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COMPLETE SPECIFICATION.

A Process for the Production of Hydrocarbons and Oxygenous Derivatives thereof.

We, N.V. DE BATAAFSCHE PETROLEUM MAATSCHAPPIJ, a Body Corporate organised under the laws of The Netherlands, of 30 Carel van Bylandtlaan, The Hague, Holland, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement :—

This invention relates to a process for the production of hydrocarbons and oxygenous derivatives thereof, particularly aldehydes and alcohols, by treating carbon monoxide with hydrogen, if desired in the presence of hydrocarbons, such as olefins, at elevated temperature and in the presence of a catalyst. The invention relates more particularly to the use of an improved catalyst.

In the industrial synthesis of hydrocarbons from monoxide and hydrogen it is known to use catalysts containing a metal of the iron group (iron, cobalt and nickel), precipitated on kieselguhr. The preparation of such catalysts presented certain difficulties, since the kieselguhr serving as support, on being contacted with acids or alkalis, separates off soluble components, which—as hitherto has been assumed—adversely affects the catalytically active metals. When, for example, the kieselguhr is added to the alkaline solution used to precipitate the catalytically active metals, part of the silicic acid of the kieselguhr is dissolved as alkali silicate, which forms with the salts of the heavy metals heavy metal silicates that are insoluble and cannot—or at least not readily—be reduced to metal. These silicates were also believed to affect the catalytic activity.

Measures have, therefore, been taken to prevent such components of the support from being dissolved. When kieselguhr is used as support, this may be attained by reducing to a minimum the period of contact of the kieselguhr with the alkaline solution which is used for the precipitation. For example, the kieselguhr is added to the solution after the precipitation of the catalytically active metals has almost or entirely been completed, since the solution is then no longer highly alkaline.

It has further been considered advantageous to use an entirely insoluble support material or to render soluble components thereof insoluble by a preliminary treatment, for example, by heating and/or removing the soluble components by extraction.

As highly insoluble support materials, compounds of alkaline earth metals and the heavy metals that are not readily soluble, such as barium sulphate, magnesium carbonate, silicon carbide (carborundum), chromium oxide, aluminium oxide, as well as silicates, for instance, steatite (magnesium hydrosilicate) potshards and the like, have already been proposed.

When using these supports, which do not contain soluble silicic acid, catalysts are obtained, however, which only retain their activity in synthesis for a short time. In practice, therefore, suitable types of kieselguhr have always been resorted to.

It was further deemed essential for the preparation of a good catalyst to carry out a very rapid filtration after the precipitation of the catalytically active metal, for example within one minute, and to rapidly wash the precipitate, as also to effect the reduction with a rapid flow of hydrogen. All these prescriptions have been issued in order to check the formation of silicate.

It has further been proposed to use catalysts which contain as an essential component a finely divided metal of the iron group and/or its oxidic compounds, and, if so desired, activators either with or without supports, particularly iron catalysts containing one or more alkali silicates, especially potassium silicate, in a proportion of approximately 2 to 60% calculated as alkali carbonate on the total weight of the catalyst.

With cobalt catalysts it was considered necessary, on account of what was hitherto known, to preclude the use of alkali silicate in the preparation of the catalyst.

It has now been surprisingly found according to this invention that in the preparation of suitable catalysts the formation of silicates of the active metals is desirable.

According to the invention the preparation of hydrocarbons and oxygenous derivatives thereof, particularly aldehydes and alcohols, by treating carbon monoxide with hydrogen, if desired in the presence of hydrocarbons such as olefines, is carried out at elevated temperature (as hereinafter defined) in the presence of a catalyst which is essentially free from alkali silicates, i.e. contains less than 2% of alkali silicate, for example less than 1% (calculated as alkali carbonate on the total weight of the catalyst) and which contains a metal of the iron group obtained by reduction, either with or without a support which does not appreciably contribute to the formation of silicates with the catalytically active metal, the metal of the iron group during the preparation of the catalyst being partly precipitated by means of a dissolved silicate so that it is partly in the form of a silicate and partly in that of a readily reducible basic compound.

In the catalyst as thus prepared the metal of the iron group is present mixed with silica. If a support is used the catalyst is present in the support.

Thus a catalyst may be employed, in the preparation of which 0.5 to 60%, preferably 5 to 30%, of the metal of the iron group is precipitated in the form of silicate.

The preparation of hydrocarbons according to the invention is technically of great advantage. Thus one is no longer tied down to the special manufacturing specifications required when using kieselguhr which has hitherto proved suitable as a support, in order to obviate as much as possible the formation of undesirable silicates; moreover the most diverse support materials may be employed with the same result as when using a known suitable kieselguhr.

Thus, according to the present invention, it is possible to obtain active catalysts even with types of kieselguhr which so far had given much inferior results as compared with the known better types of kieselguhr supports. These catalysts could be prepared with reproducible results.

