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COMPLETE SPECIFICATION

NO DRAWINGS

Improvements relating to the Production of Hydrocarbons and/or Oxygenated Hydrocarbons

We, DAVID GALL, SIDNEY LEONARD SMITH and JOHN HILDRED GEORGE CARLILE, all three of Warren Spring Laboratory, Gunnels Wood Road, Stevenage, Hertfordshire, and all British subjects 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:—

This invention relates to the production of hydrocarbons and/or oxygenated hydrocarbons from gases comprising carbon monoxide and hydrogen and/or steam, using a catalyst. The oxygenated hydrocarbons referred to comprise alcohols and carboxylic acids in particular, but also such other oxygenated compounds as aldehydes and ketones. The invention thus relates to the Fischer-Tropsch process and similar processes, such as the Fischer-Pichler, Fischer-Pichler-Ziesecke and Hydrocol processes.

According to the present invention an iron oxide catalyst intended for use in the production of hydrocarbons and/or oxygenated hydrocarbons from gases comprising carbon monoxide and hydrogen and/or steam at elevated temperature and pressure is submitted to a preliminary activating treatment comprising heating it at a pressure of from substantially one atmosphere to substantially two atmospheres in the presence of a gas of reducing character which contains carbon monoxide and hydrogen in the ratio of 0.55 to 0.75 parts by volume of hydrogen per part by volume of carbon monoxide. We have obtained particularly useful results for example from such a gas when the carbon monoxide and hydrogen together comprise 90% to 99% of the total volume.

In general it is appropriate that the temperatures at which the preliminary activating treatment is carried out should be 10 to 50 Centigrade degrees higher than the production temperature of the hydrocarbons for which production the catalyst is intended. Thus the production temperature may for example be 265°C. and in this case a suitable activating temperature is 285°C. More generally, activating temperatures within the range 260-310°C. are normally suitable. The duration which is appropriate for the preliminary activating treatment naturally varies according to the temperature used, and also according to the composition of the activating treatment gas and of the catalyst itself, but in a typical case it may for example be 15 to 20 hours. The gas mixture used for the preliminary activating treatment may contain other gaseous substances in addition to the carbon monoxide and hydrogen specified in the preceding paragraph, examples of these being carbon dioxide and nitrogen; the activating gas may thus have a composition comparable to that of water-gas except in that the ratio by volume of hydrogen to carbon monoxide is much lower than in water-gas. A specific example of a gas mixture suitable for use in accordance with the invention is that comprising (by volume) 4% CO_2, 56% CO, 37% H_2, and 3% N_2; this mixture has a H_2/CO ratio of 0.6 volumes of H_2 per volume of CO.

If the production process in question uses a slurry of catalyst in high-boiling point hydrocarbons and/or oxygenated hydrocarbons, the novel preliminary activating treatment may be carried out after the catalyst slurry has been prepared, and indeed after the slurry has been charged into the reactor to be used in production. The activating gas may then be introduced by means of the same equipment as is provided for the subsequent introduction of the production gas, the introduction of the activating gas being maintained at a rate to give a space velocity and/or linear velocity similar to that employed in production.

The iron oxide catalysts to which the invention is most particularly applicable are those composed of precipitated iron oxide (consisting predominantly of ferric oxide) together with small proportions (e.g. 1-2%) of catalyst promotors such as cupric oxide and potassium oxide, hydroxide or carbonate.

The novel preliminary activating treatment is appropriate for a catalyst for use with a variety of synthesis gases in the production of hydrocarbons and/or oxygenated hydrocarbons, ranging from ordinary water-gas to gas mixtures rich in carbon monoxide comparable with those used in the preliminary activating treatment itself. The H_2/CO ratio by volume of the synthesis gas may thus lie in the range 1.3 to 0.55.

The preliminary activating treatment of the present invention has the advantage that it makes possible a particularly high rate of conversion of synthesis gas into products in the synthesis itself.

The following Examples illustrate the invention.

