PATENT SPECIFICATION

NO DRAWINGS

Inventors: JOHANNES MULLER, FRITS EILERT ALTING VAN GEUSAU and MARIUS 't HART

1,150,972

1,150,972

Date of Application and filing Complete Specification: 4 Oct., 1967.
No. 45136/67.
Application made in Netherlands (No. 6614074) on 6 Oct., 1966.
Complete Specification Published: 7 May, 1969.
© Crown Copyright 1969.

Index at acceptance: —B1 E(20Y, 41Y, 49Y, 55Y, 283, 413, 491, 535, 536, 537, 550, 551, 563, 591)
Int. Cl: —B 01 j 11/14

COMPLETE SPECIFICATION

Process for the Regeneration and Reactivation of Deactivated Supported Platinum Group Catalysts

We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ N.V., a Company organised under the Laws of the Netherlands, of 30 Carel van Bylandtlaan, The Hague, the Netherlands, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the regeneration and reactivation of deactivated supported platinum group metal catalysts by subjecting them to chlorination and oxidation.

Platinum group metal catalysts are used extensively in processes for the conversion of hydrocarbons or hydrocarbon mixtures, such as catalytic reforming. Platinum group catalysts normally comprise a platinum group metal, usually platinum, and usually supported on a suitable base or carrier, such as alumina, and a small amount of halogen, such as chlorine and possibly fluorine, to improve the hydrocracking and isomerization activity of the catalyst.

During the course of the conversion process catalyst activity gradually declines, owing to a build-up of carbonaceous deposits on the catalyst and/or a depletion of halogen from the catalyst. Eventually it becomes necessary to regenerate the catalyst by subjecting it to an oxidizing atmosphere to remove carbonaceous deposits by burning. Normally, halogen is added to the catalyst during the regeneration procedure or by contacting the regenerated catalyst with halogen or a decomposable halogen compound. Unexpectedly, however, carbon burn and/or halogen addition may fail to restore the catalyst to initial activity and selectivity or to prevent that activity and selectivity decrease at an increased rate during subsequent use of the catalyst.

It has now been found that it is possible to regenerate and reactivate a platinum group metal catalyst in a very easy manner by effecting the overall regeneration and reactivation in a particular way, including a special kind of treatment with chlorine; this overall treatment effectively restores the activity, selectivity and stability of the catalyst (e.g. palladium or preferably platinum).

According to the invention a process for the regeneration and reactivation of deactivated supported chlorinated platinum group metal catalyst which has been used for hydrocarbon conversion comprises removing carbonaceous deposits from the catalyst by treating it at elevated temperature in the range 370° to 450°C with a gas containing oxygen and subsequently maintaining it at still higher average catalyst temperature, not exceeding 550°C, in the presence of a gas having a higher oxygen content, and thereafter chlorinating the catalyst by treating it with chlorine to an extent exceeding the chlorine treatment, if any normally effected during operation of the conversion process, for a period of at most 24 hours immediately after operation of the conversion process has been resumed.

The chlorination treatment, which is effected from the resumption of the conversion process on, i.e. from the renewed introduction into the reactor of the hydrocarbon feedstock to be reformed or otherwise converted, need never be prolonged for more than 24 hours in order to obtain good results; in many cases however, this chlorination treatment need take

[*Price 4s. 6d.*]

only the first 4—8 hours after operation of the conversion process has been resumed. The exact length of time during which chlorine injection is suitably carried out is dependent upon the hydrocarbon feed rate, the quantity of catalyst present and desired final catalyst chlorine level.

It is preferred to employ relatively large chlorine addition rates, in order to lessen the time during which chlorine must be added to obtain the desired chlorine content on the catalyst; a preferred range of rates is 100—1000 ppm by weight, calculated on the hydrocarbon feed to the conversion process.

It will generally be desired to bring the average catalyst chlorine level to the vicinity of that of the same catalyst when fresh, i.e. preferably to a value lying between 0.2% by weight below and 0.2% by weight above the chlorine content of the fresh catalyst, the high end of the range generally being the more effective; this means that, dependent on the type of catalyst employed, desirable average chlorine contents will generally lie between 0.2 and 1.1% by weight.

