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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, in which the products have a high content of oxygen-containing organic compounds.

Oxygen-containing organic compounds, particularly alcohols, may be obtained in larger or smaller quantities, in addition to hydrocarbons, in the hydrogenation of carbon monoxide. This is effected by the use of particular iron catalysts and by the application of increased synthesis pressures and suitable other synthesis conditions. Such iron catalysts are conventionally produced by the fusion process and contain promoters, for example, aluminium oxide and small quantities of alkalis. Precipitated catalysts are also known which consist chiefly of iron and contain small quantities of copper, magnesium or rare earths as promoters; these catalysts also yield larger quantities of oxygen-containing synthesis products. In addition, the precipitated iron catalysts generally contain large quantities of kieselguhr or similar inert supporting materials in an amount equal to from about 50% to 100% by weight of the total iron content. By the use of these catalysts yields of alcohols and other oxygen-containing compounds amounting to 50%—60% of the normally liquid synthesis products are obtained. All such catalysts contain only comparatively small quantities of alkalis, such as potassium hydroxide or potassium carbonate.

It has now been found, according to the invention, that a product rich in oxygen-containing organic compounds (more than 60%) may be obtained by a process which comprises contacting a synthesis gas containing at least 1.2 volumes of hydrogen per volume of carbon monoxide with a precipitated iron catalyst under synthesis conditions of temperature and pressure, which catalyst contains one or more alkali-metal compounds (as hereinafter defined) in an amount of more than 5% by weight when calculated as K_2O and based on the total iron content of the catalyst, the catalyst being unsupported or containing not more than 20% by weight of supporting material relative to the total iron content and being used as a fixed bed or as a suspension in a liquid medium.

The alkali-metal compounds which may be used in the catalyst in the process according to the invention, are those which exhibit an alkaline reaction, such as the hydroxides and carbonates, or those which are decomposed under the synthesis conditions with the formation of alkaline-reacting compounds. Examples of the latter kind of alkali-metal compounds are the alkali-metal salts of many organic acids, such as the acetates and the oxalates. Alkali-metal halides and alkali-metal salts of non-volatile acids, for example, potassium fluoride, potassium silicate and potassium phosphate, are therefore not used to promote the catalyst in the process according to the invention. The amount of alkali-metal compound or compounds incorporated in the catalyst is more than 5%, preferably from 8%—12% (calculated as K_2O and based on the total iron content).

The catalyst may also contain copper, silver or a metal of the second, fifth, sixth or seven groups of the periodic system or an oxide of such metals as promoter.

When the catalyst is provided as a fixed bed, it will be understood that the catalyst granules may be coated with or surrounded

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by a liquid medium. The synthesis gas preferably contains from 1.5 to 2 volumes of hydrogen per volume of carbon monoxide.

The catalysts used in the process according to the invention, even at low synthesis temperatures, show an activity which has not generally been attainable with iron catalysts. As the catalytic conversion of gas mixtures containing carbon monoxide and hydrogen will produce very high yields of oxygen-containing organic compounds, particularly alcohols, only at low synthesis temperatures, relatively high yields of oxygen-containing organic compounds may be produced with the iron catalysts according to the invention, particularly by a synthesis effected in several stages or with recycling of the synthesis gases. The highest yields of oxygen-containing organic compounds can be obtained with hydrogen-rich synthesis gases which contain 2 or more volumes of hydrogen for each volume of carbon monoxide. The iron catalysts hitherto known and used will, under these conditions, generally show a decrease in the alcohol yield with an undesirably high production of methane; this decrease in the alcohol yield is due to hydrogenation with the production of saturated hydrocarbons.

If the alkali-metal in the catalyst is potassium, introduced for example in the form of its hydroxide or carbonate, then it is observed that by the use of such catalysts considerably more esters are formed than by the use of similar catalysts in which the potassium compounds are replaced by the corresponding sodium compounds. Conversely, the use of sodium compounds produces large quantities of alcohols and only small quantities of esters. This fact is of considerable importance in the technical exploitation of the process according to the invention, since it makes possible the production of primary products with larger or smaller amounts of esters or increased or reduced amounts of alcohols as desired. Thus, by simply changing the catalyst, whilst allowing the other synthesis conditions to remain the same, products with a high or low ester content and a corerspondingly reduced or increased alcohol content, may be obtained.

