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(12) Patent:

(54) THORIUM CATALYST REGENERATION

(54) REGENERATION DE CATALYSEURS EN THORIUM

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In the synthesis of hydrocarbons with more than one carbon atom in the molecule from gases comprising carbon monoxide and hydrogen, thorium has hitherto been recovered from spent catalysts containing thorium, for example, beside cobalt and/or nickel, by treating the said catalysts with dilute nitric acid and subsequently precipitating thorium from the solution obtained by means of sodium carbonate.

It has, however, been observed that when the thorium thus recovered was re-employed for the preparation of catalysts, that these catalysts did not always have a satisfactory activity in the said synthesis. This was more particularly the case when the catalytic materials were regenerated from catalysts containing carriers, such as, for example, kieselguhr.

I have now found that catalysts containing thorium having a uniformly satisfactory activity in the said synthesis of hydrocarbons from gases comprising carbon monoxide and hydrogen can be prepared with thorium recovered from spent catalysts if the said recovery is carried out by treating the spent catalysts with a mineral acid to dissolve the thorium, and, if desired, the other catalyst constituents, precipitating from the acid solution thus obtained, a sludge containing large amounts of thorium, dissolving the said sludge in sulphuric acid, precipitating the thorium from the sulphuric acid solution thus obtained as thorium-potassium sulphate, separating the thorium-potassium sulphate from the solution, preparing an insoluble thorium carbonate from the sulphate and recovering the said carbonate.

The said insoluble thorium carbonate is usually obtained in the form of thorium hydrocarbonate.

The unsatisfactory activity of the catalysts prepared with thorium in the manner hitherto employed was apparently due to the fact that this thorium contained iron in disturbing amounts. When working according to the present invention thorium is recovered containing substantially no iron or only small amounts of iron.

The present invention will now be described in greater detail. The treatment of the spent catalyst with a mineral acid to

dissolve the thorium and other catalyst constituents is advantageously carried out in accordance with Specification No. 456035

The sludge containing large amounts of thorium is as a rule precipitated from the solution thus obtained by the addition of a solution of a soluble carbonate, in particular alkali metal carbonates such as sodium carbonate. If the solutions contain other catalyst constituents such as cobalt or nickel it is desirable to add only so much alkali metal carbonate solution and so slowly that the precipitate contains large amounts of thorium but that the bulk of the other catalyst constituents remain in solution.

In this way a sludge containing mainly thorium and iron, for example, in the proportions of about 1 to 3 may be precipitated. The precipitation may be carried out at suitably elevated temperatures, for example, at about 60° to 70° Centigrade.

The solution from which the sludge has been separated and which usually contains the bulk of the catalyst materials, such as cobalt, is then worked up for the recovery of these materials if this is desired.

After dissolving the said sludge in sulphuric acid, potassium sulphate or, if desired, a mixture of potassium sulphate and sodium sulphate in which the former is present in predominating amounts, may be added to the acid solution, preferably while stirring, so that thorium is precipitated as thorium-potassium sulphate but iron remains dissolved. In place of potassium sulphate mixtures furnishing potassium sulphate may be employed for precipitating the thorium-potassium sulphate as, for example, potassium chloride and sodium sulphate or potassium chloride and sulphuric acid. The precipitate is separated from the solution for example, by filtration and preferably thoroughly washed, advantageously with a saturated potassium sulphate solution, in order to remove the adhering parts of the solution in which iron is contained.

The conversion of thorium-potassium sulphate into insoluble thorium carbonate may be carried out in different ways. For Example, the said carbonate may be obtained by boiling up the

thorium-potassium sulphate with a concentrated solution of a carbonate of an alkali metal or of ammonium. Particularly good results as regards the separation from the iron and ultimately in the activity of the regenerated catalyst, are obtained if the reaction mixture during the said conversion contains more potassium sulphate than sodium sulphate or at least equal amounts by weight thereof. For example, when employing a sodium carbonate solution for the conversion, potassium sulphate may be added as such or in the form of a solution, before or during the said conversion, which is effected according to the equation:

$$(\text{Th}(\text{SO}_4)_3)_2 \text{K}_2 + 2 \text{Na}_2 \text{CO}_3 = \text{Th}(\text{CO}_3)_2 + 2 \text{Na}_2 \text{SO}_4 + \text{K}_2 \text{SO}_4$$

so that without the addition of potassium sulphate, more sodium sulphate would have been present. Also a solution containing both sodium- and potassium carbonate may be employed with advantage in place of sodium carbonate alone, in order to increase the proportion of potassium sulphate to sodium sulphate in the reaction mixture.

In order to obtain even more favourable results as regards the separation of iron and the catalyst activity the conversion of the thorium-potassium sulphate into thorium carbonate may be carried out by treating it with such an excess of alkali metal or ammonium carbonate solution that the thorium carbonate first precipitated is redissolved and then heating the solution obtained, say to about 90° Centigrade, so that the iron hydroxide colloiddally contained in solution is precipitated. After the precipitate has been removed, for example, by filtration thorium hydrocarbonate is precipitated from the solution by an addition of acid, for example, sulphuric acid or hydrochloric acid.

The iron hydroxide precipitated as aforesaid usually contains a small amount of thorium and therefore this precipitate may be worked up for the recovery of thorium together with fresh sludge to be dissolved in sulphuric acid, in accordance with the present invention.

The alkali metal sulphates contained in the solution obtained by the aforesaid conversions of thorium-potassium sulphates may be separated therefrom, for example, by cooling to low tem-

peratures, such as, for example, 5° to 10° Centigrade, and may be used again in the process.

According to the process of the present invention thorium is recovered from the spent catalysts in a sufficiently purified form for further employment in the manufacture of catalysts with satisfactory activity.

