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(54) PRODUCTION OF UNSATURATED HYDROCARBONS

(71) We, RUHRCHEMIE AKTIENGESELLSCHAFT, a German Company of 42 Oberhausen 13, Postfach 35, Germany, Federal Republic of Germany, 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 present invention relates to the production of unsaturated hydrocarbons by catalytic hydrogenation of carbon oxides.

German Patent 922,883 discloses a process for the production of unsaturated, especially gaseous hydrocarbons by reacting carbon monoxide with hydrogen in the presence of finely divided fused iron catalysts. In this process, the catalysts are periodically or continuously removed from the reaction chamber, regenerated, reduced and returned. The reaction is carried out under atmospheric or slightly elevated pressure and at temperatures above 450°C. and advantageously at 470° to 600°C.

In another process which is described in German Patent 896,338, unsaturated gaseous hydrocarbons are produced by reacting carbon monoxide with hydrogen in the presence of stable oxides of metals of groups II to VII of the Periodic Table. The reaction is carried out at substantially atmospheric pressure and at temperatures above 520°C.

Corresponding with the Boudouard equilibrium, the high reaction temperatures used in the prior art processes result in the formation of carbon from carbon monoxide. The deposition of carbon results in deactivation of the catalyst surface and, in individual cases, in disruption of the catalyst structure, which reduces considerably the lifetime of the catalyst.

According to DAS 1,271,098, catalysts consisting of at least 98% by weight of a support and 0.3 to 2% by weight of cobalt, nickel or platinum can be used for producing ethylene by hydrogenation of carbon monoxide with hydrogen. The reaction is carried out at a throughput rate of 2,500 to 3,000 liters of gas per liter of catalyst per hour at a temperature of 300° to 450°C. and pressures of 130 to 200 mm. Hg. The process is distinguished by good selectivity to lower gaseous olefins, but the conversions which can be achieved and which are in the order of 10 to 20% are unsatisfactory.

When hydrogenating carbon oxides, the conversion is highly dependent upon the hydrogen partial pressure. The higher the hydrogen partial pressure, the higher the conversions which are achieved. However, the hydrogenation of the primarily formed olefins also increases as the hydrogen partial pressure increases. Therefore, it is necessary in practice when operating in the presence of selectively acting catalysts to adjust the synthesis pressure or hydrogen partial pressure such that the hydrogenation of carbon oxide proceeds with a high conversion and, at the same time, hydrogenation of the olefins is largely suppressed.

It is additionally known, according to British Patent No. 506064, to produce hydrocarbon products (and contingently oxygen containing derivatives of hydrocarbons) by reacting carbon monoxide with hydrogen at elevated temperatures in the presence of a catalyst consisting wholly or mainly of a sintered metal of the iron group to which is added an alkali compound having particular properties set forth in British Patent No. 506064.

The combination of sintered metal of the iron group and alkali compound may, as also described in British Patent No. 506064, have added thereto an oxide or hydroxide of aluminium, silicon dioxide, kieselguhr, compounds of copper, titanium, manganese, tungsten, molybdenum, chromium, thorium, cerium, zirconium or other rare earths.

We have now discovered that, by a particular selection of conditions of temperature and pressure in conjunction with judicious selection of the catalyst type, we are able to obtain unsaturated hydrocarbons in good yield.

According to the present invention there is provided a process for the production of one or more unsaturated hydrocarbons, comprising catalytic hydrogenation of a carbon oxide with hydrogen at 250° to below 350°C and at a total pressure of 10 to 30 bars in the presence of a catalyst which contains a lower oxide of a transition metal of Group 5 or 7 of the Periodic Table hereinafter specified and a metal of Group 8 of said Periodic Table.

The Periodic Table referred to herein is that shown in Liptot, Modern Inorganic Chemistry, 1971. In the Periodic Table, Groups 5A and 7A contain transition metals, whereas Groups 5B and 7B contain non-transition elements, and Group 8 contains transition metals.

