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COMPLETE SPECIFICATION

A Process for the Production of Moulded Catalysts.

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 improved moulded catalysts and the production and application thereof.

According to the nature of the active part catalysts may be distinguished, e.g., as metal oxide catalysts, metal sulphide catalysts and catalysts containing free metals.

The Applicants have already developed catalysts containing free metals which are produced by converting metals, either entirely or partially, into hydrosilicate and subsequently subjecting the mass to a reducing treatment. These catalysts may be obtained by precipitation of an active metal from a solution of one of its salts with a precipitant consisting, either entirely or partially, of a soluble silicate. Further they may be obtained by replacing the metal of an insoluble metal hydrosilicate, either entirely or partially, by a catalytically active metal. As initial material may also be taken, for example, sintered kieselguhr, on which the active metal is precipitated in the form of a basic compound, the hydrosilicate then being prepared either by a treatment with steam or a prolonged contact of the precipitate with the solution in which the precipitate has been formed.

The production of these improved catalysts is not limited to the application of carrier material, such as kieselguhrs containing free silicic acid and capable of forming the desirable hydrocilicates when the catalysts are prepared under suitable circumstances, but the most divergent carrier materials may be used, such as alpha-aluminium oxide, carborundum, magnesium silicate, magnesium carbonate, magnesium oxide, barium sulphate, pumice stone, majolica, potsherds, active carbon and satisfactory heat conductors, such as metals, either in powdered or gritty condition.

Hitherto such catalysts were frequently prepared by starting from a solution which contained a salt of the catalytically active metal mixed with a carrier, upon which the catalytically active metal was precipitated. It was also possible to add the carrier to the suspension after precipitation of the active components.

Now it was found experimentally that in employing carriers which are suitable for the production of moulded catalysts of great mechanical strength, the catalysts obtained were not so active or could not be reduced so satisfactorily as those prepared with carriers forming moulded pieces of less mechanical strength.

Generally it was found that if carriers were used which had been strongly heated or otherwise been rendered less reactive in respect of the active catalytic metals, catalysts were obtained of less mechanical strength but adequate activity, whereas catalysts prepared with carriers giving a greater mechanical strength generally proved less active.

It has now been found that moulded catalysts containing active metals and a carrier, and having a great mechanical strength and high catalytic activity, may be produced by entirely or partially converting the active metal into a hydrosilicate by precipitating an active metal from a solution of one of its salts with a precipitant consisting entirely or partially of a soluble silicate, mixing the hydrosilicate-containing material in pulverised condition with a powdered carrier, compressing the mixture to shaped pieces and subjecting the pieces to a reducing treatment with hydrogen to obtain the active metal at least partly in the active form.

This process is particularly advantageous if carriers are employed which in the case of the above-described older method of preparation would render the catalytically active metals non- or poorly-reducible when contacted with the solution containing a salt of the catalytically active metal, thus resulting in catalysts with a lower activity. In the process according to the invention such carriers may be used without adversely affecting the reducibility and activity of the catalyst.

When employing carriers such as aluminium grits, activated aluminium oxide, gamma aluminium oxide or hydrated aluminium oxide, it is desirable to use a lubricating agent, for example, graphite, in order to enable the compressed pieces to leave the press undamaged. With carriers such as magnesium oxide, magnesium silicate and magnesium carbonate the application of a lubricating agent is generally not required and even harmful, since it slightly reduces the activity of the catalyst. In the case of beta-aluminium oxide it may sometimes be desirable to add a lubricating agent.

Catalytically active metals comprise, for example, iron, cobalt, nickel and the other metals of the eighth group of the Periodic System, as well as copper or manganese.

The compressed catalysts may, for example, have the form of pellets, tablets, cylinders or Raschig rings. Owing to their great mechanical strength they may be applied for a long time without the risk of their being pulverised when introduced into or withdrawn from the catalyst space or when used in the reaction space. Moreover the catalysts have a high resistance to temperature fluctuations.

The moulded catalysts are applicable to a large number of catalytic reactions, for example, hydrogenation reactions, such as the hardening of vegetable and animal oils; the destructive hydrogenation of hydrocarbon oils; the conversion of aldehydes and ketones into the corresponding alcohols; the conversion of olefins and di-olefins into saturated hydrocarbons, of aromatics into cyclohexane derivatives; the hydrogenation of naphthalene to tetrahydronaphthalene or decahydronaphthalene; the selective hydrogenation of di-olefins to mono-olefins and of acetylenes to mono-olefins; the dehydrogenation and the desulphurisation by hydrogenation of mineral oils and the selective desulphurisation by hydrogenation of unsaturated oils. These catalysts are particularly effective in the synthesis of hydrocarbons from carbon monoxide and hydrogen-containing gas, especially when employed according to the embodiment which comprises a fixed catalyst bed and circulation of evaporating oil or the application of a high gas-recycling ratio. They may also be employed in the isomerisation of unsaturated compounds with one or more olefinic bonds by shifting the latter. By their great mechanical strength the catalysts are eminently suitable when operating in the liquid phase.

