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THERMAL TREATMENT OF CARBONACEOUS MATERIALS

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The present invention relates to the thermal treatment of carbonaceous materials.

It is already known to carry out the destructive hydrogenation under pressure or cracking of carbonaceous materials in contact with catalysts comprising metal sulphides, for example those produced by heating thio-salts. It has further been proposed to use mixtures of sulphides of the metals of the 6th group of the periodic system (more particularly molybdenum or tungsten) with sulphides of the metals of the iron group (iron, nickel or cobalt) for this purpose. These mixtures have up to the present generally been produced by precipitation from solutions of compounds of the said metals or by sulphidizing a mixture of the metal compounds or a compound containing both metals, for example nickel tungstate.

We have now found that valuable hydrocarbons can be produced from carbonaceous materials with greater advantage by thermal treatment, i. e. by treatment with hydrogen or gases containing hydrogen or by cracking, in contact with catalysts, if as catalysts are used mixtures of metal sulphides, which have been obtained by mixing in a dry state ammonium thio-salts of metals of the 6th group of the periodic system with salts, containing carbon in combined form, such as for example carbonates or salts of organic acids, of metals of the iron group and heating the mixture, if desired after grinding, at temperatures above 300° C., at least until the formation of ammonia ceases. This method of preparation of the catalyst is in practice simpler than those referred to in the preceding paragraph and catalysts of greater activity are obtained so that economies are realized in the said hydrocarbon production.

The heating for the production of metal sulphide mixtures according to the present invention is advantageously carried out in the presence of reducing or sulphidizing gases, for example hydrogen, hydrogen sulphide and the like, or inert gases, for example carbon dioxide, and at temperatures of from about 300° to about 500° C., preferably from 375° to 475° C. The said heating may take rather a long time, for example 1 to 24 hours.

For producing the catalyst preferably ammonium thiomolybdates or tungstates are used as compounds of the metals of the 6th group, which may, for example be produced by dissolving tungstic acid in ammonium sulphide solution and introducing hydrogen sulphide. The thio-salts thus obtained are separated from the liquid and mixed in a dry state with the said salts of iron, nickel or cobalt, such as for example carbonates, oxalates or acetates, in the desired proportion. The said salts of the metals of the iron group and the compounds of the metals of the 6th group may, for example, be mixed in such amounts that the metal of the iron group and the metal of the 6th group are present in the catalyst as sulphides in the atomic proportion of 1:2. However, also other proportions may be used, for example, such proportions that the sulphide of the metal of the iron group is present in predominating amounts.

The treatment with hydrogen or gases containing hydrogen, in the presence of catalysts according to the process of the present invention, may comprise, for example simple hydrogenation or destructive hydrogenation processes and also dehydrogenation processes.

The said hydrogenation processes are as a rule carried out at temperatures of between 300° and 600° C. and in practice between about 380° and 480° C. and under high pressures of at least 50 atmospheres, say 100, 200, 300, 700 or 1000 atmospheres or more.

In the case of dehydrogenation, preferably a hydrogen pressure of about 50 atmospheres or less is used.

The catalysts according to the process of the present invention are also particularly suitable in the hydrogenation of polymerization products, such as the hydrogenation of diisobutylene, for the manufacture of iso-octane.

The following examples will further illustrate the nature of our said invention and how the same can be carried out in practice, but it should be understood that the invention is not limited to the said examples.

Example 1

1 molecular proportion of nickel carbonate is ground together with 2 molecular proportions of ammonium thio-molybdate in a ball mill and treated at 400° to 450° C. in a hydrogen stream during 3 hours, namely until the ammonia formation has ceased. The powder is cooled in the hydrogen stream and then pelleted. Over this catalyst a middle oil obtained from the low temperature carbonization of brown coal tar is passed together with hydrogen under a pressure of 250 atmospheres at a temperature of 425° C. A Diesel oil free from phenols is obtained.