Oxides of metals of Group 8 are relatively easily reducible to the corresponding metals. Lower oxides of transition metals of Groups 5 and 7 are relatively difficultly reducible to the corresponding metals. Higher oxides of transition metals of Groups 5 and 7 are relatively easily reducible to corresponding lower oxides.

The catalyst may be prepared by a known method.

The catalyst or a composition to form the catalyst may be prepared by mixing its constituents, homogenizing the mixture and mechanically shaping the homogenized mixture.

The catalyst or a composition to form the catalyst may be prepared by sintering its constituents together.

The catalyst may be prepared by contacting a composition comprising an oxide of the transition metal of Group 5 or 7 and an oxide of the metal of Group 8 with hydrogen at a temperature of 350° to 520°C, suitably at a pressure of about 1 bar, to reduce the oxide of the metal of Group 8 to the metal and, where the oxide of the transition metal of Group 5 or 7 is a higher oxide, to reduce that oxide to a lower oxide.

Alternatively the catalyst may be prepared from a composition comprising a compound of a transition metal of Group 5 or 7, the compound being converted to the lower oxide of the transition metal of Group 5 or 7 at the catalytic hydrogenation temperature. The compound to be converted to the lower oxide may be prepared by precipitation from an aqueous solution by means of a precipitating agent such as an alkali metal carbonate.

The catalyst may contain a promoter such as one or more compounds selected from carbonates of metals of Group 1A of said Periodic Table, magnesium oxide and zinc oxide.

The catalyst may contain a carrier material such as one or more materials selected from precipitated silicic acid, natural silicic acid, kieselguhr, aluminium oxide, alumina hydrate and natural and synthetic silicates such as magnesium silicate, aluminium silicate and pumice.

The lower oxide of the transition metal of Group 5 or 7 is preferably a lower oxide of vanadium and/or a lower oxide of manganese and/or a lower oxide of rhenium. The metal of Group 8 is preferably iron or cobalt.

One preferred catalyst for use in the process of the invention is described and claimed in Application No. 36209/78 (Patent No. 1553362) and comprises 100 parts by weight of iron, 50 to 100 parts by weight of vanadium as lower oxide or as a compound reducible to lower oxide, 3 to 5 parts by weight of K_2O and 5 to 15 parts by weight of ZnO.

Another preferred catalyst for use in the process of the invention is described and claimed in Application No. 36210/78 (Patent No. 1553363) and comprises 100 parts by weight of iron, substantially 100 parts by weight of manganese as lower oxide or as a compound reducible to lower oxide, substantially 4 parts by weight of K_2O and substantially 10 parts by weight of ZnO.

In carrying out the process of the invention, the catalyst is generally used in the form of a stationary bed. However, the catalyst may alternatively be used in finely divided form, a whirling motion being imparted to the catalyst by gas flowing therethrough.

For regeneration, the catalyst may be withdrawn continuously or intermittently from a reaction vessel in which the process of the invention is carried out. The withdrawn catalyst is freed from contaminant adhering to it by burning the contaminant off with air in a separate vessel.

The process of the invention is simple in operation. The process may be carried out by passing a mixture of carbon oxide and hydrogen over the catalyst, contained in a pressure reactor, at an inlet temperature of about 300°C. A feed gas containing carbon oxide and hydrogen in a ratio of from 2:1 to 1:2 by volume may be used in the process. Preferably the gas mixture contains a slight excess of the carbon oxide. The gas mixture leaving the reaction vessel is advantageously returned wholly or partially into the reaction vessel after removal of the unsaturated gaseous hydrocarbons produced.

The total conversion of carbon oxide and hydrogen in the process according to the invention is 80 to 90%. 60% to 70% of the reaction products are C_2 to C_4 olefins.

EXAMPLE 1

Iron oxide (Fe_2O_3 and Fe_3O_4), vanadium oxide (V_2O_5), zinc oxide and potassium carbonate were mixed in a ratio of 100 parts by weight of Fe, 70 parts by weight of V, 10 parts by weight of ZnO and 4 parts by weight of K_2O and homogenized. The composition obtained after moulding and sintering of the mixture at 1050°C. was subsequently reduced for several hours at 500°C with hydrogen to produce a catalyst.

