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(54) CATALYTIC CARBON MONOXIDE HYDROGENATION

(54) HYDROGENATION D'OXYDE DE CARBONE CATALYTIQUE

(72) (Country): **HERBERT SPENGLER** (Not Available)
WALTER ROTTIG (Not Available)
KARL SCHENK (Not Available)

(73) (Country): **LURGI GESELLSCHAFT FUR WARMETECHNIK M.B.H.**
RUHRCHEMIE AKTIENGESELLSCHAFT

(71) (Country):

(74) :

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This invention relates to improvements in catalytic carbon monoxide hydrogenation. It more particularly relates to a new iron catalyst.

The catalytic hydrogenation of carbon monoxide is well known. It is also known that the primary products obtained from the synthesis may be varied with respect to their chemical nature and their boiling range by varying the operating conditions. The operating conditions which effect the nature and range of the primary product include the synthesis pressure, temperature load and gas recycling. In addition catalysts of various compositions and prepared by various methods of preparation effect the formation of different types of primary products.

In general, however, a catalyst of a given composition and prepared by a given method will lead to the preferred formation of synthesis products of a certain composition. Thus for the production of primary products having a high content of oxygen containing compounds strongly alkaline iron catalysts have proven particularly effective. It is generally true that the nature of the catalysts determine the primary products formed independent of the other synthesis operating conditions and especially with respect to the gas load.

One object of this invention is a new iron catalyst which may be used for the catalytic hydrogenation of carbon monoxide and which will produce either a high content of high boiling paraffin-like hydrocarbons or a high content of low boiling gasoline-like hydrocarbons depending upon the gas load of the catalyst. This and

still further objects will become apparent from the following description:

The catalyst in accordance with the invention is an iron catalyst which is carrier free or contains only small amounts of carrier material. The catalyst is obtained by precipitation of an iron salt solution at a pH of about 6.8 to 7.5 and preferably of 6.8 to 7.1. The catalyst has an alkali content of 2 to 6% and preferably 3 to 4% calculated as K_2O and a SiO_2 content of 5 to 15%. The catalyst is reduced to a free iron content of 10 to 50% and preferably 20 to 30% based upon the total iron and has an inner surface of 180 to 230 square meters and preferably 200 to 220 square meters per gram of iron in the reduced catalyst.

The SiO_2 content of 5 to 15% is obtained by direct impregnation with an alkali silicate.

The catalyst preferably has a K_2O to SiO_2 ratio of 1 ; 1 to 1: 5.

The new catalyst may, if necessary, or desired, contain activators such as copper, silver or metals of the 5th to 7th group of the Periodic system.

The new catalyst may be used for the catalytic hydrogenation of carbon monoxide with synthesis gases at temperatures of 175° to $300^{\circ}C$. and pressures up to 100 atmospheres.

If gas flows of 10 to 200 litres of fresh gas per liter of catalyst per hour are used, the synthesis products obtained will have a high content of paraffin-like hydrocarbons.

If a catalyst load of 200 to 1000 liters and

and preferably 200 to 750 liters of fresh gas is used per liter of catalyst per hour, the synthesis products will have a high content of low boiling gasoline-like hydrocarbons.

5 Thus, with the new catalyst in accordance with the new invention, it is for the first time possible to obtain either a high yield of paraffin-like hydrocarbons which are high boiling, or a high yield of gasoline-like hydrocarbons which are low boiling merely by varying the
10 catalyst load as described.

Of decisive importance in the new catalyst is the composition and method of preparation thus resulting in the required inner surface.

15 The determination of the inner surface is effected by preparation of an adsorption isotherm and its valuation by the method of Brunauer, Emmet and Teller (the so-called BET-method). The apparatus required substantially consists
20 of a graduated buret in which the volume of gas to be absorbed such as nitrogen or argon is measured, a manometer for the determination of the gas pressure and a small flask in which the adsorbing substance to be tested is placed.

