PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Catalysts for Carbon Monoxide Hydrogenation

We, RUHRCHEMIE AKTIENGESELLSCHAFT, Oberhausen/Holten, Germany, a German Company, and LURGI GESELLSCHAFT FUER WAERMETECHNIK M.B.H., Frankfurt a.M.-Heddernheim, Germany, a German Company, 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:—

The invention relates to the catalytic hydrogenation of carbon monoxide using iron catalysts.

For carrying out the catalytic hydrogenation of carbon monoxide with hydrogen, iron catalysts of various kinds are known, such as fused catalysts, sintered catalysts or precipitated catalysts. Fused catalysts are prepared by the fusion of iron powder in an oxidising atmosphere, disintegrating the fused mass and reducing the catalyst particles thus obtained in a stream of hydrogen, the reduction being preceded, if necessary or desired, by an alkaline impregnation. In the preparation of the sintered catalysts hitherto known, only a sintering of the iron powder has been carried out, preceded, if necessary or desired, by an alkaline impregnation. The sintered mass has then been disintegrated and reduced in a stream of hydrogen.

Water-soluble iron salts, chiefly iron nitrates, have generally been used for the preparation of precipitated catalysts. Iron sulphate, iron chloride and iron salts of organic acids or mixtures of these compounds have also been suggested. Precipitation of these soluble iron salts has been carried out with alkaline-reacting compounds in the presence, if necessary or required, of promoters, such as copper, silver, calcium, barium, titanium and chromium. Alkali-metal hydroxides and carbonates, and ammonia and compounds of ammonia are known as precipitants. The precipitate obtained is in general filtered under a high degree of suction, washed and subsequently, if necessary, impregnated with alkali followed in most cases by moulding for the purpose of obtaining a particle of maximum resistance to abrasion. This moulded grain is subsequently dried at temperatures of approximately 100° C.

Prior to being used in the hydrogenation of carbon monoxide, the catalysts are pretreated with reducing gases at temperatures between 100° C and 350° C. at various flow rates.

Although having good activity, precipitated catalysts, in contrast to fused and sintered catalysts, frequently have the disadvantage of disintegrating during reduction with the formation of undersize particles or catalyst dust even though the catalyst particles have been moulded prior to reduction. Removal of these smaller particles after reduction is difficult since the reduced catalyst particle is highly pyrophoric and sensitive to air. When carrying out the reduction of the catalyst in the synthesis reactor itself, the disadvantages are particularly objectionable since, when the precipitated catalyst is being charged into the reactor, obstructions by the catalyst dust or undersize particles may occur. This may result in difficulties, not only in the synthesis itself, but chiefly in the subsequent discharging of the synthesis reactor.

It has now been found, according to the invention, that the strength of the particles of an iron-containing precipitated catalyst for use in the hydrogenation of carbon monoxide may be increased by admixing iron powder with the oxide, hydroxide or carbonate of iron which is precipitated from a solution of an iron salt by an alkaline medium, the catalyst mass being then mounded and/or dried and afterwards reduced at a temperature within the range 100°—400° C.

The iron powder may be prepared by mechanical, chemical or physical processes. Mechanical processes include all processes in which mechanical means are

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employed in the production of a fine powder, for example, the coarse and fine crushing of compact iron metal in crushers and mills, in the presence of a liquid, such as water, or otherwise. Chemical processes include the reduction of iron compounds, particularly the oxides, with gaseous reducing agents, the reduction of iron ores and technical oxides with solid reducing agents, and the decomposition of atomized carbonyls or of atomized solutions of carbonyls. Physical processes comprise electrolytic processes and the like.

The particle size of the iron powders such as are used, for example, in numerous metallurgical purposes, is preferably from 10 microns to 250 microns, advantageously between 40 microns and 80 microns. The structure exhibited by the iron powder under the microscope should be as irregular as possible, since experience has shown that the greater the irregularity of structure or shape of the powder, the greater the strength of the catalyst particles.

The iron powder is advantageously used in the form of the pure iron powder. It is possible, however, to use an iron powder which contains a catalyst promoter, such as chromium, manganese, titanium, tungsten, an alkali or an alkaline earth metal compound.

