

PATENT SPECIFICATION

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(54) CATALYST FOR REDUCING CARBON MONOXIDE WITH HYDROGEN

(71) We, HOECHST AKTIEN-GESELLSCHAFT, a body corporate organised under the laws of the Federal Republic of Germany, of D6230-Frankfurt am Main 80, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a catalyst for reducing carbon monoxide by means of hydrogen so as to obtain a mixture consisting substantially of C₁—C₄-hydrocarbons, the catalyst being made by subjecting a metal cyanide to partial or complete decomposition.

Ethylene is one of the most important lower hydrocarbons which are used as starting materials in the chemical industries for the commercial production of a wide variety of secondary products. In view of the considerable demand for ethylene, it is highly desirable to exploit raw material sources other than petroleum for making ethylene. One of such raw materials which recommend themselves is water gas which is obtained by reacting coal with steam at high temperatures.

The catalytic hydrogenation of carbon monoxide with the resultant formation of hydrocarbons has been described in the literature, e.g. by Winnacker-Weingaertner in "Chemische Technologie", vol. Organische Technologie I, pages 780—803, Carl Hanser Verlag, München, 1952. This reaction entails the formation of all hydrocarbons belonging to the olefin and paraffin series, which are obtained in quite different proportions depending on the particular catalyst and reaction conditions used. It has more specifically been

described at page 786 of the above literature reference that in those cases in which an iron or iron/copper-catalyst is substituted for a cobalt catalyst in the hydrogenation of carbon monoxide, olefins tend to be formed at an increasing rate while methane tends to be formed at a decreasing rate. The prior art catalysts are so-called precipitation catalysts. They are made, for example, by dissolving the metals in nitric acid and rapidly precipitating them, while hot, with an alkali metal carbonate solution. After precipitation, the precipitate is filtered off, washed out with water, dried at 110°C, crushed and screened. Next, the screened matter is reduced by contacting it with hydrogen or synthetic gas at 225°C under a pressure of 10 atmospheres gauge.

The iron or iron/copper-catalysts prepared in the manner just described have an unsatisfactory catalytic efficiency in the hydrogenation of carbon monoxide inasmuch as the reaction gas contains an insufficiently low proportion of C₂—C₄ hydrocarbons, especially C₂-hydrocarbons. In other words, the catalysts are insufficiently selective as regards the formation of low olefinic hydrocarbons.

The present invention obviates the disadvantageous effects referred to hereinabove and provides catalysts which by reason of the specific method selected for their preparation enable the proportion of C₂—C₄ hydrocarbons in the reaction gas obtained on hydrogenating carbon monoxide to be considerably increased.

The present invention thus provides more specifically a catalyst for reducing carbon monoxide by means of hydrogen so as to obtain a mixture consisting substantially of C₁—C₄ hydrocarbons, said catalyst being made by precipitating a salt of a

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hydrocyanic acid of the general formula $Me_1Me_n(CN)_x$, separating and drying the salt so precipitated and subjecting it to thermal decomposition, in which formula the cationic component Me_1 stands for one or more of the elements Ce, Cu, Co, Ni, Fe, Mn, Zn and Ag, or for Ca or Mg, the Ca or Mg being in admixture with (NH_4) ; the anionic component Me_n stands for one or more of the elements Cu, Co, Ni, Fe, Mn, Zn and Ag or a mixture of these elements; and x stand for the sum of the metal valencies; Me_1 and Me_n being, however, not permitted to stand for iron alone, or for a mixture of iron with copper. This catalyst may for instance be formed by subjecting the salt to thermal decomposition at 200 to 500°C, e.g. 290 to 350°C, under vacuum, e.g. 1 to less than 760 mm of mercury, or under a pressure of up to 100 atmospheres absolute. It is also possible for the catalyst to be formed in the presence of hydrogen or a mixture of hydrogen and carbon monoxide at a temperature of 200 to 500°C and under a pressure of 1 to 100 atmospheres absolute, preferably 4 to 30 atmospheres absolute.