25 The catalyst is prepared by the precipitation of an iron salt solution in the conventional manner. The alkali content of the catalyst is generally adjusted by first
30 washing the precipitated mass extensively, and thereafter impregnating with commercial alkali silicate having a ratio of K_2O to SiO_2 of 1 : 2.5 to the desired silicic acid content. The silicic acid remains quantitatively in the precipitated catalyst mass and cannot be removed therefrom by any chemical expedient in the course of the catalyst production.

The catalyst is preferably adjusted to a K_2O to SiO_2 ratio of 1 : 1 to 1 : 5. This will give particularly favorable results with respect to lifetime activity of the catalyst. To obtain a ratio of 1 : to more than 2.5, the catalyst mass is impregnated with water glass, is neutralized with dilute nitric acid while maintaining a pH value of 6.5 to 8 thereby dissolving out a more or less large alkali portion and shifting the ratio of K_2O to SiO_2 in favor of the silicic acid.

If a K_2O to SiO_2 ratio of 1 to less than 2.5 is desired, an incomplete washing of the precipitated catalyst mass is effected so that a residual alkali content of 1 to 2% will remain. By the subsequent direct impregnation with commercial water glass, it is possible to obtain K_2O to SiO_2 ratios which are lower than 1 to 2.5 such as for example 1 : 1.5 or even 1 : 1.

The content of free iron is obtained by suitable reduction conditions. The catalyst in accordance with the invention may be reduced with gases containing hydrogen and/or carbon monoxide at temperatures of between 175° to $320^\circ C$. and preferably between 200° and $250^\circ C$. A high gas velocity of for example 1 to 2 meters per second, preferably 1.2 to 1.5 meters per second calculated under standard conditions has been found to be advisable.

When using the catalyst in accordance with the invention for the hydrogenation of carbon monoxide, temperatures of 175° to $300^\circ C$. and pressures up to 100 atmospheres the result with respect to the composition of the hydrogenation product as mentioned are dependent upon the gas load.

If the gas load is 10 to 200 liters of fresh gas per liter of catalyst per hour, that is to say within the normal limits of the Fischer-Tropach synthesis, then the primary products will have a high content of high boiling paraffin-like hydrocarbons. If, however, the hydrogenation is effected with the same catalyst under the same conditions of temperature and pressure, but at a high gas load of 200 to 1000 liters and preferable 200 to 750 liters of fresh gas per liter of catalyst per hour, then primary products having a high content of low-boiling gasoline-like hydrocarbons are obtained.

Except as set forth above, all the conditions for the catalyst preparation are the same as is conventional for the production of precipitated iron catalysts. In the same manner, any mode of operation within the limits set forth above may be used for the carbon monoxide hydrogenation.

The following examples are given by way of illustration and not limitation:

Example 1.

A boiling solution which contained 45 grams of iron, 0.45 grams of copper and 2.5 grams of lime in solution in the form of their nitrates was added within 2 minutes to a boiling soda solution so that the pH value after the termination of the precipitation was 7.1. Then the mixture was heated for a short time and immediately thereafter filtered in the hot state. The filtrate was washed with hot distilled water so that the residual alkali content in the catalyst was 0.6 based on iron and calculated as K_2O .

The moist catalyst mass was cooled and impregnated with an aqueous solution of potassium water glass having a concentration of 20% and a $K_2O : SiO_2$ ratio of 1 : 2.5 in such a manner that the total alkali content of the impregnated catalyst mass was 3.6 calculated as K_2O and based on 100 parts of iron, and the content of silicic acid was 7.8% based on total iron.

The mass was dried at a temperature of $110^{\circ}C.$, crushed and sieved to a grain size of between 2 and 4 mm.

The granulated catalyst mass was reduced for 60 minutes at a temperature of $250^{\circ}C.$ with a gas mixture consisting of 75% of hydrogen and 25% of nitrogen using a superficial gas velocity of 1.4 meters/second referred to standard conditions. Thereafter, the reduced catalyst had a content of 26% of free iron.

