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PATENT SPECIFICATION

727,805

Date of Application and filing Complete Specification April 7, 1952.

No. 8898/52.

Application made in Germany on April 11, 1951.

Complete Specification Published April 6, 1955.

Index at acceptance:—Classes 1(1), F3B1; and 2(3), B1G, C3A5(B: F4B), C3A10E3,

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ERRATUM

SPECIFICATION NO. 727,805

Page 3, line 20, *after* "for" *delete* "use".

THE PATENT OFFICE,
17th June, 1955

DB 78150/2(8)/3377 150 6/55 R

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following statement:—

The invention relates to a process for the synthesis of oxygen-containing organic compounds and particularly to the synthesis of oxygen-containing compounds having a high content of esters, by the catalytic hydrogenation of carbon monoxide.

To obtain products having a high proportion of oxygen-containing organic compounds, particularly of alcohols, the catalytic hydrogenation of carbon monoxide has been carried out in different ways. On the one hand, fused catalysts, somewhat of the type of the known catalysts used in the synthesis of ammonia, have been used for this purpose, which catalysts consist essentially of iron with the addition of small amounts of aluminium oxide, silica and alkali. On the other hand, precipitated catalysts have been described which are mainly composed of iron with small amounts of promoters, such as copper, calcium, cerium vanadium, and alkali and, if necessary or desired, more or less large amounts of carrier materials such as kieselguhr, bleaching earths and the like. The yield of oxygen-containing organic compounds obtained with catalysts of this type was quantitatively about 50%, calculated on the liquid primary product. Hitherto, however, no catalyst has been found to be effective to produce esters to any considerable extent in the hydrogenation of carbon monoxide. Although esters are always contained in the primary products from the hydrogenation of carbon mon-

to keep the methane formation within the lowest possible limits and, correspondingly, to operate the synthesis at the lowest possible temperatures. For the same reasons, a high $CO + H_2$ conversion is aimed at in order to keep the number of synthesis stages low when using multi-stage operation, which method of operation is necessary in nearly all cases. Under certain circumstances, it is even possible, when using these synthesis conditions, to carry out the synthesis in single-stage operation with a very high CO conversion.

It has now been found, according to the invention, that the production of oxygen-containing organic products having a high content of esters in the higher boiling ranges by the catalytic hydrogenation of carbon monoxide with the use of precipitated iron catalysts at pressures above 5 atmospheres, may be carried out with particular advantage by the use of catalysts which, in addition to a content of free alkali (as hereinafter defined) of between 4% and 15% preferably between 6% and 12% (calculated as K_2O and based on total amount of iron in the catalyst) and, if necessary or desired, small quantities of promoters, for example, aluminium oxide, zinc oxide and other difficultly reducible metal oxides which are known as promoters for catalysts used in the hydrogenation of carbon monoxide, contain over 15%, preferably between 15% and 50% of copper. Catalysts of this kind exhibit an extremely high activity, that is to say, high conversions of $CO + H_2$ are obtained at relatively low reaction temperatures. Moreover, the methane formation which, with the conventionally known catalysts giving good yields of oxygen-containing organic compounds, is generally of the order of magnitude of 12—15% approximately, is very low in this case due to the low operating temperature. Moreover, the high copper content also permits the catalyst to be reduced in a shorter time prior to its use in the synthesis as well as permitting the synthesis to be carried out at a lower temperature.

The term "free alkali" as used in the body and claims of the present specification, is to be understood as signifying the hydroxides, carbonates and bicarbonates of the alkali-metals.

It has been found to be particularly advantageous to use iron catalysts which have a high reduction value. Thus, the content of esters in the oxygen-containing products is particularly high with catalysts which have more than 50% preferably more than 60%, of their iron content in the form of free iron.

The method of producing the catalysts according to the invention is not different from that of the known precipitated catalysts. In general one starts with salts of iron and copper, using advantageously the nitrates of the metals. The precipitation is effected in known manner from a boiling solution of the two metallic salts, preferably the nitrates, using likewise boiling solutions of alkaline reacting compounds, such as ammonia, sodium carbonate or potassium carbonate of the corresponding hydroxides. The *p*H value upon completion of the precipitation may lie within the range 7—12, advantageously within the range 7—9. The washing of the precipitated catalyst mass may be carried out as a total or partial washing and depends, *inter alia*, on the alkali compound used for the precipitation. In a partial washing, a residual alkali content of between 4% and 15%, preferably between 6% and 12%, calculated as K_2O and based on the total iron present, is allowed to remain in the mass. In a total washing, the whole of the alkali is removed from the mass, and the desired amount of alkali is then introduced into the mass by a subsequent impregnation.