With respect to the ionic components represented by Me_1 and Me_n in the general formula $Me_1Me_n(CN)_x$, it is advantageous for them to be used in various combinations. In those cases in which Me_n stands for iron, Me_1 should preferably stand for one of the following combinations:

- a) silver, zinc, cobalt or manganese, or
- b) a mixture of copper with iron and nickel, or a mixture of copper with cerium or cobalt or manganese, or
- c) a mixture of silver with cerium or iron, or
- d) a mixture of calcium or magnesium with NH_4 .

If, however, Me_n stands for cobalt, then Me_1 should more preferably stand for copper or silver. In the above general formula $Me_1Me_n(CN)_x$, it is finally preferable for Me_n to stand for manganese and for Me_1 to stand for copper, which is a preferred combination of metals.

With respect to the nature of the catalyst, it is possible for it to be used in the form of granules or pellets or to be deposited on a carrier, such as alumina, silicic acid, kieselguhr, asbestos, glass fibers, clay minerals, pumice or active carbon. In those cases in which the catalyst is deposited on a carrier, 1 to 95 weight %, preferably 5 to 30 weight %, of the catalytically active ingredient should advantageously be applied to the carrier, the percentage being based on the total weight of the catalytically active ingredient and carrier.

The following statements are intended further to illustrate the catalyst of this invention.

The catalysts prepared in the manner

described hereinabove can, for example, be applied to a carrier by precipitating the hydrocyanic acid salt in an aqueous suspension of the carrier, separating the resulting mixture of precipitated salt and carrier, drying the mixture, washing it and subjecting to thermal decomposition at the necessary temperature.

Another method of applying the catalyst to the carrier comprises impregnating preformed carrier material by first impregnating the carrier with an aqueous solution of a hydrocyanic acid salt, then drying the carrier so impregnated, and reacting it with an aqueous solution of a precipitation inducing salt, or inversely.

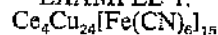
A further preferred method comprises dry-blending the active ingredient with the carrier.

The catalyst of this invention is suitable for use in the catalytic hydrogenation of carbon monoxide by means of gaseous hydrogen to give a mixture consisting substantially of C_1-C_4 hydrocarbons. The hydrogenation can preferably be effected, e.g. by contacting the catalyst at 150 to 500°C and, if desired, under a pressure of up to 100 atmospheres absolute with a gas mixture containing hydrogen and carbon monoxide in a molar ratio of 3:1 to 1:2, the gas mixture being used at a rate of 100 to 3000 normal liters (S.T.P.) per liter of catalyst per hour, and separating the C_1-C_4 hydrocarbons from the issuing gas.

It is even more preferable to contact the catalyst at 250 to 400°C and under a pressure of 1 to 30 atmospheres absolute with a gas mixture containing H_2 and CO in a molar ratio of 2:1 to 1:1, the gas mixture being used at a rate of 100 to 2000 normal liters per liter of catalyst per hour.

As more fully illustrated in the following Examples, the present catalyst compares favorably with the prior art in respect of the following points: It can be made under commercially attractive conditions and combines this with a relatively high selectivity in the reaction of carbon monoxide with hydrogen to give a mixture of C_1-C_4 hydrocarbons.

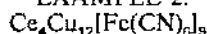
EXAMPLE 1:



34.7 g of $Ce(NO_3)_3 \cdot 6H_2O$ and 116 g of $Cu(NO_3)_2 \cdot 3H_2O$ were dissolved in 1 liter of water and the whole was introduced at 60°C, with vigorous agitation, into a solution of 126.7 g of $K_4[Fe(CN)_6] \cdot 3H_2O$ in 1 liter of water. The resulting precipitate was suction-filtered and washed with 1.5 liters of water in portions of 100 ml. The precipitate, which had the empirical formula $Ce_4Cu_{24}[Fe(CN)_6]_{15}$, was dried at 60°C and the hard mass was comminuted to give particles with a size of 1.6 to 2.5 mm. 30

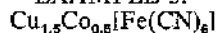
g of the product so made was contacted at 340 to 350°C under a pressure of 20 atmospheres gauge with a gas mixture consisting of 50 volume % of H₂ and 50 volume % of CO. A constant quantity of 25 normal liters of gas was taken from the apparatus per hour. The reaction gas contained 11.25 volume % of CH₄, 2.45 volume % of C₂H₄, 1.18 volume % of C₂H₆, 1.7 volume % of C₃H₈ and 0.3 volume % of C₃H₆. After an operation period of 10 hours, a further 6.4 g of an unidentified oil was obtained in a separator disposed downstream of the reactor.