Water vapour may be present during all or part of the chlorination treatment, and also during the rest of the conversion operation.

It is possible to carry out the conversion operation in such a way that no chlorine is intentionally added to the catalyst except during the chlorination treatment, however, it is also possible to add chlorine either continuously or intermittently after the chlorination proper has been terminated. For example, 1 to 5 ppm, or even up to about 10 ppm, by weight of chlorine, calculated on the hydrocarbon feed, is frequently added throughout conventional reforming runs, the latter high amounts being employed when water is present to an excessive extent, which considerably lessens the degree of chlorination effected by such chlorine addition. The degree of chlorine addition specified for the chlorination step of the present process is exclusive of all chlorine which may have been added already, but inclusive of all chlorine which at that time is being introduced from whatever source, and this chlorine treatment is such that it exceeds any chlorine treatment which may be effected regularly.

While the chlorination step is a necessary step of the process of the invention, it is insufficient by itself to restore the properties of the catalyst. Therefore, it is preceded by an oxidative treatment, carried out after the reforming or other conversion operation has been discontinued by cutting off the introduction of hydrocarbon feed, in the course of which treatment carbonaceous deposits are burned from the catalyst. Firstly, the still hot (e.g. >370°C) reactor or reactors may be purged with nitrogen or some other inert gas, to reduce the hydrocarbon and hydrogen concentration therein and also, as frequently may be required, to reduce the temperature, which should not, however, be lowered to less than 370°C. On the other hand, as long as there is still a substantial amount of carbon on the catalyst the temperature should not rise above 450°C, since otherwise the physical characteristics of the catalyst support might be deleteriously affected. The oxidative treatment of the catalyst may be carried out by introducing into the hot catalyst bed an inert gas containing only a small amount of oxygen; most economical for this purpose is nitrogen gas containing air. The average temperature of the catalyst may be regulated by adjusting the amount of oxygen in the inert gas and/or by varying the total amount of gas passed through. In commercial practice of a reforming process, the oxygen-containing gas can conveniently be passed through the reforming reactor or reactors by means of a compressor which during normal operation is used to recycle hydrogen gas to the reforming process. It is preferred also to recycle the oxygen-containing gas itself, with addition of supplementary quantities of oxygen to replace any used up in burning; in this case the gas will normally comprise carbon dioxide, arising from the burning of carbon, besides oxygen and e.g. nitrogen. The oxygen content of the inert gas will preferably be 0.2 to 1.5% by volume.

Subsequently, the catalyst is maintained at a still higher average temperature (but not higher than 550°C) in the presence of a gas having a higher oxygen content, preferably at most 6%, suitably 1 to 2%, by volume. It will ordinarily be preferred to increase the oxygen concentration slowly and stepwise so as to keep the catalyst temperature below the allowable maximum and to make a gradual transition from the lower (370° to 450°C) temperature to the higher (up to 550°C) one. After this higher temperature has been reached, a stepwise increase of the amount of oxygen in the gas which is continuously passed through the reactor or reactors may again be effected, this oxygen content then suitably first lying below 3% by volume and then between 3 and 6%. The total duration of the higher temperature treatment is preferably 2 to 8 hours; some carbon burning can take place during this part of the treatment as well. Though substantial but incomplete burning of the carbon may in some instances be sufficient or expedient, it is usually preferred to remove substantially all the burnable carbon from the catalyst.

Water vapour may be present during all or part of the overall oxidative treatment as described above.

It is preferred that, after the catalyst has been maintained in the presence of the gas having a higher oxygen content, it is treated with sulphur, suitably in the form of a decomposable compound thereof, preferably car-

bon disulphide or hydrogen sulphide. This has been found to improve the characteristics of the catalyst. At least part of this sulphur treatment should take place before operation of the conversion process has been resumed; however, it may also be advisable to prolong this sulphiding (although advantageously to a somewhat lesser extent than before) for some time after this resumption, especially when an in itself substantially sulphur-free reformer feedstock is being processed. In this case, therefore, sulphiding and chlorination partly coincide; however, sulphiding (by which here is meant intentional addition of sulphur, in excess of that which may possibly be normally present already in the hydrocarbon feedstock and/or in the hydrogen-containing gas employed) is advantageously effected during a longer period of time than chlorination (which latter is continued for 24 hours at the most, as has already been indicated above), and is preferably prolonged for up to 30 days after resumption of the conversion process, although the degree of sulphur introduction may be reduced in the course of this period.

