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PROVISIONAL SPECIFICATION

Improvements in and relating to the Preparation of Catalytic Masses for Hydrocarbon Synthesis

I, KSHITINDRA MOHAN CHAKRAVARTY, D.Sc.(Dac.), F.Inst.F. (London), of 26, Hatkhola Road, P.O. Wari, Dacca, British India, of Indian Nationality, do hereby declare the nature of this invention to be as follows:—

This invention relates to the preparation of catalytic masses suitable for promoting the reaction of carbon monoxide and hydrogen for the synthesis of hydrocarbons by the Fischer-Tropsch method. Such catalytic masses comprise as catalyst metallic nickel or other suitable metal produced by the reduction with hydrogen of a compound of the metal obtained as a precipitate by treating a solution of a salt of the metal with an alkali. Such metal catalysts, however, are not all equally suitable for promoting the formation of higher hydrocarbons. Thus, according to Fischer (Brennstoff Chemie, 1935, Vol. 16, page 1) nickel has a considerable tendency to promote the formation of methane, whereas cobalt has a greater tendency to promote the formation of the higher hydrocarbons and it retains its activity for a considerably longer time. It is thought, therefore, that certain processes for the production of higher hydrocarbons which are in operation commercially at the present time use catalytic masses which contain cobalt instead of nickel, and which are therefore relatively costly.

According to the present invention the capacity of such catalytic masses, especially those containing nickel, for promoting the formation of higher hydrocarbons is improved and their period of activity is prolonged, by removing alkali therefrom after reduction or by using as the alkali for precipitation ammonium carbonate or other volatilisable or decomposable alkali.

The beneficial effect of removing the alkali from the catalyst after its reduction, and the advantage arising from the presence of alkali during the process of reduction, have not hitherto been recognised. Thus, Fischer and Meyer (Brennstoff Chemie, 1931, Vol. 12, pages 225—232) considered a nickel catalyst to be more active when the potassium carbonate, used as the alkali for precipitation,

was not entirely removed from the precipitate by washing; whereas at a later date the same authors (Brennstoff Chemie, 1938, Vol. 14, pages 86—89) stated that the addition of potassium carbonate to the finished catalyst had a deleterious effect.

The activity of the catalyst can be still further prolonged, and its capacity for promoting the formation of higher hydrocarbons still further improved by lowering the temperature required for the reduction. In the preparation of catalytic masses in accordance with the invention the reduction can be conducted at a lower temperature by subjecting the precipitate to reduction in admixture with a quantity of a like catalytic mass which has been previously reduced.

In the case of a catalytic mass comprising nickel and thorium oxide (ThO_2) on a support of kieselguhr, the temperature at which the mass remains active and steady in its action can be raised by incorporating cerium oxide (Ce_2O_3) therewith. Such a catalytic mass containing cerium oxide is especially suitable for promoting the formation of hydrocarbons in the final stages of the reaction when the gases from the earlier stages of the reaction have attained a relatively high temperature owing to the exothermic character of the reaction. An advantageous procedure, therefore, is to conduct the early stages of the reaction with the aid of the catalytic mass free from cerium oxide and to use the catalytic mass containing cerium oxide to complete the reaction.

The alkali-free catalytic masses of the invention remain steady in action and give very good results when the reaction is conducted under a moderately raised pressure of the order of about 5 to 10 atmospheres. Furthermore, it is possible to treat gas mixtures, for example, purified blue water gas, which contain approximately equal parts by volume of carbon monoxide and hydrogen, since the customary dilution with further hydrogen to bring the ratio of carbon monoxide to hydrogen to 1:2 by volume, in order to prevent premature loss of activity with the known catalysts, is unnecessary.

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It is also possible by the invention to re-activate a catalytic mass which still contains alkali by removing the alkali in accordance with the invention.

- 5 The invention may be carried out as follows: Kieselguhr, preferably the white variety, is suspended in a solution containing the requisite quantities of pure salts of nickel and thorium, preferably 10 nickel nitrate and thorium nitrate, and a solution of potassium carbonate or sodium carbonate is added in sufficient quantity to precipitate the nickel and thorium completely in the form of their carbonates. 15 The insoluble material is separated, and washed with distilled, or preferably doubly distilled, water until it is only slightly alkaline. It is then dried and heated in a current of hydrogen in order 20 to reduce the nickel carbonate to the free metal. It will be understood that all the materials used should be free from substances having a poisoning effect on the catalyst. The slight amount of alkali 25 present, which is necessary during the process of reduction, is then removed. The more thorough the removal of alkali the more efficient and steady in action will be the resulting catalytic mass, and the 30 lower its tendency to promote the formation of methane. The catalytic mass so obtained is also less subject to loss of activity due to changes in temperature than a similar catalytic mass from which 35 alkali has not been removed.