The iron catalysts according to the invention which permit the use of synthesis temperatures of 150° C. to 225° C., are produced by precipitating a hot aqueous solution of iron nitrate or other iron salts and soluble salts of the promoters, with hot sodium carbonate or potassium carbonate solution. Other alkali compounds, such as caustic soda or caustic potash solutions, are also suitable for use as precipitants. The precipitation is suitably effected in the alkaline range, that is to say, at a pH of 9 to 11.

The high alkali content required according to the invention may be obtained by a restricted washing of the precipitated catalyst sludge to leave the required amount of alkali-metal compounds in the sludge. Such a restricted washing may be carried out, for example, by washing the moist catalyst mass, after it has been filtered in a filter press from the mother liquor, for such a period of time as serves to leave the catalyst with the desired residual content of alkali, the washing being effected by the use, for example, of hot distilled water. However, in many cases it is advantageous if the washing of the precipitated sludge is carried through in the usual manner as far as is possible, for example, to a residual alkali content of 0.5% to 1%, the precipitated mass being then impregnated with suitable alkali-metal compounds. As a certain content of free alkali in the catalyst is required, this impregnation is carried out, for example, with an alkali-metal hydroxide or advantageously an alkali-metal carbonate, or an alkali-metal salt of an organic acid, such as an oxalate or acetate, which salt may be readily decomposed under the synthesis conditions. This procedure of subsequent impregnation is particularly advantageous if the catalyst is to be impregnated with expensive alkali-metal compounds, their use in excess for precipitation being thereby uneconomic. Thus, this procedure should be followed if impregnation with lithium, rubidium, or caesium is to be effected. This particular procedure has also been found effective if several alkalis are to be used simultaneously in the catalyst.

The impregnation of the moist catalyst mass may be carried out by any of the known methods, such as by stirring in a suspension container, by mixing in a stirring apparatus or by use of a kneading machine. The alkali-metal compounds may be used in the solid, dissolved or suspended state.

When the moist catalyst mass, through restricted washing or complete washing and subsequent impregnation, has been brought to the desired alkali content, it may be dried in the usual manner and moulded. The moulding of the catalyst may be effected in a thread or cord press. Other means for moulding may also be used.

In moulding the catalyst mass, the production of a catalyst granule of the greatest possible strength is aimed at. The length of the life of the catalyst depends to a great extent on the strength of the granules. If the granule is too soft, the catalyst will tend to form a sludge due to the more or less extensive disintegration of the granules. This disintegration of the granules may be prevented to a large extent if the moulding is carried out under as high a pressure as is possible. In many cases the addition of small amounts of inert supporting materials, such as kieselguhr, "Tonsil," ceramic masses or bleaching clay, will improve the firmness and strength of the granules. Where inert supporting materials are incorporated in the catalyst, the content of these materials never exceeds 20% by weight of the total iron content of the catalyst. It is important that this amount should not be exceeded, as the addition of inert substances always results in an undesirable increase in the synthesis temperature. The inert materials used may be added during the step of precipitation or just before the moulding of the catalyst.

If the catalyst is formed into threads or filaments, the unreduced granules should have a size of about 3—8 mm. and preferably 4—5 mm. A granule of smaller size will tend to break or splinter owing to the shrinkage of the granule during the reduction of the catalyst. This shrinkage in the size of the granule may be 50% or more of the original volume of the granule. Thus a granule having an initial size of 2 mm. may under certain circumstances be reduced to a size of only about 0.5 to 1.0 mm. Catalyst granules of such small size tend to disintegrate a great deal. When using a catalyst granule of 4 mm. size, the size of the granule upon reduction will be about 2 mm., which is sufficiently large to prevent disintegration. The moulded catalyst granules are dried in continuous manner, or in stages, for example, on a band in a drying oven. The drying process is carried out at a temperature of between 80° C. and 150° C., preferably at about 100°—115° C. At the beginning of the drying process the temperature should preferably not exceed 110° C. because a too rapid escape of steam may damage the structure of the catalyst granules to such an extent that the catalyst during reduction, and particularly during synthesis, tends to disintegrate at an increased rate. It is preferred to discontinue the drying of the catalyst when the residual water content is about 4%—7%.