For example, thorium carbonate obtained by conversion of thorium-potassium sulphate according to the present process, by boiling up the same with a concentrated sodium carbonate solution as stated above, contains only about 0.8 - 1.0 parts by weight of iron oxide (calculated as Fe_2O_3) in 100 parts by weight of thorium compound (calculated as ThO_2). When adding potassium sulphate during the said conversion in amounts as above defined a thorium carbonate of higher purity can be obtained, for example containing less than 0.3 parts of iron oxide in 100 parts of thorium compound (calculated as stated above).

When thorium carbonate is prepared by precipitation from a purified solution of thorium-potassium sulphate in a carbonate solution as set out above, the thorium is obtained practically free from iron, for example, containing in 100 parts less than 0.1 part of iron oxide (calculated as stated above).

The recovered thorium is dissolved in nitric acid and the thorium nitrate solution obtained is employed in the preparation of catalysts for the synthesis of hydrocarbons by interaction of hydrogen and carbon monoxide.

The following Examples further illustrate the nature of the present invention and in what manner the same can be carried out in practice, but it should, however, be understood that the invention is not limited to said Examples.

Example 1.

360 kilograms of a moist sludge containing 50 kilograms of thorium calculated as thorium oxide, precipitated by the addition of the first portions of sodium carbonate solution from a nitric acid solution obtained in the working up of a spent thorium containing catalyst, which has been employed in the synthesis of hydrocarbons from carbon monoxide and hydrogen, are introduced while cold into 720 litres of 4-normal sulphuric acid, and are dissolved while stirring. Then 150 kilograms of potassium sulphate and 100 kilograms of sodium sulphate are introduced into the solution which is then stirred for about 1 1/2 hours. The

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thorium-potassium sulphate double salt is thereby precipitated and is separated from the iron-containing solution. The double salt is washed with a potassium sulphate solution which has been saturated at room temperature, until the washing liquid contains merely traces of iron. The practically iron-free double salt is thereupon admixed with a little water and heated at about 90° Centigrade and so much sodium carbonate solution having a concentration of about 200 grams per litre is added while stirring, until the p_H -value remains constant at 7.5 to 8.0. For this purpose about 60 kilograms of sodium carbonate are required. The thoriumhydrocarbonate thus obtained is separated by filtration, washed with hot water until it is free from sulphate and dissolved in 60 per centio nitric acid, whereupon the solution obtained is filtered. This solution is employed in the preparation of catalyst for the hydrocarbon synthesis the activity of which is equal to that from which it has been regenerated.

Example 2.

360 kilograms of the same sludge as used in Example 1 are introduced into a mixed solution which consists of 160 litres of concentrated sulphuric acid, 170 litres of a solution of potassium sulphate of slightly acid reaction, which has been used for the washing of thorium-potassium sulphate and 410 litres of a solution which has been used in the conversion of thorium-potassium sulphate. Thereupon 20 kilograms of potassium sulphate are added and after stirring for about 1 1/2 hour, the precipitated thorium-potassium sulphate is separated and further worked up to catalyst for the synthesis as stated in Example 1.

Having now particularly described and ascertained the nature of the said invention and in what manner the same is to be performed, I declare that what I claim is:

- 1.- In the synthesis of hydrocarbons with more than one carbon atom in the molecule from gases comprising carbon monoxide and hydrogen the improvement in the regeneration of catalysts con-

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taining thorium, which comprises treating the spent catalysts with a mineral acid, to dissolve the thorium, and if desired, the other catalyst constituents precipitating from the acid solution thus obtained a sludge containing large amount of thorium dissolving the said sludge in sulphuric acid, precipitating the thorium from the sulphuric acid solution thus obtained as thorium-potassium sulphate, separating the thorium-potassium sulphate from the solution, preparing an insoluble thorium carbonate from the sulphate and recovering the said carbonate.

2. A process as claimed in claim 1, which comprises precipitating the said thorium-potassium sulphate by means of potassium sulphate and/or a mixture furnishing potassium sulphate.

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3. A process as claimed in claim 1 which comprises precipitating the said thorium-potassium sulphate by means of a mixture of sulphate and sodium sulphate, in which the former is present in predominating amounts.

4. A process as claimed in claim 1 which comprises converting the said thorium-potassium sulphate by boiling up with a concentrated solution of a carbonate of an alkali metal or of ammonium.

5. A process as claimed in claim 1 which comprises converting the said thorium-potassium sulphate by boiling up with a concentrated solution of alkali metal carbonates in such amounts that the reaction mixture contains at least equal amounts by weight of potassium sulphate and sodium sulphate or still more potassium sulphate.

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6. A process as claimed in claim 5, which comprises adding potassium sulphate before and/or during the said boiling up.

7. A process as claimed in claim 1 which comprises converting the said thorium-potassium sulphate by boiling up with a concentrated solution containing potassium and sodium-carbonate.

8. A process as claimed in claim 1 which comprises converting the said thorium-potassium sulphate, by treating it with such an excess of alkali metal or ammonium carbonate solution that the thorium carbonate first precipitated is redissolved, heating the solution obtained, so that the iron hydroxide colloiddally contained in solution is precipitated, removing the ironhydroxide by filtration, and subsequently precipitating thorium hydrocarbonate from the filtrate by an addition of acid.

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9. A process as claimed in claim 1 which comprises employing a sludge which is prepared from the spent catalyst by treating the same with nitric acid and precipitation from the acid solution by means of sodium carbonats added only in such amounts and so slowly that the precipitated contains large amounts of thorium but little or nothing of the other catalyst constituents.

10. A process as claimed in claim 1 which comprises employing a sludge which contains thorium and iron in the atomic proportion of about 1 to 3.

11. Catalysts when regenerated in accordance with claim 1.