FISCHER –TROPSCH ARCHIVE

ABSTRACT OF LITERATURE & PATENTS BY K.M.CHAKRAVARTY

454. CHAKRAVARTY, K. M. [Equilibrium Constants of the Reactions $CO+3\ H_2=CH_4+H_2O$; $CO_2+4\ H_2=CH_4+2\ H_2O$; and $2\ CO+2\ H_2=CH_4+CO_2$.] Ztschr. Elektrochem., vol. 34, 1928, pp. 22-25; Chem. Abs., vol. 22, 1928, p. 4040.

Constants for the above equilibria at temperatures 800°-1,300° have been calculated: (a) From the variation with temperature of the equilibrium constants for $C+2\ H_2=CH_4$; $2\ CO=C+CO_2$; and $CO_2+H_2=CO+H_2O$; and (b) from the heats of reaction and the specific heats and chemical constants of reactants and products. The figures obtained are compared and discussed.

455. ---------------.[CHAKRAVARTY, K. M.] Catalytic Reduction of Carbon Monoxide. Sci. and Culture, vol. 4, 1938, pp. 300-301; Chem. Zentralb., 1939, I, p. 3996.

CO can be reduced at 248° by means of a Ni-Cu catalyst activated and reduced at 275° to a gas mixture, which contains more olefins (3.7%) than CH_4 (1.7%).

456. ---------------.[CHAKRAVARTY, K. M.] Hydrogenation of Nickel Carbonyl. Ind. Eng. Chem., vol. 31, 1939, pp. 1059-1060; Chem. Abs., vol. 33, 1939, p. 7498.

Evidence is given to show that the principal reactions in the process of Litkenhous and Mann (*see* abs. 2122) are $CO+H_2=C+O_2$ and $2\ CO+2H_2=CO_2+CH_4$. (*See* abs. 2121.)

457. ---------------.[CHAKRAVARTY, K. M.] Synthetic-Fuel Industry in India. Sci. and Culture, vol. 4, 1939, pp. 573-581; Chem. Abs., vol. 33, 1939, p. 5153.

Bergius, Fischer-Tropsch process for hydrogenating coal, the preparation and use of alcohol motor fuels, compressed-fuel gases, and sewage-disposal gas, and their applications to motors are discussed with particular reference to Indian conditions. Of 103,000,000 gal. of gasoline consumed in 1937, about 15.4 million gal. was produced in India and 38.1 million gal. imported from Burma. The erection of a plant like that at Billingham, England, is recommended as a means for protecting the motor-fuel supply both in peace and war.

458. ---------------.[CHAKRAVARTY, K. M.] Conversion of Coal Into Oil. The Fischer-Tropsch Process. Jour. Indian Chem. Soc., Ind. and News Ed., vol. 3, 1940, pp. 185-192; Chem. Abs., vol. 37, 1943, p. 4878.

Ni can replace Co in the $Co-ThO_2$ catalyst. At 1 atm. the yield of solid paraffins reaches a maximum at about 170°; that of liquefiable hydrocarbons, at 180°. Pressures greater than 15 atm. are not advantageous. Briefly reviews large-scale operation in the Ruhr.

----------. Catalytic Formation of Methane From Carbon Monoxide and Hydrogen. IV. Specific Nature of Promoter Effect on a Nickel Catalyst Using as Reactants Water Vapor and Equal Volumes of Carbon Monoxide and Hydrogen. *See* abs. 463.

----------. Catalytic Formation of Methane From Carbon Monoxide and Hydrogen. V. Study of the Promoter Effect on Nickel Catalyst. *See* abs. 464.

----------. Catalytic Formation of Methane From Carbon Monoxide and Hydrogen. VI. Poisoning by Carbon Deposition. *See* abs. 465.

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459. CHAKRAVARTY, K. M., AND CHAKRAVARTY, P. B. Effect of Potassium Carbonate on Nickel Catalysts for the Fischer-Tropsch Synthesis. Sci. and Culture, vol. 12, 1946, pp. 110-111; Chem. Abs., vol. 41, 1947, p. 1989.

Catalysts containing traces of K_2CO_3 were found to lose their activity after passage of small volumes of H_2-CO mixture. The deactivated catalyst, after being washed with distilled water and reduced at 200°, was negligibly active at first but rose in activity to a steady value somewhat below that found with the original preparation. The catalyst composition was: Kieselguhr, 46%; Ni, 45.77%; ThO_2, 8.3%; and K_2CO_3, traces. A similar preparation containing 0.0823% CeO_2 behaved in the same manner; the reactivated catalyst was not very active at 178°-180° but was steadily active at 219°-220°. The presence of K_2CO_3 causes the formation of C, CO_2, and H_2O rather than hydrocarbons.