The moulded and dried catalyst must be reduced in a suitable manner. Practically all known reduction methods are suitable. Particularly favourable catalyst properties are obtained when the reduction is carried out with pure hydrogen or with mixtures of hydrogen and nitrogen, such as are used in the synthesis of ammonia. With the iron catalyst used according to the invention, it is possible to use low synthesis temperatures and thus particularly high yields of oxygen-containing organic compounds, if the reduction is carried through until more than 60%, preferably more than 80%, of the iron in the catalyst is in the metallic state. For this purpose, the temperature of reduction lies within the range 250°—350° C. and is preferably about 300°—320° C. During the reduction, the linear speed of the reduction gases should be 30—150 cm./sec., preferably 100 cm./sec., at 760 mm. Hg and 0° C.

With the iron catalyst used according to the invention good yields of oxygen-containing organic products can be obtained from synthesis gases which contain the minimum of 1.2 volumes of hydrogen per volume of carbon monoxide. This is in contrast with the prior art which places particular emphasis on the use of gases rich in carbon monoxide for the manufacture of oxygen-containing synthesis products.

The catalysts described can be used with much higher loads or throughputs than the normal load of 100 volumes of gas per volume of catalyst per hour, for example, the process may be operated with 200 to 400 volumes of gas per volume of catalyst per hour. In operating with such higher throughputs, correspondingly higher synthesis temperatures may be used without any appreciable reduction in the yield of oxygen-containing organic compounds. This is also in contrast with the catalysts hitherto known.

With the catalyst used according to the invention high ($CO + H_2$) conversions may be obtained in single stage operation. It is, however, of greater advantage to use a two or three stage operation. In this manner, conversions of 90% ($CO + H_2$) and higher may be obtained without difficulty. At a synthesis pressure of between 10—100 kg. per sq. cm. and preferably between 20—50 kg. per sq. cm. yields of about 190—210 grams per cubic metre (760 mm. Hg and 20° C.) can be obtained. These high yields have hitherto been technically impossible. This is due to the fact that synthesis pressures considerably above 10 kg. per sq. cm. have the advantage of a much higher conversion. If a constant conversion rate is desired, the synthesis temperatures can be lowered considerably. In this connection the ratio of make-up CO and H_2 may be influenced towards an increased H_2 consumption. In view of the favourable properties of gases rich in hydrogen, this appears to be particularly advantageous.

In multi-stage operation it is advantageous to remove the carbon dioxide from the exit gases at least after the second stage and preferably after the first stage. In this manner a synthesis gas with a high content of carbon monoxide and hydrogen is provided for each stage. If the gas has a sufficiently high hydrogen content before the last stage, this stage can be operated with a single pass without recycling.

In contrast to the technical methods of today in the process according to the invention for the manufacture of products with a high content of oxygen-containing compounds, recycling of the gases is advantageous. In recycling, the ratio of 1 volume of fresh gas to 1—10 volumes of recycle gas and preferably 1 volume of fresh gas to 3—5 volumes of recycle gas is used. With recycling of the gas, an increase of the temperature is not required. By keeping the temperature constant, the conversion according to the process of the invention is somewhat increased by the recycling. In particular, the consumption ratio is considerably improved. This fact is particularly advantageous for the catalysts used according to the invention because, by their use, gases rich in hydrogen can be converted particularly well and produce high yields of oxygen-containing organic compounds. By this method a conversion up to 90% ($CO+H_2$) can be obtained. Known catalysts, which operate with gases rich in carbon monoxide, cannot be used for such high ($CO+H_2$) conversions because, by recycling the conversion ratio is altered towards an increased consumption of hydrogen.

For the process according to the invention it is of utmost importance that the heat of reaction be quickly and effectively removed. To carry out the synthesis, the well-known carbon monoxide hydrogenation reactors with double or single tubes of 10—20 mm. diameter, can be used.

The invention is illustrated by the following examples:—

EXAMPLE 1.

An iron catalyst containing 100 parts of iron (Fe), 5 parts of copper (Cu), 10 parts of calcium oxide (CaO) and 10 parts of kieselguhr, was precipitated from a solution of the corresponding metal nitrates containing the kieselguhr in suspension, by means of a boiling sodium carbonate solution. Upon completion of the precipitation, the pH was 9.2. The precipitated mass was immediately filtered in a filter press, the mother liquor being discarded. The filter cake was partially washed with distilled water to a residual alkali content, calculated as K_2O and based on the total iron content of the mass, of 8.4%. This partially washed mass was pre-dried to a residual water content of 60% H_2O and moulded into threads 3.5 mm. thick, in a thread press. The catalyst moulded in this manner was then finally dried at 110° C., broken into small pieces and screened through a sieve.

