PATENT SPECIFICATION

Inventor: WALTER ROTTIG

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COMPLETE SPECIFICATION

Process for the Catalytic Hydrogenation of Carbon Monoxide

We, RUHRCHEMIE AKTIENGESELLSCHAFT, of Oberhausen-Holten, Germany, a German joint-stock Company, and LURGI GESELLSCHAFT FÜR WÄRMETECHNIK M.B.H., of 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 a process for the catalyic hydrogenation of carbon monoxide.

It is known to obtain oxygen-containing organic compounds by reacting carbon monoxide and hydrogen in the presence of iron catalysts, the iron catalysts used being generally mixed, for the usual alkali impregnation, with potassium hydroxide or with potassium compounds of acids that are readily volatile, for example, potassium carbonate or potassium bicarbonate. Alcohols form the greater part, frequently 85%—90%, of the oxygen compounds obtained.

For many industrial purposes, however, an increased formation of esters is desirable, esters being extensively used, for example, as solvents or as starting materials in the production of artificial resins. Furthermore, carboxylic acids which, owing to their straight-chain nature are particularly valuable, may be obtained in a simple manner from esters produced by the catalytic hydrogenation of carbon monoxide.

It has now been found that a considerable increase in the formation of esters is obtained if, at a synthesis pressure of 10—50 kg./sq. cm., preferably of 20—30 kg./sq. cm., iron catalysts are used which, relative to their total iron content, contain more than 60%, preferably more than 80% of free iron and 0.5% to 10%, preferably 2%—5% of a halogen-free alkali-metal compound (calculated as K_2O) of one of the phosphoric acids, boric acids, tungstic acids or molybdic acids. The preferred alkali-metal compound is a potassium compound. It is most surprising that, with iron catalysts reduced to such an extent, and which at normal pressure effect only an increased paraffin yield and a reduction in the methane formation, there is a much higher yield in esters at superatmospheric pressure such as has not been observed hitherto.

According to the invention, therefore, a process is provided for the catalytic hydrogenation of carbon monoxide to yield a product having a relatively high content of esters, in which a synthesis gas containing carbon monoxide and hydrogen is contacted, at a temperature within the range 165° C.—240° C., and at a pressure within the range of 10 kg. to 50 kg. per sq. cm., with a precipitated iron catalyst containing a halogen-free alkali-metal compound introduced into the catalyst in the form of a salt of one of the phosphoric acids, boric acids, tungstic acids or molybdic acids, more than 60% of the iron being in the metallic state and the alkali-metal compound, calculated as K_2O, being present in a proportion of from 0.5% to 10% by weight of the total iron content of the catalyst. The preferred temperature range for the process is 190° C. to 220° C.

Iron catalysts having a reduction value of 60% to more than 80% free iron show, under suitable synthesis conditions, a four to five times higher formation of oxygen-containing organic compounds. Apart from the increase in the yield of oxygen-containing compounds, the indicated increase in the reduction value of the iron catalyst also permits a decrease the reaction temperature of approxi-

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mately 15° C. to 20° C., if the synthesis is carried out with the degree of conversion usual at the present time. Furthermore, a change occurs in the composition of the hydrocarbons produced. With iron catalysts of high reduction value only a small yield in organic products boiling above 320° C. is obtained in spite of the working temperature being considerably below the normal synthesis temperature. Compared with this, iron catalysts of normal reduction value, the metallic iron content of which amounts to 25%—45% of their total iron content, generally yield at 10—20 kg./sq. cm., according to the kind of catalyst used in any given case, a product predominating in hydrocarbons which boil for the greater part above 320° C.

To obtain satisfactory ester yields, it is advantageous to effect the usual reducing pre-treatment of the catalyst with hydrogen, carbon monoxide or mixtures of these two gases, using high gas velocities at temperatures within the range 200° C.—320° C., preferably within the range 250° C.—300° C. In this case, at temperatures between 200° C. and 210° C. the subsequent synthesis yields a $(CO+H_2)$ conversion of between 60% and 70% which is equivalent to a pure carbon monoxide conversion of 80%—88%. It is preferred to use a gas rich in carbon monoxide for the reduction of the catalyst.