In the preparation of the catalysts according to the invention, the initial precipitate, with or without promoters, is prepared in the usual manner, the quantity of iron in the solution of the iron salt from which the precipitate is produced being less by that quantity which is to be added as iron powder. The precipitation is carried out in known manner from solutions of the iron salts hereinbefore referred to, at temperatures of, for example, from 50° C. to 100° C. with use of a hot solution of an alkali-metal hydroxide or alkali-metal carbonate as precipitant. Immediately upon precipitation, the iron powder is stirred into and admixed with the precipitate, an efficient stirrer being advantageously used for this purpose in order to distribute the iron powder as uniformly as possible throughout the precipitate. The quantity of iron used in the form of iron powder may be as high at 80 per cent. Experiments have shown, however, that optimum effect is obtained by adding approximately 25—50 per cent. of the total iron content of the catalyst in the form of iron powder.

The catalyst mass is then processed in known manner, that is to say, it is washed several times, followed, if necessary or desired, by an impregnation with a promoter or with promoters to give a catalyst of the desired constitution. In certain circumstances, the extent of washing of the catalyst mass may be reduced so that a part of the alkali-metal compound used as precipitant or produced during precipitation, remains in the catalyst mass. The step of washing is expediently followed by moulding. It has been found, however, that by drying the moist catalyst mass at approximately 110° C., crushing the dried mass and screening the crushed mass to a particle size of approximately 1 to 3 mm., a catalyst is obtained, the strength of the particles of which, particularly upon reduction, is considerably superior to that of precipitated catalysts prepared without admixture of iron powder.

The process according to the invention is suitable for the preparation of catalysts which promote the formation of hydrocarbons as well as those which promote the formation of oxygen-containing organic compounds in the hydrogenation of carbon monoxide. Where the synthesis is to be carried out for the preferred formation of hydrocarbons, the iron powder is admixed with a precipitate which contains more or less large quantities of alkali, preferably K_2O, together with more or less large amounts of a radical of a non-volatile acid, such as a silicate, a borate or a phosphate. The catalyst should have a comparatively low reduction value, that is to say, not more than 50% of its total iron content should be in the form of free iron. When the catalyst is to be effective to promote the formation of hydrocarbons having boiling points not exceeding 200° C., the iron powder is admixed with a precipitate to yield a catalyst which contains from 1 to 6 parts, preferably from 2 to 4 parts, of alkali (calculated as K_2O) per 100 parts of the total iron content and from 3 to 15 parts, preferably 3 to 8 parts, of the radical of the non-volatile acid (calculated as the acidic oxide) per 100 parts of the total iron content of the catalyst. If the catalyst is to promote the formation of hydrocarbons having boiling points higher than 200° C., the iron powder is admixed with a precipitate to yield a catalyst which contains more than 15 parts, preferably from 15 to 30 parts, of the radical of the non-volatile acid (calculated as the acidic oxide) per 100 parts of the total iron content of the catalyst and from 4 to 10 parts, preferably from 5 to 8 parts, of alkali (calculated as K_2O) per 100 parts of the total iron content of the catalyst. When the catalyst is to be used to promote the formation of oxygen-containing organic compounds, the iron powder is admixed with a precipitate to yield a catalyst which contains from 3 to 15 parts, preferably from 6 to 12 parts, of an alkali-metal compound or compounds (calculated at K_2O) per 100 parts of its total iron content. The compounds employed are preferably potassium compounds.

Catalysts of this kind may also be used with particular advantage in a synthesis in which ammonia and/or an organic amine which is gaseous under the synthesis conditions, is or are added to the synthesis gas; such a synthesis is described in Patent Application No. 6932/50 (Serial No. 672,405). In such a synthesis, the alkali is preferably introduced into the catalyst as an alkali-metal salt of a non-volatile acid, for example, as a phosphate or a silicate.

Reduction of the catalyst according to the invention is carried out in known manner using reducing gases, such as hydrogen, carbon monoxide or their mixtures. Reduction temperatures are between 100° C. and 400° C., preferably between 200° C. and 350° C. The use of a high gas velocity in the reduction (approximately 50—150 metres per second) is of advantage, chiefly because the reduction may then be carried out with the catalyst particles in a layer of a thickness of 1 metre or more.

The catalyst may be used in synthesis carried out at atmospheric pressure. However, elevated pressures between 5 and 100 atmospheres gauge, preferably between 10 and 40 atmospheres gauge, are of particular advantage in the synthesis. Gas loads or space velocities may be varied within wide limits depending on the purpose and the object of the synthesis; the gas load may be from 10 to 1000 volumes per volume of catalyst per hour, and is advantageously from 100 to 500 volumes per volume of catalyst per hour. The synthesis may be carried out as a single pass operation, that is to say, without recycling of exit gases, or exit gases may be recycled using a recycle ratio (recycle gas/synthesis gas) of from 0.5:1 to 10:1, preferably however with a recycle ratio from 1:1 to 4:1.

