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(54) CATALYST AND PROCESS FOR REDUCING CARBON MONOXIDE

(71) We, HOECHST AKTIENGESELLSCHAFT, 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 containing iron or a mixture of iron and copper as its catalytically active ingredient, and to a process for reducing carbon monoxide by means of hydrogen with the resultant formation of a mixture substantially of hydrocarbons containing 1 to 4 carbon atoms.

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 fully described, for example, by Winnacker-Weingaertner in "Chemische Technologie", vol. Organische Technologie I, pages 780—803, published by Carl Hauser 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 is more specifically stated at page 786 of the above publication 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 a higher rate while methane tends to be formed at a lower 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 with water, dried at 110°C, crushed and screened. Next, the screened matter is reduced by contacting it with hydrogen or synthesis 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 C_2—C_4 hydrocarbons, especially C_2-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 iron/copper-catalysts which by reason of the specific method selected for their preparation enable the proportion of C_2—C_4 hydrocarbons in the reaction gas obtained on hydrogenating carbon monoxide to be considerably increased.

The present invention thus provides a catalyst containing iron or a mixture of iron and copper as its catalytically active ingredient for reducing carbon monoxide by means of hydrogen with the resultant formation of a mixture substantially of hydrocarbons having 1 to 4 carbon atoms, said catalyst being made by contacting one or more complex salts of the following general formula:

$$Me_x[Fe(CN)_6]_y$$

in which Me stands for an iron and/or copper ion, x stands for 1 to 4, and y stands for 1 to 3, with hydrogen or a hydrogen/carbon monoxide-mixture, at a temperature of 200 to 500°C, under a pressure of 1 to 100 atmospheres absolute and over a period of 2 to 20 hours and thereby reducing the complex salt(s) to elementary iron or copper.

In the above general formula, the parameters x and y stand more preferably for 2 or 4, and for 1 or 3, respectively. The particular compounds concerned in this case have approximately the following constitution:

$Fe_4[Fe(CN)_6]_3$, $CuFe[Fe(CN)_6]$,

$Cu_2[Fe(CN)_6]$, $Cu_4[Fe(CN)_8]$

in which the water of hydration and residual alkali metal contents remain unmentioned.

A preferred form of catalyst preparation comprises contacting the said one or more complex salts with at least stoichiometric proportions of hydrogen or a hydrogen/carbon monoxide-mixture in a preferred molar ratio of 3:1 to 1:2 at a temperature of 350 to 400°C, under a pressure of 5 to 50 atmospheres gauge, and over periods of 3 to 10 hours.

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, a clay mineral, pumice or active carbon. In those cases in which the catalyst is deposited on a carrier, it is preferable for 20 to 95 weight % of catalytically active ingredient to be applied to the carrier, the percentage being based on the total weight of catalytically active ingredient and carrier. The catalyst of the present invention is a precipitation catalyst since it is possible to obtain the one or more complex salts of the above general formula by precipitating it or them from an aqueous alkali metal ferrocyanide solution by means of an aqueous solution of an iron and/or copper salt, and separating and drying the precipitated salt or salts.

The present invention also provides a process for the catalytic reduction of carbon monoxide by means of hydrogen with the resultant formation of a mixture substantially of hydrocarbons containing 1 to 4 carbon atoms by contacting a carbon monoxide/hydrogen mixture at elevated temperature, at atmospheric or higher pressure with a catalyst containing iron or a mixture of iron and copper as its catalytically active ingredient and being deposited on a carrier, if desired, which process comprises: contacting the gas mixture containing hydrogen and carbon monoxide in a molar ratio of 0.5—3:1, at a temperature of 200 to 500°C, and under atmospheric pressure or a superatmospheric pressure of up to 100 atmospheres absolute, with a catalyst, the gas mixture being used at a rate of 100 to 10000 normal liters (S.T.P.) per liter of catalyst per hour, and separating hydrocarbons having from 1 to 4 carbon atoms from the issuing gas, said catalyst having been made by contacting one or more complex salts of the following general formula:

$$Me_x[Fe(CN)_6]_y$$

in which Me stands for an iron and/or copper ion, x stands for 1 to 4, and y stands for 1 to 3, with hydrogen or a hydrogen/carbon monoxide mixture, at a temperature of 200 to 500°C, under atmospheric pressure or a superatmospheric pressure of up to 100 atmospheres absolute, and over a period of 2 to 20 hours and thereby reducing the complex salt(s) to elementary iron or copper.