A layer of the catalyst of 30 cm. depth was filled into a test furnace of 1 m. in length and 10 mm. in inside diameter. The reactor was brought to the reaction temperature by means of an electrical heater. Under a pressure of 10 bars and at a temperature of 320°C., a CO/H_2 mixture (molar ratio, 1:1) was passed over the catalyst at a space velocity of 500 standard liters of gas mixture per liter of catalyst per hour. The conversion of $CO + H_2$ was 85% and the yield 152 g. The reaction product contained.

C_2H_4	26.1% by weight
C_3H_6	18.6% by weight
C_4H_8	14.4% by weight
C_2—C_4 saturated	13.2% by weight
total	72.3% by weight

The proportion of methane was 12% by weight, the balance being hydrocarbons having more than 4 carbon atoms.

EXAMPLE 2

The conditions of Example 1 were maintained except that a catalyst was prepared from a mixture consisting of 100 parts by weight of Fe, (as oxide), 100 parts by weight of Mn (as oxide), 10 parts by weight of ZnO and 4 parts by weight of K_2O (as K_2CO_3) was used. The conversion of $CO+H_2$ was 86%, the yield 164 g.

The reaction product contained the following gaseous hydrocarbons having 2 to 4 carbon atoms:

C_2H_4	31.3% by weight
C_3H_6	22.2% by weight
C_4H_8	17.4% by weight
C_2—C_4, saturated	15.7% by weight
total	86.6% by weight

In addition, 9.6% by weight of methane were obtained, the balance being hydrocarbons having more than 4 carbon atoms.

WHAT WE CLAIM IS:—

1. A process for the production of one or more unsaturated hydrocarbons, comprising catalytic hydrogenation of a carbon oxide with hydrogen at 250° to below 350°C and at a total pressure of 10 to 30 bars in the presence of a catalyst which contains a lower oxide of a transition metal of Group 5 or 7 of the Periodic Table hereinbefore specified and an elemental metal of Group 8 of the said Periodic Table.

2. A process according to claim 1, wherein the metal of Group 8 is iron or cobalt.

3. A process according to claim 1 or 2, wherein the catalyst contains a lower oxide of vanadium.

4. A process according to any preceding claim, wherein the catalyst contains a promoter.

5. A process according to Claim 4, wherein the promoter is selected from carbonates of metals of Group 1A of the Periodic Table, magnesium oxide and zinc oxide.

6. A process according to claim 4, wherein the catalyst contains 100 parts by weight of iron, 50 to 100 parts by weight of vanadium, 3 to 5 parts by weight of K_2O and 5 to 15 parts of ZnO.

7. A process according to any of claims 1 to 4, wherein the catalyst contains a lower oxide of manganese and/or a lower oxide of rhenium.

8. A process according to claim 7, wherein the catalyst contains 100 parts by weight of iron, substantially 100 parts by weight of manganese, substantially 4 parts by weight of K_2O and substantially 10 parts by weight of ZnO.

9. A process according to any preceding claim, wherein the catalyst comprises a carrier material.

10. A process according to claim 9, wherein the carrier material is one or more materials selected from precipitated silicic acid, natural silicic acid, kieselguhr, aluminium oxide, alumina hydrate, natural silicates and synthetic silicates.

11. A process according to any preceding claim, wherein the ratio of carbon oxide to hydrogen is from 2:1 to 1:2 by volume.

12. A process according to any preceding claim, wherein the catalyst has been prepared by contacting a composition comprising an oxide of the transition metal of Group 5 or 7 and an oxide of the metal of Group 8 with hydrogen at a temperature of 350° to 520°C to reduce the oxide of the metal of Group 8 to the metal and, when the

oxide of the transition metal of Group 5 or 7 is higher oxide, to reduce that oxide to a lower oxide.

13. A process according to claim 1, substantially as described herein in Example 1 or 2.

14. An unsaturated hydrocarbon produced by a process according to any of claims 1 to 13.

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