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COMPLETE SPECIFICATION

Process for the Hydrogenation of Carbon Monoxide

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The invention relates to a process for the hydrogenation of carbon monoxide carried out in the presence of copper-containing fused and/or sintered iron catalysts.

In the hydrogenation of carbon monoxide with hydrogen, particularly with the use of iron catalysts, the use of fused and sintered catalysts, as well as the use of precipitated catalysts, is known. Fused and sintered catalysts are in practice exclusively used, for example, in the so-called "fluidized synthesis" since the mechanical strength the precipitated catalysts is not sufficient to withstand the conditions which occur in this process. Fused and sintered catalysts, in both the pulverulent and the granular state, have also been used for the wet synthesis with moving or fixed-bed catalysts. For synthesis with a stationary catalyst disposed in tubes, the use of a fused or sintered catalyst has been suggested as yet only in a few cases. The reason for this might be that catalysts of this kind generally require a higher operating temperature than precipitated catalysts to yield a $CO+H_2$ conversion of a commercially usable level.

The fused and sintered catalysts hitherto proposed have in practice consisted to the extent of more than 90%, preferably even more than 95%, of iron. Promoters such as aluminium oxide, titanium oxide, zirconium oxide as well as silicon dioxide and other compounds have been suggested as catalyst additives. An alkali content which is not very high and which has generally been limited to 1% based on the iron present, has also been stated to have a promoting or activating effect. These catalysts, namely the type of conventional fused catalyst used in the synthesis of ammonia, are prepared by melting iron or iron powder, or, if desired, iron oxide powder, separately or in admixture, in an oxidising atmosphere, whilst the addition of promoters is effected before or during the melting process. It has also been proposed to heat the corresponding powders only to a temperature at which sintering occurs rather than to melt them, in order to obtain a more porous catalyst structure. However, up to the present these methods seem to have found no use on a commercial or industrial scale in the preparation of catalysts for the hydrogenation of carbon monoxide.

It is an object of the invention to provide a process for the hydrogenation of carbon monoxide in the presence of a fused or sintered iron catalyst, in which good yields of hydrocarbons and/or oxygen-containing organic compounds may readily be obtained.

According to the invention, a process for the hydrogenation of carbon monoxide with the production of hydrocarbons and/or oxygen-containing organic compounds containing more than one carbon atom in the molecule, comprises effecting the hydrogenation at a temperature in the range 150°—350° C. and at a pressure in the range 1—200 atmospheres absolute in the presence of a fused or sintered iron catalyst containing more than 20% by weight of copper relative to the total amount of iron in the catalyst, which catalyst has been reduced at a temperature not exceeding 350° C. prior to use in the hydrogenation.

The hydrogenation is preferably effected at a temperature in the range 180°—270° C. and at a pressure in the range 10—50 atmospheres. The reduction of the catalyst is preferably effected with a gas containing hydrogen and/or carbon monoxide and the temperature during the reduction of the catalyst is preferably below 300° C.

The process according to the invention enables the hydrogenation of carbon monoxide to be effected at temperatures which are appreciably lower than those required with fused and sintered catalysts which have previously been used or proposed for use in the synthesis of hydrocarbons and oxygen-containing organic compounds by the hydrogenation of carbon monoxide. At the same time, the addition of copper has the effect of considerably reducing the proportion of undesirable C_1—C_2 compounds in the primary products. Furthermore, this eliminates or appreciably reduces the troublesome property of the fused and sintered catalysts hitherto disclosed of causing the separation of carbon to a relatively high extent during the synthesis, which carbon leads to considerable practical difficulties and results in a severe reduction of the activity of the catalyst. Due to the high copper content, it is now possible in contrast to the prior art, to effect the reducing pretreatment of the catalyst at a low temperature of below 350° C. in the synthesis reactor itself.

It is of particular advantage that catalysts of this kind show substantially no shrinkage during the reduction which could cause the formation of voids or channels in reactors which, for example are provided with tubes into which the catalyst is charged prior to reduction.

It is very remarkable that the process may be carried out with excellent yields, especially of synthesis products containing increased proportions of high molecular weight oxygenated products and particularly of esters, if more than 4% and preferably 6—10% of alkali, calculated as K_2O, and preferably more than 25% of copper, based in each case on the total iron present, are contained in the catalyst with at least 80% of the total iron being in the metallic state after reduction.