The synthesis may be carried out in one or more stages, scrubbing of the gases for the removal of CO_2 being carried out between the individual synthesis stages. Both gases rich in hydrogen and gases rich in carbon monoxide may be used as synthesis gases. A $CO:H_2$ ratio of approximately 1:1 to 1:2 is of advantage.

The invention is illustrated by the following examples:—

EXAMPLE 1.

Iron nitrate was dissolved in water and precipitated with an aqueous solution of sodium carbonate at boiling temperature, in such a manner that the pH value during and after the precipitation was 7. The same quantity of iron as that present in the precipitate was then added in the form of a powder of from 20 to 60 microns particle size, while vigorously stirring with a turbo stirrer. The catalyst mass was filtered and largely freed from precipitation alkali by repeated washing with hot distilled water. The washed catalyst mass was then impregnated with a solution of potassium silicate to give the mass a content of 3 per cent. of K_2O and 7.6 per cent. of SiO_2 based on the total iron content of the catalyst mass. The catalyst mass then dried at 105° C. for 24 hours. After crushing and sieving to a particle size of between 2 and 4 mm. the catalyst was charged into a synthesis reactor and reduced for 4 hours at a temperature which was increased from 200° C. to 230° C. using water gas at flow rates of 1.2 metres per second. The catalyst was then placed on stream at a synthesis pressure of 20 atmospheres and at a temperature of 246° C. using a gas load of 100 litres/hr. of gas per litre of catalyst. The conversion obtained was 68 per cent. $(CO+H_2)$, while 6 per cent. by volume of methane, calculated on $(CO+H_2)$ converted, were formed.

Upon completion of this run the same catalyst was used with twice the load of water gas and at a synthesis temperature of 264° C. A conversion of 65 per cent. $(CO+H_2)$ was obtained, the methane formation being 7 per cent.

When the synthesis was carried out with gas recycling the same conversion as that obtained in the first run (68%) was attained at a temperature which was approximately 10° C. lower, with a methane formation reduced to approximately 4.5 per cent. When the synthesis was carried out with the fresh synthesis gas load used in the second run but with gas recycling (ratio of synthesis gas to recycled gas approximately 1:3), the same conversion (65%) was obtained at a temperature which was 12° C. lower, namely at 252° C., with a methane formation of approximately 6 per cent.

EXAMPLE 2.

A catalyst mass of the same composition as that used in Example 1 was reduced in a separate reduction apparatus and not in the reactor itself. The reduction was carried out at 280° C. for a period of 75 minutes with a gas mixture consisting of three volumes of hydrogen and one volume of nitrogen at a linear gas velocity of 1.2 metres per second. Using water gas at a synthesis pressure of 20 atmospheres a gas load of 100 litres of gas per litre of catalyst per hour and a temperature of 248° C., a $(CO+H_2)$ conversion of 64 per cent. was obtained, with a methane formation of approximately 7 per cent.

EXAMPLE 3.

100 parts of iron and 20 parts of copper in the form of their nitrates, were precipitated from a boiling aqueous solution by a boiling solution of sodium carbonate. The pH of the solution upon completion of the precipitation was 9.1 Immediately thereafter 100 parts of iron powder of a particle size of 40—60 microns were added with vigorous stirring and the whole mixture was filtered in the hot state. The catalyst mass was thoroughly washed with hot distilled water and was then impregnated with K_2CO_3 so that the mass contained 10 parts of the alkali-metal compound (calculated at K_2O) per 100 parts of the total amount of iron present. The catalyst mass was moulded in an extrusion press into thread-like particles of 3.5 mm. diameter and subsequently dried for 24 hours at 110° C. In a reduction apparatus the catalyst was reduced for 1 hour at 300° C. using a hydrogen/nitrogen mixture at a linear gas velocity of 1.3 metres per second. 72 per cent. of the iron content of the catalyst was then present in the metallic form. The catalyst was charged into a synthesis reactor and operated with water gas at a synthesis pressure of 30 atmospheres with a space velocity of 100 volumes of gas per volume of catalyst per hour. At a reaction temperature of 195° C., a $(CO+H_2)$ conversion of 62 per cent. was obtained with a methane formation of 7 per cent. The reaction product contained approximately 27 per cent. of alcohols, and approximately 3 per cent. of aldehydes in addition to approximately 20 per cent. of esters.