A preferred feature of the present process provides for the gas mixture to contain hydrogen and carbon monoxide in a molar ratio of 0.8—3:1 and to be contacted at a temperature of 250 to 450°C under a pressure of 5 to 50 atmospheres gauge with the catalyst at a rate of 200 to 5000 normal liters per liter of catalyst per hour.

The following statements are intended further to illustrate the catalyst and process of the present invention.

The catalyst can be prepared, for example, by precipitating copper ferrocyanide from an aqueous solution of a copper (II) salt by means of an aqueous solution of potassium ferrocyanide. The resulting red-brown precipitate is suction-filtered, washed and dried. Next, the precipitate is reduced in a copper-lined steel tube at 350—400°C over a period of about 2 hours with the use of hydrogen.

Another method of preparing a very good hydrogenation catalyst comprises producing an almost white precipitate from an ammoniacal solution of copper (I) chloride and potassium ferrocyanide (molar ratio = 4:1), drying the precipitate and reducing it by means of hydrogen.

A still further method of preparing an effective hydrogenation catalyst comprises reacting an aqueous solution of a copper (II) salt and iron (II) salt with potassium ferrocyanide in a molar ratio of 1:1:1, separating the resulting blackish blue precipitate, drying the precipitate and reducing it with hydrogen. The blackish blue precipitate contains iron and copper in an atomic ratio of 1:2. If the atomic ratio of Cu:Fe is further reduced, the catalyst becomes less selective relative to the formation of C_2-hydrocarbons. Even those catalysts which are prepared from ferri-/ferrocyanide have however been found to possess good hydrogenating properties.

The catalysts prepared in the manner described hereinabove can, for example, be applied to a carrier by precipitating the complex cyanide(s) in an aqueous suspension of the carrier, separating the resulting mixture of precipitated cyanide and carrier, drying the mixture, washing it and reducing the cyanide(s) by means of hydrogen at the necessary temperature.

Another method of applying the catalyst to the carrier comprises impregnating preformed carrier material with the complex cyanide(s) by first impregnating the carrier with an aqueous solution of potassium ferrocyanide, then drying the carrier so impregnated and reacting the carrier with an aqueous solution of a copper salt.

A still further method comprises mixing the aqueous solution of potassium ferrocyanide with a copper salt in the presence of ammonia (precipitation is obviated, e.g. in those cases in which a copper (II) salt and potassium ferrocyanide are used), impregnating the carrier with the resulting solution and precipitating the copper-cyanide complex by evaporation of the ammonia.

It is not absolutely necessary for the dry catalyst to be treated with hydrogen. It may well be contacted immediately with the CO/H_2-mixture at the necessary reaction temperature to effect reduction of the cyanide complex. A catalyst so prepared was taken from a reactor after about 8 hours of operation and found to be pyrophoric in contact with air. The nitrogen content of the catalyst was found to have dropped to (e.g.) 0.2—0.4 weight %, i.e. the complex cyanide compound was found to have been extensively destroyed.

As more fully illustrated in the following Examples, the present iron/copper catalysts compare favorably with the prior art catalysts in respect of the following points: They can be prepared under commercially attractive conditions and combine this with a relatively high selectivity in the reaction of carbon monoxide with hydrogen with the resultant formation of C_1—C_4 hydrocarbons.

EXAMPLE 1.

Particulate pumice (particle size = 2—3 mm) was introduced into an aqueous solution of potassium ferrocyanide (a saturated hot solution was used), the supernatant liquid was poured off, and the remaining material was dried and mixed with a $FeCl_3$ solution in excess. The resulting blue mass was water-washed and dried in a drying cabinet at 120°C. 30 g of the product so obtained was placed in a copper-lined tube 16 mm wide and reduced by means of hydrogen over a period of 3 hours at 250—300°C under a pressure of 5 atmospheres gauge.

The catalyst so made was contacted with 30 normal liters per hour of a H_2/CO-mixture (molar ratio = 1:1) under a pressure of 10 atmospheres gauge. The reaction temperature was 385°C. The gas issuing from the reactor contained 1.8% by volume of ethylene and ethane, 7.2% by volume of methane, 1% by volume of C_3 hydrocarbons and 0.8% by volume of C_4 hydrocarbons. Liquid hydrocarbons could not be found to have been formed. The hydrogenation was accomplished by the formation of CO_2.

The experiment was repeated under the reduction conditions described, but the molar ratio of $H_2:CO = 1:1$ was changed to 3:1. The quantity of C_2, C_3 and C_4 hydrocarbons remained unchanged, but 9.3% by volume of CH_4 was obtained. Less CO_2 was found to have been formed; water was formed in a substantial proportion, however.