A carbon monoxide/hydrogen mixture as rich as possible in carbon monoxide is particularly advantageous for use as synthesis gas, as too high a content of hydrogen increases the formation of olefinic hydrocarbons. A gas rich in carbon monoxide also gives an increased formation of hydrocarbons of high molecular weight. The gas load may be greater than the usual catalyst load of 100 litres of synthesis gas per litre of catalyst per hour, and may occasionally be increased to 500 litres of synthesis gas per litre of catalyst per hour or even more.

When using water gas, a liquid product may be obtained at a synthesis pressure of 10 kg./sq. cm. which, apart from approximately 20% alcohols, contains about 20% esters. Furthermore, the product contains about 5% of other oxygen-containing compounds such as ketones, aldehydes and acids.

High yields are best obtained when the synthesis is effected with temperatures increasing in the direction of the gas flow. At the present time the hydrogenation of carbon monoxide is mostly effected in water-cooled reaction chambers, in which the gas-conversion takes place substantially in the upper third of the catalyst mass. In contrast to this, where catalyst temperatures increase in the direction of the gas flow, uniformly high conversions over the greater part of the total catalyst mass result, so that side reactions and undesired decompositions of the primary products formed are avoided. The increase of catalyst temperature in the direction of gas flow may be obtained in known manner by special cooling media or zone-wise cooling of the reaction chamber.

In contrast to other iron catalysts, which mainly yield alcohols, the process of the invention results in a very small formation of methane. In present-day synthesis with iron catalysts, at a conversion of 55%—60% $(CO+H_2)$ in once-through operation, methane is formed to the extent of approximately 8%—12%. In the process of the invention, however, with conversions of 60% to 65% the quantity of methane formed may be reduced to 5% or less.

It is most advantageous to effect the synthesis with recycling of the synthesis gases. Even when working with once-through passage of the gas, the process of the invention yields 60%—65% of the liquid synthesis products in the form of compounds of high molecular weight. If the gas is recycled, the yield in compounds of high molecular weight increases to 70%—75%, the great economic advantage being that the esters formed lie substantially in the boiling range of the products of high molecular weight.

The process according to the invention is illustrated by the following examples:

EXAMPLE 1.

To effect the interaction of carbon monoxide and hydrogen a catalyst consisting of 100 parts of iron and 5 parts of copper was used. This catalyst was prepared by precipitation with sodium carbonate from a hot solution of the metal nitrates. The precipitate was freed from alkali by washing. It was then impregnated with potassium dihydrogen phosphate (KH_2PO_4) so that it contained 7.9 parts of potassium calculated as potassium monoxide K_2O to 100 parts of iron. The catalyst so formed was reduced for one hour at 300° C. with a gas mixture consisting of 3 volumes of hydrogen and one volume of nitrogen. The flow velocity of the reduction gas amounted to 1.2 metres per second (760 mm. Mg/0°). After reduction, the catalyst contained 62% of the iron in the metallic state.

The synthesis pressure was 10 kg./sq. cm. and the synthesis temperature 205° C. The synthesis gas used was water gas and it was passed over the catalyst at a space velocity of 100 normal litres of gas per litre of catalyst per hour, a $(CO+H_2)$, conversion of 61% being obtained and 4.9% of methane being formed. The liquid synthesis products obtained contained on an average 17% esters, 28% alcohols and 4% of other oxygen-containing organic compounds. 57% of the liquid products of the synthesis boiled above 320° C.

EXAMPLE 2.

A catalyst containing 100 parts of iron, 25 parts of copper, 20 parts of chromic oxide, (Cr_2O_3) and 20 parts of Kieselguhr (relative to metallic iron) was produced by precipitation with hot sodium carbonate solution from a hot solution of the corresponding nitrates, the precipitate being then thoroughly washed to remove traces of alkali and afterwards impregnated with a solution of potassium phosphate to give a content of 2 parts of potassium monoxide K_2O. The catalyst was then reduced with hydrogen for a period of three hours at 300° C. using a gas flow velocity of 1.5 metres per second. Its reduction value thereupon amounted to 85% of free iron.

When water gas was passed over this catalyst at a pressure of 20 kg./sq. cm., and at a temperature of 211° C. a $(CO+H_2)$ conversion of 65% to 70% was obtained. The product obtained contained a large quantity of oxygen-containing organic compounds, for example, the C_8 hydrocarbon fraction contained 50% oxygen-containing organic compounds, and the C_{10} hydrocarbon fraction approximately 40% oxygen-containing organic compounds. The proportion of esters amounted to approximately 5% of the liquid product. Approximately 25% of the liquid product boiled above 320° C.