460. CHAKRAVARTY, K. M., AND GHOSH, J. C. Catalytic Formation of Methane From Carbon Monoxide and Hydrogen. I. Quart. Jour. Indian Chem. Soc., vol. 2, 1925, pp. 150-156; Chem. Abs., vol. 20, 1926, pp. 860-861.

Sugar charcoal-Ni catalyst for the reaction $CO+3\ H_2 \rightarrow CH_4+H_2O$ retained its activity undiminished for months when the ratio H_2:CO was 3:1. The critical space velocity ($cm.^3$ gas mixture per cc. catalyst per minute) below which CO disappeared was fairly great (1.3 at 300°, 1.7 at 335°, 3.6 at 358°, >4.3 at 400°). This catalyst entirely suppressed the reaction $2\ CO \rightarrow C+CO_2$ and prevented deposition of C on the Ni surface. CeO_2 acted as a promoter for this catalyst increasing the critical space velocity at 355° from 3.5 to 4.4. Some CO_2 about 9 volume % of exit gas, was produced, owing mainly to the reaction $2\ CO+2\ H_2 \rightarrow CO_2+CH_4$ and partly to the reaction $C+2\ H_2O \rightarrow CO_2+2\ H_2$.

461. ---------------.[CHAKRAVARTY, K. M., AND GHOSH, J. C.] Catalytic Formation of Methane From Carbon Monoxide and Hydrogen. II. Production of Fuel Gases Rich in Methane. Quart. Jour. Indian Chem. Soc., vol. 2, 1925, pp. 157-164; Chem. Abs., vol. 20, 1926, p. 861.

Use of sugar charcoal-pumice-Ni catalyst for the formation of CH_4 was studied with equimolal mixtures of H_2 and CO, with view to its use in enriching blue water gas (H_2 49%, CO 42%). This catalyst was not as efficient as a sugar charcoal-Ni catalyst for promoting the reaction $2\ CO+2\ H_2 > CH_4+CO_2$ (I) and was little improved by addition of CeO_2. Pumice-V_2O_5-Ni (A) was at first very effective but rapidly lost its activity; as reaction (I) was retarded, the undesirable reaction $CO+3\ H_2 > CH_4+H_2O$ (II) was favored, though with a smaller total conversion. A sugar charcoal-pumice-V_2O_5-Ni catalyst (B) at 400°-450° retained for months the initial activity of (A). Increasing space velocity favored reactions

(II), but even with a space velocity of over 25 cc. gas per cm.^{3} catalyst per min. only 20% of the CH_4 was formed by reaction (II). If sugar charcoal was replaced by coconut charcoal the catalyst deteriorated rapidly; Fe_2O_2 in place of V_2O_5 made (II) the chief reaction. The gas obtained by use of catalyst (B) was comparable in calorific value to carbureted water gas, though much less poisonous; removal of CO_2, present in amounts as great as 33%, would give a gas of very high calorific value.

462. ---------------.[CHAKRAVARTY, K. M., AND GHOSH, J. C.] Catalytic Formation of Methane From Carbon Monoxide and Hydrogen. III. Study of Various Catalysts. Quart. Jour. Indian Chem. Soc., vol. 4, 1927, pp. 431-436; Chem. Abs., vol. 22, 1928, p. 1085.

Catalysts as follows were invested at 300° on asbestos: $Ni(OH)_2$, $Ni(OH)_2$ and $Mn(OH)_2$, $Ni(OH)_2$ on $Mn(OH)_2$, MnO_2 on $Ni(OH)_2$, $Ni(OH)_2$ and $Mg(OH)_2$, $Ni(OH)_2$ on $Mg(OH)_2$, $Mg(OH)_2$ on $Ni(OH)_2$, $Ni(OH)_2$ and $Zn(OH)_2$, $Ni(OH)_2$ on $Zn(OH)_2$, $Ni(OH)_2$ and $Pb(OH)_2$, NH_4VO_3 on $Ni(OH)_2$, $Cr(Oac)_3$ on $Ni(OH)_2$, $(NH_4)_2MoO_4$ on $Ni(OH)_2$, $Ni(OH)_2$ and $Al(OH)_3$, $Ni(OH)_2$ on $Al(OH)_3$, $Al(OH)_3$ on $Ni(OH)_2$, $Ni(NO_3)_2$ on $Al(OH)_3$. Those with Al were most promising. A rapid fall of activity occurred in all cases. The pumice-sugar carbon-Ni catalyst at 400° did not show marked increase of activity with Ni about 10:2:0.65. Loss of activity was slow, but C always deposited on the catalyst.