Normally gaseous, liquid and solid compounds are obtained in the synthesis and comprise gaseous hydrocarbons, liquid hydrocarbons and alcohols, and solid high molecular weight hydrocarbons the normally liquid compounds forming the bulk of the synthesis product. Valuable low molecular weight alcohols are contained in the water formed in the reaction. Of the greatest practical interest is the composition of the main product, namely the liquid hydrocarbons and alcohols. Increased alkali content of the catalysts, depending on the conditions of the preparation of the catalysts and the kind of alkali used, permits the yield of the normally liquid product to be increased and the proportions of its constituents to be varied.

Fused and sintered catalysts which have been subjected to a short-time, more or less complete reduction, that is to say, catalysts having a reduction value of more than 80% (more than 80% of the iron being in the elementary state), and a high copper content and a high alkali content of more than 4%, calculated at K_2O and based on the total iron, effect, for example, to an increased extent the formation of oxygenated compounds boiling above 320° C. of which esters constitute not only a very high percentage, for example, more than 25% by weight and often more than 35% by weight, but also exceed to a considerable extent the amount of alcohols boiling above 320° C. The total amount of the products boiling above 320° C. may also constitute 25% or more of the total yield of liquid products, a result which is very surprising for fused and sintered catalysts. In the fraction boiling between 30° C. and 180° C., the alcohols are the main oxygenated products in this case. In this fraction boiling in the range 180°–320° C. the ester content amounts to approximately 20—30% and is thus nearly always higher than that of the alcohols.

If the alkali component in fused catalysts is added in the form, for example, of potassium silicate rather than, for example, as KOH or K_2CO_3, then the formation of high molecular weight hydrocarbons increases at the expense of the esters content.

Furthermore, an incomplete reduction of the same catalyst makes possible a high content of oxygenated compounds in the synthesis products; however, in this case the proportion of esters in the oxygenated products decreases whilst the proportion of alcohols increases considerably. When such a synthesis is desired, that is to say, when the synthesis is operated for the production of synthesis products which contain more than 50% of oxygenated compounds without having a particularly high proportion of esters, then fused and sintered catalysts must be used the alkali content (based on the total iron and calculated as K_2O) of which is more than 1.5% and preferably more than 4%, and the content of free iron of which is less than 80% and preferably between 20% and 60% of the total iron.

In contrast to the synthesis with the use of precipitated iron catalysts in which it is generally essential that more than 60% and preferably more than 80% of the iron present should be in the free state for the synthesis of a product which contains more than 50% of oxygenated compounds, it is very surprisingly possible when operating with fused and sintered catalysts to obtain a marked increase in the formation of oxygenated compounds and to obtain a product containing 60% or more of such compounds with the use of the iron-copper-alkali catalysts according to the invention having reduction values of only 20%—60%.

A further advantage of the process according to the invention consists in that the methane formation, which is generally undesired in the hydrogenation of carbon monoxide, is only very low and constitutes only a fraction of the methane formation hitherto observed. Moreover, the content of products having a boiling point in excess of 320° C is in general higher than with the hitherto known fused and sintered catalysts. Yields of more than 30% are obtainable without difficulty.

The process, in accordance with the invention, is advantageously carried out with the catalysis in a fixed bed which, however, under certain circumstances may be surrounded by a liquid cooling agent. The process of the invention is also applicable to a synthesis with a pulverulent catalyst ("fluidized synthesis"). In the first case, particle sizes of between approximately 0.5—6 mm. and preferably between 1—4 mm. are used. The fluidized synthesis uses a particle size of below 0.5 mm. and preferably below 0.2 mm. Finally, the so-called "wet synthesis process" may be carried out with any particle size.

The reduction of the catalysts according to the invention, which may be carried out, if desired, in the synthesis reactor itself, is preferably effected with the use of a high gas velocity of above 50 cm./second and preferably above 120 cm./second (measured at room temperature and at atmospheric pressure). The reduction may be effected at atmospheric pressure, superatmospheric pressure or at subatmospheric pressure. Gas velocities of 50—150 cm./second are preferably used when operating at atmospheric pressure, and velocities of 5—40 cm./second when operating at superatmospheric pressure, the gas velocity in each case being measured at room temperature and at the pressure at which the reduction is effected. The H_2O content of the reduction gas is maintained below 1 gram/cu. m. and preferably below 0.1 gram/cu.m.