On the other hand it is preferred that not too much sulphur be present when the regeneration and reactivation treatment is initiated, since it has been found that this may interfere with the efficacy of this treatment; hence, at least during a final period of the conversion process, i.e. until the introduction of hydrocarbon feedstock to the reactor or reactors is discontinued so that the reactivation and regeneration treatment may be initiated, a hydrocarbon feedstock is preferably employed which has a sulphur content of 40 ppm by weight at most, advantageously for the last 5 to 50 days of operation. It is of course possible that during the whole of the conversion operation a feedstock having such a low sulphur content is being processed. It may also be advantageous to clean the apparatus or parts thereof, especially those situated before the reactor or reactors proper, such as heaters and heat exchangers, before the regeneration and reactivation treatment is initiated, with a view to removing sulphur compounds such as iron sulphide which may have been deposited there.

Since the present regeneration and reactivation has been found to give best results with a catalyst not too far depleted in chlorine, it may be advantageous to effect an additional treatment with chlorine exceeding the normally effected chlorine treatment, if any, during a terminal period of the conversion process as well, i.e. until the discontinuation of introducing hydrocarbon feedstock; this additional treatment therefore coincides in part with the processing of low sulphur feedstock, if such is effected, but preferably lasts for a shorter time, viz. for the last 30 to 60 hours, before this discontinuation.

While for either of the chlorine treating steps described above chlorine gas may be used, it is preferred to employ a chlorine-containing compound, preferably normally liquid, which, upon exposure to the reaction conditions of the conversion process, will be decomposed to form hydrogen chloride. By this means, more precise metering of the chlorine into the process is possible. Chlorine-containing compounds which are especially suitable for this purpose are C_{1-3} chlorinated hydrocarbons, such as trichloroethylene and ethylene dichloride.

The following Examples illustrate the invention.

EXAMPLE I

A commercial reforming catalyst comprising platinum on an alumina support and containing 0.9% wt of chlorine when fresh had become deactivated after extensive use in reforming a hydrotreated naphtha having a boiling range of 90—165°C and comprising 28% wt naphthenes and 12% wt aromatics; about 19300 litres of feed per kg of catalyst had been treated. The catalyst deactivation was such that the average catalyst temperature, required to produce a liquid product having a Research octane number (unleaded) of 92, had risen from 481°C to about 503°C and the yield of debutanized liquid product had dropped from about 83% to about 73% by weight, calculated on the hydrocarbon feedstock.

During the run in question, the liquid hourly space velocity was 1.5 volume of feed per volume of catalyst per hour, and the reactor outlet pressure was 28 kg/cm² gauge.

In order to ensure that the catalyst did not have too low a chlorine content at the start of the regeneration/reactivation step proper, during the last 32 hours of the reforming run a total amount of 0.1% wt (calculated on the catalyst) of chlorine in the form of ethylene dichloride was introduced, after which the unit was shut down. Subsequently, the unit was evacuated and then purged with nitrogen, after which 0.5% volume of oxygen was added to the nitrogen stream when a temperature of 38°C was reached; the temperature was then slowly increased to 510°C, which took 2 hours. At this same temperature, the oxygen content was gradually increased to 2% volume over a period of one hour, and kept at this value for one hour more, after which oxygen was increased to, and subsequently kept at, 5% volume over 1 and 2 hours, respectively. The total period of keeping the catalyst in contact with a gas containing more oxygen than did the gas initially employed (0.5%) was therefore 5 hours.

