27, p. 5.

[66] Work cited in footnote 18, p. 41.

ature constant for 2 hours when the contraction reaches 20 percent, then again constant for 2 hours at 30 percent, 40 percent, and so on. In this way it has been possible to induce oil formation in a minimum of time on any sample of active catalyst.

Most investigators agree that the first step in the synthesis of hydrocarbons from hydrogen and carbon monoxide is that proposed by Fischer and his coworkers;[67] [68] namely, the formation of relatively unstable metal carbides as, for example: $3Co+CO=Co_2C+CoO$. Craxford[69] wrote the primary reaction as $2Co+CO+H_2=Co_2C+H_2O$. It is conceivable that hydrogen acts as catalyst for metal carbide formation by forming an unstable metal hydride.[70]

Eidus and his coworkers[71] [72] wrote that the formation of cobalt carbide in the presence of carbon monoxide was too slow a reaction to be intermediate in the synthesis. On iron catalysts, however, they agreed that the carbide formed by carbon monoxide alone is an intermediate. It was learned from Dr. Pichler and Dr. Koch of the Kaiser Wilhelm Institut für Kohlenforschung, Mülheim,[73] that magnetic-chemical studies showed that the carbide, Fe_3C, is the only stable phase between 300° and 400° C.; further, that most active iron catalysts were those containing the most Fe_3C. Catalysts pretreated at 1/10 atmosphere[74] [75] contained more Fe_3C than did catalysts pretreated at atmospheric pressure. An electrical isolation method for the determination of iron carbide is reported by Houdremont and his coworkers.[76]

At the Bureau of Mines laboratories, investigations[77] [78] of the properties of metal carbides are in progress, with particular emphasis on their significance in the Fischer-Tropsch synthesis. Weller[77] has compared data obtained from a study of the kinetics of carbiding on cobalt catalysts with similar investigations by Craxford and Rideal[79] and Eidus and Zelinskii.[80] Craxford and Rideal reported that the initial rate of carbiding in carbon monoxide was 20 to 30 times slower and that the steady carbiding rate reached after a few hours was 200 times less than the synthesis rate (at 200° C.). As the reaction between carbon monoxide and cobalt was too slow to account for the rate of hydrocarbon formation, they postulated the primary reaction $2Co + CO + H_2 = Co_2C + H_2O$. They used a static system in their investigations. Eidus and Zelinskii, using a flowing system,

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[67] Work cited in footnote 11, p. 3.

[68] Work cited in footnote 12, p. 3.

[69] Work cited in footnote 19, p. 47.

[70] Storch, H. H., Catalysis in Synthetic Liquid Fuel Processes: Ind. Eng. Chem., vol. 37, 1945, pp. 340-351.

[71] Work cited in footnote 91, p. 37.

[72] Eidus, Y. T. [Mechanism of the Synthesis of Aliphatic Hydrocarbons by the Contact Hydrogenation of Carbon Monoxide]: Uspekhi Khim., vol. 9, 1940, pp. 673-681.
Eidus, Y. T., and Zelinskii, N. D. [The Reaction of Carbon Monoxide with Cobalt Catalysts Used in the Synthesis of Gasoline from Water Gas]: Bull. Acad. Sci. U. R. S. S., Classe Sci. Chim., 1942, pp. 45-54. [Carbide Formation as an Intermediate Stage in the Catalytic Synthesis of Hydrocarbons from Water Gas]: Bull. Acad. Sci. U. R. S. S., Classe Sci. Chim., 1942, pp. 190-194.

[73] Haensel, V. [Kaiser Wilhelm Institut für Kohlenforschung, Mülheim, Ruhr]: Combined Intelligence Objectives Subcommittee Report 25/1, Item 30, 1945, 16 pp.
Korber, F., Wiemer, H., and Fischer, W. A. [The Thermal Disintegration of CO on Fe and Its Alloys and in Mixtures with C]: Arch. Eisenhüttenw., vol. 17, 1943, pp. 43-52.

[74] Work cited in footnote 99, p. 39.

[75] Work cited in footnote 4, p. 39.

[76] Houdremont, E., Klinger, P., and Blaschczyk, G. [New Electrolytic Isolation Procedure for Determining Iron Carbide]: Tech. Mitt. Krupp. Forschungsber., vol. 4, 1941, pp. 311-328. Arch. Eisenhüttenw., vol. 15, 1941, pp. 257-270. Brennstoff Chem., vol. 23, 1942, p. 8.

[77] Work cited in footnote 35, p. 44.

[78] Hofer, L. J. E., The Preparation and Properties of Metal Carbides, with Critical Comment as to Their Significance in the Fischer-Tropsch Synthesis: Bureau of Mines Rep. of Investigations 3770, 1944, 39 pp.

[79] Work cited in footnote 63, p. 51.

[80] Work cited in footnote 72, p. 52.

found that the steady rate of carbiding was about 10 times slower than the synthesis rate; the initial carbiding rate was not measured. They concluded that carbide was not formed as an intermediate product in the synthesis.

