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PATENT SPECIFICATION

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PROVISIONAL SPECIFICATION

Improvements in or relating to the Treatment of Gases containing Sulphur

We, WALTER HENRY GROOMBRIDGE and RONALD PAGE, both British subjects, of the Works of British Celanese Limited, Spondon, near Derby, England, do hereby declare the nature of this invention to be as follows:—

This invention relates to the treatment of gases and in particular to the treatment of gas mixtures comprising hydrogen and carbon monoxide to render them suitable for conversion into hydrocarbons.

It is known that mixtures of carbon monoxide and hydrogen, if caused to react in the presence of suitable catalysts, can be converted either into methane or into higher hydrocarbons or, especially when high pressures are employed, into oxygenated organic compounds, for instance lower aliphatic alcohols. Gas mixtures comprising carbon monoxide and hydrogen which are relatively easily obtained, for example water gas, are however not as a rule altogether suitable for immediate conversion. For example they may contain sulphur in amount sufficient to poison the catalyst and/or, as in the case with water gas, the proportion of carbon monoxide to hydrogen in the mixture may be too high.

The present invention provides a means whereby in a single stage a large proportion of the sulphur contained in such mixtures can be converted into a form in which it is readily removable by treatment with alkali and at the same time the amount of carbon monoxide in the mixture may be decreased and that of hydrogen increased.

According to the invention the gases are passed at an elevated temperature over a catalyst comprising iron oxide. If the carbon monoxide content is to be decreased the gases are passed over the catalyst in admixture with water vapour.

Although a catalyst consisting solely of iron oxide may be employed it is very much better to use in association with the iron oxide a further oxide of a metal, e.g. chromic oxide or magnesium oxide or best of all zinc oxide. Catalysts comprising for example between 60 and 80% of ferric oxide and between 40 and 20% of zinc oxide are particularly valuable.

Among the catalysts which do not comprise zinc oxide there may be mentioned naturally-occurring iron oxides, for example spathic iron ore, or naturally-occurring mixtures of iron oxide with some other metal oxide, for example chromic iron ore. Such minerals are preferably broken down to about 8—12 mesh before being used. Another mineral which may be employed is "ankerite" which appears to be a complex carbonate of calcium, iron and magnesium. If desired, instead of using minerals, synthetic mixtures of similar compositions, prepared for example by igniting mixtures of the carbonates of the metals, may be employed.

The ferric oxide-zinc oxide catalysts, which have been found to give the best results, are preferably made by precipitation; for instance a mixture of the oxides may be precipitated from a solution containing ferric chloride and zinc chloride by means of an alkali, for example sodium carbonate or ammonium hydroxide. The precipitate so obtained may be washed by decantation or filtration or in any other way until it is free from chloride. Preferably it is then compressed into tablets or otherwise shaped and dried in an air oven, for example at temperatures above about 80° C., and especially temperatures of about 100° C. Like the mineral catalysts, it may advantageously be broken down and graded to 8—12 mesh before use.

When treating a gas containing sulphur it is preferable first to wash the gas with an alkaline solution in order to remove as much of the sulphur as possible before subjecting it to the process of the present invention. For example the gas may be caused to flow up a tower in counter-current to a stream of caustic soda solution. It may then be passed in admixture with the desired amount of water over one of the catalysts specified above, especially the iron oxide-zinc oxide catalyst, preferably at a temperature between about 400° and 550° C. and especially at about 500° C. After leaving the catalyst the gases may again be washed with an alkali, pre-

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ferably caustic soda, so as to remove the sulphur compounds formed in the reaction.

When treating water gas to produce a gas more suitable for conversion into methane or higher hydrocarbons, it is preferable to add water vapour in at least the same amount by volume as the carbon monoxide. Preferably considerably more water vapour is employed, good results being obtained when the volume of water vapour is between twice and three times that of the carbon monoxide. Using this high proportion of water vapour at a temperature between 400° and 500° C. over an iron oxide-zinc catalyst, there may be obtained a gas, containing very approximately twice as much hydrogen as carbon monoxide, which is suitable for the hydrocarbon synthesis.

It appears that the reaction between the water vapour and carbon monoxide proceeds considerably faster than the conversion of sulphur compounds into alkali-soluble and therefore easily removable sulphur compounds, and the latter reaction therefore determines the rate at which the gas may be passed over the catalyst. This rate will also depend on the temperature and the precise properties of the catalyst employed and the particular rate necessary in any particular set of conditions may be readily determined by simple test. Generally speaking, when employing a temperature of about 500° C. a space velocity between about 50 and 100 and particularly between about 50 and 80 will be found to reduce the sulphur content to a suitable level. Still lower space velocities may be employed if desired, especially when using catalysts other than the iron oxide-zinc oxide catalyst described above.

Dated this 17th day of December, 1937.
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COMPLETE SPECIFICATION

Improvements in or relating to the Treatment of Gases containing Sulphur

We, WALTER HENRY GROOMBRIDGE and RONALD PAGE, both British subjects, of the Works of British Celanese Limited, Spondon, near Derby, 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:—

This invention relates to the treatment of gases containing sulphur, and especially to the treatment of sulphur-containing gas mixtures comprising hydrogen and carbon monoxide, with a view to rendering them suitable for conversion into hydrocarbons or other compounds.