A nitrogen purge was then again effected and the unit evacuated and subsequently pressurized with hydrogen to 7 kg/cm² gauge, the temperature being 370°C; 0.2% wt of

sulphur (calculated on the catalyst) in the form of hydrogen sulphide was injected, the temperature being gradually raised to 400°C. Under these conditions, which were still somewhat different from those normally employed, the reforming operation was resumed by the introduction of the same naphtha as before. Some hydrogen sulphide was still injected at first, and later on some extra sulphur was dissolved in the hydrocarbon feed, until 20 days after operation of the reforming process had been resumed. Together with the naphtha feed, chlorine was introduced during a period of 6 hours at a rate of about 600 ppm wt, calculated on the feed introduced, in the form of trichloroethylene, leading to an average chlorine content on the catalyst of 0.9% wt. Also, operating conditions were gradually brought to normal; it was then found that the average operating temperature required to obtain once more an octane number of 92 was as low as 479°C, the yield of debutanized liquid product having again increased to about 83% by weight, so that catalyst reactivation was complete in both respects; its stability turned out to be even better than before, for after about 19300 litres of feed per kg of catalyst had again been treated the average temperature required for maintaining the same octane number of 92 had risen to 496°C only, as compared to the 503°C just before regeneration. On the other hand, a temperature rise to 503°C was in this case required only after 26300 litres of feed per kg of catalyst had been treated; similar results were obtained with respect to yield.

EXAMPLE II

A commercial catalyst of the same type as that employed in the process described in Example I was employed in reforming a naphtha having a high sulphur content of 40—60 ppm wt. at a reactor outlet pressure of 29 kg/cm² gauge and a volume space velocity of 18. In order to ensure a low sulphur as well as a high chlorine content on the catalyst at the start of the regeneration/reactivation procedure, during the last 28 days of the reforming run a naphtha was employed having similar characteristics to the original one, but the sulphur content of which was 20—30 ppm wt only, and during the last 57 hours of this run a total amount of 0.15% wt, calculated on the catalyst, of chlorine in the form of trichloroethylene was introduced, after which the unit was shut down, evacuated, purged with nitrogen and cooled; subsequently, the unit was in part subjected to a pressurized water wash in order to remove any iron sulphide which might still be present. The catalyst was then subjected to an oxidative treatment and the unit prepared for the renewed introduction of naphtha feed in a manner substantially similar to that described in Example I, sulphur being injected in the form of carbon disulphide. Since, as indicated above, the normal feed had a high sulphur content, no extra sulphur was injected after the reforming operation had been resumed; on the other hnad, during the first 6 hours of operation chlorine in the form of trichloroethylene was injected at a rate of about 600 ppm, calculated on the hydrocarbon feed, the average catalyst chlorine content at the end of this period being 1.0% by weight.

The average temperature for obtaining a Research octane number (unleaded) of 90, which before regeneration/reactivation had risen to 508°C, was in this way reduced to 486°C; the yield of debutanized product was increased again from 77% by weight, calculated on hydrocarbon feedstock, to 82% by weight, all under the same operating conditions as before regeneration.

EXAMPLE III

A commercial reforming catalyst of the type employed according to Examples I and II was employed in reforming a naphtha boiling between 88° and 148°C and containing 20% wt naphthenes, 10% wt aromatics and 30 ppm wt sulphur, at a reactor outlet pressure of 28 kg/cm² gauge and a volume space velocity of 1.2. The catalyst was deactivated to such an extent that for obtaining a Research octane number (unleaded) of 96 on average temperature of 518°C was required, as compared to 498°C when the catalyst was fresh under the same operating conditions.

In this case, no chlorine was added in the last period before the regeneration/reactivation; unit shut down, evacuation, purge and cooling, oxidative and sulphur treatments were carried out in a manner substantially similar to that of Example I. Subsequently the reforming operation was resumed, about 500 ppm wt of chlorine, calculated on the hydrocarbon feed, being injected during the first 6 hours, at the end of which period the average catalyst chlorine content was 0.9% wt. The average temperature required for obtaining an octane number of 96 had then dropped again to 497°C, i.e. even better than with fresh catalyst; after processing 3500 litres of feed per kg of catalyst, this temperature was still as low as 505°C.