463. CHAKRAVARTY, K. M. Catalytic Formation of Methane From Carbon Monoxide and Hydrogen. IV. Specific Nature of Promotor Effect on a Nickel Catalyst Using as Reactants Water Vapor and Equal Volumes of Carbon Monoxide and Hydrogen. Science and Culture, vol. 3, 1938, p. 396; Ztschr. Anorg. Chem., vol. 237, 1938, pp. 381-387; Chem. Abs., vol. 32, 1938, pp. 2818, 6535.

Apart from CH_4 formation a C-Ni catalyst containing thoria and ceria accelerates the formation of CO, CO_2, and H_2 from H_2O and C, but with K_2CO_3 the formation of C and CO_2 from CO is promoted. The addition of a small quantity of a mixture of Ce nitrate and NH_4 vanadate or of Ce nitrate and $Cr(OAc)_3$ to the $Ni(Oac)_2$ used in preparing the catalyst brings about a more complete reduction of the Ni at 300°. The formation of CO_2 and CH_4 is indirectly helped by them. The thoria-ceria mixture increases the uniformity of the Ni particles, prevents granule formation on the surface and clogging of the pores of the pumice used, and prevents sintering. At 400°-450° the Ni catalysts adsorb much CO_2.

464. ---------------.[CHAKRAVARTY, K. M.] Catalytic Formation of Methane From Carbon Monoxide and Hydrogen. V. Study of the Promotor Effect on Nickel Catalyst. Jour. Indian Chem. Soc., vol. 15, 1938, pp. 245-248; Chem. Abs., vol. 32, 1938, p. 8742.

Reduction of Ni catalyst at a temperature of 300° is incomplete when it is prepared from pure Ni acetate. Addition of a small quantity of a mixture of Ce nitrate and NH_4 vanadate or of Ce nitrate and Cr acetate helps in bringing about a more thorough reduction. Thus catalysts of a reaction $2CO+2H_2=CO_2+CH_4$ is accelerated by these promoters through their influence on the preparation of the Ni. Whether the promoters have a direct effect on the reaction has not been settled.

465. ---------------.[CHAKRAVARTY, K. M.] Catalytic Formation of Methane From Carbon Monoxide and Hydrogen. VI. Poisoning by Carbon Deposition. Jour. Indian Chem. Soc.,

vol. 16, 1939, pp. 663-670; Chem. Zentralb., 1940, II, p. 723; Chem. Abs., vol. 34, 1940, p. 4723.

Deposited C may be adsorbed on Ni particles or may form a simple layer on the surface. Moreover, Ni may undergo carbide formation and Ni_3C may have catalytic activity. It has been shown that the reaction $2CO=C+CO_2$ is catalyzed by Ni and also by Ni_3C. The reaction $CO+3H_2=CH_4+H_2O$ is 2.50, Cu 0-1.50, Mg 0.70-1.30, Si 0.10-0.35, and Fe 0.10-0.50%. Al is the remainder, but so that if Cu is near its maximum, the total of the Ni, Sb, and Si is near the lower limit and vice versa. The alloy may also contain Mn up to 0.25%.

466. CHAKRAVARTY, K. M., AND SARKER, J. M. Catalytic Formation of CH_4 From CO and H_2 – a Study of Ni and Ni- Alumina Catalysts Prepared From the Hydroxide, Using KOH, NaOH and NH_4OH as Precipitants. Current Sci., vol. 13, 1944, p. 127; Chem. Abs., vol. 38, 1944, p. 6178.

In a mixture of CO, H_2, and H_2O, roughly 1:1:1, 2 reactions occur in the presence of Ni catalysts: (1) $2CO+2H_2 \rightarrow CH_4+CO_2$. (2) $CO+H_2O \rightarrow CO_2+H_2$. The influence of KOH, NaOH, and NH_4OH, used to precipitate Ni, was small. Alumina promotes reaction (1); its maximum activity occurs at a concentration below 0.16%. Addition of K_2CO_3 to the catalyst promotes reaction (2). Results of 11 runs are tabulated, with analyses of reactants and resultants, weight and volume of catalyst, rate of flow and total volume of gases, and reaction temperatures.

467. CHAKRAVARTY, K. M., AND SEN, R. X-Ray Diffraction Studies of a Nickel-Thoria-Kieselguhr Catalyst for Fischer-Tropsch Synthesis. Nature, vol. 160, 1947, pp. 907-908; British Abs., 1948, A I, p. 155.

