

[54] **HYDROGENATION OF COAL**

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[58] **Field of Search**..... 208/9, 10

[57] **ABSTRACT**

A process of catalytic hydrogenation of coal comprising impregnating a water-soluble iron salt (chloride, nitrate, sulphate) into discrete coal particles, chemically converting such water-soluble iron salt into iron oxide and generating activated iron oxide catalyst by subjecting the iron oxide coated coal particles to pressure-temperature conditions in a hydrogen-hydrogen sulfide atmosphere.

11 Claims, No Drawings

[56] **References Cited**

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HYDROGENATION OF COAL

This invention relates to the hydrogenation of coal. It is well-known that hydrogenation of coal can be carried out with iron catalysts besides many others requiring costlier elements. Iron catalysts for this process have been used in the form of powdered oxide prepared from its compounds, or as iron ore, or obtained as industrial wastes or by-products like 'red mud' from aluminium industry.

In an alternative practice, powdered coal can be impregnated with iron salts like ferrous sulphate from their solution in water. Such impregnated iron salts have also been used along with powdered oxide with or without the addition of sodium sulphide or elemental sulphur.

For liquid phase hydrogenation of coal tar, extraneous carbonaceous matter such as coal or coke dust from gas producers, has been soaked with ferrous sulphate solution, mixed with caustic soda solution, dried and used as catalyst.

In all cases, the operating pressure is normally maintained as high as 700 kg. per sq. cm.

This invention has for its object improvements whereby the hydrogenation of coal may be carried out at considerably lower operating pressures.

This invention is based on the discovery that in the process of hydrogenation of coal, the catalytic action of the iron catalysts can be enhanced by the deposition of the metal in the form of hydrated iron oxide, on the surface of powdered coal, before it is subjected to the hydrogenation step.

Based on this discovery, this invention consists of a process of catalytic hydrogenation of coal wherein, as a preliminary step prior to the step of hydrogenation, an iron catalyst comprising hydrated iron oxide is applied in a thoroughly distributed state over the coal, by the interaction of hydroxide ions with an iron salt solution. The active form of the catalyst is generated in situ by reaction with hydrogen sulfide and hydrogen under the conditions of hydrogenation.

The said deposition of the hydrated iron oxide is effected by the following consecutive steps:

1. Mixing powdered coal with a solution of an iron salt.
2. Gradually adding ammonium hydroxide to the resulting mixture.
3. Allowing the contents to settle, filtering and washing, if desired, with a wash liquor containing NH_4NO_3 , until the washings remain at a pH between 7 and 8.
4. Drying the washed product in a vacuum dryer or under an atmosphere of inert gas.

The hydrated iron oxide deposited on coal is converted into the active form of the catalyst in situ by reaction with hydrogen sulphide and hydrogen under the condition of hydrogenation.

The details of the above-mentioned steps may be varied as follows:

1. The coal may be powdered to a 60–200 mesh B.S., or 250 to 75 microns, before it is mixed with the solution of the iron salt.
2. The iron salt used may be ferrous sulphate, ferric chloride or ferric nitrate.
3. The iron solution may be heated to a temperature of 80°–100°C before it is added to the powdered coal and is maintained at this temperature during the precipitation.

4. The strength of the ammonium hydroxide solution used may be about 1:1.

5. The mass resulting from the addition of ammonium hydroxide solution, may be allowed to settle for 1 to 2 hours.

6. The washing of the filtered mass may be carried out until the pH value of the washings is between 7 and 8, and in case the iron salt used is ferric chloride, until the washings are free from chloride ion.

7. The drying of the washed mass may be carried out at about 110°C, until its moisture content is about 2–3%.

The hydrogenation of the coal particles impregnated with the catalyst as explained above, may be carried out as usual, with or without the use of a vehicle oil.

It is well known that the presence of sulphur promotes the catalytic action of the iron catalyst, and that for ensuring the presence of the required amount of sulphur during the hydrogenation process, this element may be added to the coal mass before it is subjected to hydrogenation. Accordingly, for ensuring the presence of sulphur in desired concentration during the hydrogenation by the improved process according to this invention, a predetermined quantity of sulphur or sulphur bearing compounds capable of producing hydrogen sulphide under the conditions of reaction may be added to the catalyst deposited-coal particles before they are subjected to hydrogenation. Alternatively, gaseous hydrogen sulphide may be used.