When the catalyst is to contain less than 80%, and preferably from 20% to 60% of its iron in the free state it has been found to be particularly advantageous to effect the reduction with hydrogen and/or carbon monoxide-containing gases for 30—90 minutes in the temperature range 300°—350° C., for about 90—240 minutes in the temperature range 250°—300° C., and for more than 240 minutes to as long as 600 minutes at temperatures below 250° C. With all fused or sintered iron-copper-alkali catalysts according to the invention, synthesis gases rich in carbon monoxide are or may be used for the purpose of obtaining an increased yield of high molecular weight oxygenated compounds, particularly of esters. The same catalysts are suitably used with hydrogen-rich gases if less high molecular weight products having a reduced content of esters, but an increased content of alcohols, particularly C_6—C_{18} alcohols are to be recovered

The promoters for the catalysts mentioned above include, for example, chromium oxide, manganese oxide, aluminium oxide, calcium oxide, titanium dioxide, silicon dioxide, alkalis or alkaline earths.

The production of the fused catalysts used is simplified by the fact that a part of the mixture of the components consists of a salt or salts which exhibit oxidising properties. Nitrites, nitrates, or perborates have been found to be particularly suitable for this purpose.

The carrying out of the reduction in the synthesis reactors proper eliminates the necessity of a specific reduction apparatus, which has hitherto been required in most cases.

The production of the catalysts used in accordance with the invention follows partly the known methods, but is fundamentally different in several details. The iron present in the catalyst may be used in the metallic state but is preferably used in the form of oxide. The copper may likewise be used in the form of its monovalent oxide or its bivalent oxide. However, in certain cases the use of metallic copper is particularly advantageous. For the purpose of the oxidation it is frequently of advantage to use a certain part of the metals in the form of salts such as in the form of nitrates or perborates. This applies in particular if the proportion present as metal is high.

For the production of fused catalysts, the starting material may be in the form of powder as well as in the form of lumps. For the production of sintered catalysts, it has been found to be particularly advantageous to add the iron and copper used as the starting material in the form of a powder of the smallest possible particle size of below 100μ, preferably below 10μ.

In the production of sintered catalysts, the sintering temperature and sintering period are of considerable importance. When starting with metals, lower temperatures are required than with metal oxides. The sintering time is determined by the grain structure desired. The grain or particle size increases and the pore volume decreases as the sintering time increases. The atmosphere used for the fusion and sintering should be oxidising in character in order to convert the metallic components largely into oxides and to prevent a premature reduction of the metal oxides. The addition of promoters, which are the conventional elements and their compounds known from the literature as promoters in the catalytic hydrogenation of carbon monoxide, may be effected before the fusion as well as during the fusion step. With sintered catalysts, it is generally preferred to add the promoters before the step of sintering. In a few cases it is also possible, for example, to soak or impregnate the sintered material after the sintering with aqueous solutions of the promoters and to subject the material to an after-sintering. In this way, the addition of alkali such as in the form of potassium carbonate and potassium silicate or sodium nitrate, is possible.

The cooling of the molten mass is most suitably effected in the air. This is followed by crushing of the fused or sintered mass. When the synthesis is to be carried out with the catalyst disposed in tubes, the catalyst particles should have a diameter of between approximately 0.5 mm. and 5 mm., preferably between 1 mm. and 3 mm. In a liquid phase syntheses, the particle size may advantageously be considerably lower such, for example, as below 100μ. The pulverulent material produced during the crushing of the catalyst may be added to a new melt.

Due to their low tendency to form carbon deposits, the catalysts in accordance with the invention may also be used for the fluidized synthesis. It is also possible to use them in processes of carbon monoxide hydrogenation which operate with a gas velocity which lies considerably above that of the fluidized system. The use of the catalysts according to the invention for a carbon monoxide hydrogenation in the liquid prase, and particularly in an oily phase, is possible with catalysts in either the pulverulent or granular state.