Weller's measurements were performed on a pelleted 100Co–18ThO$_2$–100 kieselguhr catalyst in an all-glass apparatus, including a circulating pump. The gases were circulated over the catalyst and then through liquid-nitrogen traps so as to condense all products except 1 centimeter partial pressure of methane. The initial carbiding rate was found to be of the same order of magnitude as the synthesis rate, but the subsequent "steady-state" rate of carbiding of the bulk of the catalyst was about 10 times lower than the rate of the synthesis. In view of the high rate of hydrogenation of the carbided catalyst, the diffusion of carbidic carbon through the lattice structure probably is rapid and is not the rate-determining step in the carbiding.

Assuming that the first step in the synthesis is carbide formation, the second step is the reduction of the carbide to a methylene group. That toluene was formed when a mixture of $2H_2 + 1CO$ was passed over a nickel–cobalt–aluminum catalyst in the presence of benzene at 190° C. is claimed by Eidus and Zelinskii[81] as evidence of the intermediate formation of methylene radicals during catalytic hydrogenation of carbon monoxide. Craxford[82] postulated in 1939 that this reaction is with molecular hydrogen, $Co_2C + H_2=CH_2 + 2Co$, because his work on the ortho-para-hydrogen conversion on hydrocarbon synthesis catalysts showed that the concentration of atomic hydrogen decreased when higher hydrocarbons were produced. He predicted that no tertiary carbon should appear in the products and that some quaternary carbon should be obtained. Koch and Hilberath[83] in 1941 made a detailed analysis of the hydrocarbons boiling below 100° C., obtained by synthesis on a cobalt catalyst. Appreciable percentages of isoparaffins were found, including tertiary carbon, but no quaternary carbon compounds. Matsumura[84] pointed out that Craxford's observations do not necessarily imply that methylene cannot be formed by reaction of the carbide with atomic hydrogen produced by activated adsorption on the catalyst surface. Indeed, such participation of active hydrogen is very probable, since the temperature range for active higher-hydrocarbons synthesis (175° to 200° C.) coincides with that for the maximum amount of activated adsorption of hydrogen. The somewhat higher optimum temperature for iron as compared with cobalt catalysts was explained by Matsumura[84] as being due to the higher temperature necessary for maximum chemisorption of carbon monoxide on iron. The extent of the polymerization of the methylene groups is determined by the rate of desorption of the $(CH_2)_n$. Therefore, on the catalyst surface a "steady state" is set up which involves polymerization, reduction, and desorption of the methylene and polymethylene groups. If the extent of carbide formation is small, or if the rate of desorption of the

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[81] Eidus, Y. T., and Zelinskii, N. D. [Intermediate Formation of Methylene Radicals During the Catalytic Synthesis of Aliphatic Hydrocarbons from Carbon Monoxide and Hydrogen]: Bull. Acad. Sci. U. R. S. S., Classe Sci. Chim., 1940, pp. 289-293.

[82] Work cited in footnote 49, p. 47.

[83] Work cited in footnote 21, p. 4.

[84] Work cited in footnote 58, p. 50.

methylene group is rapid, the concentration of methylene groups on the catalyst surface is low, polymerization is therefore retarded, methane is the main product, and there is an ample supply of active surface on which the ortho-para-hydrogen reaction may proceed. The absence of higher hydrocarbon formation during the initial period of operation with an active catalyst is to be explained by the time necessary for covering most of the catalyst surface with polymethylene groups so as to slow up the reduction of methylene to methane. Predominant methane formation at higher temperatures, above 250°C., is due to the very rapid desorption of methylene groups.

Robinet [85] proposed a mechanism in which a primary complex is formed upon the active centers of the catalyst; the complex grows by a kind of copolymerization under the influence of carbon monoxide and hydrogen and free radicals that originate simultaneously in other active centers. If the growth of the complex is not stopped by the cleavage of water or carbon dioxide, the evolution of heat becomes so great that a sudden decomposition of the complex takes place, so that all the active centers form only methane, water, and carbon dioxide. Eidus reported [86] that methyl alcohol, acetic acid, and ethyl alcohol are not intermediates in the synthesis of hydrocarbons from water gas over cobalt catalysts, as these compounds produced liquid hydrocarbons in smaller amounts than those obtained directly from water gas.

Matsumura [87] and Pospekhov [88] preferred to postulate the transient existence of the metal oxide instead of carbide. Subsequent reduction with hydrogen to form chemisorbed water would account for elimination of the oxygen as water on cobalt catalysts. However, on iron catalysts the chemisorption of water at 200° C. is much larger than for cobalt at the same temperature, and hence there is more opportunity for carbon monoxide to form carbon dioxide by reaction with the oxygenated areas on the catalyst surface; this accounts for the fact that for iron catalysts the oxygen appears in the reaction products largely as carbon dioxide.