The following Examples illustrate the invention and the manner in which it may be carried out into practice:

EXAMPLE 1

11 g. of ferric nitrate [$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$] in 200. c.c. distilled water is heated to 80°–100°C. 1–2 c.c. of concentrated nitric acid is added to the solution. 82 g. of powdered coal is added in small portions with mechanical stirring to 100 c.c. distilled water at 80°C. containing 5 g. of ammonium nitrate. The ferric nitrate solution is added to the coal suspension.

1:1 ammonium hydroxide is now added to the suspension in a mixer under conditions of rapid agitation at a rate of 3–4 c.c. per minute till a pH of 8–9 is attained. After being allowed to settle for 1–2 hours the mixture is filtered and washed with 1 percent aqueous ammonium nitrate solution, till the washings showed a pH of 7–8. The residue is washed 1–2 times with distilled water and then dried in an atmosphere of nitrogen at 110°C till the moisture content falls to 2–3 percent.

The above dried mass was mixed with 123 g. of carrier or vehicle oil and made into a paste. 0.83 g. of elemental sulphur was added and mixed. The paste was transferred into a rocking type 1 litre autoclave with liner. The autoclave was closed, flashed with hydrogen and finally pressurized to 100 kg/cm² with hydrogen gas at room temperature. A test for leakproofness was carried out at this stage.

The autoclave was heated electrically at a rate of 3°–4°C/min. with rocking. The temperature was brought to 400°C and maintained at this level for 3 hours, the inside pressure being measured at every 10 minutes. The heating was stopped but the rocking carried on till the temperature dropped to about 150°C. At this stage the rocking was also stopped and the autoclave was allowed to cool to room temperature.

The autoclave was depressurized and the total amount of H₂S determined idometrically. The contents were transferred to a distillation flask. The dissolved H₂S was removed under reduced pressure and determined.

The product was distilled upto 210°C at 10 mm of Hg. The residue was combined with that from the autoclave and Soxhleted with benzene. The organic benzene insolubles (OBI) calculated from the extraction residue, after correction for ash and catalyst, is used to determine the percent conversion of dried, ash free coal according to the expression.

$$\text{Conversion} = \frac{\text{d.a.f. coal} - \text{OBI}}{\text{d.a.f. coal}} \times 100$$

The conversion achieved in the above sequence was 80.7 percent using a catalyst concentration of 1.86 g. of Fe and 0.83 g of sulphur per 100 g. of coal. The atomic S/Fe ratio was 0.78.

EXAMPLE 2

Example 1 was repeated except that hydrated iron oxide was precipitated separately and not on the coal. The precipitate was dried at 110°C, powdered to the same fineness as that of the coal and mechanically mixed with it. Using the same concentration of iron and sulphur as in Example 1, the conversion in this case was 69.0 percent.

EXAMPLE 3

Example 1 was repeated with gradual increase in the amount of sulphur keeping the concentration of iron at 1.86 g. per 100 g. coal. A maximum conversion of 91.3 percent was achieved under the experimental conditions described in Example 1 at a catalyst concentration of 1.86 g Fe and 4.33 g. sulphur per 100 g. coal corresponding to an atomic S/Fe ratio of 4.

EXAMPLE 4

Example 1 was repeated under identical conditions of applying hydrated iron oxide on coal but the hydrogenation test was carried out without the use of carrier or vehicle oil in a 2 litre shaking autoclave. In this case 100 g. of powdered coal was used and the corresponding amount of ferric nitrate was 13.42 g. The amount of water and other reagents were adjusted accordingly.

The method of hydrogenation, recovery and analysis of the products were exactly similar to that in Example 1.

In this case, the catalyst concentration was 1.86 g. of Fe and 2.196 g. of sulphur per 100 g. of coal. S/Fe atomic ratio was 2 and the corresponding conversion of coal was 94.7 percent.