In a suitable reduction apparatus this catalyst was reduced at a temperature of 310° C. with a gas mixture consisting of 75% hydrogen and 25% nitrogen, and with a linear speed of the gas of 1.20 metres per second (calculated at 760 mm. Hg. and 0° C.). The duration of the reduction period was 90 minutes. The reduced catalyst contained 70% of the iron in the metallic state.

When this catalyst was used with 100 litres (760 mm. Hg., 20° C.) of water gas ($CO:H_2 = 1:1.2$) per litre of catalyst per hour with a recycle ratio of 3 volumes of recycle gas to 1 volume of fresh gas under a pressure of 30 kg. per sq. cm. and at a temperature of 210° C., synthesis products with a total content of oxygen-containing organic compounds of 64% were obtained. When, under otherwise the same conditions, a synthesis gas having the ratio $CO:H_2=1:2$ was used, the yield of oxygen-containing organic compounds increased to 73%. When processing a gas mixture having a carbon monoxide: hydrogen ratio of 1:0.85, the yield of oxygen-containing organic compounds decreased to 53%. In each of these cases the ($CO+H_2$) conversion was about 57%.

EXAMPLE 2.

A catalyst which consisted of 100 parts Fe, 10 parts Cu and 10 parts of kieselguhr, was precipitated from a solution of the corresponding metal nitrates containing the kieselguhr in suspension, by means of a hot sodium carbonate solution to an end-point of pH=9.2. The precipitated mass was immediately separated from the mother liquor in a filter press and washed to a residual alkali content of 1%, the alkali being calculated as K_2O and relative to the iron present. The mass was then impregnated with a solution of potassium carbonate in such manner that the finished catalyst had an alkali content of 7% calculated as K_2O and relative to the total iron content. The mass was then sieved to recover granules of 3—4 mm. and dried to a residual water content of about 6% at a temperature of 110° C.

This catalyst was reduced for 3 hours at 310° C. with a gas mixture containing 75% hydrogen and 25% nitrogen. The reduction gases had a linear speed of 1.4 metres/sec. The reduction value, that is, the amount of the iron in the metallic state, was 78%.

When this catalyst was used in single-pass operation with 100 litres of water gas ($CO:H_2 = 1:1.2$) per litre of catalyst per hour at a temperature of 198° C. and at a pressure of 20 kg. per sq. cm., the liquid synthesis products contained approximately 62% of oxygen-containing organic compounds. With a synthesis gas having a ratio of $CO:H_2=1:2.0$, the content of oxygen-containing organic compounds in the products increased to about 75%. With a gas rich in carbon monoxide ($CO:H_2=1:0.85$) only 55% of oxygen-containing organic compounds were obtained. The $CO+H_2$ conversion was between 58%—60% in each case.

EXAMPLE 3.

Four catalysts were prepared, each having a basic composition of 100 parts Fe, 5 parts Cu and 10 parts CaO. The catalysts were obtained by precipitation from a boiling solution of the corresponding metal nitrates by means of a boiling sodium carbonate solution at a pH of about 9. The residual alkali present in the precipitates was practically entirely removed by a subsequent, thorough washing. Each of the four catalysts was then impregnated with a different alkali-metal compound so that each catalyst contained 10 parts of alkali, calculated as K_2O, per 100 parts of the total iron content. The first catalyst was impregnated with KOH, the second with K_2CO_3, the third with NaOH and the fourth with Na_2CO_3.

Each catalyst mass was then dried for 24 hours at temperatures between 100° C. and 110° C. and was reduced for 4 hours with hydrogen at a linear speed of 1.3 metres/

second at temperatures around 310° C. The free iron content of each catalyst was approximately 45%—50%. The catalysts were used for the synthesis in an experimental reactor having a catalyst volume of 5 litres. The synthesis pressure was 20 atmospheres, the gas load was 10° volumes per volume of catalyst per hour. A recycle ratio of 1:1 was used.