After the impregnation or the partial washing, the moist catalyst mass is advantageously brought to a water content of between 55% and 70% and is subsequently moulded. Moulding into particles of cylindrical form has been found to be particularly suitable. The use of moulded catalyst particles is advantageous because only small amounts of catalyst dust are formed in this case. By sieving the moulded catalyst mass, catalyst particles of substantially uniform size are obtained which, after reduction, permit trouble-free operation in the synthesis reactor.

The reduction of the moulded catalyst particles is effected at temperatures between 200° C. and 350° C. by the action of reducing gases, preferably of carbon monoxide, hydrogen or hydrogen-nitrogen mixtures or mixtures of these gases, for example, water gas and the like. Temperatures between 250° C. and 300° C. are particularly advantageous. The proportion of metallic iron in the reduced catalyst should be more than 50%, calculated on total iron.

The reduction may be carried out in catalyst layers of approximately 30 centimeters thick, but also in layers of a thickness of more than 1 metre and up to a maximum of 12 meters, if desired in the synthesis reactor itself. The gas used for the reduction should be as free as possible from H_2O and CO_2.

After the reduction, the catalysts may then be immediately used in the synthesis. Because of their high activity they must carefully be started up since even at temperatures of approximately 190° C. conversion rates of approximately 60% $CO+H_2$ will be obtained. The catalysts exhibit a long life.

The gas load of the catalyst in accordance with the invention may be varied within wide limits. While, for example, a load of 10 volumes of gas per volume of catalyst per hour may be used, the load may be increased to 100 times this figure.

The synthesis pressures may be in the range 5—100 atmospheres; they may also be higher than 100 atmospheres. The pressure is preferably greater than 10 atmospheres; pressures between 30 and 50 atmospheres have been found to be advantageous. Single-stage and multi-stage operation and gas compositions between 0.5 and 2 parts of H_2 for each part of CO, may be used. The synthesis is preferably effected at temperatures in excess of 170° C. In multi-stage operation it is of advantage to remove the carbon dioxide between the individual stages. Morever, operation with gas recycling has been found to increase the active life of the catalyst.

The invention is illustrated by the following examples:—

EXAMPLE 1

A boiling solution of the nitrates of iron and copper, containing 50 parts by weight of Cu for every 50 parts by weight of Fe, was precipitated at a *p*H value 7.1, with the use of a boiling solution of sodium carbonate. Immediately thereafter, the precipitated catalyst mass was carefully washed free of alkali and impregnated with potassium carbonate in such a manner that 8% of K_2O in the form of K_2CO_3, calculated on the iron present, were uniformly incorporated into the moist catalyst mass. After short-time drying to a water content of approximately 60%, the catalyst mass was moulded in an extruding press into small cylinders of 5 mm length which were dried for 24 hours at a temperature of 105° C. and then sieved by means of a vibrator to uniformly sized particles. The dust formed was approximately 4% of the charge.

The moulded catalyst was then reduced in a reduction apparatus for use one hour at a temperature of 280° C., using a gas mixture consisting of 75% of hydrogen and 25% of nitrogen and a gas velocity of 1.4 metres per second, measured in the cold state. The reduction value of the finished catalyst was approximately 80%, calculated on total iron.

This catalyst was then charged into a double-tube reactor 4.5 meters in length for the synthesis. The synthesis pressure was 30 atmospheres, and the gas load was 100 litres per litre of catalyst per hour. The experimental run was carried out without gas recycling.

With the use of water gas ($CO : H_2 = 1 : 1$ to $1 : 1.2$), a $CO + H_2$ conversion of 66% to 67% corresponding to a CO conversion of 88% to 90%, was obtained at a temperature of 195° C. The methane formation was approximately 5—6%, calculated on $CO + H_2$ converted.