EXAMPLE 2:



As described in Example 1, a solution of 52.05 g of Ce(NO₃)₃·6H₂O and 87.0 g of Cu(NO₃)₂·3H₂O in 1 liter of water was united with a solution of 114 g of K₄[Fe(CN)₆]·3H₂O in 1 liter of water. The resulting precipitate was suction-filtered, washed, dried and fragmented. 30 g of the product so obtained was contacted at 315°C under a pressure of 30 atmospheres gauge with a gas mixture of 50 volume % of H₂ and 50 volume % of CO. The issuing gas was removed at a rate of 33 normal liters per hour. It contained 11.7 volume % of CH₄, 2.7 volume % of C₂H₄, 1.38 volume % of C₂H₆, 1.78 volume % of C₃H₈ and 0.52 volume % of C₃H₆. After an operation period of 30 hours, a further 60 g of high-boiling hydrocarbons were obtained.

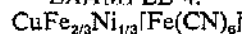
EXAMPLE 3:



A solution of 0.75 mol of CuSO₄ and 0.25 mol of Co(NO₃)₂ in 1 liter of water was stirred into a solution of 0.4 mol of K₄[Fe(CN)₆] in 1 liter of water. The resulting precipitate was suction-filtered, thoroughly washed with water and the filter cake was mixed, while moist, in a laboratory kneader with 125 g of asbestos and 125 g of fine silicic acid, the resulting mixture was dried and made into pellets 3 mm in diameter. The filter cake corresponded approximately to the formula Cu_{1.5}Co_{0.5}[Fe(CN)₆]. 40 g of pelletized material was placed in a reactor and contacted therein with gaseous hydrogen at 320°C under a pressure of 10 atmospheres gauge. The efficiency of the catalyst so made was tested by contacting it at 300 to 310°C under a pressure of 7 atmospheres gauge with a CO/H₂-mixture (1:1). A constant quantity of 25 normal liters of reaction gas was removed per hour. It contained 11.5 volume % of CH₄, 2.86 volume % of C₂H₄, 0.74 volume % of C₂H₆, 2.14 volume % of C₃H₈ and 0.31 volume % of C₃H₆. Under a pressure of 4 atmospheres gauge, at 290°C and gas removal at a

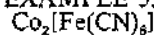
constant rate of 10 normal liters/h, the issuing gas was found to contain 9.38 volume % of CH₄, 2.0 volume % of C₂H₄, 0.32 volume % of C₂H₆, 1.37 volume % of C₃H₈ and 1.37 volume % of C₃H₆.

EXAMPLE 4:



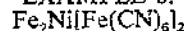
A solution of 211.2 g of K₄[Fe(CN)₆] in 1 liter of water was admixed, with thorough agitation, with 2 l of an aqueous solution containing 137.3 g of CuSO₄·5H₂O, 93.2 g of FeSO₄·7H₂O, and 51.2 g of NiSO₄·7H₂O. The resulting precipitate was suction-filtered and washed with water, and the filter cake, which had the empirical formula Cu₁Fe_{2/3}Ni_{1/3}[Fe(CN)₆], was mixed with 125 g of asbestos and 125 g of silicic acid. The mixture obtained was dried and made into pellets. 40 g of pelletized material was placed in the reactor and treated for 2 hours with H₂ at 320°C under a pressure of 10 atmospheres gauge. The pelletized material was contacted at 340°C under a pressure of 10 atmospheres gauge with a gas mixture of H₂ and CO, which was used in a ratio by volume of 1:1. The issuing gas was removed at a constant rate of 10 normal liters/h and found to contain: 13.6 volume % of CH₄, 0.81 volume % of C₂H₄, 2.56 volume % of C₂H₆, 1.61 volume % of C₃H₈ and 0.35 % of C₃H₆.

