PATENT SPECIFICATION

1,076,848

1,076,848

Date of Application and filing Complete Specification: January 8, 1964. *No. 49780/63*
Application made in Germany (No. P30986ivd/39c) on January 22, 1963.
Application made in Germany (No. P32286ivd/39c) on July 26, 1963.
Complete Specification Published: July 26, 1967.

Index at Acceptance:—C5 EB1G.
Int. Cl.:—C 07 c 1/06, C 07 c 9/22.

COMPLETE SPECIFICATION

NO DRAWINGS

Process for Preparing High-moleculare Weight Paraffinic Hydrocarbons from Carbon Monoxide and Hydrogen

I, HELMUT PICHLER, of German nationality, of Kaiserstrasse 12, 75, Karlsruhe, Germany, do hereby declare the invention, for which I pray that a patent may be granted to me, 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 synthesis of high-molecular weight, i.e. at least 50,000 paraffinic hydrocarbons from carbon monoxide and hydrogen using ruthenium catalysts. Ruthenium catalysts have long been known for this synthesis, see, for example, German Specification 705,528. In these operations the ruthenium catalyst is made by precipitating RuO from potassium ruthenate solution. Comparatively high temperatures have hitherto been used for the synthesis, because the catalysts used were relatively inactive at low temperatures, and because one had to keep above the melting point of the paraffin formed in order to prevent the paraffin from being deposited on the catalyst. The necessary operating pressures were approximately 100 to 2000 atmospheres (H. Pichler and H. Buffleb, Brennstoff-Chemi *21*, 257 (1940); P. Guyer, D. Thomas and A. Guyer, Helv. Chim. Atac *42*, 481 (1959)). The solid paraffins of high melting point made by this process had maximum molecular weights of about 20,000, but the yields of high-molecular weight paraffin hydrocarbons were low. If the ruthenium catalyst was alkalised before use, for example by adding 5% of K_2O, then a reaction product containing 20% of paraffin having a molecular weight of 43,600 would be obtained. Even at 1000 atmospheres comparatively high temperatures of e.g., 150-180°C had to be used.

It has now been found that one can operate within the pressure range of 100 to 3000 atmospheres or more and preferably 100 to 2000 but at substantially lower temperatures of from 80-135°C., i.e., below the melting range of the high-melting paraffins, provided that certain conditions are observed:

(1) One must operate in the presence of solvents for the high-molecular weight paraffins, i.e., solvents which dissolve the high-molecular weight paraffins under the reaction conditions. The solubility of the high-molecular weight synthesised products in the solvent determines the lower temperature limit of the reactions according to the invention since below 80-90°C the products are virtually insoluble.

(2) It is necessary to use a highly active ruthenium catalyst prepared *in situ* in the solvent medium by reacting the medium with a ruthenium oxide which is especially activated to such an extent that it reacts with the solvent as soon as they are brought together. Only with these particularly active catalysts is it possible to operate at the low temperatures mentioned, i.e. below the melting range of the high-molecular weight products formed (maximum melting point approximately 135°C).

As a ruthenium-hydrocarbon complex is first formed during the synthesis, subsequent treatment must also be carried out to separate the ruthenium from the reaction product.

Finally, it is advantageous to ensure that contact between the gaseous reactants and the suspension of the catalyst in the solvent is as intimate as possible. This may be done by shaking the reaction vessel or preferably by vigorous stirring, for example, by means of magnetic agitators.

Suitable solvents are organic compounds which easily dissolve the resultant products under reaction conditions and which do not have too high a vapour pressure, such as paraffinic hydrocarbons such as nonane, and aromatic and halogenated hydrocarbons.

From the point of view of synthesis, it is very important to use highly active ruthenium catalysts. Ordinary ruthenium catalysts obtained by precipitating RuO_2 may be activated by irradiation with proton, neutron or electron rays or electromagnetic radiation, for example γ rays from a Co^{60}—source, or by heating in a high vacuum at from 100-130°C. Such catalysts are so reactive that they react immediately on being brought together with the solvent such as nonane to form carbon dioxide and water. Catalysts made in this way are several times more active in the synthesis than ordinary RuO_2 catalysts, which, it should be pointed out, do not react with nonane.