Upon termination of this run, the same catalyst was used with the water gas at double the space velocity of the previous run, at the same synthesis pressure but with a synthesis temperature of 215° C. 57 per cent. of $(CO+H_2)$ were converted. Approximately 25 per cent. of alcohols and approximately 3 per cent. of aldehydes in addition to 23 per cent. of esters were contained in the reaction product.

EXAMPLE 4.

A boiling solution containing 40 grams of iron, 2 grams of copper and 4 grams of CaO in the form of nitrates was rapidly added to a boiling solution of sodium carbonate containing 92 grams/litre of anhydrous Na_2CO_3. Upon termination of the precipitation the pH value was 7.1. Immediately following this, a technical-grade iron powder of a particle size of between 20 and 60 microns was stirred into the precipitate in such a quantity that 40 per cent. of the total iron present in the mixture was in the form of iron powder. The catalyst slurry was washed with hot distilled water until the residual content of alkali was approximately 0.5 per cent (calculated as K_2O) based on the total iron present.

10 kilograms of this catalyst mass having an Fe content of approximately 25 per cent. were stirred by means of a turbo stirrer with 10 litres of distilled water at a temperature of about 50° C. to give in a homogeneous suspension. To this suspension technical-grade potassium silicate containing about 8 per cent. of K_2O and about 20 per cent. of SiO_2 was added in an amount to give 25 parts by weight of SiO_2 per 100 parts by weight of total iron. The pH of the suspension was adjusted to 7.1 by the addition of nitric acid of a concentration of about 50 per cent., whereupon the suspension was filtered after being quickly heated to 80° C. After a brief period of intermediate drying, the catalyst mass was moulded into filaments by means of an extrusion press, and the moulded particles were dried for 24 hours at 105° C.

The reduction of the catalyst was carried out for 90 minutes at a linear gas velocity of 1.5 metres per second and at a temperature of 310° C. with a gas mixture consisting of three volumes of hydrogen and one volume of nitrogen.

Using a gas load of 200 litres of water gas per litre of the catalyst per hour, a synthesis pressure of 30 atmospheres and a temperature of 265° C., a $(CO+H_2)$ conversion of 63 per cent. was obtained. Methane formation was approximately 5 per cent.

What we claim is:—

1. A process for the production of an iron catalyst for use in the catalytic hydrogenation of carbon monoxide, which comprises precipitating an oxide, hydroxide or carbonate of iron from a solution of an iron salt by means of an alkaline medium, admixing iron powder with the precipitate, moulding and/or drying the catalyst mass, and reducing the catalyst mass at a temperature within the range 100°—400° C.

2. A process according to claim 1, in which the added iron powder constitutes not more than 80% by weight of the total quantity of iron in the catalyst.

3. A process according to claim 2, in which the added iron powder constitutes from 25% to 50% by weight of the total quantity of iron in the catalyst.

4. A process according to any one of the preceding claims, in which the particle size of the added iron powder is within the range 10—250 microns.

5. A process according to claim 4, in which the particle size of the iron powder is within the range 40—80 microns.

6. A process according to any one of the preceding claims, in which a promoter, such as chromium, manganese, titanium, tungsten, an alkali or an alkaline earth metal compound, is contained in the added iron powder.

7. A process according to any one of the preceding claims, in which the iron powder is admixed with a precipitate which yields a catalyst effective to promote the formation of hydrocarbons in the hydrogenation of carbon monoxide, the catalyst containing, in addition to an alkali (preferably K_2O), a radical of a non-volatile acid, such as a silicate, a borate or a phosphate, not more than 50% of the total iron in the catalyst being in the form of free iron.

8. A process according to claim 7, in which the catalyst is effective to promote the formation of hydrocarbons boiling below 200° C., the catalyst containing from 1 to 8 parts of alkali (calculated as K_2O) and from 3 to 15 parts of the radical of the non-volatile acid (calculated as the acidic oxide) per 100 parts of the total iron content of the catalyst.

9. A process according to claim 8, in which the catalyst contains from 3 to 8 parts of the radical of the non-volatile acid, preferably SiO_2, and from 2 to 4 parts of alkali, preferably K_2O, per 100 parts of the total iron content of the catalyst.