The regeneration of the spent, fused catalysts may be effected in accordance with the prior art by oxidising re-melting preceded, if necessary or desired, by a treatment with hydrogen. In particular cases, it is sufficient to subject the catalysts to a careful oxidising treatment with gases which contain only small amounts of oxygen such as 0.5%—5%, in order to burn off the carbon deposited on the catalyst. Thereafter, a reactivation with reducing gases is required. This latter expedient may also be used in certain circumstances with sintered catalysts. When completely working up the catalyst mass, it may be sufficient in particular cases to crush the mass to the particle size stated above and then to subject it to a new sintering. Since such catalysts, owing to their structure being somewhat different from that of the original catalysts, frequently give somewhat different synthesis results, a chemical processing with the separation into the individual starting components cannot be avoided in particular cases.

Pressures of as low as 1 atmosphere absolute may be used in the carbon monoxide hydrogenation. The synthesis results improve, however, when operating above 5 atmospheres such, for example, as in the range 10—40 atmospheres. The gas load or space velocity may be varied within wide limits such, for example, as between 10 and 1000 volumes of gas per volume of catalyst per hour. The temperature, when operating with fixed-bed catalysts is preferably between 180° C. and 270° C., while the $CO:H_2$ mol ratio may range between approximately 1:05 and 1:5. The use of gas recycling with a recycle ratio (vol. fresh gas: vol. recycle gas) which may range, for example, between 1:1 and 1:4, is advantageous in any case. It is also possible, however, to operate on a once-through basis. When operating the fluidized synthesis and, under certain circumstances, the so-called wet synthesis, the synthesis temperature is preferably maintained in the higer part of the range 150°—350° C.

When operating with fixed-bed catalysts, it is possible to use long and wide tubes in the reactor such, for example, as tubes of 10—25 metres length while the diameter of the tubes may be approximately 10—100 mm. and preferably 30—50 mm. Of course, short and narrow tubes may also be used.

The invention is illustrated by the following examples.

EXAMPLE 1.

1000 grams of a mixture consisting of 130

Fe_2O_3 (jeweller's rouge), CuO and potassium carbonate, the ratio of $Fe:Cu:K_2O$ being 100:25:8, were fused in the presence of oxygen. The fusing temperature of the mixture was approximately 1600° C. The particle sizes of Fe_2O_3 and CuO were approximately 1—3μ and 18μ, respectively.

After cooling the melt, the fused cake was crushed to a particle size of between 1.0 mm. and 2 mm. The reduction was effected for 2 hours at 350° C. with a H_2/N_2 mixture (75% H_2, 25% N_2 by weight) using a gas velocity of 1.5 metres/second (standard conditions). Thereafter, the reduction value of the catalyst was approximately 100%, that is to say, approximately all of the iron was in the metallic state.

This catalyst was charged into the annular space of a double-tube reactor formed by two concentric tubes, the inner tube having an outer diameter of 24 mm. and the outer having an inner diameter of 44 mm. When super-purified water gas was passed through the catalyst at a synthesis pressure of 20 atmospheres gauge in single-pass operation, a CO conversion of 81% ($CO + H_2$ conversion = 61.5%) was obtained at a temperature of 207° C The composition of the liquid primary products was as follows:—

Fraction	Weight % of total liquid product	Aliphatic Esters %	Alcohols %
above 320° C.	26.2	40	2
180°—320° C.	25.8	25	10
30°—180° C.	48.0	10	33

When using a standard ammonia synthesis catalyst consisting of approximately 96% Fe and small amounts of Al_2O_3, SiO_2, etc., a synthesis temperature higher by 12° C. was required under otherwise the same synthesis conditions to obtain the same conversion. In this case the yield of compounds boiling above 320° C. was below 19%; the ester content was approximately 20%.

EXAMPLE 2.

A catalyst which contained 5.2 parts K_2O instead of 8 parts K_2O and, in addition, 10 parts of ZnO (particle size about 1μ) based on 100 parts of iron, was prepared in the manner described in Example 1. Under the same reduction and synthesis conditions as described in Example 1, the following results were obtained:—

CO conversion - - -	81.5%
$CO + H_2$ conversion - -	63%
Synthesis temperature -	207° C.

