PATENT SPECIFICATION

THE PATENT OFFICE LONDON

641,333

Date of Application and filing Complete Specification: July 7, 1948.

Application made in Netherlands on July 10, 1947.

No. 18294/48

Complete Specification Published: Aug. 9, 1950.

2467

Index at acceptance:—**Class 1(i),** F3B1.

COMPLETE SPECIFICATION.

Improvements in or relating to 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:—

The invention relates to improved moulded catalysts and to their production and application.

Catalysts may be distinguished according to the nature of the active component. Thus, for example, metal oxide and metal sulphide catalysts and catalysts containing free metals may be distinguished.

Catalysts containing free metals may be produced by completely or partially converting metals into hydrosilicates and then subjecting the mixture to a reducing treatment. Such catalysts may be produced by precipitation of an active metal from a solution of one of its salts with a precipitating agent completely or partially consisting of soluble silicate. Further they may be obtained by replacing the metal in an insoluble metal hydrosilicate completely or partially by a catalytically active metal. Another initial material is, for example, sintered kieselguhr, on which the active metal is precipitated in the form of a basic compound, whereupon the hydrosilicate is formed, either by a treatment with steam or by prolonged contact of the precipitate with the solution in which the precipitate has been formed.

The production of these improved catalysts is not restricted to the use of carrier materials, such as kieselguhr, which contain free silicic acid and which, under suitable conditions, may yield the desired hydrosilicates in the production of the catalysts, but the most widely varied carrier materials may be used, such as alpha-aluminium oxide (corundum), carborundum, magnesium silicate, magnesium carbonate, magnesium oxide, barium sulphate, pumice stone, majolica, potsherds, active carbon and substances with a good heat conductivity, such as metals in the form of powder or grit.

Hitherto, the production of such catalysts often started from a solution containing a salt of the catalytically active metal, to which a carrier was added, after which precipitation of the catalytically active metal took place. In some cases the carrier was added to the suspension after the precipitation of the active components.

Now, operating in this manner, it was found that if carriers which are suitable for the production of moulded catalysts of great mechanical strength are used, the catalysts obtained have lower activity or are more difficult to reduce than catalysts produced while using carriers giving rise to mouldings of lower mechanical strength.

In general, carriers which had been heated to high temperatures or had been rendered less active with repect to the active catalytically acting metals were found to yield catalysts of lower mechanical strength, but of good activity, whereas carriers yielding catalysts of great mechanical strength are generally found to be less active.

On further investigation it was found that catalysts containing active metals and produced by the method described above, in the production of which the metals are completely or partially converted into hydrosilicates, can be obtained with great activity and with great mechanical strength, if beta-aluminium oxide is used as carrier and is added at any stage of the production, but before separating the precipitate from the mother liquor.

Beta-aluminium oxide may be produced in known manner as described in Specification No. 571,352 by bringing an aluminium oxide, either containing water of

[*Price 2/-*]

hydration or not, of the gamma-type according to Haber into intimate contact for some time with a compound of an alkali metal ,such as potassium or sodium, capable of being converted to the oxide by heating, for example in the form of hydroxide, at a temperature between 800 and 1400°C. The alkali is then absorbed into the crystal lattice of the aluminium oxide and prevents the recrystallisation to alpha-aluminium oxide. The beta-aluminium oxide may also be prepared by the use of an alkaline earth metal, such as calcium, strontium or barium. If a micro-crystalline gamma-aluminium oxide is used as initial material, beta-aluminium oxide is formed, which is only partially sintered and still has a largely micro-crystalline structure. It is also owing to this property that mouldings of great mechanical strength are obtained during compression.

The beta-aluminium oxide surprisingly combines the properties of yielding mouldings of great mechanical strength when it is used in the production of catalysts described above while the final catalyst has great activity. Moreover, mouldings can be made with the use of little or no lubricating means, such as graphite.

As compared with an aluminium oxide of the gamma-type, the beta-aluminium oxide has greatly reduced reactivity with respect to the compounds of catalytically active metals, so that in the production of the catalyst it may advantageously be added to the aqueous suspension of the hydrosilicate-containing compounds of the active metals or to the solutions from which these compounds are produced. Thus products are formed which may readily be reduced and at the same time give rise to catalysts of high activity.

Catalytically active metals that can be employed are, for example, iron, cobalt, nickel and the other metals of the eighth group of the periodic system, and/or copper and/or manganese.

The compressed catalysts may, for example, have the shape of lozenges, tablets, cylinders or Raschig rings. Owing to their great mechanical strength they may be used for a long period without any pulverisation occurring during the filling or emptying of the catalyst space or during its use in the reaction space. The catalysts are also highly stable against temperature changes.

The moulded catalysts may be employed in a large number of catalytic reactions, for example in 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 olefines and di-olefines into saturated hydrocarbons, of aromatics into cyclohexane derivatives, the hyrdogenation of naphthalene into tetrahydronaphthalene or decahydronaphthalene, the selective hydrogenation of di-olefines to mono-olefines and of acetylenes to mono-olefines, in dehydrogenation and in the hydrogenation desulphurisation of mineral oils and for the selective hydrogenation desulphurisation of unsaturated oils. These catalysts are particularly suitable for use in the synthesis of hydrocarbons from carbon monoxide and hydrogen-containing gas, especially according to the embodiment in which use is made of a fixed catalyst bed and of circulation of evaporating oil or of a high gas recirculation ratio. They may also be employed in the isomerisation of unsaturated compounds with one or more double bonds by a shifting of the latter. Owing to their great mechanical strength the catalysts are highly suitable for operating in the liquid phase.