Example 2

A benzine produced in the destructive hydro-

genation of bituminous coal, which boils within the range of 70° to 215° C. and which contains 15 per cent by weight of phenols, is passed over the catalyst described in Example 1 together with hydrogen under a pressure of 50 atmospheres at 490° C. A light-colored benzine which is practically free from phenols and which conforms completely with the commercial requirements, is obtained. The octane number has been increased from 75 to 90.

Example 3

Over the catalyst described in Example 1, diisobutylene is passed together with hydrogen in the proportion of 5 cubic meters of hydrogen per kilogram of diisobutylene at a temperature of 215° C. and under a pressure of 250 atmospheres and with a throughput of 1 kilogram of diisobutylene per liter of reaction space and per hour. Practically pure iso-octane is obtained together with only 0.5 per cent of gaseous hydrocarbons. The bromine number of the obtained product is 0.2.

Example 4

A benzine obtained from bituminous coal by destructive hydrogenation, which boils within the range of 60° to 200° C., and contains 15 per cent of phenols, and has an aniline point of 13.5° C. and an octane number of 72, is passed over the catalyst described in Example 1, together with hydrogen in the proportion of 1 liter of benzine (measured in the liquid phase) to 3 cubic meters of hydrogen (measured at atmospheric pressure), at a temperature of 475° C. and under a hydrogen pressure of 50 atmospheres. A benzine free from phenols with an aniline point of 6° below zero C. and an octane number of 90 is obtained.

What we claim is:

1. A process for the production of hydrocarbons from a carbonaceous material by thermal treatment at temperatures of between 300° and 600° C., in the presence of a catalyst, which comprises using as catalyst a mixture of metal sulphides, which has been obtained by mixing in a dry state an ammonium thio-salt of a metal of the 6th group of the periodic system with a salt, containing carbon in combined form, of a metal of the iron group and heating the mixture at temperatures above 300° C., at least until the formation of ammonia ceases.

2. A process as claimed in claim 1, wherein the salt, which contains carbon in combined form, is a carbonate.

3. A process as claimed in claim 1, wherein the salt, which contains carbon in combined form, is a salt of an organic acid.

4. A process as claimed in claim 1, which comprises heating the mixture in the presence of a reducing gas.

5. A process as claimed in claim 1, which comprises heating the mixture in the presence of an inert gas.

6. A process as claimed in claim 1, which comprises heating the mixture in the presence of a sulphidizing gas.

7. A process as claimed in claim 1, which comprises heating the mixture at temperatures of from 375° to 475° C.

8. A process as claimed in claim 1, which comprises using a catalyst in which the metal of the iron group and the metal of the 6th group are present as sulphides in the atomic proportion of 1:2.

9. A process for the production of hydrocarbons from a carbonaceous material by thermal treatment at temperatures of between 300° and 600° C. in the presence of hydrogen in the presence of a catalyst, which comprises using as catalyst a mixture of metal sulphides, which has been obtained by mixing in a dry state an ammonium thio-salt of a metal of the 6th group of the periodic system with a salt, containing carbon in combined form, of a metal of the iron group and heating the mixture at temperatures above 300° C., at least until the formation of ammonia ceases.

10. A process as claimed in claim 9, wherein the thermal treatment is a destructive hydrogenation under a pressure of at least 50 atmospheres.

11. A process as claimed in claim 9, wherein the thermal treatment is a dehydrogenation under a pressure up to about 50 atmospheres.

12. A process for the production of hydrocarbons of lower boiling point from hydrocarbons of higher boiling point by cracking in the presence of a catalyst, which comprises using as catalyst a mixture of metal sulphides, which has been obtained by mixing in a dry state an ammonium thio-salt of a metal of the 6th group of the periodic system with a salt, containing carbon in combined form of a metal of the iron group and heating the mixture at temperatures above 300° C., at least until the formation of ammonia ceases.

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