Canadian Patents Database

12/19/2001 - 10:05:03

(12) **Patent:** (11) **CA 634593**

(54) PROCESS FOR THE CATALYTIC HYDROGENATION OF CARBON MONOXIDE

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(71) (Country):	
(74)	
(45)	**Jan. 16, 1962**
(22)	
(43)	
(52)	**260/678.7**
(51)	**N/A**
	No
(30)	**None**
	N/A
	Unknown

*** Note: Data on abstracts and claims is shown in the official language in which it was submitted.

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The invention relates to a process for the production or synthesis of hydrocarbons and oxygen-containing organic compounds from carbon monoxide and water vapour or steam, particularly from carbon monoxide-containing industrial gases and water vapour or steam, in which the activation, that is to say the reduction of the catalysts prior to use in the synthesis, is carried out with industrial gases which contain carbon monoxide.

Application No.600393 relates to a process for the production of hydrocarbons and oxygen-containing organic compounds by the reaction of carbon monoxide with water vapour in the presence of a catalyst at elevated temperature and at normal or elevated pressure, in which with the use of temperatures in the range 150° - 400°C. and pressures of from 1 to 200 atmospheres, the mixture of carbon monoxide and water vapour is contacted with a catalyst which contains a metal of the eighth group of the periodic system of elements, preferably cobalt, iron, nickel or ruthenium, and which may also contain supporting substances and/or promoters, and which has first been activated by treatment with carbon monoxide and, if necessary or desired, with hydrogen, or with a mixture of CO and H_2, at a temperature in the range 150° - 500°C. Suitable promoters are compounds of alkali metals, alkaline earth metals and magnesium, difficultly reducible oxides, such as thorium oxide, cerium oxide, aluminium oxide, or chromium oxide; as well as compounds of the elements

magnesium, vanadium, boron, copper, nickel, silver, or gold. The hydrogenation of carbon monoxide may be carried out in one or more stages as well as with recycling, the carbon monoxide/water vapour ratio being adjusted after each stage. The carbon monoxide/water vapour ratio may be from 1 to 4 volumes of carbon monoxide per volume of water vapour; however, it has been found to be particularly advantageous to use at least 2 volumes of carbon monoxide for each volume of water vapour or steam. The production of hydrocarbons and oxygen-containing organic compounds by reacting carbon monoxide with water vapour may be carried out in the presence of fixed-bed catalysts as well as in the liquid phase with the use of catalysts which are suspended in a liquid medium. However, a fluidized-bed catalysis may also be employed.

Therefore, the preliminary treatment of the catalysts was carried out in such manner that they were reduced with hydrogen or with carbon monoxide, or with carbon monoxide and subsequently with hydrogen, or with mixtures of CO and H_2. However, such a preliminary reducing treatment for the activation of the catalysts renders it necessary at the beginning of the actual synthesis to change over to a completely new gas if it is desired to carry out the synthesis with industrial carbon monoxide-containing gases which are substantially free from hydrogen and rich in inert gases, such, for example, as producer gas or blast-furnace gas, and water vapour or steam.

It has now been found that this disadvantage is

substantially completely avoided by carrying out the preliminary reducing treatment of the catalyst directly with the gases which are subsequently used with water vapour in the synthesis.

It was by no means to be expected that it would be possible to activate the catalysts in this manner with carbon monoxide-containing industrial gases; rather was it assumed that, for example by treatment with a blast-furnace gas containing only 32% by volume of carbon monoxide, the degree of reduction necessary for the synthesis would not be obtained due to the high nitrogen content of the blast-furnace gas.

However, according to the invention, an additional advantage of the preliminary treatment of the catalysts resides in the discovery that it is exactly the high nitrogen-content of the industrial gases by which, even during the activating period, any excessive and harmful separation of carbon is suppressed to a high degree.

The activation is carried out with particular advantage at normal pressure; however, superatmospheric pressures may also be used. The temperatures used range between the synthesis temperature subsequently employed and 100°C., advantageously 20° - 30°C., above the synthesis temperature.

According to the invention, the preliminary treatment of the catalysts is suitable for all methods of carrying out the synthesis from carbon monoxide and water vapour or steam, that is to say, it may be used in a synthesis carried out in the gaseous

phase with fixed-bed catalysts, in a synthesis carried out in the liquid phase using a suitable liquid medium, and in the fluidized process and moving bed process, as well as in all processes in which the gas and/or the catalyst suspension are recycled.