Example 1

The catalyst used consisted of precipitated iron oxide together with 1.0 part of copper as cupric oxide 1.5 parts of K_2O per 100 parts of iron, the parts being by weight. It was dispersed in a melted wax derived from a Fischer-Tropsch synthesis in the approximate proportion of 100 grams of catalyst per litre. The catalyst slurry was submitted to a preliminary activating treatment comprising heating at 285°C. and 1 atmosphere pressure for 16 hours in the presence of a gas mixture comprising (with a variation of $\pm$ 0.5%) by volume 35.6% hydrogen, 57.5% carbon monoxide, 4.9% carbon dioxide, and 2.0% nitrogen, the H_2/CO ratio being 0.62 volumes of H_2 per volume of CO. After activation, the catalyst was used for synthesis with water-gas (comprising by volume, 6.1% CO_2, 39.9% CO, 49.0% H_2 and 5.0% N_2; $H_2/CO = 1.23$) at 265°C. and 10 atmospheres gauge pressure, with a synthesis gas space velocity of about 275 volumes (at S.T.P.) per volume of slurry per hour. The catalyst was found to have an activity, with respect to the conversion of the water-gas into synthesis products, of 12.3 arbitrary units. To enable a comparison to be made it may be mentioned here that when a similar catalyst was activated using water-gas with a H_2/CO ratio of 1.15 volumes of H_2 per volume of CO, but otherwise under similar conditions, its activity was only 4.1 arbitrary units.

Example 2

The procedure followed was similar to that of Example 1, except in that the catalyst was used on synthesis not with water gas but with the same CO-rich gas as was used for activation. After 32 hours on synthesis the catalyst was found to have an activity of 12.0 arbitrary units, and after 104 hours an activity of 9.9 arbitrary units.

Example 3

The procedure followed was similar to that of Example 2, except in that the activating treatment was carried out at 310°C. instead of 285°C. After 25 hours on synthesis the catalyst was found to have an activity of 9.7 arbitrary units, and after 98 hours an activity of 12.1 arbitrary units. It will be noted that as a result of the higher activating temperature the activity increases over the approximate period of 100 hours on synthesis instead of decreasing.

The same arbitrary units are used in all the Examples.

WHAT WE CLAIM IS:—

1. A preliminary activating treatment for an iron oxide catalyst intended for use in the production of hydrocarbons and/or oxygenated hydrocarbons from gases comprising carbon monoxide and hydrogen and/or steam at elevated temperature and pressure, said treatment comprising heating the catalyst at a pressure of from substantially one atmosphere to substantially two atmospheres in the presence of a gas of reducing character which contains carbon monoxide and hydrogen in the ratio of 0.55 to 0.75 parts by volume of hydrogen per part by volume of carbon monoxide.

2. A treatment according to claim 1 and in which the carbon monoxide and hydrogen together comprise 90 to 99% of the total volume.

3. A treatment according to claim 1 or claim 2 which is carried out at 10 to 50°C. higher than the temperature of the production of said hydrocarbons and/or said oxygenated hydrocarbons in which the catalyst is to be employed.

4. A treatment according to claim 3 and in which the treatment is carried out at a temperature in the range 260 to 310°C.

5. A treatment according to claim 3 and in which the production temperature is 265°C. and the treatment temperature 285°C.

6. A treatment according to any of the preceding claims in which the duration of the treatment is from 15 to 20 hours.

7. A treatment according to any of the preceding claims and in which the gas mixture contains additional gaseous substances not of a reducing character.

8. A treatment according to any of the preceding claims and in which the gas mixture comprises the following percentages by volume:— 4% CO_2, 56% CO, 37% H_2 and 3% N_2.

9. A treatment according to any preced-

ing claim and in which the hydrocarbon production process uses a slurry of the catalyst in high-boiling point hydrocarbons and/or oxygenated hydrocarbons, the preliminary activating treatment being carried out after the catalyst slurry has been prepared and preferably after the slurry has been charged into the reactor used in the production.

10. A treatment according to claim 9 and in which the activating gas is introduced by the same equipment as is provided for the introduction of the production gas, the activating gas being introduced at a rate at least sufficient to keep all the catalyst particles in suspension.

11. A treatment according to any of the preceding claims and in which the iron oxide catalysts are composed of precipitated iron oxide, consisting predominantly of ferric oxide, together with catalyst promoters.

12. A treatment according to claim 11 and in which the catalyst promoters consist of one or more of the following:— cupric oxide, potassium oxide, potassium hydroxide, potassium carbonate.