The composition of the synthesis product obtained was as follows:—

Fraction	Weight % of total liquid product	Esters %	Alcohols %
above 320° C.	28	25	10
180°—320° C.	26	22	22
30°—180° C.	46	13	30

When this catalyst was reduced in a synthesis reactor of 5 metres length (tube diameter 14 mm.) for 30 hours at 250° C. with a mixture consisting of 75% H_2 and 25% N_2 by weight (reduction value of catalyst 85%) and subsequently used in synthesis under the conditions given above, the following results were obtained:—

CO conversion - - - -	84%
$CO + H_2$ conversion - - -	63%
Synthesis temperature - -	231° C.

(With a reduction time of 48 hours, the synthesis temperature could be lowered to 225° C.). The composition of the liquid products obtained was similar to that given above.

EXAMPLE 3.

A mixture consisting of Fe_2O_3, CuO (particle size of Fe_2O_3 about 3μ of CuO about 2μ and K_2CO_3 in a ratio of 100:25:5 calculated as $Fe:Cu:K_2O$, was pasted with a little water, dried for 5 hours at 100°—120° C. and sintered for 60 minutes at a temperature of 1150° C. in the presence of air. The cooled mass was crushed and sieved to a particle size of between 1 mm. and 2 mm.

The reduction of the granular catalyst was effected for 120 minutes at a temperature of 350° with a mixture consisting of 75% H_2 and 25% N_2 by weight at atmospheric pressure using a linear gas velocity of 1.5 metres/second. The reduction value of the reduced catalyst was about 80%.

When this catalyst was used at a synthesis pressure of 20 atmospheres gauge with water gas on a once-through basis, a $CO + H_2$ conversion of 61% was obtained at 215° C. The gas load was 200 litres of gas per litre of catalyst per hour. The liquid product obtained had the following composition:—

Fraction	Weight % of total liquid product	Esters %	Alcohols %
above 320° C.	29	45	1
180°—320° C.	20	33	5
30°—180° C.	51	11	35

When the same catalyst was reduced in a synthesis reactor for 30 hours at 250° C. with H_2/N_2 (reduction value of the catalyst 82%), the $CO + H_2$ conversion under the same conditions as set forth above was 63% at a synthesis temperature of 230° C. The yield of high boiling products and of oxygenated compounds in the liquid product was somewhat reduced.

Example 4.

A hot aqueous solution containing, per litre, 40 grams Fe and 10 grams Cu in the form of their nitrates, was poured into a likewise hot solution of 100 grams of soda/litre of water. The quantities were so proportioned that the pH value after the precipitation was approximately 7—7.2. The precipitated catalyst mass was filtered in the hot state, freed by washing from the alkali to about 0.5 grams residual alkali based on 100 grams of iron, and divided into two parts. The first part was impregnated with KOH in such a manner that 6 parts calculated as K_2O were contained therein per 100 parts of iron. The second portion was impregnated with potassium waterglass in such a manner that 5 parts K_2O (calculated) and 25 parts SiO_2 were present for every 100 parts of Fe. The moist mass was dried at about 120° C.

The two masses were separately fused at about 1500° C. in the presence of air as oxidising agent. The melt obtained was crushed and sieved to a particle size of between 1 mm. and 2.5 mm. (The undersized particles and the dust may be added to a new melt.)

The reduction was carried out for 120 minutes at 350° C. with a mixture consisting of 75% H_2 and 25% N_2 by weight. The reduction value of each catalyst was 85%.

When the catalyst which had been impregnated with KOH was used in synthesis with water gas at 210° C., a pressure of 20 atmospheres gauge and a gas load of 200 volumes of gas per volume of catalyst per hour, a $CO + H_2$ conversion of 63% was obtained. The liquid product obtained had the following composition:

Fraction	Weight % of total liquid product	Esters %	Alcohols %
above 320° C.	28	41	small amount
180°—320° C.	72	29	10
30°—180° C.		8	80

In addition, all fractions contained small amounts of ketones, aldehydes and acids.

With the use of gas recycling (1 vol. fresh gas:2 vols recycle gas) the other conditions being the same, the yield of high molecular weight compounds boiling above 320° C. increased somewhat (to 31%); moreover, the yield of oxygenated compounds increased to a certain extent.