EXAMPLE 2.

The procedure was as described in Example 1, but granular pumice was charged with $K_4[Fe(CN)_6]$ and the granular material was introduced into an aqueous solution of copper and iron sulfates (molar ratio = 1:1). The cyanide complex applied to the granular pumice corresponded approximately to the following formula $CuFe[Fe(CN)_6]$. The dry granular material was contacted with 30 normal liters per hour of a H_2/CO-mixture (molar ratio = 1:1) at 345°C under a pressure of 9.5 atmospheres gauge. The gas issuing from the reactor contained 2.4% by volume of C_2 hydrocarbons, 1.3% by volume of C_3 hydrocarbons, 1.1% by volume of C_4 hydrocarbons and 6.4% by volume of methane.

EXAMPLE 3.

0.5 mole of $K_4[Fe(CN)_6]$ was dissolved in a suspension of 90 g of very finely divided silicic acid (AEROSIL, a product of Degussa, Frankfurt/Main) in 2 liters of water. (The word "Aerosil" is a registered Trade Mark.) Next, a solution of 0.5 mole of $CuSO_4$ and 0.5 mole of $FeSO_4$ was stirred thereinto. The resulting precipitate was filtered off together with silicic acid, thoroughly washed with water and dried. 30 g of the product so obtained was contacted at 340°C and under a pressure of 9.5 atmospheres gauge with 30 normal liters per hour of a H_2/CO-mixture (molar ratio = 1:1). The issuing gas contained 4.4% by volume of C_2 hydrocarbons, 2.2% by volume of C_3 hydrocarbons, 1.2% by volume of C_4 hydrocarbons and 13.2% by volume of methane. Liquid higher hydrocarbons could not be found to have been formed. The reaction was accompanied by the formation of CO_2.

EXAMPLE 4.

The procedure was as described in Example 3, but the water-washed mixture was mixed with agitation with 5 weight %, based on the dry mixture, of potassium waterglass, which was a 28 weight % aqueous solution; the whole was dried and comminuted. The dry product was contacted at 360°C with a H_2/CO-gas mixture to effect reduction of the cyanide complex to the catalytically active material. The resulting reaction gas contained 3.5% by volume of C_2 hydrocarbons together with 9.6% by volume of CH_4.

EXAMPLE 5.

The procedure was as described in Example 3, but the AEROSIL silicic acid was replaced by hydrate of alumina (a commercially available product of Condea Petrochemie Gesellschaft mbH, Brunsbüttel). The reaction temperature was 315°C. The reaction gas contained 2.8% by volume of C_2 hydrocarbons together with 7.8% by volume of methane.

EXAMPLE 6.

An aqueous solution of 2 mol of $CuSO_4$ was mixed with agitation with an aqueous solution of 1 mol of $K_4[Fe(CN)_6]$ and copper ferrocyanide corresponding approximately to the formula $Cu_2[Fe(CN)_6]$ was found to have been precipitated. The precipitate was filtered off, washed with water, dried and tabletted. 30 g of the tabletted material was contacted at 360°C and under a pressure of 9.5 atmospheres gauge with 30 normal liters per hour of a H_2/CO-mixture. The resulting reaction gas contained 2.66% by volume of C_2 hydrocarbons and 11.7% by volume of methane. The hydrogenation was accompanied by the formation of water.

EXAMPLE 7.

An aqueous copper sulfate solution was introduced into an aqueous solution of potassium ferrocyanide, which had fine particulate pumice suspended therein, to cause precipitation of copper ferrocyanide which was deposited on the pumice. The mixture of pumice and copper ferrocyanide was filtered off, washed with water and dried at about 60°C. 30 g of the product so obtained was contacted at 320°C under a pressure of 9.5 atmospheres gauge with 30 normal liters per hour of a H_2/CO-mixture (molar ratio $\simeq$ 3:1). The resulting reaction gas contained 3% by volume of C_2 hydrocarbons and 10.5% by volume of methane. The oxygen contained in the CO-gas which underwent reaction was converted to CO_2.

EXAMPLE 8.