13. The preliminary activating treatment for a catalyst substantially as hereinbefore particularly described in Example 1 in the Complete Specification.

14. The preliminary activating treatment for a catalyst substantially as hereinbefore particularly described in Example 2 in the Complete Specification.

15. The preliminary activating treatment for a catalyst substantially as hereinbefore particularly described in Example 3 in the Complete Specification.

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PROVISIONAL SPECIFICATION

Improvements relating to the Production of Hydrocarbons and/or Oxygenated Hydrocarbons

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According to the present invention an iron oxide catalyst intended for use in the production of hydrocarbons and/or oxygenated hydrocarbons from gases comprising carbon monoxide and hydrogen and/or steam at elevated temperature and pressure is submitted to a preliminary activating treatment comprising heating it at a pressure of the order of one atmosphere in the presence of a gas of reducing character which contains carbon monoxide and hydrogen in the ratio of 0.55 to 0.75 parts by volume of hydrogen per part by volume of carbon monoxide. We have obtained particularly useful results for example from such a gas when the carbon monoxide and hydrogen together comprise 90% to 95% of the total volume.

The preliminary activating treatment, which is in the nature of a reduction, is, as already specified, carried out at a pressure of the order of one atmosphere; by a pressure of the order of one atmosphere we mean a pressure not exceeding two atmospheres. In general it is appropriate that the temperatures at which the preliminary activating treatment is carried out should be 10 to 50 Centigrade degrees higher than the operating temperatures in the synthesis proper for which the catalyst is intended. Thus the operating temperature may for example be 265°C. and in this case a suitable activating temperature is 285°C. More generally, activating temperatures within the range 260-310°C. are normally suitable. The duration which is appropriate for the preliminary activating treatment naturally varies according to the temperature used, and also according to the composition of the activating treatment gas and of the catalyst itself, but in a typical case it may for example be 15 to 20 hours. The gas mixture used for the preliminary activating treatment may contain other gaseous substances in addition to the carbon monoxide and hydrogen specified in the preceding paragraph, examples of these being carbon dioxide and nitrogen; the activating gas may thus have a composition comparable to that of water-gas except in that the ratio by volume of hydrogen to carbon monoxide is much lower than in water-gas. A specific example of a gas mixture suitable for use in accordance with the invention is that comprising (by volume) 4% CO_2, 56% CO, 37% H_2, and 3% N_2; this mixture has a H_2/CO ratio of 0.66 volumes of H_2 per volume of CO.

If the synthesis process in question uses a slurry of catalyst in high-boiling hydrocarbons and/or oxygenated hydrocarbons, the novel preliminary activating treatment may be carried out after the catalyst slurry has been prepared, and indeed after the slurry has been charged into the reactor to be used in actual production. The activating gas may then be introduced by means of the same equipment as is provided for the subsequent introduction of the synthesis gas itself, the introduction of the activating gas being maintained at a rate sufficient to keep all the catalyst particles in suspension.

The iron oxide catalysts to which the invention is most particularly applicable are those composed of precipitated iron oxide (consisting predominantly of ferric oxide) together with small proportions (e.g. 1-2%) of catalyst promoters such as cupric oxide and potassium oxide, hydroxide or carbonate.

The novel preliminary activating treatment is appropriate for a variety of synthesis gases, ranging from ordinary water-gas to gas mixtures rich in carbon monoxide comparable with those used in the preliminary activating treatment itself. The H_2/CO ratio by volume of the synthesis gas may thus lie in the range 1.3 to 0.55.

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Example 2

The procedure followed was similar to that of Example 1, except in that the catalyst was used on synthesis not with water gas but with the same CO-rich gas as was used for activation. After 32 hours on synthesis the catalyst was found to have an activity of 12.0 arbitrary units, and after 104 hours an activity of 9.9 arbitrary units.

Example 3

The procedure followed was similar to that of Example 2, except in that the activating treatment was carried out at 310°C. instead of 285°C. After 25 hours on synthesis the catalyst was found to have an activity of 9.7 arbitrary units, and after 98 hours an activity of 12.1 arbitrary units. It will be noted that as a result of the higher activating temperature the activity increases over the approximate period of 100 hours on synthesis instead of decreasing.

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