Although both cobalt and iron form metal carbides, evidence exists that the mechanism of the synthesis on cobalt catalysts differs qualitatively from that on iron catalysts. The first difference is that ordinarily, during the synthesis, water is the chief oxygenated product from cobalt catalysts, whereas that from iron catalysts is carbon dioxide. Operative conditions can be varied so that either carbon dioxide or water is produced on cobalt or iron catalysts. Only a very small percentage of ethylene and ethane appears in the products from a cobalt catalyst, the ratio of the partial pressures of methane to ethane plus ethylene in the off-gases from the synthesis being about 10, as shown in table 9. This ratio for cobalt is 20 times larger than that for iron:copper. Addition of ethylene to the synthesis gas passed over a cobalt-copper–manganese oxide catalyst results chiefly in conversion of the ethylene to higher molecular weight hydrocarbons, only little being hydrogenated to ethane, whereas on an iron–copper catalyst the ethylene is largely converted to ethane. It is apparent that ethylene plays an important role in the synthesis on cobalt, but not on iron–copper catalysts.

TABLE 9.—*Bureau of Mines analyses of residual hydrocarbon gas from Fischer-Tropsch synthesis after one pass through catalysts, in percent by volume*

Catalyst	Co–ThO$_2$–kieselguhr	Fe	Fe–Cu
Methane	76.0	66.0	20.2
Ethane	5.7	7.3	31.5
Ethylene	1.9	7.3	9.3
Propane	5.8	6.7	12.4
Propylene	8.6	11.0	21.2
Butanes	.7	----------	1.5
Butenes	1.3	1.7	3.9
Ratio, $C_1 : C_2$	10.0	4.5	.5

According to Hamai,[89] synthesis of hydrocarbons from carbon monoxide and hydrogen involves the same mechanism on iron, cobalt, and nickel, the oxygen of carbon monoxide always forming water. However, on iron catalysts the final product, Hamai reported, is not water, but carbon dioxide, owing to the water-gas equilibrium, $CO+H_2O=CO_2+H_2$.

An analysis was made [90] of the data obtained by Japanese investigators [91] in their study of the behavior of precipitated nickel–manganese–thoria–kieselguhr and nickel-cobalt alloy catalysts for the Fischer-Tropsch hydrocarbon synthesis. Computations of the rate of formation of water (cubic centimeters per hour per gram of catalyst) indicate the following trends: (1) That the rate of formation of water passes through a maximum at a relatively short contact time; (2) that the rate of formation of water may be zero at zero time; (3) that, therefore, water may not be a primary product of the reaction, but may be produced subsequently in the dehydration of the primary product which would be an oxygenated hydrocarbon. The validity of this analysis depends on the precision with which water formation was measured by the Japanese investigators.

When carbon monoxide is absorbed in the outer adsorption layers and not in direct contact with the catalyst surface, its reduction leads to compounds containing oxygen rather than hydrocarbons. These are the conditions that exist when an appreciable concentration of ethylene is provided in the synthesis gas, and when pressures of 100–200 atmospheres are employed, as in the synthesis of methanol.

ENERGY OF ACTIVATION

The apparent energy of activation of the synthesis of 29 kilocalories per mole for iron-copper-thoria–potassium carbonate–kieselguhr

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[85] Robinet, P. [Hydropolymerization of Carbon Monoxide]: Chim. et ind., vol. 47, 1942, pp. 480–482.

[86] Eidus, Y. T. [The Reactions of Some O-Containing Organic Compounds Over the Cobalt Contact Catalysts Used for the Synthesis of Gasoline from Water Gas]: Bull. Acad. Sci. U. R. S. S., Classe Sci Chim., 1943, pp. 65–73.

[87] Work cited in footnote 58, p. 50.

[88] Pospekhov, D. A. [The Mechanism of Catalytic Syntheses from Hydrogen and Carbon Monoxide. (A Preliminary Report.)]: Sbornik. Nauch.-Issledovatel. Rabot Kiev. Tekh. Inst. Kozhevenno-Obuvnoi Prom., vol. 3, 1940, pp. 261–267. Khim. Referat. Zhur., vol. 4, No. 5, 1941, p. 12.

[89] Hamai, S. [Physicochemical Investigations on Catalytic Mechanism. I. Fischer-Tropsch Synthesis of Hydrocarbons with Special Reference to Its Mechanism]: Jour. Chem. Soc., Japan, vol. 62, 1941, pp. 516–518. Physicochemical Investigations on Catalytic Mechanism. II. The Fischer-Tropsch Synthesis of Hydrocarbons with Special Reference to Its Reaction Mechanism]: Bull. Chem. Soc. Japan, vol. 16 1941, pp. 213–228.

[90] Elliott, M. A., Unpublished Report to Research and Development Division: Bureau of Mines, Office of Synthetic Liquid Fuels.

[91] Work cited in footnotes 56, p. 31; 44 and 45, p. 29.