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Published May 25, 1943

Serial No. 384,741

ALIEN PROPERTY CUSTODIAN

PRODUCTION OF CATALYSTS

Mathias Pier, Heidelberg, Wilhelm v. Fuener and Kurt Peters, Ludwigshafen-on-Rhine, Germany; vested in the Alien Property Custodian

No Drawing. Application filed March 22, 1941

The present invention relates to a process for the production of catalysts possessing good mechanical strength, i. e. high stability of shape.

We have found that catalysts of high activity and high stability of shape are obtained by admixing an iron salt in the presence of water with ammonium sulphide, eliminating the ammonium salt formed either by carefully washing the precipitate with water or by decomposing it by an addition of oxides or hydroxides of such polyvalent metals as form salts with the acid radicle of the ammonium salt which are stable up to at least about 500° C, preferably up to about 600° C, mixing the precipitate with one or more thio salts of ammonium containing metals of the 6th group of the periodic system in their acid radicle, heating the mixture to temperatures of more than 300° C until the evolution of ammonia subsides or comes to an end, and shaping the mass so obtained, if desired.

The iron salt may be dissolved in water or suspended therein, ferrous sulphate being preferred, but other salts, as for example, the chloride, nitrate, carbonate, acetate, formate, oxalate of divalent or trivalent iron or salts of other organic acids may be employed as well. According to the invention, it is essential in order to obtain a catalyst of good efficiency and mechanical strength that the ammonium salt, for example ammonium sulphate, contained in the ferrous or ferric sulphide obtained by preicpitation which still adheres to the precipitate separated, should be completely eliminated. This is achieved, for example, by thoroughly washing the precipitate with water after it has been separated by filtration or centrifuging, ammonia or ammonium sulphide being added to the washing water, if desired. This washing generally must be done for at least 8 to 20 hours, until the acid ion of the ammonium salt at the most in traces be found in the washing water. As an alternative, the ammonium salt may be decomposed by admixing the precipitate, after or before its separation from the solution, with oxides or hydroxides of magnesium, calcium, barium, strontium, beryllium, cerium, lanthanum or zirconium or mixtures thereof, in an amount of about 0.5 to 20 per cent, calculated with reference to the ferrous or ferric sulphide. The ammonium salts, for example ammonium sulphate, are thereby converted into magnesium, calcium or barium sulphate etc. which do no harm to the catalyst and remain stable even at temperatures above 500° C.

The mixture, if desired after being freed from water by filtration, or after being purified by prolonged washing as set forth above, is then mixed with solid ammonium thiomolybdate or ammonium thiotungstate or both in an amount of from 10 to 40 per cent, especially from 15 to 30 per cent. In addition, the mixture may be admixed with nickel or cobalt carbonate, nitrate, oxalate, acetate or formate in an amount of from 0.1 to 10 per cent, especially from 0.5 to 4 per cent. These metals are advantageously added in the form of complex salts, for example nickel-ammonium oxalate, formate or acetate, and such addition is preferably made only after the addition of the molybdenum or tungsten compounds. The resulting mixture, either in the moist state or after having been dried, for example, at from 100 to 200° C, is then heated, preferably in a finely ground state and advantageously in a current of inert or reducing gases, as, for example, hydrogen or hydrogen sulphide or carbon dioxide or nitrogen or mixtures thereof, at temperatures of from 300 to 500°, preferably 375 to 475° C, for a substantial length of time until the evolution of ammonia subsides or comes to an end. The heating is advantageously carried on until the amorphous iron sulphide has been converted practically completely into the crystalline (hexagonal) form. The time of heating required for this purpose may vary between about 1 and about 24 hours. The mixture thus treated is then shaped, if desired, for example with the aid of a pill-press. The moist mass containing iron may also be admixed with a small quantity of graphite prior to drying, which causes the mass to solidify to hard pieces on drying and eliminates the necessity of an additional shaping.