90 g of AEROSIL was suspended in a solution of 0.5 mole of $K_4[Fe(CN)_6]$ in 2 liters of water. The suspension was admixed with agitation with a solution of 1 mole of $CuSO_4$ and 2 liters of water and $Cu_2[Fe(CN)_6]$ was precipitated. The suspension was filtered, and the filter residue was washed with water and dried. The dry product was contacted at 320°C under a pressure of 9.5 atmospheres gauge with 30 normal liters per hour of a CO/H_2-gas mixture (molar ratio of $H_2:CO \approx$ 1:1). After reduction of the dry product to catalytically active material, the catalyst produced a reaction gas which contained 2.7% by volume of C_2 hydrocarbons, 1.5% by volume of C_3 hydrocarbons, 0.7% by volume of C_4 hydrocarbons and 4.6% by volume of CH_4.

EXAMPLE 9.

The procedure was as described in Example 8 but Al_2O_3 was substituted for the AEROSIL carrier. (The Al_2O_3 used was a product of Degussa, Frankfurt/Main, commercially available under the designation "Aluminiumoxid C".) The resulting reaction gas contained 3.5% by volume of C_2 hydrocarbons and 11.5% by volume of CH_4.

EXAMPLE 10.

0.5 mole of $Cu(NO_3)_2$ was dissolved in water and admixed with ammonia, and the resulting deep blue solution was decolorized by means of hydroxylamine hydrochloride. Next, the solution was admixed with 0.125 mole of $K_4[Fe(CN)_6]$ in 200 ml of water. The resulting white precipitate of the approximate formula $Cu_4[Fe(CN)_6]$ was filtered off, washed with water, dried and tabletted. 30 g of the tabletted product was contacted at 340°C under a pressure of 9.5 atmospheres gauge with 30 normal liters per hour of a H_2/CO-mixture (molar ratio = 1:1). The resulting reaction gas contained 2.5% by volume of C_2 hydrocarbons and 10% by volume of CH_4.

EXAMPLE 11.

1.2 mole of $Cu(NO_3)_2$ was dissolved in water and admixed with ammonia, and the resulting deep blue solution was decolorized by means of hydroxylamine sulfate. 90 g of AEROSIL was suspended in the solution and the resulting suspension was admixed with 0.3 mole of $K_4[Fe(CN)_6]$. The suspension was filtered and the filter residue was washed with water and dried. 30 g of the dry product was contacted at 325°C under a pressure of 9.5 atmospheres gauge with 30 normal liters per hour of a H_2/CO-gas mixture (molar ratio = 1:1). The resulting reaction gas contained 2.6% by volume of C_2 hydrocarbons and 11.2% by volume of CH_4.

EXAMPLE 12.

The procedure was as described in Example 11, but the AEROSIL was replaced by alumina (a product of Degussa, commercially available under the designation of "Aluminiumoxid C"). The resulting reaction gas contained 2.5% by volume of C_2 hydrocarbons and 9.2% by volume of CH_4.

EXAMPLE 13.
(Comparative Example)

A hot solution of 1 mole of $Cu(NO_3)_2$, 0.5 mole of $Fe(NO_3)_3$, and 6 g of $Zr(NO_3)_4$ in 2 liters of water was admixed with thorough agitation with 2.5 liters of an aqueous solution containing 2 moles of Na_2CO_3. Next, the mixture was stirred into 100 g of kieselguhr. The resulting precipitate was suction-filtered, thoroughly washed with water and dried. 30 g of the dry product was reduced by means of hydrogen over a period of 2 hours, at 300°C and under a pressure of 5 atmospheres gauge. The catalyst so obtained was contacted with 30 liters per hour of a H_2/CO-mixture (molar ratio = 2:1). The resulting reaction gas contained the following quantities of C_2 hydrocarbons, methane and CO_2, depending on the reaction temperature used in each particular case.

TABLE :

Temp. °C	Pressure atm. gauge	C_2-hydrocarbons % by volume	CH_4 % by vol.	CO_2 % by vol.
350	9.5	0.22	0.98	0.93
390	9,5	0.35	1.60	1.64
410	9,5	0.33	1.65	1.55

The water of hydration present in the salts specified in the above Examples and used for making the catalysts has been disregarded for reasons of simplicity.

WHAT WE CLAIM IS:—

1. Catalyst containing iron or a mixture of iron and copper as its catalytically active ingredient for reducing carbon monoxide by means of hydrogen with the resultant formation of a mixture substantially of hydrocarbons having 1 to 4 carbon atoms, said catalyst being made by contacting one or more complex salts of the following general formula:

$$Me_x[Fe(CN)_6]_y$$

in which Me stands for an iron and/or copper ion, x stands for 1 to 4, and y stands for 1 to 3, with hydrogen or a hydrogen/carbon monoxide-mixture, at a temperature of 200 to 500°C, under a pressure of 1 to 100 atmospheres absolute and over a period of 2 to 20 hours and thereby reducing the complex salt(s) substantially to elementary iron or copper.