With the use of a CO-rich gas containing 0.82 parts of H_2 for each part of CO, a $CO + H_2$ conversion of approximately 69% to 70%, corresponding to a CO conversion of 80%, was obtained at a temperature of 198° C. The methane formation in this case was about 4% to 5%, calculated on $CO + H_2$ converted.

Finally, with the use of a hydrogen-rich gas containing 2 parts of H_2 for each part of CO, a $CO + H_2$ conversion of 53% was obtained at a temperature of 195° C. The methane formation was approximately 6% to 6.5%, the CO conversion in this case being 93%.

The yield of oxygen-containing organic compounds, including the water-soluble alcohols, was 55% when using water gas, 53% when using the gas rich in CO, and 59% when using the gas rich in hydrogen.

The percentage proportion of esters, based on the total oxygen-containing organic products, was approximately 30% in the first case, approximately 40% in the second case, and approximately 22% in the third case.

When the precipitation was carried out at a *p*H value of 9.1 instead of 7.1, using potassium carbonate as the precipitant and thereafter washing the precipitated mass only partially to leave a residual alkali content of approximately 9%, calculated as K_2O and based on the iron present, the same conversion rates were obtained at temperatures which, on an average, were approximately 5° C. higher, the yield of oxygen-containing organic compounds being somewhat lower.

EXAMPLE 2

Water gas passed over a catalyst as described in Example 1 and containing 8% of K_2O in the form of potassium carbonate, calculated on the total iron content of the catalyst. A synthesis pressure of 10 atmospheres and a gas load of 150 normal litres of gas per litre of catalyst per hour were used. A conversion of 60% $CO + H_2$ was obtained at a temperature of 220° C. The resulting liquid product contained 1.7% of aldehydes and ketones and 16.7% of esters in addition to 20.9% of alcohols. The ester content of the individual fractions boiling above 200° C. was more than 35%; in some of the fractions boiling above 250° C. the ester content was 45% or higher.

By increasing the synthesis pressure to 30 atmospheres, the same rate of conversion was obtained at a temperature of 201° C. The methane formation in this case was approximately 4—5%. The resulting liquid product contained 1.9% of aldehydes and 28.6% of esters in addition to 15.7% of alcohols.

Moreover, certain amounts of alcohols and esters were present in the aqueous product of the reaction.

What we claim is:—

1. A process for the synthesis of oxygen-containing organic compounds having a high content of esters by the hydrogenation of carbon monoxide in the presence of a precipitated, copper-containing iron catalyst at a synthesis pressure greater than five atmospheres, in which the catalyst contains more than 15% of copper and between 4% and 15% of free alkali (as hereinbefore defined), the alkali being calculated as K_2O and with reference to the total iron content of the catalyst.

2. A process according to claim 1, in which the catalyst contains between 15% and 50% of copper.

3. A process according to claim 1 or claim 2, in which the catalyst contains between 6% and 12% of free alkali.

4. A process according to any one of

the preceding claims, in which more than 50%, preferably more than 60%, of the iron in the catalyst is in the metallic state.

5. A process according to any one of the preceding claims, in which the synthesis pressure is greater than 10 atmospheres.

6. A process according to any one of the preceding claims, in which the synthesis pressure is within the range 30—50 atmospheres.

7. A process according to any one of the preceding claims, in which the catalyst contains no support or carrier material.

8. A process for the synthesis of esters which comprises passing a synthesis gas containing hydrogen and carbon monoxide over a precipitated iron catalyst containing copper and a free alkali (as hereinbefore defined) with the use of a synthesis pressure in excess of five atmospheres and a synthesis temperature in excess of 170° C. the content of copper in the catalyst being 15% or more by weight and the content of free alkali in the catalyst being between 4% and 15% by weight of the total iron content of the catalyst when the free alkali is calculated as the equivalent quantity of K_2O.

9. A process according to any one of the preceding claims, in which the catalyst containing small quantities of promoters (as hereinbefore defined).

10. A process for the synthesis of oxygen-containing compounds having a high content of esters, substantially as hereinbefore described.

11. A process for the hydrogenation of carbon monoxide, substantially as described in Example 1 or Example 2.

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**Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press.—1955.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.**