10. A process according to claim 7, in which the catalyst is effective to promote the formation of hydrocarbons boiling above 200° C., the catalyst containing from 4 to 10 parts of alkali (calculated as K_2O) and more than 15 parts of the radical of the non-volatile acid (calculated as the acidic oxide) per 100 parts of the total iron content of the catalyst.

11. A process according to claim 10, in which the catalyst contains from 15 to 30 parts of the radical of the non-volatile acid, preferably SiO_2, and from 5 to 8 parts of alkali, preferably K_2O, per 100 parts of the total iron content of the catalyst.

12. A process according to any one of claims 1 to 6, in which the iron powder is admixed with a precipitate which yields a catalyst effective to promote the formation of oxygen-containing organic compounds in the hydrogenation of carbon monoxide, the catalyst containing from 3 to 15 parts of an alkali-metal compound or compounds (calculated at K_2O) per 100 parts of the total iron content of the catalyst.

13. A process according to claim 12, in which the alkali-metal compounds are potassium compounds.

14. A process according to claim 12 or claim 13, in which the catalyst contains from 6 to 12 parts of the alkali-metal compound or compounds per 100 parts of the total iron content of the catalyst.

15. A process according to any one of the preceding claims, in which the catalyst mass is reduced at a temperature within the range of 200°—350° C.

16. A process for the production of an iron catalyst, substantially as hereinbefore described in Example 1, Example 3, or Example 4.

17. A process for the production of an iron catalyst, substantially as hereinbefore described.

18. An iron catalyst whenever produced by the process claimed in any one of the preceding claims.

19. A process for the hydrogenation of carbon monoxide, whenever carried out in the presence of an iron catalyst produced by the process of any one of claims 1 to 17.

20. A process according to claim 19, in which ammonia and/or an organic amine which is gaseous under the synthesis conditions, is added to the synthesis gas.

21. A process according to claim 19 or claim 20, in which the hydrogenation is effected at a gauge pressure within the range 5—100 atmospheres.

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COMPLETE SPECIFICATION

ERRATUM

SPECIFICATION NO. 718,386

Page 1, line 92, *for* "mounded" *read* "moulded".

THE PATENT OFFICE,
2nd December, 1954

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genation of carbon monoxide with hydrogen, iron catalysts of various kinds are known, such as fused catalysts, sintered catalysts or precipitated catalysts. Fused catalysts are prepared by the fusion of iron powder in an oxidising atmosphere, disintegrating the fused mass and reducing the catalyst particles thus obtained in a stream of hydrogen, the reduction being preceded, if necessary or desired, by an alkaline impregnation. In the preparation of the sintered catalysts hitherto known, only a sintering of the iron powder has been carried out, preceded, if necessary or desired, by an alkaline impregnation. The sintered mass has then been disintegrated and reduced in a stream of hydrogen.

Water-soluble iron salts, chiefly iron nitrates, have generally been used for the preparation of precipitated catalysts. Iron sulphate, iron chloride and iron salts of organic acids or mixtures of these compounds have also been suggested. Precipitation of these soluble iron salts has been carried out with alkaline-reacting compounds in the presence, if necessary or required, of promoters, such as copper, silver, calcium, barium, titanium and chromium. Alkali-metal hydroxides and carbonates, and ammonia and compounds of ammonia are known as precipitants. The precipitate obtained is in general filtered under a high degree of suction.

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Price 25p

the disadvantage of disintegrating during reduction with the formation of undersize particles or catalyst dust even though the catalyst particles have been moulded prior to reduction. Removal of these smaller particles after reduction is difficult since the reduced catalyst particle is highly pyrophoric and sensitive to air. When carrying out the reduction of the catalyst in the synthesis reactor itself, the disadvantages are particularly objectionable since, when the precipitated catalyst is being charged into the reactor, obstructions by the catalyst dust or undersize particles may occur. This may result in difficulties, not only in the synthesis itself, but chiefly in the subsequent discharging of the synthesis reactor.

It has now been found, according to the invention, that the strength of the particles of an iron-containing precipitated catalyst for use in the hydrogenation of carbon monoxide may be increased by admixing iron powder with the oxide, hydroxide or carbonate of iron which is precipitated from a solution of an iron salt by an alkaline medium, the catalyst mass being then mounded and/or dried and afterwards reduced at a temperature within the range 100°—400° C.

The iron powder may be prepared by mechanical, chemical or physical processes. Mechanical processes include all processes in which mechanical means are