WHAT WE CLAIM IS:—

1. A process for the regeneration and reactivation of deactivated supported chlorinated platinum group metal catalyst which has been used for hydrocarbon conversion, which process comprises removing carbonaceous deposits from the catalyst by treating it at elevated temperature in the range 370° to 450°C with a gas containing oxygen and subsequently maintaining it at still higher average catalyst temperature, not exceeding

sulphur (calculated on the catalyst) in the form of hydrogen sulphide was injected, the temperature being gradually raised to 400°C. Under these conditions, which were still somewhat different from those normally employed, the reforming operation was resumed by the introduction of the same naphtha as before. Some hydrogen sulphide was still injected at first, and later on some extra sulphur was dissolved in the hydrocarbon feed, until 20 days after operation of the reforming process had been resumed. Together with the naphtha feed, chlorine was introduced during a period of 6 hours at a rate of about 600 ppm wt, calculated on the feed introduced, in the form of trichloroethylene, leading to an average chlorine content on the catalyst of 0.9% wt. Also, operating conditions were gradually brought to normal; it was then found that the average operating temperature required to obtain once more an octane number of 92 was as low as 479°C, the yield of debutanized liquid product having again increased to about 83% by weight, so that catalyst reactivation was complete in both respects; its stability turned out to be even better than before, for after about 19300 litres of feed per kg of catalyst had again been treated the average temperature required for maintaining the same octane number of 92 had risen to 496°C only, as compared to the 503°C just before regeneration. On the other hand, a temperature rise to 503°C was in this case required only after 26300 litres of feed per kg of catalyst had been treated; similar results were obtained with respect to yield.

EXAMPLE II

A commercial catalyst of the same type as that employed in the process described in Example I was employed in reforming a naphtha having a high sulphur content of 40—60 ppm wt. at a reactor outlet pressure of 29 kg/cm² gauge and a volume space velocity of 18. In order to ensure a low sulphur as well as a high chlorine content on the catalyst at the start of the regeneration/reactivation procedure, during the last 28 days of the reforming run a naphtha was employed having similar characteristics to the original one, but the sulphur content of which was 20—30 ppm wt only, and during the last 57 hours of this run a total amount of 0.15% wt, calculated on the catalyst, of chlorine in the form of trichloroethylene was introduced, after which the unit was shut down, evacuated, purged with nitrogen and cooled; subsequently, the unit was in part subjected to a pressurized water wash in order to remove any iron sulphide which might still be present. The catalyst was then subjected to an oxidative treatment and the unit prepared for the renewed introduction of naphtha feed in a manner substantially similar to that described in Example I, sulphur being injected in the form of carbon disulphide. Since, as indicated above, the normal feed had a high sulphur content, no extra sulphur was injected after the reforming operation had been resumed; on the other hnad, during the first 6 hours of operation chlorine in the form of trichloroethylene was injected at a rate of about 600 ppm, calculated on the hydrocarbon feed, the average catalyst chlorine content at the end of this period being 1.0% by weight.

The average temperature for obtaining a Research octane number (unleaded) of 90, which before regeneration/reactivation had risen to 508°C, was in this way reduced to 486°C; the yield of debutanized product was increased again from 77% by weight, calculated on hydrocarbon feedstock, to 82% by weight, all under the same operating conditions as before regeneration.

EXAMPLE III

A commercial reforming catalyst of the type employed according to Examples I and II was employed in reforming a naphtha boiling between 88° and 148°C and containing 20% wt naphthenes, 10% wt aromatics and 30 ppm wt sulphur, at a reactor outlet pressure of 28 kg/cm² gauge and a volume space velocity of 1.2. The catalyst was deactivated to such an extent that for obtaining a Research octane number (unleaded) of 96 on average temperature of 518°C was required, as compared to 498°C when the catalyst was fresh under the same operating conditions.

In this case, no chlorine was added in the last period before the regeneration/reactivation; unit shut down, evacuation, purge and cooling, oxidative and sulphur treatments were carried out in a manner substantially similar to that of Example I. Subsequently the reforming operation was resumed, about 500 ppm wt of chlorine, calculated on the hydrocarbon feed, being injected during the first 6 hours, at the end of which period the average catalyst chlorine content was 0.9% wt. The average temperature required for obtaining an octane number of 96 had then dropped again to 497°C, i.e. even better than with fresh catalyst; after processing 3500 litres of feed per kg of catalyst, this temperature was still as low as 505°C.