EXAMPLE 5

Example 4 was repeated under identical conditions except that ferrous sulphate instead of ferric nitrate was used for the precipitation of hydrated iron oxide.

The conversion in this case was 95.2 percent for the same S/Fe ratio as in Example 4.

EXAMPLE 6

Example 4 was repeated under identical conditions except that instead of hydrated iron oxide, ferrous sulphate was impregnated on the coal in the conventional manner. 1.146 g. of elemental sulphur was added in ad-

dition to the stoichiometric amount present in ferrous sulphate to bring the S/Fe atomic ratio to 2. The conversion in this case was 88.0 percent.

EXAMPLE 7

Example 5 was repeated under identical conditions except that no nitric acid and ammonium nitrate were used during the precipitation and washing. Using the same S/Fe atomic ration, the conversion in this case was 95.5 percent.

EXAMPLE 8

Example 7 was repeated under identical conditions except that ferric chloride was used in the place of ferrous sulphate. The corresponding conversion was 97.8 percent.

It will be seen from the foregoing Examples that a. the activity of the catalyst of the present invention is higher than that of the conventional process as indicated by the percentage conversion; and

b. the activity of the improved catalyst is not appreciably effected by the nature of the iron salt used for precipitating the hydrated iron oxide.

The Examples given hereinbefore are merely by way of illustrations for carrying out the present invention and they should not be treated as limitative of the scope of the invention. For instance, the hydrogenation experiments as described in the Examples indicate that the use of vehicle oil is an optional feature for carrying out the invention into practice. Further, it is also possible to carry out the precipitation and washing of the hydrated iron oxide without the use of nitric acid and ammonium nitrate.

As already mentioned, the hydrated iron oxide deposited on coal is converted into the active form of the catalyst in situ by reaction with hydrogen sulphide and hydrogen under the condition of hydrogenation.

We claim:

1. A process of catalytic hydrogenation of coal comprising: substantially uniformly impregnating coal particles with hydrated iron oxide by precipitation of said iron oxide from an iron solution; adding a sulfur-yielding material to said iron oxide-impregnated coal particles; and subjecting the resultant mixture to coal catalytic hydrogenation conditions.

2. A process of catalytic hydrogenation of coal comprising the sequential steps of:

i. mixing powdered coal with a solution of an iron salt so that said salt impregnates said coal;

ii. gradually adding ammonium hydroxide to the resultant mixture in an amount sufficient to achieve effective conversion of the iron salt to hydrated iron oxide;

iii. allowing solids within said mixture to settle, filtering and washing said solids until the filter washings remain at a pH between about 7 and 8;

iv. drying the washed solids in the absence of oxygen; and

v. adding a sulfur-yielding material to the dried solids and subjecting the resultant mixture to coal catalytic hydrogenation conditions.

3. A process as claimed in claim 2, wherein the washing referred to in step (iii) is effected with an ammonium nitrate solution.

4. A process as claimed in claim 2, wherein the coal is powdered to a 60-200 mesh or 250-75 micron size, before it is mixed with the solution of iron salt.

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5. A process as claimed in claim 2, wherein the iron salt is selected from the group consisting of ferrous sulfate, ferric chloride and ferric nitrate.

6. A process as claimed in claim 2, wherein the solution of the iron salt is heated to a temperature of 80°-100°C before the powdered coal is added to it and is maintained at this temperature during step (ii).

7. A process as claimed in claim 2, wherein the ammonium hydroxide solution used for interaction with the iron salt is of a strength of about 1:1.

8. A process as claimed in claim 2, wherein the mixture to which ammonium hydroxide has been added is

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allowed to settle for 1 to 2 hours.

9. A process as claimed in claim 2, wherein the iron salt used is ferric chloride, and the washing of the solids is effected until the washings are free of chloride ion.

10. A process as claimed in claim 2, wherein the drying of the washed solids is carried out at a temperature of 110°C.

11. A process as claimed in claim 2, wherein the drying of the washed solids is carried out until its moisture content is about 2 to 3 percent.

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