When the catalyst was reduced at 240° C. with a gas consisting by weight of 27% CO and 52% H_2, the remainder being inerts, at a linear gas velocity of 1.3 metres/second based on standard conditions, 24 hours were required. The reduction value of the cataylst was then 80%. The yield of high molecular weight compounds boiling above 320° C. increased by 3% while the yield of oxygenated compounds decreased somewhat in favour of the olefins.

The second catalyst which was reduced under the same conditions set forth above, gave in each of the three experiments an increased yield of products boiling above 320° C. The proportion of the other fractions, particularly that of the fraction boiling in the range 30°—180° C., decreased correspondingly. The yield of oxygenated compounds was likewise reduced in all fractions.

EXAMPLE 5.

A mixture of 100 parts of iron in the form of Fe_2O_3 having a particle size of 1—3μ, 25 parts of copper in the form of CuO having a particle size of about 8μ, and potassium carbonate in a quantity of 5% by weight calculated as K_2O and based on the total amount of iron, was rapidly melted in the presence of ample oxygen. After cooling and crushing to a particle size of 1.5—2 mm., the mass was reduced in a reduction apparatus for 10 hours at a temperature of 240° C. with a gas mixture consisiting of 75% H_2 and 25% N_2 by weight at a linear gas velocity of 1.5 metres/second based on standard conditions. The reduction value of the catalyst was then 23%. When the reduction was effected at a temperature of 290° C. for 3 hours, the reduction value was 44%, while reduction at 350° C. for 90 minutes gave a reduction value of 60%.

These three catalysts were tested in reactors of 1.5 metres length and a tube diameter of 12 mm. The synthesis gas was super-purified water gas; the synthesis pressure was 20 atmospheres gauge and the gas load was 200 volumes of gas per volume of catalyst per hour, the synthesis being carried out on a once-through basis. The CO conversion was 81—84% with a comsumption ratio of 0.7—0.75, and the methane formation was between 6 and 8%. A comparative experiment carried out at a temperature which was only 20° C. higher with a standard ammonia synthesis catalyst which was reduced to yield about 20% Fe, gave in all fractions substantially lower yields (only about half as high) of oxygenated compounds, considerably lower yields of high molecular weight compounds boiling above 320° C. (only about 15%) and a substantially greater formation of methane (about 15%).

EXAMPLE 6.

A mixture consisting of Fe_2O_3 having a particle size of 1—3μ, CuO having a particle size of about 8μ, and potassium carbonate in a ratio of 100:22:5 calculated as $Fe:Cu:K_2O$, was pasted with a little water, granulated to a particle size of 1.5—2 mm., dried at 130° C. for several hours and sintered at 1250° C. for 60 minutes.

The reduction was effected at 240° C. for 9 hours (reduction value of the catalyst 25%), at 230° C. for 3 hours (reduction value of the catalyst 39%) and at 340° C. for 75 minutes (reduction value of the catalyst 57%).

Comparative tests were carried out in a reactor of 12 mm. inside diameter and 1.5 metres length which was heated with water under pressure. Highly-purified water gas was used as synthesis gas, the synthesis pressure was 20 atmospheres gauge and the gas load was 200 volumes of gas per volume of catalyst per hour. The synthesis was effected without gas recycling, the following results being obtained:—

Reduction value of the catalyst %	Synthesis temperature °C.	Content of oxygenated compounds (chiefly alcohols) in the liquid product, %	High molecular weight compounds boiling above 320% C. %	Methane formation based on $CO + H_2$ charged %
25	218	61	35	5
39	215	57	32	6.5
57	212	52	28	8

The CO conversion was about 85% with the consumption ratio being 0.7.

With one-stage operation, conversion rates of 90% and more such as, for example, 95% may be obtained without difficulty. In multi-stage operation, a partial removal of the carbon dioxide between the stages is advantageous under certain circumstances.