EXAMPLE 5:



A solution of 1/5 mol of K₄[Fe(CN)₆] in 0.8 liter of water was united with a solution of 2/5 mol of Co(NO₃)₂ in 0.5 liter of water. The resulting precipitate was suction-filtered, thoroughly washed with 1.5 liters of water, which contained 1/5 mol of Co(NO₃)₂ per liter, and then mixed with 50 g of asbestos and 50 g of silicic acid. The mixture obtained was dried and made into pellets. The pelletized material was treated at 280°C as described in Example 4, and the resulting reaction gas was found to contain: 12.32 volume % of CH₄, 1.66 volume % of C₂H₄, 0.96 volume % of C₂H₆, 1.96 volume % of C₃H₈ and 0.35 volume % of C₃H₆. 36 g of higher-boiling hydrocarbons were obtained over an operation period of 55 hours.

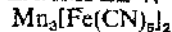
EXAMPLE 6:



As described in Example 1, a complex cyanide of the empirical formula Fe₂Ni[Fe(CN)₆]₂ was made from Fe(NO₃)₃·9H₂O, Ni(NO₃)₂·6H₂O and K₄[Fe(CN)₆] and the complex cyanide was contacted, as described in Example 1, with a CO and H₂ gas mixture. The issuing reaction gas contained 32.48 volume % of CH₄, 0.06 volume % of C₂H₄, 3.44 volume % of C₂H₆,

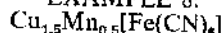
1.47 volume % of C_2H_6 and 1.05 volume % of C_3H_8 . A further 10 g of liquid hydrocarbons were obtained within 20 hours.

EXAMPLE 7:



As described in Example 1, an aqueous solution of 0.3 mol of $MnSO_4$ was united with an aqueous solution of 0.2 mol of $K_3[Fe(CN)_6]$ and a precipitate of the empirical formula $Mn_3[Fe(CN)_6]_2$ was obtained. The precipitate was washed dried and comminuted. 30 g of the comminuted material was contacted at $310^\circ C$ under a pressure of 4 atmospheres gauge with a CO and H_2 gas mixture which was used in a ratio by volume of 1:1. A constant quantity of 10 normal liters/h of gas was taken from the reactor. The gas contained 6.76 volume % of CH_4 , 0.52 volume % of C_2H_6 , 1.96 volume % of C_3H_8 , 1.68 volume % of C_3H_8 and 0.77 volume % of C_3H_8 .

EXAMPLE 8:



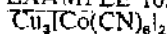
0.2 mol of $K_3[Fe(CN)_6] \cdot 3H_2O$, 0.3 mol of $CuSO_4 \cdot 5H_2O$ and 0.1 mol of $MnSO_4 \cdot H_2O$ were reacted in aqueous solution so as to obtain a precipitate of the empirical formula $Cu_{1.5}Mn_{0.5}[Fe(CN)_6]$. The precipitate was further treated as described in Example 7. The issuing reaction gas contained 8.4 volume % of CH_4 , 2.04 volume % of C_2H_6 , 1.3 volume % of C_2H_6 , 3.8 volume % of C_3H_8 and 0.49 volume % of C_3H_8 . A further 25.5 g of liquid hydrocarbons were obtained during an operation period of 62 hours.

EXAMPLE 9:



40 g of the complex salt of the empirical formula $Cu_{1.5}Ni_{0.5}[Fe(CN)_6]$ described in Example 3 was contacted at $320^\circ C$ under a pressure of 4 atmospheres gauge with a gas mixture of CO and H_2 , which was used in a ratio by volume of 1:1. The issuing gas was removed at a constant rate of 25 normal liters/h. The reaction gas contained 17.78 volume % of CH_4 , 0.04 volume % of C_2H_6 , 2.2 volume % of C_2H_6 , 0.35 volume % of C_3H_8 and 0.91 volume % of C_3H_8 . Higher oily hydrocarbons could not be found to have been formed.