The advantage and the practical importance of a preliminary treatment of the catalysts with carbon monoxide-containing industrial gases are illustrated by the following example:-

EXAMPLE

An alkalised Fe-Cu-Kieselguhr catalyst of the composition : 100 Fe : 0.5 Cu : 2 K_2CO_3: 100 Kieselguhr which was obtained in known manner by precipitation with sodium carbonate from the nitrate solutions iron and copper was divided into two portions a) and b) which were respectively subjected to preliminary treatment in the following manner:-

a) 24 hours with blast-furnace gas at 270°C. under normal pressure and at a space velocity of 100 based on the carbon monoxide present in the blast-furnace gas, and

b) with pure carbon monoxide, the conditions being otherwise the same as those used with a).

After this activation, the catalyst presents the following picture:

Catalyst	Degree of reduction of the catalyst %	Content of elementary carbon in the catalyst wt.%
a) pre-treated with blast-furnace gas	75	2.8
b) pre-treated with CO	87	15.7

When, using a gauge pressure of 20 atmospheres and a temperature of 240° - 260°C., a mixture of blast-furnace gas and water vapour in the ratio 3 volumes of CO to 1 volume of H_2O was passed over these catalysts at a space velocity of 200 based on the CO content of the blast-furnace gas, the catalyst a), pre-treated with blast-furnace gas, gave, with an average CO-conversion of 90% by volume, a yield of 300 kilograms of hydrocarbons per kilogram of Fe, while the catalyst b), activated with pure carbon monoxide, gave a yield of 220 kilograms of hydrocarbons per kilogram Fe.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:-

1. A process for the synthesis of hydrocarbons by the reaction of carbon monoxide with steam in the presence of a catalyst containing a metal of the eighth group of the periodic system, in which the catalyst used in the synthesis has been previously reduced and activated by treatment with a carbon monoxide-containing industrial gas rich in one or more inert gases.

2. A process according to claim 1, in which the industrial gas used in the reduction and activation is producer gas or blast-furnace gas.

3. A process according to claim 1 or claim 2, in which the reduction and activation of the catalyst is carried out at a temperature in the range 150° - 500°C.

4. A process according to claim 1, in which the reduction and activation of the catalyst is carried out at a temperature which is higher than the temperature of the synthesis in which the catalyst is used and which is not more than 100°C above that synthesis temperature.

5. A process according to claim 1 or claim 2, in which the reduction and activation of the catalyst is carried out at or about normal atmospheric pressure.

6. A process for the synthesis of hydrocarbons with or without the synthesis of oxygen-containing organic compounds, which comprises

contacting steam and a carbon monoxide containing industrial gas rich in one or more inert constituents in synthesis proportions of CO/H_2O with a catalyst containing a metal of the eighth group of the periodic system at a temperature in the range 150° - $400^{\circ}C$ and at a pressure within the range from normal atmospheric pressure to about 200 atmospheres gauge, the catalyst having been activated prior to use in the synthesis by treatment, at a temperature within the range 150° - $500^{\circ}C$., with a carbon monoxide-containing industrial gas rich in one or more inert constituents.

7. A process according to claim 6, in which the industrial gas employed for the activation of the catalyst and for the synthesis is blast-furnace gas.

8. A process according to claim 6, in which the industrial gas employed for the activation of the catalyst and for the synthesis is blast-producer gas.

9. A process according to any one of claims 6, 7 and 8, in which the activation of the catalyst is effected at or about normal atmospheric pressure.

10. A process according to any one of claims 6, 7 and 8, in which CO/H_2O ratio in the synthesis gas lies between 1:1 and 4:1.

11. A process according to any one of claims 6, 7 and 8, in which the CO/H_2O ratio in the synthesis gas is at least 2.

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12. A process according to any one of claims 6, 7 and 8, in which the CO/H_2O ratio in the synthesis gas is not less than 2 and is not greater than 3.

13. A process according to any one of claims 6, 7 and 8, in which the temperature used in the activation of the catalyst is higher than the synthesis temperature but is not more than 100°C. higher than the synthesis temperature.

14. A process according to any one of claims 6, 7 and 8, in which the activation of the catalyst is carried out at a temperature which is from 20°C to 30°C higher than the synthesis temperature.

15. A process according to any one of claims 6, 7 and 8, in which the synthesis is effected at a temperature in the range 180° - 280°C.

16. A process according to any one of claims 6, 7 and 8, in which the synthesis is effected at a pressure not substantially in excess of 100 atmospheres gauge.

17. A process according to any one of claims 6, 7 and 8, in which the metal of the eighth group in the catalyst is iron.

18. A process according to any one of claims 6, 7 and 8, in which the duration of the period of activation of the catalyst is such as to convert more than 50% of the metal of the eighth group into one or more of the forms selected from the group consisting of (a) the free element, (b) definite compounds with carbon, and (c) indefinite compounds with carbon.

19. A process according to any one of claims 6, 7 and 8, in which the carbon monoxide-containing industrial gas is relatively free from hydrogen.

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