2. Catalyst as claimed in claim 1, wherein the parameter x stands for 2 or 4 and the parameter y stands for 1 or 3.

3. Catalyst as claimed in claim 1 or 2, the catalyst having been made by contacting the said one or more complex salts with at least stoichiometric proportions of hydrogen or a hydrogen/carbon monoxide-mixture at a temperature of 350 to 400°C, under a pressure of 5 to 50 atmospheres gauge and over a period of 3 to 10 hours.

4. Catalyst as claimed in any one of claims 1 to 3, having been made by contacting the said one or more complex salts with a hydrogen/carbon monoxide mixture in a molar ratio of 3:1 to 2:1.

5. Catalyst as claimed in any one of claims 1 to 4, wherein the said one or more complex salts are made by precipitating it or them from an aqueous alkali metal ferrocyanide solution by means of an aqueous solution of an iron and/or copper salt, and separating and drying the precipitated salt or salts.

6. Catalyst as claimed in any one of claims 1 to 5, the catalyst being in the form of granules or pellets.

7. Catalyst as claimed in any one of claims 1 to 5, the catalyst being deposited on a carrier.

8. Catalyst as claimed in claim 7, wherein the carrier is alumina, silicic acid, kieselguhr, asbestos, glass fibers, a clay mineral, pumice or active carbon.

9. Catalyst as claimed in claim 7, wherein 20 to 95 weight % of catalytically active ingredient is applied to the carrier, the percentage being based on the total weight of catalytically active ingredient and carrier.

10. Process for the catalytic reduction of carbon monoxide by means of hydrogen with the resultant formation of a mixture substantially of hydrocarbons containing 1 to 4 carbon atoms by contacting a carbon monoxide/hydrogen-mixture at elevated temperature, at atmospheric or higher pressure with a catalyst containing iron or a mixture of iron and copper as its catalytically active ingredient and being deposited on a carrier, if desired, which process comprises: contacting the gas mixture containing hydrogen and carbon monoxide in a molar ratio of 0.5—3:1, at a temperature of 200 to 500°C, and under atmospheric pressure or a superatmospheric pressure of up to 100 atmospheres absolute, with a catalyst, the gas mixture being used at a rate of 100 to 10 000 normal liters (S.T.P.) per liter of catalyst per hour, and separating hydrocarbons having from 1 to 4 carbon atoms from the issuing gas, said catalyst having been made by contacting one or more complex salts of the following general formula:

$$Me_x[Fe(CN)_6]_y$$

in which Me stands for an iron and/or copper ion, x stands for 1 to 4, and y stands for 1 to 3, with hydrogen or a hydrogen/carbon monoxide mixture, at a temperature of 200 to 500°C, under atmospheric pressure or a superatmospheric pressure of up to 100 atmospheres absolute, and over a period of 2 to 20 hours and thereby reducing the complex salt(s) to elementary iron or copper.

11. Process as claimed in claim 10, wherein the gas mixture contains hydrogen and carbon monoxide in a molar ratio of 0.8—3:1.

12. Process as claimed in claim 10 or 11, wherein the catalyst is contacted at a temperature of 250 to 450°C under a pressure of 5 to 50 atmospheres gauge with 200 to 5000 normal liters of gas mixture, per liter of catalyst per hour.

13. Process as claimed in any one of claims 10 to 12, wherein the parameter x stands for 2 or 4 and the parameter y stands for 1 or 3.

14. Process as claimed in any one of claims 10 to 13, wherein the said one or more complex salts are contacted with at least stoichiometric proportions of hydrogen or a hydrogen/carbon monoxide mixture at a temperature of 350 to 400°C, under a pressure of 5 to 50 atmosphéres gauge and over a period of 3 to 10 hours.

15. Process as claimed in any one of claims 10 to 14, wherein the said one or more complex salts are contacted with a mixture of hydrogen and carbon monoxide in a molar ratio of 3:1 to 1:2.

16. Process as claimed in any one of claims 10 to 15, wherein the said one or more complex salts are made by precipitating it or them from an aqueous alkali metal ferrocyanide solution by means of an aqueous solution of an iron and/or copper salt, and separating and drying the precipitated salt or salts.

17. A process for the catalytic reduction of carbon monoxide conducted substantially as described in any one of Examples 1 to 12 herein.

18. Catalyst as claimed in any one of claims 1 to 9 herein and whenever obtained by a process as described in any one of Examples 1 to 12 herein.

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