The invention will be further illustrated with reference to an Example.

EXAMPLE.

A comparison was made between moulded catalysts produced according to the known process of adding the carrier material to catalytic material freshly precipitated from a solution and moulded catalysts obtained by the process of the invention. In the production of the catalysts such quantities were used that the resultant catalysts contained 100 gms, of cobalt per litre.

1*a*. The following initial solutions were used:

A. an aqueous solution of 80 gms. of cobalt, 4 gms. of thorium oxide and 8 gms. of magnesium oxide in the form of nitrates up to a total volume of 2 litres.

B. a solution of 165 gms. of anhydrous sodium carbonate dissolved in 1800 ccs. of water.

C. 156 gms. of sodium silicate solution, containing 151 mgs. of SiO_2/gm. and 156½ mgm. of Na_2O/gm. was diluted to 200 ccs.

To solution B, heated to 90-95°C., solution C and subsequently solution A, heated to 90-95°C., were rapidly added, stirring being effected during the whole operation.

Subsequently the suspension was vigorously stirred for 1 minute and mixed with 520 gms. of powdered activated aluminium oxide which had previously been heated to 600°C. for 2 hours and then cooled. After being stirred for a short time the suspension was rapidly filtered and thoroughly washed with water at 95°C., whereupon the precipitate was dried at 105-110°C. for 3 hours. After pulverisation 3% by weight of graphite was added as a lubricating agent, and the catalytic mass was compressed into pellets having a diameter of 5 mms. and a height of 4 mms. These pellets were reduced with hydrogen of 430°C. during one hour (1100 litres of hydrogen being used per hour per 70 ccs.), which caused 40% of the total quantity of cobalt present to be converted into the metallic form.

The catalyst was composed of 100 parts by weight of cobalt, 650 parts by weight of activated aluminium oxide, 8 parts by weight of magnesium oxide, 5 parts by weight of thorium oxide, 28 parts by weight of SiO_2.

The pellets could withstand a maximum

pressure in radial direction of 5 kgms.

1b. A catalyst of similar composition was prepared as follows according to the process of the invention.

The same solutions as referred to under *1a.* were mixed in an analogous manner and then filtered, washed, dried and pulverised without the addition of a carrier, whereby 220 gms. of a dry, powdered, active material was obtained. 160 gms. of powdered activated aluminium oxide, which had been subjected to the same heating treatment as mentioned under *1a*, was mixed with 70 gms. of the active powder in a dry state, to which 3% by weight of graphite was added. The mixture was then compressed into pellets of the same size. The reducing treatment was carried out in the same manner as under *1a*, although in view of the desirable reduction of approximately 60%, the reduction had to be effected at only 400°C. for one hour. The catalyst was composed of 100 parts by weight of cobalt, 8 parts by weight of magnesium oxide, 5 parts by weight of thorium oxide, 28 parts by weight of SiO_2 and 700 parts by weight of activated aluminium oxide.

The pellets could withstand a maximum pressure of 8 kgms.

2a. 1 Litre of aqueous solution containing 40 gms. of cobalt, 2 gms. of thorium oxide and 4 gms. of magnesium oxide in the form of nitrates was introduced in the same manner as indicated under *1a* in to 900 ccs. of a solution of sodium carbonate containing 83 gms. of sodium carbonate, to which 78 gms. of a sodium silicate solution, containing 151 mgms. of SiO_2 per gm. and 156½ mgms. of Na_2O per gm., had previously been added upon being diluted to 100 ccs. In accordance with the process described under *1a*, after the precipitation of the catalytic constituents 220 gms. of dry magnesium oxide was added, filtered, washed and dried at 110°C.

The pellets formed by compression were reduced in an analogous manner with hydrogen at the maximum temperature of 430°C. Thus only 17½% by weight of the cobalt present could be reduced to the metallic form.

The catalyst was composed of 100 parts by weight of cobalt, 8 parts by weight of magnesium oxide, 5 parts by weight of thorium oxide, 28 parts by weight of SiO_2 and 550 parts by weight of magnesium oxide carrier. The pellets could withstand a maximum pressure of 12 kgms.

2b. 70 gms. of the active material obtained according to the process described under *1b* was mixed in a dry state with 150 gms. of powdered magnesium oxide and subsequently compressed to pellets. The reduction was effected in the same manner as referred to under *1a* and *1b*. In order to obtain a reduction of 60% it was necessary to carry out the reducing treatment at 375°C. for one hour.