Before subjecting the material to reduction it is of advantage to mix with it a small quantity of a powdered catalytic mass which has previously been prepared and reduced in the manner described 40 above. The resulting mixture is then subjected to reduction in hydrogen at a lower temperature, and alkali is thereafter removed as described above. The catalytic mass so obtained possesses the 45 above mentioned advantageous properties in an even greater degree.

By using in the above procedure ammonium carbonate, instead of potassium carbonate or sodium carbonate, to precipitate the metal carbonates the removal of alkali subsequently to reduction becomes unnecessary. 50

Although the invention is applicable in general to all catalytic masses of the kind 55 above referred to for the synthesis of hydrocarbons from mixtures of carbon monoxide and hydrogen, it is of especial importance in its application to the preparation of catalytic masses containing 60 nickel, since they are rendered suitable for the production of higher hydrocarbons, and can therefore be used in place of the more costly catalytic masses containing cobalt. 65

Dated this 7th day of July, 1944.

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COMPLETE SPECIFICATION

Improvements in and relating to the Preparation of Catalytic Masses for Hydrocarbon Synthesis

- I, KSHITINDRA MOHAN CHAKRAVARTY, D.Sc(Dac.), F.Inst.F. (London), of 26, Hatkhola Road, P.O. Wari, Dacca, British India, of Indian Nationality, do hereby 70 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:—
- 75 This invention relates to the preparation of catalytic masses comprising as catalyst metallic nickel or cobalt or other metal suitable for promoting the reaction of carbon monoxide and hydrogen for the 80 synthesis of hydrocarbons by the Fischer-Tropsch process. Such catalytic masses which may contain the metal catalyst on a support, for instance of kieselguhr, are prepared by the reduction, for example, 85 with hydrogen, of a compound of the metal obtained as a precipitate by treating a solution of a salt of the metal with

an alkali carbonate. Such metal catalysts, however, are not all equally suitable for promoting the formation of higher hydrocarbons. Thus, according to Fischer (Brennstoff Chemie, 1935, Vol. 16, page 1) 90 nickel has a greater tendency than cobalt to promote the formation of methane, and cobalt has a greater tendency than nickel to promote the formation of higher 95 hydrocarbons. Moreover, cobalt retains its activity for a considerably longer time when used for promoting the formation of higher hydrocarbons. It is thought, 100 therefore, that certain processes for the production of higher hydrocarbons which are in operation commercially at the present time use catalytic masses which contain cobalt instead of nickel, and which 105 are therefore relatively costly.

According to the present invention the capacity of such catalytic masses, especially those containing nickel, for promot-

ing the formation of higher hydrocarbons is improved and their period of activity is prolonged, by conducting at least a part of the reduction in presence of residual alkali, and removing substantially the whole of the residual alkali from the mass after or during the reduction.

The beneficial effect of removing the residual alkali, and the advantage arising from the presence of alkali during the whole or a part of the process of reduction, have not hitherto been recognised. Thus, Fischer and Meyer (*Brennstoff Chemie*, 1931, Vol. 12, pages 225—232) considered a nickel catalyst to be more active when the potassium carbonate, used as the alkali for precipitation, was not entirely removed from the precipitate by washing; whereas at a later date the same authors (*Brennstoff Chemie*, 1933, Vol. 14, pages 86—89) stated that the addition of potassium carbonate to the finished catalyst had a deleterious effect.

In order to remove substantially the whole of the residual alkali from the mass after reduction, the mass may be washed with water, preferably accompanied by boiling, until the washings have a pH value of substantially 7. For removing the alkali from the mass during the reduction there may be used for the precipitation an alkali carbonate, for example, ammonium carbonate, which volatilises during the reduction with or without decomposition. If, in this case, it is found that the alkali has not been entirely removed during the reduction, any traces of alkali which remain may be subsequently removed, for example, by washing with water as described above. It will be understood that oxidation of the reduced mass should be substantially avoided during and after the washing, and especially during the drying or partial drying of the mass which follows the washing. If, however, some slight oxidation has occurred the mass may be subjected to subsequent reduction.

As will be understood from the foregoing description, it is necessary that some alkali should be present during at least a part of the reduction, and it is preferable that the quantity of alkali should be equivalent to that which remains after washing the precipitate with water until the washings have a pH value of about 10.