The invention will be explained more in detail with reference to an example.

EXAMPLE.

A comparison was made of compressed catalysts produced with activated aluminium oxide, with alpha- and with beta-aluminium oxide as carrier, all of which contained 100 gms. of cobalt per litre.

In the production the following solutions were used as initial materials:

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 in a total volumn 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, which contained 151 mgms. of SiO_2/gm. and 156 1/2 mgm. of Na_2O/gm., was diluted to 200 ccs.

When the B solution had been heated to 90-95°C., the C solution was rapidly added to it while stirring and subsequently the A solution, after having been heated to 90-95°C., was also rapidly added while stirring. After 1 minute's thorough stirring 520 gms. of pulverised activated aluminium oxide, which had first been heated for 2 hours to 600°C. and subsequently cooled, was added to the suspension and the latter was rapidly filtered off after being stirred for a short time. After being thoroughly washed with water at 95°C., the precipitate was dried for 3 hours at 105-110°C. and pulverised. In order to obtain strong lozenges it was necessary to add graphite as lubricating means to the mixture to be compressed. After addition of 3% by weight of graphite, lozenges with a diameter of 5 mms. and a height of 4 mms. were obtained from the catalyst mixture by compression. These lozenges were reduced for 1 hour with hydrogen of 439°C. (1100 litres of hydrogen per hour were used per 70 ccs. of lozenges), 40% of the total amount of cobalt present thus being converted into 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 and 28 parts by weight of SiO_2.

The maximum force in the radial direction at which the lozenges were not broken to pieces was 5 kgms.

The production of the catalyst with alpha-aluminium oxide as carrier took place completely analogously to that described for activated aluminium oxide as carrier. Immediately after the precipitation a powder consisting of 700 gms. of alpha-aluminium oxide, prepared by heating activated aluminium oxide for 12 hours to 1200°C., was introduced into the suspension. For 60% of the cobalt to be reduced to metal it was necessary to reduce for 1 hour at 375°C.

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 875 parts by weight of alpha-aluminium oxide. The maximum force in the radial direction at which the lozenges were not broken to pieces was 2 kgms.

Starting from gamma-aluminium oxide, beta-aluminium oxide was produced in the following manner.

612 grams of gamma-aluminium oxide were heated for 3 hours to 700°C. ground and subsequently impregnated with a solution of 40 gms. of NaOH in 200 gms. of water. After drying at 110°C. the mixture was heated for 12 hours to 1000°C. The cooled mass was washed out with water until practically no alkali separated. Subsequently the mixture was heated for one more hour to 650°C.

With this beta-aluminium oxide as carrier material a catalyst was produced according to the process described above. The only difference was that instead of activated aluminium oxide 520 gms. of beta-aluminium oxide in pulverised condition was added immediately after the precipitation. It was not necessary to add a lubricating means before the compression. For the cobalt to reach a degree of reduction of 60% it was necessary to reduce for 1 hour at 400°C.

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 650 parts by weight of beta-aluminium oxide. The maximum force in the radical direction at which the lozenges were not broken to pieces was 9 kgms.

An investigation was carried out into the activities of the above mentioned catalysts for the synthesis of hydrocarbons at atmospheric presure from synthesis gas. The synthesis gas consisted of 1 part by vol. of CO and 2 parts by vol. of H_2. The sulphur content was less than 1 mgm. of sulphur per cubic metre of gas. The temperature at which the reaction was carried out was 185°C. The rate at which the synthesis gas was fed to the reactor was 100 parts by vol. per part by vol. of catalyst.

The following results were obtained:

Catalyst Carrier	Maximum allowable force in kgm.	Vol. % of contraction of the synthesis gas during the period in hours from.			Yield of hydrocarbons higher than C_4 relative to synthesis gas introduced in gm. cubic metre.		
		0-50	100-150	200-300	0-50	100-150	200-300
1 activated Al_2O_3	5	72	71	68	80	85	82
2 alpha-Al_2O_3	2	83	83	82	115	115	113
3 beta-Al_2O_3	9	82	83	81	105	113	112

From this table it is clear that the hard lozenges produced with beta-aluminium oxide as carrier have an equally high initial activity as the lozenges produced with alpha-aluminium oxide but have a higher mechanical strength, while the high initial activity is preserved a long time.

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 on a carrier, wherein in the production the metals are completely or partially converted into hydrosilicates on beta-aluminium oxide as carrier by precipitation of the active metal from a solution of one of its salts with a precipitating agent completely or partially consisting of a soluble silicate and adding the carrier at any stage of the production but before

separating the precipitate from the mother liquor, whereupon the mixture is dried and compressed into pellets which are subjected to a reducing treatment with hydrogen to obtain the active metal at least in part in metallic form.

2. A process as claimed in Claim 1 wherein metals of the iron group and/or copper and/or manganese are used as active metals.

3. A process for the production of moulded catalysts as claimed in Claim 1 substantially as described with reference to the Example given.

4. Moulded catalysts when produced by the process claimed in any one of the preceding claims.

5. A process for the hydrogenation of organic compound wherein a moulded catalyst as claimed in Claim 4 is employed.

6. A process for the production of hydrocarbons from carbon monoxide and hydrogen-containing gas mixtures wherein a moulded catalyst as claimed in Claim 4 is employed.

Dated the 7th day of July, 1948.

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**Printed for His Majesty's Stationery Office by Wickes & Andrews, Ltd., E.C.4. 39/244.—1950.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies,
price 2s. 0d. each (inland), 2s. 1d. (abroad) may be obtained.**