Another highly reactive catalyst may be formed by introducing gaseous ruthenium tetroxide into the solvent which is to be used in the synthesis. The RuO_4 reacts vigorously with the solvent to form extremely finely dispersed and extremely active ruthenium. The solvents which may be used are, for example, hydrocarbons having 6-12 carbon atoms in the molecule, particularly n-nonane.

The RuO_4 is made from ruthenate solutions by oxidation, for example with chlorine and by distilling the RuO_4.

Thus three ways of preparing active ruthenium catalysts which can be used in the process of the invention are:—

1. Subjecting RuO_2 to irradiation by proton, neutron or electron rays or by electromagnetic radiation, followed by reaction with the solvent medium.

2. Heating the RuO_2 in a high vacuum followed by reaction with the solvent medium.

3. Reacting RuO_4 with the solvent medium.

The effectiveness of catalysts made from RuO_4 can be further increased by irradiation with the agents hereinbefore mentioned. Irradiation during the reaction or irradiation of the reaction suspension outside the reaction zone during circulation, may also be advantageous.

In the case of catalysts made from RuO_4, the addition of alkali, for example, 1-5% of K_2CO_3 (based on the ruthenium in the catalyst material), was also found to aid the formation of high-molecular weight hydrocarbons.

The synthesis itself is effected in the usual manner, by passing a mixture of carbon monoxide and hydrogen into a suspension of the active ruthenium catalyst in the said solvent at a temperature of 80-135°C.

Up to 30% and more, based on the total product, of high molecular weight paraffin having a molecular weight of 50,000 to more than 100,000 can be obtained in this way at low temperatures of 120-130°C.

Due to the low reaction temperatures, especially below 150°C, the reaction product is dark in colour and it is hardly possible to separate the catalyst, which is thought to be chemically bonded to the high-molecular weight paraffin. However, if the reaction produce is then treated with hydrogen at temperatures of from 120 to 150°C or even higher, and at pressures of from 100 to 200 atmospheres for a short time, for example, about 15 minutes, then the catalyst easily separates from the solution of the reaction products in nonane. A pure white, extremely high-molecular weight paraffin is then obtained. The temperature used must be as low as possible, as the long hydrocarbon chains otherwise split and thus cause the molecular weight to be lowered. This reaction is very obvious even at 160°C.

Another method of splitting the ruthenium-hydrocarbon complexes is treatment with alcoholic potash lye.

The initially dark products of ruthenium and ruthenium compounds are liberated by this treatment and give a clear colourless high-molecular weight paraffin.

In the practical performance of the invention it has ben found to be especially advantageous to use two reactors both filled with the solvent medium containing the catalyst material and feeding to the first reactor the reaction gas containing carbon monoxide and hydrogen and feeding to the second reactor containing the reaction produce hydrogen gas in order to split the ruthenium-hydrocarbon complex, removing the product and cycling the catalyst together with the solvent medium for the second to the first reactor. During the splitting of the ruthenium-hydrocarbon complex a reactivation of the catalyst takes place so that, after treatment and separation of the resulting high molecular weight paraffinic hydrocarbons, the catalyst-solvent medium can be recycled.

Example I

A ruthenium catalyst was made by precipitating RuO_2 from a potassium-ruthenate solution with methanol. The precipitate was washed and dried. The RuO_2 catalyst was irradiated for 65 hours with the γ-rays from a Co^{60} source (dose: 4×10^5 r/h), in the presence of air or, with the same results, in an evacuated glass tube. The irradiated catalyst was extremely active with hydrocarbons. It reacted at room temperatures with nonane, causing the catalyst to glow and the nonane to decompose into carbon dioxide and water.