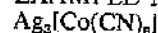
EXAMPLE 10:



$K_3[Co(CN)_6]$ was reacted with copper acetate in aqueous solution and the resulting precipitate was made into pellets in the manner described in Example 3. 40 g of the pelletized material was contacted at $340^\circ C$ under a pressure of 10 atmospheres gauge with a gas mixture of CO and H_2 ,

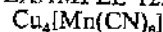
which was used in a ratio of 1:1. The issuing gas was removed at a constant rate of 10 l/h and found to contain 16 volume % of CH_4 , 0.16 volume % of C_2H_6 , 1.70 volume % of C_2H_6 , 0.63 volume % of C_3H_8 and 0.32 volume % of C_3H_8 . 2.1 g of higher liquid hydrocarbons were obtained within 13 hours.

EXAMPLE 11:



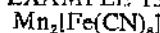
$K_3[Co(CN)_6]$ was precipitated with $AgNO_3$ in a dilute aqueous solution of acetic acid so as to obtain a complex salt of the empirical formula $Ag_3[Co(CN)_6]$. As described in Example 3, the precipitate was mixed with asbestos and silicic acid and made into pellets. 40 g of the pelletized material was contacted at $320^\circ C$ under a pressure of 10 atmospheres gauge with a gas mixture of CO and H_2 , which was used in a ratio by volume of 1:1. The issuing gas was removed at a constant rate of 10 normal liters/h and found to contain 12.3 volume % of CH_4 , 0.05 volume % of C_2H_6 , 1.06 volume % of C_2H_6 , 0.35 volume % of C_3H_8 and 0.49 volume % of C_3H_8 .

EXAMPLE 12:



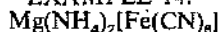
$K_4[Mn(CN)_6]$ was precipitated with the use of an ammoniacal Cu(I) salt solution to obtain a complex salt which was contacted under the conditions described in Example 11 with a gas mixture of CO and H_2 . The issuing gas contained 1.6 volume % of CH_4 , 0.3 volume % of C_2H_6 , 0.4 volume % of C_2H_6 , 0.3 volume % of C_3H_8 and 0.12 volume % of C_3H_8 . Higher liquid hydrocarbons could not be found to have been formed.

EXAMPLE 13:



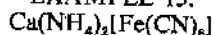
A solution of 0.2 mol of $K_4[Fe(CN)_6]$ in 1 liter of water was admixed, while stirring, with a solution of 0.4 mol of $MnSO_4$ in 1 liter of water. The resulting white precipitate, which had the empirical formula $Mn_2[Fe(CN)_6]$ was suction-filtered, washed, mixed, in the manner described in Example 5, with asbestos and silicic acid and made into pellets. 50 ml of the pelletized material was contacted at $310^\circ C$ under a pressure of 4 atmospheres gauge with a gas mixture of 50 volume % of CO and 50 volume % of H_2 . The issuing gas was removed at a rate of 10 l/h. The reaction gas contained 4.74 volume % of CH_4 , 1.76 volume % of C_2H_6 , 0.72 volume % of C_2H_6 , 2.59 volume % of C_3H_8 and 0.24 volume % of C_3H_8 . A further 28.3 g of liquid hydrocarbons were obtained over an operation period of 100 hours.

EXAMPLE 14:



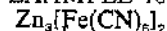
Aqueous solutions which contained stoichiometric proportions of MgCl_2 , ammonium chloride and potassium ferrocyanide, respectively, were united so as to produce magnesium-ammonium ferrocyanide. The complex salt was dried and 10 g thereof with a particle size of 2 mm was placed in a reactor, in which it was contacted at 320°C under a pressure of 20 atmospheres gauge with a gas mixture of CO and H_2 in a ratio by volume of 1:1. The issuing gas was removed at a constant rate of 20 normal liters/h. The reaction gas contained 15.9 volume % of CH_4 , 0.5 volume % of C_2H_6 , 2.35 volume % of C_3H_8 , 0.3 volume % of C_4H_{10} and 0.77 volume % of C_5H_{12} . A further 19 g of higher liquid hydrocarbons were obtained within 22 hours.