Kieselguhr may be employed as a support if it has been sintered since it then no longer gives rise to the formation of silicates. Other suitable supports are: aluminium oxide, carborundum, magnesium silicate, magnesium carbonate, barium sulphate and other known supports that are free from silicic acid. A support material with a high heat conductivity is particularly advantageous, such as a metallic support, for example, either in the form of powder or grit.

The formation of a silicate from the active catalytic component resulted in catalysts with a high stability. Thus the catalysts obtained according to the invention are marked by a very long period of activity not calling for any intermediate regeneration.

A proper control of the quantity of silicate affects the properties of the catalyst, resulting, for example, in the formation of less paraffin wax and also of paraffin wax having a low molecular weight, which is of advantage since paraffin wax of high molecular weight checks the activity of the catalyst owing to clogging of the pores. The amount of silicate may be regulated by the proportion of alkali silicate used for precipitation instead of the usual precipitating agent, such as soda. Part of the soda, e.g. 10, 20 or 30%, may be replaced by alkali silicate, for example, water glass. With the aid of much alkali silicate the precipitation proved capable of being carried out rapidly, while on the other hand for a somewhat longer duration less alkali silicate may be applied.

So far it had not been possible to apply the known cobalt-kieselguhr catalyst in a fluidised state. By using support material capable of being fluidised, it is possible according to the invention to effect the reaction with fluidised cobalt catalysts, thus attaining the combined advantages attached to the application of both cobalt and the fluid technique.

Moreover the hitherto known catalysts supported on kieselguhr could not readily be applied in a suspended state in either a boiling or non-boiling liquid, for which purpose a mechanically much stronger sintered catalyst was used. With catalysts according to the invention the support as such may have great mechanical stability and supports may be used which on precipitation of the active constituents thereon may be given the form of pressed particles, such as tablets. The pressed particles may be obtained by means of an extruding process or a pelletting machine. These catalysts in the form of pressed particles may be conveniently used for carrying out the process of the invention in the liquid phase.

The process according to the invention may be carried out at normal as well as elevated pressure, for example, at a pressure, for example, at a pressure of 10, 20 atms. or 50 atms. or higher.

The process according to the invention may be advantageously applied to the preparation of oxygenous compounds by passing olefines together with carbon monoxide and hydrogen over a catalyst which has been prepared by giving part of the active metal the form of silicate.

The process according to the invention

may also be used for the removal of CO from gases containing CO by conversion into methane with H_2. Thus, coal gas may be methanised by applying the improved catalysts, for which purpose precipitated nickel catalysts are particularly suitable.

The following examples illustrate how the process of the invention may be carried into effect:

EXAMPLE 1.

A comparison will be made of three embodiments of the synthetic preparation of hydrocarbons from CO and H_2 by using a cobalt catalyst supported on a kieselguhr hitherto deemed suitable for this process (Experiment *a*) on the one hand and an aluminium oxide on the other (Experiment *b*), whilst a third embodiment (Experiment *c*) shows the improvement of the latter catalyst by using part of the cobalt in the form of a silicate.

The catalyst for Experiment *a* was prepared by heating to 95° C. a solution of cobalt, magnesium and thorium nitrates containing 40 gms. of cobalt per litre and for every 100 parts by weight of cobalt 10 parts by weight of magnesium oxide and 5 parts by weight of thorium oxide, and then introducing it into a solution of soda which contained 104 gms. per litre and had likewise been heated to 95° C., after which stirring was effected for ½ minute. While intensively stirring, 200 parts by weight of kieselguhr per 100 parts by weight of cobalt were added within 1½ minutes and stirring continued for another ½ to 1 minute, a subsequent filtration being carried out as quickly as possible. Within 15 minutes the precipitate was washed with distilled water of 90° C. The filter cake was removed by suctional filtration until a substance was formed which with the aid of an extruding press was pressed into strands. The strands were dried at a temperature of at most 105° C. and then broken into 5 mm. pieces. The catalyst was subjected to a reducing treatment with hydrogen which was passed through the catalyst at a linear velocity of 250 cms./sec. for 1 hour at 320° C.

As a suitable kieselguhr one of the following compositions was taken:

SiO_2	78.8%
FeO_3	0.82%
Al_2O_3	2.5%
CaO	7.5%
MgO	—
H_2O and CO_2	Remainder.

By means of acetic acid, $CaCO_3$ was removed, the kieselguhr then having a surface 14 sq. m/gm. (measured according to the method of Emmett, Brunauer and Teller, described in Journal American Chemical Society, 60, page 309, 1938) and a bulk weight of 320 gms. per litre.