What we claim is:—

1. A process for the hydrogenation of carbon monoxide with the production of hydrocarbons and/or oxygen-containing organic compounds containing more than one carbon atom in the molecule, in which the hydrogenation is effected at a temperature within the range 150°—350° C. and at a pressure within the range 1—200 atmospheres absolute in the presence of a fused or sintered iron catalyst containing more than 20% by weight of copper based on the total amount of iron in the catalyst, which catalyst has been reduced at a temperature not exceeding 350° C. prior to use.

2. A process according to Claim 1 in which the hydrogenation is effected at a temperature within the range 180°—270° C.

3. A process according to Claim 1 or

Claim 2 in which the hydrogenation is effected at a pressure within the range 10—50 atmospheres absolute.

4. A process according to any one of the preceding claims, in which the reduction of the catalyst is effected at a temperature below 300° C.

5. A process according to any one of the preceding claims, in which the catalyst contains one or more elements or compounds known to be effective as promoters of iron catalysts in the hydrogenation of carbon monoxide.

6. A process according to any one of the preceding claims, in which the catalyst contains more than 4% by weight of an alkali-metal compound calculated as K_2O, based on the total amount of iron in the catalyst, more than 80% of the iron being in the free state after the reduction.

7. A process according to Claim 6, in which the catalyst contains more than 25% by weight of copper and from 6% to 10% by weight of the alkali-metal compound (calculated as K_2O), both based on the total amount of iron in the catalyst.

8. A process according to any one of claims 1 to 5, in which the catalyst contains more than 1.5% by weight of an alkali-metal compound (calculated as K_2O) based on the total amount of iron in the catalyst, less than 80% of the iron being in the free state.

9. A process according to Claim 8, in which 20—60% of the iron in the catalyst is in the free state.

10. A process according to Claim 8 or Claim 9, in which the catalyst contains more than 4% by weight of an alkali-metal compound (calculated as K_2O) based on the total amount of iron in the catalyst.

11. A process according to any one of the preceding claims, in which the reduction of the catalyst is effected at atmospheric pressure with a velocity of the reducing gas of not less than 50 centimetres/second (measured at room temperature and atmospheric pressure).

12. A process according to Claim 11, in which the velocity of the reducing gas is more than 120 centimetres/second.

13. A process according to any one of the preceding claims, in which the reduction of the catalyst is effected in the reactor in which the hydrogenation of the carbon monoxide is to be effected.

14. A process according to any one of claims 1 to 10, in which the reduction of the catalyst is effected under superatmospheric pressure at a gas velocity in the range 5—40 centimetres/second (measured at room temperature and at the superatmospheric pressure).

15. A process according to any one of claims 1 to 10, in which the reduction of the catalyst is effected at subatmospheric pressure.

16. A process according to any one of the preceding claims, in which the gas used for the reduction of the catalyst has a water-vapour content of less than 1 gram per cubic metre of gas.

17. A process according to Claim 16, in which the water vapour content of the gas is less than 0.1 gram per cubic metre.

18. A process according to any one of the preceding claims, in which the reduction of the catalyst is effected with a gas containing hydrogen and/or carbon monoxide at a temperature in the range 300°—350° C. for a period of about 30—90 minutes.

19. A process according to any one of Claims 1 to 17, in which the reduction of the catalyst is effected with a gas containing hydrogen and/or carbon monoxide at a temperature within the range 250—300° C. for a period of about 90—240 minutes.

20. A process according to any one of Claims 1 to 17, in which the reduction of the catalyst is effected with a gas containing hydrogen and/or carbon monoxide at a temperature below 250° C. for a period longer than 240 minutes and not longer than about 600 minutes.

21. A process according to any one of the preceding claims, in which the components used in the production of the catalysts consist in part of a salt or salts having oxidising properties, for example nitrates, nitrites and perborates.

22. A process according to any one of the preceding claims, in which a sintered catalyst is used, the iron and copper and/or their compounds from which the catalyst is produced, being in the form of a powder having a particle size below 100μ.

23. A process according to Claim 22, in which the particle size of the powder is below 10μ.

24. A process according to any one of the preceding claims, in which the catalyst is used in a fixed bed.

25. A process for the synthesis of esters of high boiling point, which comprises reacting hydrogen and carbon monoxide at a temperature within the range 150°—350° C. and at a pressure within the range 10—50 atmospheres absolute in the presence of a fused or sintered iron-copper-alkali metal catalyst, more than 80% of the iron in the catalyst being brought into the metallic state prior to use in the synthesis by treatment with

a gas containing hydrogen and/or carbon monoxide at a temperature not exceeding 350° C., the amount of copper in the catalyst being more than 25% by weight of the total amount of iron in the catalyst and the amount of alkali-metal, calculated as K_2O, in the catalyst being from 6% to 10% by weight of the total amount of iron.