The catalyst prepared according to the present invention possesses both a high efficiency and a very great mechanical strength. It is excellently suitable for carrying out reactions with carbonaceous materials in which deposition of carbon is liable to occur, especially for the cracking of hydrocarbon oils, the destructive hydrogenation of coals, tars and mineral oils or the reforming, isomerization, dehydrogenation and alkylation of hydrocarbons. The catalyst can be employed with special advantage in the refining hydrogenation.

The following examples serve to illustrate how the present invention may be carried out in practice, but the invention is not restricted to these examples.

Example 1

From an aqueous solution of ferrous sulphate

($FeSO_4 \cdot 7H_2O$) of 30 per cent strength, ferrous sulphide is precipitated by means of a solution of ammonium sulphide of 15 per cent strength at from 60° to 80° C. The excess ammonium sulphide is removed by evaporation, the ferrous sulphide precipitated is filtered off in a filter press and washed with water until a sample of the washing water, upon addition of barium chloride and hydrochloric acid, no longer yields a precipitate but only shows a slight turbidity. The filter cake is sucked off until it is substantially dry, the percentage of iron sulphide therein is determined analytically, and the mass is well mixed with solid ammonium thiotungstate and a small amount of dissolved ammonium-nickel oxalate. The mixture is heated at 120° C approximately to dryness, ground through a screen and treated with hydrogen at 440° C in a tubular kiln with an internal conveyor worm; the hydrogen is then displaced by nitrogen, whereupon the mass is completely cooled and pressed to pills in a dry state. The solid catalyst contains 75 per cent of ferrous sulphide, 22 per cent of tungsten sulphide and 3 per cent of nickel sulphide.

Over this catalyst are then passed the vapors of a distillate of a heavy oil which had been obtained by the destructive hydrogenation of mineral coal according to the method described in the copending application Ser. No. 318,831, filed February 14, 1940, together with 3 cubic meters of hydrogen for each kilogram of initial material per hour, under a pressure of 600 atmospheres, at a rate of 0.5 kilogram of initial material per liter of catalyst space and per hour, the temperature in the reaction space being raised from 400 to 440° C. The reaction product obtained contains 68 per cent of constituents boiling up to 325° C. They are an excellent Diesel oil. The higher-boiling constituents are recycled to the reaction chamber for further treatment.

A catalyst composed of the same percentages as mentioned above of ferrous sulphide, tungsten sulphide and nickel sulphide, but prepared with the aid of the finished sulphides (the tungsten sulphide being precipitated from ammonium thiotungstate and the ferrous sulphide and nickel sulphide being precipitated from a solution of ferrous sulphate and ammonium-nickel oxalate, respectively), in contrast to the foregoing, yields a product which only contains 59.5 per cent of constituents boiling up to 325° C. This catalyst presents the further disadvantage of being inferior in strength and falling to small pieces or powder after some time.

Example 2

The ferrous sulphide precipitated according to Example 1 is filtered off and mixed, without being washed, with 2 per cent of magnesium oxide. The mixture is then worked up as in Example 1 with ammonium thiotungstate and a solution of ammonium-nickel oxalate.

Over this catalyst are passed the vapors of a middle oil obtained by the destructive hydrogenation of mineral coal and containing 16 per cent of phenol and 1.5 per cent of organic nitrogen compounds, together with hydrogen under a pressure of 250 atmospheres, at a rate of 0.8 kilogram of initial material per liter of catalyst space and per hour, at a temperature of 430° C. A middle oil free from phenol and organic nitrogen compounds is obtained along with slight quantities of gasoline. The middle oil is then passed, together with hydrogen, over a bleaching earth known in the trade as "Terrana," which is provided with 10 per cent of tungsten sulphide, under a pressure of 250 atmospheres at 400° C and thus converted into a gasoline boiling up to 190° C and having an octane number of 74, which is raised to 90 by the addition of 0.09 per cent by volume of tetraethyl lead.

MATHIAS PIER.
WILHELM v. FUENER.
KURT PETERS.