(1) The catalyst impregnated with KOH gave with a reaction temperature of 204° C., a $CO+H_2$ conversion of 58%. The reaction product contained about 17% of esters and 30% of alcohols, in addition to other oxygen-containing organic compounds most of which were in solution in the aqueous phase.

(2) The catalyst impregnated with K_2CO_3 gave a $CO+H_2$ conversion of 53% at a temperature of 221° C. The reaction product contained about 20% of esters and 27% of alcohols, in addition to other oxygen-containing organic compounds, most of which were in solution in the aqueous phase.

(3) The catalyst impregnated with NaOH gave a $CO+H_2$ conversion of 59% at a temperature of 213° C. The reaction product contained about 38% of alcohols, about 10% of esters, in addition to other oxygen-containing organic compounds most of which were in solution in the aqueous phase.

(4) The reaction temperature with the catalyst impregnated with Na_2CO_3 was 224° C. and the $CO+H_2$ conversion was 57%. The reaction product contained 42% of alcohols and 7% of esters, together with other oxygen-containing organic compounds, most of which were in solution in the aqueous phase.

What we claim is:—

1. A process for the synthesis of a product rich in oxygen containing organic compounds, which comprises contacting a synthesis gas, containing at least 1.2 volumes of hydrogen per volume of carbon monoxide, under synthesis conditions of temperature and pressure with a precipitated iron catalyst containing one or more alkali-metal compounds (as hereinbefore defined) in an amount of more than 5% by weight when calculated as K_2O and based on the total iron content of the catalyst, the catalyst being unsupported or containing not more than 20% by weight of supporting material relative to the total iron content and being used as a fixed bed or as a suspension in a liquid medium.

2. A process according to claim 1, in which the synthesis gas contains 1.5—2 volumes of hydrogen per volume of carbon monoxide.

3. A process according to claim 1 or claim 2, in which the catalyst contains from 8% to 12% of the alkali-metal compounds, calculated as K_2O and based on the total iron content of the catalyst.

4. A process according to any one of the preceding claims, in which the catalyst contains copper, silver or a metal of the second, fifth, sixth and seventh groups of the Periodic System, as promoter.

5. A process according to any of the preceding claims, in which the catalyst is dried at a temperature within the range 80°—150° C. to a residual water content of 4% to 7%.

6. A process according to Claim 5, in which the catalyst is dried at a temperature of 100°—115° C.

7. A process according to any one of the preceding claims, in which the catalyst contains supporting material, the supporting material being incorporated in the catalyst when the catalyst is moulded to the desired form.

8. A process according to any one of the preceding claims, in which the catalyst, prior to use, is reduced with hydrogen or a hydrogen/nitrogen mixture at temperatures within the range 250°—350° C.

9. A process according to any one of the preceding claims, in which the catalyst, prior to use, is reduced by a stream of gas having a linear velocity of 30—150 centimetres per second.

10. A process according to claim 8 or claim 9, in which the catalyst is reduced at a temperature within the range 300°—320° C. by a stream of gas having a linear velocity of about 100 centimetres per second.

11. A process according to any one of the preceding claims, in which the catalyst, prior to use, is reduced until more than 60%, preferably more than 80% of the iron is in the metallic state.

12. A process according to any one of the preceding claims, in which the process is effected at a pressure within the range 10—100 kg. per sq. cm.

13. A process according to claim 12, in which the pressure is within the range 20—50 kg. per square centimetre.

14. A process according to any one of the preceding claims, in which the unconverted synthesis gas is recycled.

15. A process according to claim 14, in which the recycle ratio is 1—10 volumes of recycle gas to 1 volume of fresh synthesis gas.

16. A process according to claim 15, in which the recycle ratio is 3—5 volumes of recycle gas to 1 volume of fresh synthesis gas.

17. A process according to any one of the preceding claims, in which the space velocity is 200 to 400 volumes of gas per volume of catalyst per hour.

18. A process according to any one of the preceding claims, in which the process is carried out at a temperature within the range 150°—225° C.

19. A process for the hydrogenation of carbon monoxide, substantially as hereinbefore described.

20. A process for the hydrogenation of carbon monoxide, substantially as hereinbefore described with reference to any one of Examples 1 to 3.

21. Oxygen-containing organic compounds and hydrocarbons whenever produced by the process of any preceding claims.

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