It is known that mixtures of carbon monoxide and hydrogen, if caused to react in the presence of suitable catalysts, can be converted either into methane or into higher hydrocarbons, or, especially when high pressures are employed, into oxygenated organic compounds, for instance lower aliphatic alcohols. Gas mixtures comprising carbon monoxide and hydrogen which are relatively easily obtained, for example water gas, are however not as a rule altogether suitable for immediate conversion. For example they usually contain sulphur in amount sufficient to poison the catalyst and/or the proportion of carbon monoxide to hydrogen in the mixture may be too high, as it is for example in water gas.

The present invention provides a means whereby in a single stage a large proportion of the sulphur contained in such mixtures, or in other gases, can be converted into a form in which it is readily removable by treatment with alkali, and at the same time the amount of carbon monoxide in carbon monoxide-hydrogen mixtures may be decreased and that of hydrogen increased.

According to the invention the gases are passed at an elevated temperature over a catalyst comprising ferric oxide and zinc oxide. Catalysts comprising between 60 and 80% of ferric oxide and between 40 and 20% of zinc oxide are especially good. When the gases contain carbon monoxide, part of which is to be converted into hydrogen, they are passed over the catalyst in admixture with water vapour.

The ferric oxide-zinc oxide catalysts are preferably made by precipitation; for instance a mixture of the oxides may be precipitated from a solution containing ferric chloride and zinc chloride by means of an alkali, for example sodium carbonate or ammonium hydroxide. The precipitate so obtained may be washed by decantation or filtration or in any other way until it is free from chloride. Preferably it is then compressed into tablets or otherwise shaped and dried in an air oven, for example at temperatures above about 80° C., and especially temperatures of about 100° C. Before use it may advantageously be broken down and graded to 8—12 mesh.

When, as is usual, part of the sulphur content of a gas is in a form such that it is removable by alkali, it is preferable first to wash the gas with an alkaline solution in order to remove as much of the sulphur as possible before subjecting it to the process of the present invention. For example the gas may be caused to flow up a tower in counter-current to a stream of caustic soda solution. It may then be passed, if desired, in admixture with water, over the catalyst preferably at a temperature between about 400° and 600° C. and especially between 500° and 550° C. After leaving the catalyst the gases may again be washed with an alkali, preferably caustic soda, so as to remove the alkali-soluble sulphur compounds formed in the reaction.

When treating water gas to produce a gas more suitable for conversion into methane or higher hydrocarbons, it is preferable to add water vapour in at least the same amount by volume as the carbon monoxide. Generally speaking good results are obtained when the volume of water vapour is equal to or up to twice or three times that of the carbon monoxide. Using these proportions of water vapour at a temperature between 500° and 550° C. over a ferric oxide-zinc oxide catalyst, there may be obtained a gas, containing very approximately twice as much hydrogen as carbon monoxide, which is suitable for the hydrocarbon synthesis. Even higher proportions of water may be used, especially in conjunction with yet higher temperatures.

It appears that the reaction between the water vapour and carbon monoxide proceeds considerably faster than the conversion of sulphur compounds into alkali-soluble and therefore easily removable sulphur compounds, and the latter reaction therefore determines the rate at which the gas may be passed over the catalyst. This rate will also depend on the temperature and the precise properties of the catalyst employed, and the particular rate necessary in any particular set of conditions may be readily determined by simple test.

The following Examples illustrate the invention without in any way limiting it.

EXAMPLE 1.

Water gas containing approximately 300 mg. sulphur in each cubic metre of gas is passed up a scrubbing tower in counter-current to a solution of caustic soda, whereby the greater part of the sulphur is removed. The gas is mixed with about 75% by volume of water vapour, and is passed at a space velocity of 50 over a ferric oxide-zinc oxide catalyst (Fe:Zn=7:4) heated to 500° C. After a final alkali wash the resulting gas has a low sulphur content and a carbon monoxide-hydrogen ratio of the order of 1:2.

EXAMPLE 2.

Water gas, after as much sulphur as possible has been removed by scrubbing with caustic soda, is mixed with about its volume of water vapour and passed, at a space velocity of 30—50, over the same ferric oxide-zinc oxide catalyst at a temperature of 550° C. The greater part of the sulphur is converted into a form easily removed with alkali, and the carbon monoxide-hydrogen ratio approximates to 1:2.

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. Process for the treatment of gas mixtures containing sulphur which comprises passing the gases at elevated temperatures in contact with a catalyst comprising ferric oxide and zinc oxide.

2. Process for the treatment of gas mixtures comprising hydrogen and carbon monoxide, which comprises passing them in admixture with water vapour at an elevated temperature in contact with a catalyst comprising ferric oxide and zinc oxide.

3. Process according to Claim 1 or 2, wherein the catalyst contains 60—80% of ferric oxide and 40—20% of zinc oxide.

4. Process according to any of Claims 1—3, wherein the catalyst is heated to 400—600° C.

5. Process according to any of the preceeding Claims wherein the catalyst is heated to 500°—550° C.

6. Process according to any of Claims 2—5, wherein the volume of water vapour mixed with the gases equals or exceeds the volume of carbon monoxide contained in the gases.

7. Process according to any of the preceding Claims, wherein the catalytic treatment of gases containing sulphur is preceded and followed by a wash with an alkali solution.

8. Process for the treatment of gas mixtures containing sulphur substantially as described.

9. Gas mixtures having a relatively low content of sulphur whenever prepared by the process of any of the preceding Claims.

Dated this 28th day of October, 1938.

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