EXAMPLE 15:



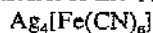
As described in Example 14, calcium-ammonium ferrocyanide was prepared and the complex salt was contacted with a CO/ H_2 gas mixture under the conditions described in that Example. The reaction gas, which was removed at a constant rate of 20 normal liters/h, contained 11.2 volume % of CH_4 , 1.02 volume % of C_2H_6 , 0.85 volume % of C_3H_8 , 0.77 volume % of C_4H_{10} and 0.43 volume % of C_5H_{12} . A further 19.6 g of liquid hydrocarbons were obtained over an operation period of 27 hours.

EXAMPLE 16:



0.6 mol of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ was reacted with 0.4 mol of $\text{K}_3[\text{Fe}(\text{CN})_6]$ in aqueous solution, which contained 279 g of SiO_2 (Ketjen SiO_2Fx), so as to obtain a precipitate of the empirical formula $\text{Zn}_3[\text{Fe}(\text{CN})_6]_2 \cdot x\text{SiO}_2$. (The word "Ketjen" is a registered Trade Mark). 27 g of the mixture was contacted at 340°C under a pressure of 9.5 atmospheres gauge with a gas mixture containing CO and H_2 in a ratio of 1:1. The issuing gas was removed at a rate of 15 normal liters/h. It contained 8.0 volume % of CH_4 , 1.6 volume % of C_2H_6 , 1.4 volume % of C_3H_8 and higher hydrocarbons.

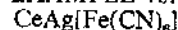
EXAMPLE 17:



An aqueous solution of $\text{K}_4[\text{Fe}(\text{CN})_6]$ was admixed with AgNO_3 so as to cause precipitation of a complex salt of the empirical formula $\text{Ag}_4[\text{Fe}(\text{CN})_6]$, which was washed with water, admixed with asbestos and silicic acid and made into pellets 3 mm in diameter. 15 g of the pelletized material was placed in a reactor and contacted

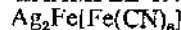
therein at 340°C under a pressure of 20 atmospheres gauge with a gas mixture containing CO and H_2 in a ratio by volume of 1:1. The issuing gas was removed at a rate of 10 normal liters/h and found to contain 10.71 volume % of CH_4 , 0.7 volume % of C_2H_6 , 1.9 volume % of C_3H_8 , 1.71 volume % of C_4H_{10} and 0.5 volume % of C_5H_{12} .

EXAMPLE 18:



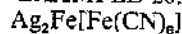
Cerium(III) nitrate, AgNO_3 and $\text{K}_4[\text{Fe}(\text{CN})_6]$ were reacted in aqueous solution so as to obtain a precipitate of the empirical formula $\text{CeAg}[\text{Fe}(\text{CN})_6]$, which was washed and dried at 60°C and then comminuted to fragments with a size of 1 to 2.5 mm. 30 g of the splintered fragments were contacted at 370°C under a pressure of 10 atmospheres gauge with a gas mixture containing 33 volume % of CO and 67 volume % of H_2 . The issuing gas was removed at a rate of 15 normal liters/h and found to contain 11.9 volume % of CH_4 , 2.62 volume % of C_2H_6 , 0.6 volume % of C_3H_8 , 1.25 volume % of C_4H_{10} and 0.25 volume % of C_5H_{12} .

EXAMPLE 19:



0.5 mol of a precipitate of the empirical formula $\text{Ag}_2\text{Fe}[\text{Fe}(\text{CN})_6]$ was mixed with 250 g of alumina (Condea NG) and the mixture was pelletized. 30 g of the pelletized material consisting of particles with a diameter of 1.5 to 2.5 mm was placed in a reactor and contacted therein at 320°C under a pressure of 20 atmospheres gauge with a gas mixture consisting of 50 volume % of CO and 50 volume % of H_2 . The reaction gas which was removed at a rate of 30 normal liter/h contained 24.1 volume % of CH_4 , 0.99 volume % of C_2H_6 , 4.32 volume % of C_3H_8 , 2.04 volume % of C_4H_{10} and 1.18 volume % of C_5H_{12} . A further 25 g of liquid higher hydrocarbons were obtained within an operation period of 26 hours.