4.8 liters of this reduced catalyst mass were operated in a so-called double tube with water gas at a synthesis pressure of 30 atmospheres, a recycle ratio of 1 : 2.5, and at a temperature of $212^{\circ}C.$ The $CO : H_2$ ratio in the water gas was 1 : 1.19. The catalyst load was 100 parts of fresh gas per part by volume of catalyst per hour.

The $CO \downarrow H_2$ conversion obtained under these conditions were 65%, the methane formation was 4.0%, the usage ratio was 1 : 1.53. The proportion of products boiling above $320^{\circ}C.$ contained in the liquid product was above 75%.

Example 2.

5 If the same catalyst as in Example 1 is operated with a catalyst load of 500 parts by volume of water gas per part by volume of catalyst per hour, other conditions being identical, then a $\text{CO}+\text{H}_2$ conversion of 61.5% was obtained. The methane formation under these conditions is 7%.

10 The quantity of high boiling hydrocarbons contained in the reaction product under these conditions is only 55% as contrasted to 75% in Example 1.

Example 3.

15 A catalyst which was prepared in a manner similar to that of the above-mentioned catalyst, but which had been washed only to residual K_2O content of 1.5% instead of 0.6%, was impregnated with the same quantity of potassium water glass as described above.

20 While a somewhat higher portion of paraffin was found with normal gas load, the difference as compared with the catalyst of Example 1 was unimportant when using a high gas load.

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

1. A substantially free reduced iron catalyst for the hydrogenation of carbon monoxide at temperatures of 175 to 300°C., at a catalyst load of 10 to 200 liters of synthesis gas per liter of catalyst per hour for recovery of high boiling paraffin-like hydrocarbons, and at a catalyst load of 200 to 1000 liters of synthesis gas per liter of catalyst per hour for recovery of gasoline-like hydrocarbons, said catalyst having an alkali content of 2 to 6% calculated as K_2O , an SiO_2 content of 5 to 15%, a content of free iron of 10 to 50% and an inner surface of 180 to 230 square meters per gram of iron.
2. Catalyst according to claim 1 in which said content of said iron is 20 to 30%.
3. Catalyst according to claim 1 in which said alkali content is 3 to 4% calculated as K_2O .
4. Catalyst according to claim 1 in which said inner surface is 200 to 220 square meters per gram of iron.
5. Catalyst according to claim 1 having a K_2O ; SiO_2 ratio of 1:1 to 1:5.
6. Process for the production of a substantially carrier free iron catalyst which comprises precipitating an iron salt solution at a pH of about 6.8 to 7.5, washing the precipitate, impregnating the washed precipitate with alkali silicate, adjusting the alkali content to 2 to 6% calculated as K_2O and the SiO_2 content to 5 to 15%, thereafter reducing the catalyst to a free iron content of 10 to 50% of the total iron, and recovering a reduced iron catalyst having an inner surface of 180 to 230 square meters per gram of iron.

Process according to claim 6 in which the iron salt solution is precipitated at a pH of 6.8 to 7.1.

8. Process according to claim 6 in which the alkali content is adjusted to 3 to 4% calculated as K_2O .

9. Process according to claim 6 in which the SiO_2 content is adjusted by direct impregnation with alkali silicate.

10. Process according to claim 6 in which the K_2O : SiO_2 ratio is adjusted to 1:1 to 1:5.

11. Process according to claim 10 in which the K_2O : SiO_2 ratio is adjusted to 1: less than 2.5 by partial washing of the precipitate and subsequent impregnation with water glass.

12. Process according to claim 10 in which the K_2O : SiO_2 ratio is adjusted to 1: more than 2.5 by substantially complete washing of the precipitate, impregnation with water glass and final neutralization with nitric acid while maintaining a pH of 6.5 to 8.

Alex. E. MacRae & Co.,
56 Sparks Street,
Ottawa, Ontario, ~~Canada~~,
Patent Agents for Applicants.
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