26. A process for the synthesis of oxygen-containing organic compounds, which comprises reacting hydrogen and carbon monoxide at a temperature within the range 180°—270° C. and at a pressure within the range 10—50 atmospheres absolute in the presence of a fused or sintered iron-copper-alkali metal catalyst, between 20% and 80% of the iron in the catalyst being brought into the metallic state prior to use in the synthesis by treatment with a gas containing hydrogen and/or carbon monoxide at a temperature not exceeding 350° C., the copper content of the catalyst being more than 20% by weight of the total amount of iron therein and the alkali-metal content of the catalyst, calculated as K_2O, being more than 1.5% by weight of the total amount of iron.

27. A process according to Claim 25 or Claim 26 in which the alkali-metal is introduced into the catalyst in the form of the hydroxide or carbonate.

28. A process according to any one of the preceding claims, in which tail gas of the process is recycled.

29. A process according to any one of the preceding claims, carried out in two or more stages.

30. A process for the production of hydrocarbons and/or oxygen-containing organic compounds by the reaction of hydrogen and carbon monoxide, substantially as hereinbefore described.

31. A process for the hydrogenation of carbon monoxide, substantially as hereinbefore described with reference to any one of the examples.

32. Hydrocarbons and/or oxygen-containing organic compounds whenever produced by the process claimed in any one of the preceding claims.

33. A process for the production of a fused or sintered iron catalyst containing copper, substantially as hereinbefore described in any one of the examples.

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PATENT SPECIFICATION

728,715

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Application made in Germany on Jan. 19, 1953.

ERRATA

SPECIFICATION NO. 728,715

Ind

Page 1, line 25, *for* "the" *read* "of".

Page 2, line 110, *for* "esters" *read* "ester".

Page 4, line 118, *for* "higer" *read* "higher".

Page 5, line 88, *after* "$3/\mu$" *insert* ",".

Page 5, line 89, *after* "$2/\mu$" *insert* ")".

Page 5, line 100, *for* "350°" *read* "350°C.,".

Page 7, line 79, *for* "320%C." *read* "320°C.".

THE PATENT OFFICE,
17th June, 1955

DB 78150/2(15)/3377 150 6/55 R

and sintered catalysts are in practice exclusively used, for example, in the so-called "fluidized synthesis" since the mechanical strength the precipitated catalysts is not sufficient to withstand the conditions which occur in this process. Fused and sintered catalysts, in both the pulverulent and the granular state, have also been used for the wet synthesis with moving or fixed-bed catalysts. For synthesis with a stationary catalyst disposed in tubes, the use of a fused or sintered catalyst has been suggested as yet only in a few cases. The reason for this might be that catalysts of this kind generally require a higher operating temperature than precipitated catalysts to yield a $CO+H_2$ conversion of a commercially usable level.

The fused and sintered catalysts hitherto proposed have in practice consisted to the extent of more than 90%, preferably even more than 95%, of iron. Promoters such as aluminium oxide, titanium oxide, zirconium oxide as well as silicon dioxide

paration of catalysts for the hydrogenation of carbon monoxide.

It is an object of the invention to provide a process for the hydrogenation of carbon monoxide in the presence of a fused or sintered iron catalyst, in which good yields of hydrocarbons and/or oxygen-containing organic compounds may readily be obtained.

According to the invention, a process for the hydrogenation of carbon monoxide with the production of hydrocarbons and/or oxygen-containing organic compounds containing more than one carbon atom in the molecule, comprises effecting the hydrogenation at a temperature in the range 150°—350° C. and at a pressure in the range 1—200 atmospheres absolute in the presence of a fused or sintered iron catalyst containing more than 20% by weight of copper relative to the total amount of iron in the catalyst, which catalyst has been reduced at a temperature not exceeding 350° C. prior to use in the hydrogenation.