EXAMPLE 20:



The precipitate prepared in the manner described in Example 19 was mixed with asbestos and silicic acid and the mixture was made into pellets 3 mm in diameter. 0.5 mol of $\text{Ag}_2\text{Fe}[\text{Fe}(\text{CN})_6]$ was blended with 125 g of asbestos and 125 g of silicic acid. 30 g of the pelletized material was contacted at 320°C under a pressure of 20 atmospheres gauge with a gas mixture containing CO and H_2 in a ratio by volume of 1:1. The reaction gas, which was removed at a rate of 30 normal liters/h, contained 10.62 volume % of CH_4 , 2.64 volume % of C_2H_6 , 1.95 volume % of C_3H_8 , 2.52 volume % of C_4H_{10} and 0.67

volume % of C_3H_8 . A further 6.8 g of higher hydrocarbons were obtained within an operation period of 18 hours.

WHAT WE CLAIM IS:—

5 1. Catalyst for reducing carbon monoxide by means of hydrogen so as to obtain a mixture consisting substantially of C_1 — C_4 -hydrocarbons, the catalyst being made by precipitating a salt of a hydrocyanic acid of the general formula $Me_1Me_{II}(CN)_x$, separating and drying the salt so
10 precipitated and subjecting it to thermal decomposition, in which formula the cationic component Me_1 stands for one or more of the elements Ce, Cu, Co, Ni, Fe, Mn, Zn and Ag, or for Ca or Mg, the Ca or Mg being in admixture with (NH_4) ; the anionic component Me_{II} stands for one or
15 more of the elements Cu, Co, Ni, Fe, Mn, Zn and Ag or a mixture of these elements; and x stands for the sum of the metal valencies; Me_1 and Me_{II} being not permitted to stand for iron alone, or for a mixture of iron with copper.

25 2. Catalyst as claimed in claim 1, the catalyst being formed by subjecting the salt to thermal decomposition at 200 to 500°C, under vacuum or under a pressure of up to 100 atmospheres absolute.

30 3. Catalyst as claimed in claim 1, the catalyst being formed in the presence of hydrogen or a mixture of hydrogen and carbon monoxide at a temperature of 200 to 500°C and under a pressure of 1 to 100 atmospheres absolute.

35 4. Catalyst as claimed in claim 3, the catalyst formation pressure being 4 to 30 atmospheres absolute.

40 5. Catalyst as claimed in any of claims 1 to 4, wherein Me_{II} stands for iron and Me_1 stands

a) for silver, zinc, cobalt or manganese, or
b) for a mixture of copper with iron and nickel or a mixture of copper with cerium or cobalt or manganese, or

45 c) for a mixture of silver with cerium or iron, or

d) for a mixture of calcium or magnesium with NH_4 .

6. Catalyst as claimed in any of claims 1 to 4, wherein Me_{II} stands for cobalt and Me_1 stands for copper or silver.

7. Catalyst as claimed in any of claims 1 to 4, wherein Me_{II} stands for manganese and Me_1 stands for copper.

8. Catalyst as claimed in any of claims 1 to 7, wherein the salt is thermally decomposed at 290 to 350°C.

9. Catalyst as claimed in any of claims 1 to 8, the catalyst being in the form of granules or pellets, or deposited on a carrier.

10. Catalyst as claimed in claim 9, wherein the carrier substance is selected from alumina, silicic acid, kieselguhr, asbestos, glass fibers, clay minerals, pumice or active carbon.

11. Catalyst as claimed in claim 9 or 10, wherein 1 to 95 weight % of the catalytically active ingredient is applied to the carrier, the percentage being based on the total weight of the catalytically active ingredient and carrier.

12. Catalyst as claimed in claim 11, wherein the said percentage of the catalytically active ingredient which is applied to the carrier is 5 to 30 weight %.

13. Catalyst as claimed in claim 2, the catalyst being formed under a vacuum of 1 to less than 760 mm of mercury.

14. A process for catalytically reducing carbon monoxide so as to obtain a mixture consisting substantially of C_1 — C_4 -hydrocarbons with the use of a catalyst as claimed in any of claims 1 to 13.

15. Hydrocarbon mixtures consisting substantially of C_1 — C_4 -hydrocarbons whenever obtained by reducing carbon monoxide with hydrogen in contact with a catalyst as claimed in any of claims 1 to 14.

16. Catalyst substantially as described in any of Examples 1 to 20 herein.

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