The invention also comprises subjecting the precipitated metal carbonate to the reduction process in admixture with a previously reduced catalytic mass comprising a metal suitable for the Fischer-Tropsch process, and from which mass the residual alkali may or may not have been previously removed. The presence of the

previously reduced catalytic mass accelerates the reduction process, and this advantage can be utilised to improve still further the capacity of the catalyst for promoting the formation of higher hydrocarbons. Thus, this acceleration enables the reduction to be conducted under milder conditions, for example, at a lower temperature or for a shorter period, which conditions favour the formation of catalyst particles having an enhanced capacity for promoting higher hydrocarbon formation. Alternatively, without altering the conditions of reduction, the reduction can be brought more nearly to completion and the capacity of the catalyst for promoting higher hydrocarbon formation correspondingly enhanced. A convenient quantity of the added catalytic mass is such that the final catalytic mass will contain 0.5—5.0 per cent. by weight of the added mass.

It is known that catalytic masses suitable for the Fischer-Tropsch process may contain thorium oxide (ThO_2) and/or another oxide or oxides in addition to the metal catalyst, and in the case of these catalytic masses the removal of residual alkali as described above also leads to the improvements hereinbefore referred to. In the case of catalytic masses containing thorium oxide, for example, one comprising nickel and thorium oxide on a support, for example of kieselguhr, the invention also comprises incorporating in the mass a small proportion of cerium oxide (Ce_2O_3) relatively to the thorium oxide, the cerium oxide having the effect of raising the temperature at which the catalytic mass remains active for long periods. An advantageous proportion is substantially 1 per cent. of cerium oxide based on the combined weights of the oxides of cerium and thorium. Such a catalytic mass may be prepared by treating a solution of a salt of the catalyst metal, for instance nickel or cobalt, also containing a thorium salt and a cerium salt in the presence of kieselguhr with an alkali carbonate to precipitate a mixture of the metal carbonates, and reducing the precipitate with hydrogen to yield the metallic catalyst together with the oxides of thorium and cerium. The residual alkali in the mass is removed after or during the reduction in accordance with the invention.

Such a catalytic mass containing cerium oxide is especially suitable for promoting the formation of hydrocarbons in the final stages of the reaction when the gases from the earlier stages of the reaction have attained a relatively high temperature owing to the exothermic character of the reaction. An advantageous

procedure, therefore, is to conduct the early stages of the reaction with the aid of the catalytic mass free from cerium oxide and to use the catalytic mass containing cerium oxide to complete the reaction.

The alkali-free catalytic masses of the invention remain active for long periods and give very good results when the reaction is conducted under a moderately raised pressure of the order of about 5 to 16 atmospheres. Furthermore, it is possible to treat gas mixtures, for example, purified blue water gas, which contains approximately equal parts by volume of carbon monoxide and hydrogen, the customary dilution with further hydrogen to bring the ratio of carbon monoxide to hydrogen to 1:2 by volume, in order to prevent premature loss of activity with the known catalysts, being unnecessary.

It is also possible by the invention to re-activate a used catalytic mass which still contains alkali, by washing it with water, preferably accompanied by boiling, until the washings have a pH value of substantially 7.

The following Examples illustrate the invention:

EXAMPLE 1.

Kieselguhr, preferably the white variety, is suspended in a solution containing pure salts of nickel and thorium, preferably nickel nitrate and thorium nitrate, the quantities of the salts and kieselguhr being so chosen that the ratio by weight of nickel: thorium oxide: kieselguhr in the final catalytic mass is 100:18:100. A solution of potassium carbonate or sodium carbonate is then added to the mixture in sufficient quantity to precipitate the nickel and thorium completely in the form of their carbonates. The insoluble material is separated, and washed with distilled, or preferably doubly distilled, water until the washings have a pH value of about 10. The material is then dried and heated at 400° C. in a current of hydrogen in order to reduce the nickel carbonate to the free metal, the thorium being converted into its oxide. It will be understood that all the materials used should be free from substances having a poisoning effect on the catalyst. The slight amount of alkali present, which is necessary during the process of reduction, is then substantially completely removed by washing the material with distilled or preferably doubly distilled water, while boiling, until the washings have a pH value of substantially 7. The more thorough the removal of alkali the more efficient and prolonged will be the activity of the resulting cata-

lytic mass, and the lower its tendency to promote the formation of methane. The mass is then dried or brought to a low moisture content by heating it under non-oxidising conditions, for example, in a current of hydrogen. The catalytic mass so obtained is also less subject to loss of activity due to changes in temperature than a similar catalytic mass from which the alkali has not been substantially completely removed.