The suspension of the resultant ruthenium catalyst in nonane was placed in a shaking autoclave and gaseous reactant mixture ($H_2/CO=2$) was passed into it under a pressure of 1000 atmospheres. A good reaction was obtained at 132°C. The amount of carbon monoxide and hydrogen reacted by the catalyst per gram per hour was 8 to 10 times the amount reacted by a non-irradiated catalyst.

The reaction product which was soluble in nonane at the reaction temperature was precipitated on cooling in the form of a solid dark deposit. By subsequently treating this dark product with hydrogen at 145°C and 200 atmospheres for 15 minutes, it was possible to separate pure white paraffin from the catalyst.

27.4 per cent of the resultant paraffin was insoluble in toluene at 85°C. This fraction had a mean molecular weight of 51,900. At 88°C, 9.4% with a molecular weight of 84,700. was still insoluble in toluene.

Example 2

A RuO_2 catalyst made in the usual way by precipitation was heated for five hours at 110°C in a high vacuum (at least 10^{-4} Torr). The thus activated catalyst also reacted when brought together with nonane, causing combustion of the hydrocarbon.

Even at 120°C, the suspension of this catalyst in nonane showed high activity in the paraffin synthesis. When fresh synthesis gas had ben passed into it several times under pressure (the pressure dropped from 1000 to 500 atmospheres each time) a dark reaction product was obtained.

The dark paraffin was boiled under reflux with a solution of 50% KOH in isopropanol for five hours in order to separate the ruthenium. Of the clear paraffin obtained 40.3% was insoluble in toluene at 85°C. This fraction had a mean molecular weight of 58,000.

Example 3

Gaseous RuO_4 was led into nonane in a stream of nitrogen. The resultant suspension of the ruthenium catalyst in the solvent catalysed a carbon monoxide-hydrogen reaction even at 100°C. In order to make larger quantities of high molecular paraffins, fresh synthesis gas was passed in several times under a pressure of 1000 atmospheres at 120°C. In addition to small quantities of methane a reaction product was formed which was solid at room temperature. This was hydrogenated at 140°C in order to separate the ruthenium. A pure white high-molecular paraffin was obtained, 39.2% of which was still insoluble in toluene at 85°C. This fraction had a mean molecular weight of 105,000.

Example 4.

RuO_4, made by oxidising a perruthenate solution with chlorine and distilling, was mixed with nonane, giving rise to a violent reaction and leaving extremely finely dispersed ruthenium in suspension.

The suspension was then placed in an autoclave and a mixture of carbon monoxide and hydrogen in a ratio of 1:2 was passed into it under a pressure of 1000 atmospheres. The autoclave was shaken. A carbon monoxide-hydrogen reaction was observed even at 100°C. At 120°C the speed of the reaction was great enough for the synthesis to be carried out. Synthesis gas was passed in several times under pressure in order to give larger quantities of a paraffin having a (CH_2) repeating unit. A reaction product consisting almost exclusively of solid paraffin was obtained in addition to small quantities of methane. According to the length of the reaction, the reaction product contained 10-25% of paraffin hydrocarbon with a mean molecular weight of more than 100,000.

In a modification of the invention, it has now been found that catalysts from other elements from Group VIII of the Mendeleeft Periodic Table, for example, catalysts containing iron, cobalt, nickel or osmium, possibly together with activators, can be activated by irradiation like the ruthenium catalysts and can then advantageously be used for synthesising higher hydrocarbons from hydrogen and carbon monoxide. Lower reaction temperatures can be used than would be used for non-irradiated catalysts, and this aids the formation of very high molecular hydrocarbons.

Besides irradiation with γ rays, the catalysts used in this invention may be activated by irradiation with proton rays, e.g. α rays, neutron rays or high energy electron rays, i.e. 1 mega-electron-volt or over.

There are various possible ways of carrying out the process.

1. Irradiating the catalyst before it is used for the reaction;
2. Irradiating the catalyst during the catalytic reaction;
3. Incorporating a radioactive isotope, particularly radioactive ruthenium, in the catalyst.