The Catalyst was composed of 100 parts by weight of cobalt, 8 parts by weight of magnesium oxide, 5 parts by weight of thorium oxide, 28 parts by weight of SiO_2 and 550 parts by weight of magnesium oxide. The pellets could withstand a maximum pressure of 12 kgms.

3a. The same solutions as mentioned under *1a* were mixed in an analogous manner and the precipitate filtered and washed. The resultant precipitate was suspended in 700 ccs. of water of 20°C., into which 450 gms. of degreased aluminium grits of a particle size of less than 1 mm. was introduced while stirring. The aluminium grits cannot be introduced into the hot solution immediately after the precipitation and prior to the filtration, since under these circumstances the aluminium is rapidly dissolved.

After filtering and washing drying was effected at 110°C. in the same manner as referred to under *1a*, upon which the mass was mixed with 3% of graphite and compressed to pellets. The reduction was carried out in the same way as mentioned under *1a*. For the purpose of obtaining a reduction of 60% of the cobalt the reduction had to be effected at 400°C. for one hour.

The catalyst was composed of 100 parts by weight of cobalt, 8 parts by weight of magnesium oxide, 5 parts by weight of thorium oxide, 28 parts by weight of SiO_2 and 570 parts by weight of aluminium. The pellets could withstand a maximum pressure of 10 kgms.

3b. 50 gms. of the active material obtained according to *1b* was mixed in the dry state with 100 gms. of degreased aluminium grits, to which 3% of graphite was added. The mass was then compressed to pellets. It was necessary to carry out a reducing treatment at 370°C. for one hour in order to obtain a reduction of 60%. The catalyst was composed of 100 parts by weight of cobalt, 8 parts by weight of magnesium oxide, 5 parts by weight of thorium oxide, 28 parts by weight of SiO_2 and 500 parts by weight of aluminium. The pellets could withstand a maximum pressure of 20 kgms.

The above catalysts were tested as to their activity for the synthesis of hydrocarbons from synthesis gas at atmospheric pressure. This gas was composed of 1 part by vol. of carbon monoxide and 2 parts by vol. of hydrogen, the sulphur content being less than 1 mgm. of sulphur per cu. metre of gas. The reaction was carried out at a temperature of 185°C. and the synthesis gas was passed through the reactor at the rate of 100 parts by vol. per part by vol. of catalyst. The following results were obtained.

Catalyst-carrier	Maximum permissible pressure in kg.	Vol. % of contraction of the synthesis gas during the following periods of hours.			Yield of hydrocarbons higher than C_4 in respect of synthesis$_3$ gas supplied in g/m.		
		0-50	100-150	200-200	0-50	100-150	200-300
1*a* activated aluminium oxide	5	72	71	—	80	85	—
1*b*	8	84	79	—	20	105	—
2*a* Mg0	12	11	(Test interrupted)		10	—	—
2*b*	12	85	85	81	120	118	105
3*a* A1	10	65	60	55	80	75	70
3*b*	20	84	82	77	120	110	100

From the above tests it appears that the catalyst pellets prepared according to the process of the invention are much more active than those obtained by mixing the active constituents and the carrier in a wet state. Moreover the catalyst pellets according to the invention retain their activity for an appreciably longer time than the others.

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 moulded catalysts containing active metals and a carrier, wherein the active metal is entirely or partially converted into a hydrosilicate by precipitation of an active metal from a solution of one of its salts with a precipitant consisting entirely or partially of a soluble silicate and the hydrosilicate-containing material is then mixed in a pulverised condition with a powdered carrier, whereupon the mixture is compressed to shaped pieces and these are subjected to a reducing treatment with hydrogen to obtain the active metal at least partly in the metallic form.

2. A process as claimed in Claim 1 wherein a powdered substance capable of being formed into particles of great mechanical strength is employed as carrier.

3. A process a claimed in Claim 1 or 2 wherein activated aluminium oxide, gamma-aluminium oxide, magnesium oxide, hydrated aluminium oxide or aluminium grits is applied as carrier.

4. A process a claimed in any one of the preceding claims wherein the active metal consists of a metal of the iron group and/or copper and/or manganese.

5. A process for the production of moulded catalyts substantially as described with reference to any one of the Examples 1*b*, 2*b* and 3*b*.

6. Moulded catalysts, such as pellets, tablets, cylinders and Raschig rings, when obtained by the process claimed in any one of the preceding claims.

7. A process for carrying out catalytic reactions, wherein moulded catalysts, claimed in Claim 6 are employed are catalysts.

8. A process as claimed in Claim 7, wherein the catalytic reaction is a hydrogenation reaction.

9. A process for the catalytic production of hydrocarbons from carbon monoxide and hydrogen-containing gas mixtures, wherein moulded catalysts claimed in Claim 6 are employed as catalysts.

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