EXAMPLE 2.

A solution of pure salts of nickel and thorium containing kieselguhr suspended therein is treated with a solution of potassium carbonate or sodium carbonate, the insoluble material is separated, washed with distilled water and dried, all in the manner described in Example 1. Before its reduction in hydrogen, the resulting material is then mixed with a powdered catalytic mass which has been previously prepared and reduced in the manner described in Example 1, except that the washing operation after reduction may, if desired, be omitted. The quantity of the added catalytic mass is such that it will constitute 0.5—5.0 per cent. of the weight of the final catalytic mass. The resulting mixture is then subjected to reduction in hydrogen at a temperature of 350° C., and the alkali is thereafter substantially completely removed in the manner described in Example 1. The catalytic mass so obtained possesses in an even greater degree the advantageous properties of the catalytic mass obtained as described in Example 1.

In order to produce catalytic masses which can be used at higher temperatures than the products of Examples 1 and 2, the procedures of these Examples may be repeated with the addition of a cerium salt to the solution of nickel and thorium salts, the quantity of the cerium salt being so chosen that the ratio by weight of thorium oxide to cerium oxide in the final catalytic mass is substantially 99:1.

By using ammonium carbonate, instead of potassium carbonate or sodium carbonate, to precipitate the metal carbonates in the procedures described in the foregoing Examples, the alkali will be substantially completely removed from the mass during the reduction, but if any traces remain after the reduction they may be removed by washing with distilled water, while boiling, until the washings have a pH value of substantially 7.

Whilst the advantages obtained by the invention apply in general to catalytic masses comprising as catalyst a metal suitable for the Fischer-Tropsch process, the invention is of especial importance in its

application to the preparation of catalytic masses containing nickel, since they are rendered suitable for the production of higher hydrocarbons, and can therefore be used in place of the more costly catalytic masses containing cobalt.

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

1. A process for preparing catalytic masses comprising as catalyst a metal suitable for the Fischer-Tropsch process and produced by the reduction of the metal carbonate obtained as a precipitate by treating a solution of a salt of the metal with an alkali carbonate, which comprises conducting at least a part of the reduction in presence of residual alkali, and removing substantially the whole of the residual alkali from the mass after or during the reduction.

2. A process as claimed in Claim 1, wherein nickel is used as the catalyst metal.

3. A process as claimed in Claim 1 or 2, wherein the residual alkali is removed from the mass after the reduction by washing it with water, preferably accompanied by boiling, until the washings have a pH value of substantially 7.

4. A process as claimed in Claim 1 or 2, wherein the residual alkali is removed from the mass during the reduction by using for the precipitation an alkali carbonate which volatilises during the reduction with or without decomposition.

5. A process as claimed in any of the preceding Claims, wherein the mass comprising the precipitated metal carbonate is subjected to the reduction process in admixture with a previously reduced catalytic mass comprising a metal suitable for the Fischer-Tropsch process.

6. A process as claimed in any of the preceding Claims, wherein thorium oxide and a small proportion of cerium oxide relatively to the thorium oxide are also

incorporated in the catalytic mass.

7. A process as claimed in Claim 6, wherein the proportion of the cerium oxide amounts to substantially 1 per cent. of the combined weights of the oxides of cerium and thorium.

8. A process for preparing a catalytic mass conducted substantially as described in either of the Examples herein.

9. A process for preparing a catalytic mass wherein a used catalytic mass which comprises as catalyst a metal suitable for the Fischer-Tropsch process and produced by the reduction of the metal carbonate obtained as a precipitate by treating a solution of a salt of the metal with an alkali carbonate, and which still contains residual alkali, is re-activated by washing it with water, preferably accompanied by boiling, until the washings have a pH value of substantially 7.

10. Catalytic masses whenever prepared or produced by the process of manufacture particularly described and ascertained herein or by any process which is an obvious equivalent thereof.

11. A process for the synthesis of hydrocarbons, which comprises subjecting a gaseous mixture containing carbon monoxide and hydrogen to the action of a catalytic mass claimed in Claim 10.

12. A process as claimed in Claim 11, wherein the catalytic mass comprises metallic nickel.

13. A process as claimed in Claim 11, or 12, wherein the gaseous mixture is subjected in the final stages of the reaction to the action of a catalytic mass prepared by the process claimed in Claim 6.

14. A process as claimed in Claim 11, 12 or 13, wherein the gaseous mixture contains approximately equal parts by volume of carbon monoxide and hydrogen.

Dated this 18th day of May, 1945.

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