The first method is technically the simplest but is not equally successful in all cases. With methods 2 and 3 the activation is maintained during the catalytic hydrogenation of the carbon monoxide.

WHAT I CLAIM IS:—

1. A process for preparing high molecular weight paraffinic hydrocarbons which

comprises reacting carbon monoxide and hydrogen at a temperature of from 80°-135°C and a pressure of from 100-3000 atmospheres, the reaction being carried out in the presence of an organic hydrocarbon or halohydrocarbon solvent medium capable of dissolving the high molecular weight paraffinic hydrocarbon product at the reaction temperature and in the presence of a finely divided ruthenium catalyst prepared *in situ* by reacting a highly active ruthenium oxide with said organic solvent medium, the high molecular weight paraffinic hydrocarbon subsequently being recovered from the ruthemium hydrocarbon complex formed.

2. A process according to Claim 1, wherein the catalyst is prepared by activating RuO_2 by irradiation with proton, neutron or electron rays or with electromagnetic radiation and reacting the activated RuO_2 with said solvent medium.

3. A process according to Claim 1, wherein the catalyst is prepared by activating RuO_2 by heating under vacuum at 100-130°C and reacting the activated RuO_2 with the organic solvent medium.

4. A process according to Claim 3, in which the RuO_2 is activated by heating for 5 hours at 110°C in a vacuum of at least 10^{-4} Torr.

5. A process according to Claim 1, wherein the catalyst is prepared by introducing gaseous RuO_4 into the solvent medium.

6. A process according to Claim 5, wherein the reaction medium contains an alkali.

7. A process according to Claim 6, where the reaction medium contains from 1-5% by weight of K_2CO_3 based on the weight of ruthenium present in the catalyst material.

8. A process according to Claims, 5, 6 or 7 wherein the catalyst is activated during the reaction by irradiation with γ rays.

9. A process according to any one of the preceding claims, wherein the solvent medium is nonane.

10. A process according to any one of the preceding claims, wherein the high molecular weight product paraffinic hydrocarbon is recovered from the reaction mixture by treatment of the product ruthenium hydrocarbon complex with hydrogen at a temperature of from 120-150°C.

11. A process according to any one of Claims 1-9, wherein the high molecular weight product paraffinic hydrocarbon is recovered from the reaction mixture by treating the product ruthenium-hydrocarbon complex with an alcoholic alkaline lye.

12. A process according to Claim 11, wherein the product ruthenium-hydrocarbon complex is treated with an alcoholic potassium hydroxide solution.

13. A process according to any one of the preceding claims, wherein the reaction between the carbon monoxide and hydrogen is conducted at a pressure in the range 100-2000 atmospheres.

14. A modification of the process according to any one of the preceding claims, in which in place of the ruthenium catalyst there is used as catalyst a compound of an element from Group VIII of the Mendeleeft Periodic Table, other than ruthenium, activated by irradiation with proton, neutron or electron rays or with electromagnetic radiation.

15. A process according to Claim 14, wherein the catalyst is activated by γ radiation before being used in the reaction.

16. A process according to Claim 15, wherein the calatysts are activated by γ radiation during the reaction.

17. A process according to any one of Claims 1-16, wherein there are used two reactors both filled with the solvent medium containing the catalyst material and feeding to the first reactor the reaction gas containing carbon monoxide and hydrogen and feeding to the second reactor containing the reaction product hydrogen gas in order to split the ruthenium-hydrocarbon complex, removing the product, and cycling the catalyst together with the solvent medium from the second to the first reactor.

18. A process according to Claim 1, substantially as hereinbefore described in any one of the Examples.

For the Applicant,
D. YOUNG & CO.,
Chartered Patent Agents
9 Staple Inn,
London, W.C.1.

Berwick-upon-Tweed: Printed for Her Majesty's Stationery Office by The Tweeddale Press Ltd.—1967
Published at the Patent Office, 25 Southampton Buildings, London, W.C.2 from which copies may be obtained.