The catalyst for Experiment *b* was prepared in the same way, the only difference being that for every 100 parts by weight of cobalt 875 parts by weight of alpha—Al_2O_3 were now used as support. The catalyst was subjected to a reducing treatment with hydrogen which was passed through the catalyst at a linear velocity of 250 cms./sec. for 10 minutes at 320° C.

The catalyst of Experiment *c* was prepared in the same way as that of Experiment *b* except that part of the soda employed for the precipitation was replaced by sodium meta-silicate, resulting in 20 and 10 parts by weight respectively of sodium of the soda being replaced by sodium of the meta-silicate. The catalyst was subjected to a reducing treatment with hydrogen which was passed through the catalyst at a linear velocity of 250 cms./sec. for 55 minutes at 320° C.

The hydrogen reduction was carried out in such a way that about 60% of the cobalt was obtained as a metal in all three cases.

With the aid of the catalysts prepared in this manner the synthesis of hydrocarbons was carried out at a temperature of 185° C. and a pressure of 1 atm., with a gas consisting, besides some proportions of impurities, of CO and H_2 in the ratio of 1 : 2. The gas was passed through the reactor in a quantity of 1 litre per gram cobalt per hour.

The following results were obtained:

Experiment a.

The contraction rose to 88% in 30 hours, and subsequently dropped slowly and continuously, until after more than 300 hours a contraction of 82% had been attained. The initial yield of normally liquid products amounted to 124 gms. per cu. m. of synthesis gas supplied, which gradually dropped to 116 gms.

Experiment b.

Within 20 hours the contraction rose to 85% and subsequently dropped to less than 50% within 100 hours.

After hydrogen regeneration the contraction again amounted to 80% but dropped then still more rapidly, however, than in the first period; after an additional 100 hours it had dropped to 30%.

The yield of normally liquid products dropped from 70 to 56 gms. in the first period and to less than 40 gms. per cu. m. of synthesis gas supplied in the second period of 100 hours.

Experiment c.

By supplying 28 parts by weight of SiO_2 per 100 parts by weight of Co to the catalyst a catalyst was obtained giving the following results:

In about 20 hours the contraction rose to 85% to remain entirely constant at 83% for 300 hours after an initial slight drop.

The yield of normally liquid products was constantly maintained at 110 gms. per cu. m.

of synthesis gas.

With the catalyst containing a quantity of 14 parts by weight of SiO_2 a yield was obtained which dropped from a maximum of 130 gms. to 110 gms. the contraction likewise showing a slow drop from a maximum of 85% to 78%.

EXAMPLE 2.

In removing carbon monoxide from gases by hydrogenation to methane a comparison was made between the activities of two catalysts containing nickel and magnesium oxide supported on aluminium oxide, in one case with and in the other case without addition of sodium silicate to the precipitant.

The catalysts were prepared as follows :

1. 87 Ccs. of nickel nitrate solution having a concentration of 115 mgms. of nickel per cc. and 15.8 ccs. of magnesium nitrate solution with a concentration of 95 mgms. of magnesium oxide per cc. were mixed and so much distilled water was added until the mixture amounted to 125 ccs. After heating at boiling temperature a boiling solution of 32 gms. of sodium carbonate in 125 ccs. of water was quickly added. Then 21 gms. of alpha - aluminium oxide prepared from "activated alumina" by heating it to 1200° C. during 10 hours was added to the solution. After 5 minutes the liquid was removed by suctional filtration, followed by 10 minutes' washing with 12 litres of boiling water. After pressing into strands and drying at 110° C. the catalyst was reduced with hydrogen at 350° during 2½ hours.

2. The silicate-containing catalyst was prepared in the same way as under (1), with the exception that the precipitation was now carried out at boiling temperature with a solution of 7.4 gms. of sodium metasilicate and 25.6 gms. of soda in 125 ccs. of water.

To obviate flocculation of kieselgel in the sodium silicate-soda solution the sodium-silicate solution was added to the sodium carbonate solution just prior to the precipitation.

The following results were obtained :

Series of Experiments A.

The coal gas to be converted was composed of 2.5% of CO_2, 1% of O_2, 17% of CO, 63% of H_2, 9% of CH_4, the remainder being N_2. The sulphur content was less than 1 mgm. per cu. m. This gas was passed over catalyst *1* at a rate of 540 vol/vol of catalyst/hour (=6.5 litre gas/gm. nickel/hour). Below 230° C. no conversion occurred, at 234° C. the contraction amounted to about 12%. The final gas contained 12% of CO and 15% of CH_4. The reactor had to be heated to 260° to effect a contraction of 60%. The final gas contained 1% of CO and 76% of CH_4.

In the same test carried out with catalyst 2 no reaction took place at 185° C. ; with a temperature of the reactor of 200° C., however, the hydrogenation was complete at the rate of supply of 540 vol/vol of catalyst/hour (=6.05 litres of gas/nickel/hour).