WHAT WE CLAIM IS:—

1. A process for the regeneration and reactivation of deactivated supported chlorinated platinum group metal catalyst which has been used for hydrocarbon conversion, which process comprises removing carbonaceous deposits from the catalyst by treating it at elevated temperature in the range 370° to 450°C with a gas containing oxygen and subsequently maintaining it at still higher average catalyst temperature, not exceeding

* C L M S *

550°C, in the presence of a gas having a higher oxygen content, and thereafter chlorinating the catalyst by treating it with chlorine to an extent exceeding the chlorine treatment, if any, normally effected during operation of the conversion process, for a period of at most 24 hours immediately after operation of the conversion process has been resumed.

2. A process according to Claim 1 in which the said treatment with chlorine lasts for the first 4—8 hours after operation of the conversion process has been resumed.

3. A process according to Claim 1 or Claim 2 in which the rate of chlorine addition in the said chlorine treatment is between 100—1,000 ppm by weight, calculated on the hydrocarbon feed to the conversion process.

4. A process according to any of Claims 1 to 3 in which the average chlorine content of the catalyst at the end of the said chlorine treatment is from 0.2% by weight below to 0.2% by weight above that of the fresh catalyst.

5. A process according to any of Claims 1 to 4 in which during the said treatment at elevated temperature the oxygen content of the treating gas is 0.2 to 1.5% by volume.

6. A process according to any of Claims 1 to 5 in which the said gas containing oxygen comprises air and nitrogen.

7. A process according to any of Claims 1 to 6 in which the said gas having a higher oxygen content contains at most 6% by volume of oxygen.

8. A process according to Claim 7 in which the said higher oxygen content is in the range of from 1 to 2% by volume.

9. A process according to any of Claims 1 to 8 in which the catalyst is maintained in the presence of the said gas having a higher oxygen content for 2 to 8 hours.

10. A process according to any of Claims 1 to 9 in which after the catalyst has been maintained in the presence of the said gas having a higher oxygen content it is treated with sulphur, at least part of this treatment being effected before operation of the conversion process has been resumed.

11. A process according to Claim 10 in which the said sulphur treatment is prolonged for at most 30 days after operation of the conversion process has been resumed.

12. A process according to Claim 10 or Claim 11 in which the sulphur is at least in part in the form of a decomposable sulphur compound.

13. A process according to Claim 12 in which the decomposable sulphur compound is carbon disulphide.

14. A process according to Claim 12 in which the decomposable sulphur compound is hydrogen sulphide.

15. A process according to any of Claims 1 to 14 in which during a final period of the conversion process a hydrocarbon feedstock is employed having a sulphur content of not more than 40 ppm by weight.

16. A process according to Claim 15 in which the said hydrocarbon feedstock is employed for the last 5 to 50 days before the conversion process is discontinued.

17. A process according to any of Claims 1 to 16 in which at least during a terminal period of the conversion process the catalyst is treated with chlorine to an extent exceeding the chlorine treatment, if any, normally effected during operation of the conversion process.

18. A process according to Claim 17 in which the said treatment with chlorine lasts for the last 30 to 60 hours before the conversion process is discontinued.

19. A process according to any of Claims 1 to 18 in which the chlorine is used in the form of a decomposable chlorine compound.

20. A process according to Claim 19 in which the said chlorine compound is a chlorinated hydrocarbon having 1 to 3 carbon atoms per molecule.

21. A process according to any of Claims 1 to 20 in which the catalyst comprises platinum.

22. A process according to Claim 1 substantially as described.

23. A process for the regeneration and reactivation of supported platinum group catalysts by subjecting them to chlorination and oxidation, substantially as described in any of the Examples.

24. Supported platinum group catalysts which have been regenerated and reactivated by means of a process according to any of Claims 1 to 23.

25. A process for the catalytic conversion of hydrocarbon materials in which a catalyst is employed which has been regenerated and reactivated by means of a process according to any of Claims 1 to 23.

26. A process according to Claim 25 in which the conversion is catalytic reforming.

27. Hydrocarbon materials which have been catalytically converted by means of a process according to Claim 25 or Claim 26.

KILBURN & STRODE,
Chartered Patent Agents,
Agents for the Applicants.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1969.
Published by the Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.