The presence of a few diffraction lines of kieselguhr on the X-ray diffraction diagram shows that, in the process of depositing Ni on kieselguhr, the structure has undergone a change. The 2 lines of the kieselguhr shown in the photograph are identified as the strong lines of ferric oxide present in the kieselguhr. The lines of silica on the kieselguhr are absent in that of the catalyst. It is concluded from this that during deposition of metallic Ni and Th on the kieselguhr the crystalline portion of silica becomes amorphous, while the structure and the crystallinity of the ferric oxide remain unchanged. The broadness of the lines indicates, however, that the crystal particles of ferric oxide have disintegrated, yielding crystallites of smaller size. The change in structure was brought about, not by the heating of the kieselguhr in H_2 during the deposition of Ni and Th, but by the disintegration caused by the decomposition of the carbonates of Ni and Th deposited as an initial step in the preparation of the catalyst. Ni is present as is Th in crystalline form in these samples.

CHAKRAVARTY, P. B. *See* abs. 459.

1184. GHOSH, J. C., AND CHAKRAVARTY, K. M. Catalytic Preparation of a Gas Rich in Methane From a Mixture of Water Gas and Steam. Proc. Indian Sci. Cong., 15th Cong., 1928, pp. 148-149; Chem. Abs., vol. 25, 1931, p. 2835.

The authors have previously shown that a gas mixture containing CO and H_2 1:1 by vol. can be made to yield a fuel gas containing over 25% CH_4 if passed over suitable catalysts at temperatures 350°-450°. The efficiency and life of certain catalysts have now been increased very considerably by introducing steam in suitable proportions in the reacting gas mixture. The following reactions take place simultaneously on the catalyst surface: (1) $2CO \rightarrow CO_2+C$; (2) $C+H_2O \rightarrow CO+H_2$; (3) $CO+3H_2 \rightarrow CH_4+H_2O$; (4) $2CO+2H_2 \rightarrow CH_4+CO_2$. It is seen from (1) and (2) that CO reacts with steam, giving CO_2 and H_2. The H_2 so produced increases the ratio of H_2 to CO in the reacting gases and prolongs the life of the catalyst by preventing deposition of C. Catalysts (not mentioned) have been found which so regulate the rates of the reaction given above that the resulting fuel gases, after removal of CO_2, contain more than 50% CH_4.

1190. GHOSH, J. C., CHAKRAVARTY, K. M., AND BAKSHI, J. B. [Catalytic Formation of Methane From Carbon Dioxide and Hydrogen : Simultaneous Acceleration of the Water Gas and Armstrong-Hilditch Reactions.] Ztschr. Elektrochem., vol. 37, 1931, pp. 775-779; Chem. Abs., vol. 26, 1932, p. 648.

Catalysts I, II and III were prepared respectively by impregnating pumice with nitrate solutions, drying in air at 110°, then heating for 16 hr. at 300° in pure H_2. The weights of catalyst used were 0.6440, 0.7100, 0.6565 gm., the densities after reduction 0.4155, 0.4438, 0.4646, % Ni 8.882, 8.433, 8.030, % Ce --, 0.0687, 0.1308, % Th ---, 4.978, 9.479, and % pumice 91.11, 86.52, 82.37, respectively for I, II, and III. The reaction tube was maintained at 405° and the catalyst at 471°. Equal volumes of H_2 and CO, saturated with water vapor, were admitted at constant velocity. With catalyst I, reactions (1) $CO+H_2=C+H_2O$ and (2) $CO_2+2H_2=C+2H_2O$ did not take part because no free C was deposited in disagreement with Randall and Gerhard (*see* abs. 2769). Catalyst I lost its CH_4-forming properties with use but was still capable of promoting the water-gas reaction. Catalysts II and III showed no loss of CH_4-forming properties. After 180 l. had passed, II gave 32.02% CO_2, 9.65% CO, 25.58% CH_4, 22.52% H_2, 10.23% H_2O from 44.48% CO, 44.48% H_2, and 11.03% H_2O. II gave after 190 l., 36.19% CO_2 5.43% CO, 30.12% CH_4, 17.38%. H_2, 10.78% H_2O from 44.78% CO, 44.78% H_2 and 10.46% H_2O.

1191. ---------------. [GHOSH, J. C., CHAKRAVARTY, K. M., AND BAKSHI, J. B.] [Simultaneous Determination of the Equilibrium Constants of the Reactions $CO+H_2O=CO_2+H_2$; $2CO+2H_2=CO_2+CH_4$; $CO+3H_2=CH_4+H_2O$; $CO_2+4H_2=CH_4+2H_2O$ by Using Activated Nickel Catalysts.] Ztschr. Anorg. Chem., vol. 217, 1934, pp. 277-283; Chem. Abs., vol. 28, 1934, p. 6613.

Experimental arrangement was similar to that previously described (*see* abs. 1190) but the gas mixture was passed much more slowly over the Ni-ThO_2-CeO_2 catalyst to insure that the temperature of the gases should be the same as that of the furnace. The required equilibrium constants were determined at temperatures 400°-490°.

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Abstract of Literature # 454 to 467, 1184, 1190 & 1191

Abstract of Patents #357