The above proves that the silicate-containing catalyst is more active at lower temperature than the non-silicate-containing catalyst, it being moreover striking that with the former complete conversion already occurs at the initial temperature, such in contrast with the no-silicate containing catalyst.

Scale of Experiments B.

The gas supplied was a carbon monoxide hydrogen mixture composed of ½% of CO_2, 10% of CO, 87% of H_2, the remainder being N_2, O_2, and saturated hydrocarbons.

When applying catalyst 1 no reaction occurred at 195° C. ; with a temperature of 210° C. prevailing in the reactor the contraction amounted to 6.8% with a temperature of 226° C. to 33% ; the final gas contained 0.5% of CO and 19% of CH_4. The gas rate remained constant at 555 vol/vol of catalyst/hour (=6.7 litre of gas/gm. of nickel/hour).

At the rate of supply of 1140 vol/vol catalyst/hour (=13.7 litres of gas/gm. of nickel/hour) and a temperature of 226° C. in the reactor the contraction amounted to 36% ; the final gas contained 0.4% of CO and 19% of CH_4.

At the rate of supply of 278 vol/vol of catalyst/hour (=3,341 litres of gas/gm. of nickel/hour) and a temperature of 225° C. the contraction amounted to 33% ; the final gas was composed of 0.6% of CO, 17% of CH_4.

With catalyst 2, the same gas mixture and a through-put of 555 vol/vol of catalyst/hour (=6.2 litre of gas/gm. of nickel/hour) the contraction was found to be 9% of 196° C. The final gas consisted of 8% of CO and 3% of CH_4.

With a temperature of 200° C. in the reactor the contraction amounted to 35% ; the final gas contained 0.3% of CO and 18.5% of CH_4.

At a throughput of 1110 vol/vol of catlyst/hour (=12.4 litre of gas/gm. of nickel hour) the contraction amounted to 35% with a temperature of 199° C. in the reactor. The final gas contained 19% of CH_4 and 0.4% of CO.

From the above tests it appears that the silicate-containing catalyst is far more active than the silicate-free catalyst.

The term "elevated temperature" as used herein means the temperatures usually employed in processes of the kind herein described, i.e. temperatures between 100 and 350° C., more particularly temperatures between 140 and 250° C.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:

1. A process for the production of hydrocarbons and oxygenous derivatives thereof, particularly aldehydes and alcohols, by treating carbon monoxide with hydrogen, if desired in the presence of hydrocarbons such as olefines, at elevated temperature (as hereinbefore defined) and in the presence of a catalyst which is essentially free from alkali silicates, i.e. contains less than 2% of alkali silicate (calculated as alkali carbonate on the total weight of the catalyst), and which contains a metal of the iron group obtained by reduction, either with or without a support not appreciably contributing to the formation of silicates with the catalytically active metal, characterised in that in the preparation of the catalyst the metal of the iron group is partly precipitated by means of a dissolved silicate so that it is partly in the form of a silicate and partly in that of a readily reducible basic compound.

2. A process as claimed in claim 1 wherein the catalyst contains less than 1% of alkali silicate.

3. A process as claimed in Claim 1 or 2 wherein a cobalt-containing catalyst is used.

4. A process as claimed in any one of the preceding claims wherein sintered kieselguhr, aluminium oxide, carborundum, magnesium silicate, magnesium carbonate or barium sulphate is used as support.

5. A process as claimed in any one of the preceding claims wherein the silicate of the metal of the iron group is obtained by the precipitation of the metal from a solution of a salt thereof by means of an alkali silicate, such as water glass.

6. A process as claimed in any one of the preceding claims wherein a catalyst is used which is prepared by precipitating 0.5 to 60%, preferably 5 to 30% of the metal of the iron group in the form of a silicate.

7. A process as claimed in any one of the preceding claims wherein the catalyst is used in a fluidised state.

8. A process as claimed in any one of the preceding Claims wherein the catalyst is used in the form of pressed particles, such as are obtained with an extruding press or a pelleting machine.

9. A process as claimed in Claim 8 wherein the process is carried out in the liquid phase.

10. A process as claimed in any one of the preceding Claims wherein substances with a high heat conductivity, such as metals, either in the form of powder or grit, are used as catalytic support material.

11. A process as claimed in any one of the preceding Claims 1 to 8 and 10 wherein the process is applied to carbon monoxide-containing gases, such as coal gas, for the purpose of freeing them from CO by conversion with H_2 into methane, preferably by using a nickel catalyst.

12. A process for the production of hydrocarbons and oxygenous derivatives thereof substantially as described.

13. Hydrocarbons and oxygenous derivatives thereof when produced by the process claimed in any one of the preceding claims.

Dated the 15th day of January, 1948.

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