An iron catalyst produced in a similar manner, but with a shorter reduction period and a lower reduction temperature, had a reduction value of only 40%. A reaction temperature of 280° C. was required with this catalyst to give the same conversion. The liquid product obtained in the fractions with the corresponding number of carbon atoms contained, however, only approximately a quarter to a fifth of the above-mentioned content of oxygen-containing organic compounds. The content in compounds boiling above 320° C. amounted to 45% of the liquid synthetic product.

In the foregoing description, the term "reduction value" means the percentage of the total iron content of the catalyst which is in the metallic state.

What we claim is:—

1. A process for the catalytic hydrogenation of carbon monoxide to yield a product having a relatively high content of esters, in which a synthesis gas containing carbon monoxide and hydrogen is contacted, at a temperature in the range 165°—240° C. and at a pressure in the range 10—50 kg. per sq. cm., with a precipitated iron catalyst containing a halogen-free alkali-metal compound introduced into the catalyst in the form of a salt of one of the phosphoric acids, boric acids, tungstic acids or molybdic acids, more than 60% of the iron being in the metallic state and the alkali-metal compound, calculated as K_2O, being present in a proportion of from 0.5% to 10% by weight of the total iron content of the catalyst.

2. A process according to Claim 1, in which more than 80% of the iron is in the metallic state.

3. A process according to Claim 1 or Claim 2, in which the pressure lies within the range 20—30 kg. per sq. cm.

4. A process according to any of the preceding claims, in which the temperature lies within the range 190° C.—220° C.

5. A process according to any of the preceding claims, in which the alkali-metal calculated as K_2O comprises 2% to 5% by weight of the total iron content of the catalyst.

6. A process according to any of the preceding claims, in which the alkali-metal is potassium.

7. A process according to any of the preceding claims, in which the alkali-metal compound is introduced into the catalyst by impregnating it with a solution of an alkali-metal salt.

8. A process according to any of the preceding claims, in which the catalyst, prior to use, is reduced in a gas stream of high velocity, the gas containing hydrogen or carbon monoxide, or a mixture of both.

9. A process according to Claim 8, in which the catalyst is reduced at a temperature within the range 200° C.—320° C.

10. A process according to claim 8 or Claim 9, in which the gas used in the reduction contains an excess of carbon monoxide.

11. A process according to any of the preceding claims, in which the synthesis gas fed to the process contains more carbon monoxide than hydrogen.

12. A process according to any of the preceding claims, in which the temperature of the catalyst increases in the direction of gas flow.

13. A process for the catalytic hydrogenation of carbon monoxide, substantially as described with reference to Example I or Example II.

14. A process for the catalytic hydrogenation of carbon monoxide, substan-

tially as hereinbefore described.

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

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Process for the Catalytic Hydrogenation of Carbon Monoxide

ERRATUM

SPECIFICATION NO. 712,686

Page 2, line 123, *for* "(760 mm Mg/0°)" *read* "(760 mm Hg/0°)".

THE PATENT OFFICE,
9th September, 1954

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taining organic compounds by [illegible] carbon monoxide and hydrogen in the presence of iron catalysts, the iron catalysts used being generally mixed, for the usual alkali impregnation, with potassium hydroxide or with potassium compounds of acids that are readily volatile, for example, potassium carbonate or potassium bicarbonate. Alcohols form the greater part, frequently 85%—90%, of the oxygen compounds obtained.

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yield a product [illegible] content of esters, in which a synthesis gas containing carbon monoxide and hydrogen is contacted, at a temperature within the range 165° C.—240° C., and at a pressure within the range of 10 kg. to 50 kg. per sq. cm., with a precipitated iron catalyst containing a halogen-free alkali-metal compound introduced into the catalyst in the form of a salt of one of the phosphoric acids, boric acids, tungstic acids or molybdic acids, more than 60% of the iron being in the metallic state and the alkali-metal compound, calculated as K_2O, being present in a proportion of from 0.5% to 10% by weight of the total iron content of the catalyst. The preferred temperature range for the process is 190° C. to 220° C.

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