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REACTIVATING A SILICA-ALUMINA CATALYST BY IMPREGNATION WITH BORIC ACID

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This invention relates to the reactivation of catalysts and more particularly to the reactivation of silica-alumina catalysts such as those used in petroleum cracking.

In the usual commercial catalytic cracking processes a heavy hydrocarbon oil such as a gas oil wholly or partly in vapor phase is contacted with a cracking catalyst at an elevated temperature which may operatively range from 700° to 1100° F., but which in commercial practice does not normally go below 800° F. or above 1000° F. The oil is cracked to gas, gasoline hydrocarbons and heavier liquid hydrocarbons, and a hydrocarbonaceous material generally called "coke" is deposited on the catalyst. This coke deposit temporarily deactivates the catalyst and makes necessary its regeneration. The regeneration is usually carried out by contacting the coked catalyst with air so as to burn off the coke. In this regeneration step the temperature usually goes as high as 1000° F. and may reach 1100° F. or somewhat above. The activity of the catalyst following any one regeneration is substantially the same as the activity of the catalyst prior to the preceding cracking step. Thus the deactivation of the catalyst in a single cracking cycle is a temporary condition which is readily corrected by means of regeneration.

It has been found, however, that when a silica-alumina cracking catalyst is subjected to cycles of cracking and regeneration steps over a long period of time a different and permanent deactivation of the catalyst takes place. These cycles of cracking and regeneration are continued for an extended period of time with the permanent deactivation of the catalyst becoming progressively more serious. For example, in the Houdry fixed-bed type of operation the permanent deactivation continues until at the end of about 18 months it is no longer feasible to continue operation. It is the practice when operating such a process to shut the unit down and replace the permanently deactivated catalyst with fresh catalyst. This operation usually necessitates a shut-down time of several weeks in the Houdry-type process. This is an expensive operation not only because of the cost of labor and of fresh catalyst but also because of production loss. The continuing permanent deactivation of the catalyst also has another undesirable effect. Since the permanent deactivation of a catalyst begins long before this deactivation has progressed to a point making it necessary to replace the catalyst, it is the practice to gradually increase the severity of conditions such as temperature and

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pressure in order to compensate for the loss in activity of the catalyst. Such an increase in severity of conditions is usually undesirable, as the product distribution is inevitably affected.

It is an object of the present invention to reactivate a silica-alumina catalyst.

It is a further object of this invention to reactivate a silica-alumina cracking catalyst in situ.

These and other objects of the present invention are achieved by the process herein described, comprising reactivating a permanently deactivated silica-alumina catalyst by impregnating boric acid on the interior and exterior surfaces of the catalyst. We have found that by impregnating a permanently deactivated silica-alumina catalyst with a solution of boric acid and then heating said catalyst impregnated with said boric acid to decompose the boric acid, the activity of the catalyst can be substantially increased, in certain cases to equal the activity of the catalyst prior to permanent deactivation. The boric acid from an economic standpoint is advantageously applied to the permanently deactivated catalyst in the form of an aqueous solution. However, solvents for boric acid other than water may be used, such as, for example, methyl alcohol, ethyl alcohol, and glycerin.

The process of the invention is applicable to the reactivation of a wide variety of silica-alumina catalysts, particularly silica-alumina cracking catalysts which may or may not contain other metal oxides such as zirconia, magnesia, thorium, and the like. Important silica-alumina cracking catalysts include the so-called natural catalysts which are prepared by conventional acid treatment of acid-activable montmorillonite clays, which clays are usually referred to as sub-bentonites to distinguish them from the Wyoming or swelling-type bentonites. Before use and after pelleting, if pelleted catalysts are desired, the acid-treated clay material is usually calcined in air at a temperature of 800° to 1100° F., ordinarily about 1000° F.

It has been proposed to manufacture synthetic silica-alumina catalysts by a variety of methods. Although the invention includes the reactivation of the general class of synthetic silica-alumina catalysts, we have discovered that the process is especially advantageous when applied to the treatment of silica-alumina catalysts manufactured by forming a silica-alumina hydrogel; i. e., combining precipitated hydrated silica gel and precipitated hydrated alumina gel without drying the gels. These catalysts may be manufactured by processes including precipitating one

hydrogel in the presence of the other as by co-precipitating the gels, separately precipitating the hydrogels and combining the undried hydrogels, or by first precipitating the silica hydrogel and then forming the silica-alumina hydrogel by precipitating a gel or gelatinous precipitate of alumina in the presence of the silica hydrogel. The combined gels are then dried, pelleted, if pellets are desired, and then usually calcined in the manner described above in connection with the natural catalyst. These catalysts are usually made from raw materials containing alkali metals, and it is the normal practice to remove such metals from the gels either before or after drying by treatment with an acid or a material that has base exchange properties such as ammonium hydroxide or ammonium chloride.

Synthetic silica-alumina cracking catalysts of the class described above are composite materials which are referred to as calcined composites of undried hydrous silica and alumina gels. The materials are amorphous and reasonable variation in the proportions of silica and alumina does not materially affect their properties, indicating that they are not true chemical compounds, yet there appears to be some sort of union resulting from combining the hydrous gels which is not readily possible when silica and alumina are combined by other methods. The more important catalysts contain a greater proportion of silica than alumina; preferably they contain about 80 to 95 per cent by weight silica and especially about 85 to 90 per cent.

Catalysts having somewhat similar characteristics can be prepared by precipitating a silica hydrogel, drying this gel, and then combining the resulting dry silica gel with alumina in a form which is generally referred to and is referred to herein as the hydrogel but which may be a gelatinous precipitate of aluminum hydroxide. This may be done by mixing the silica gel with a solution of a soluble aluminum salt such as aluminum nitrate and then precipitating the alumina hydrogel by treating the resulting mixture with an alkaline material, preferably ammonium hydroxide.

The boric acid may be applied to the permanently deactivated catalyst by pouring a solution of boric acid over the catalyst. The preferred method for treating catalysts disposed in a fixed bed, however, is vacuum impregnation of a catalyst. While vacuum impregnation of the deactivated catalyst is the preferred method for fixed-bed catalysts, other methods such as impregnation at atmospheric or superatmospheric pressure with a solution of boric acid followed by a procedure to decompose the boric acid give satisfactory results. The decomposition of the boric acid may be accomplished by drying the impregnated catalyst at a temperature below the decomposition point (approximately 185° C.) of the boric acid followed by raising the temperature above the decomposition point, for example, to a temperature in the range where it is to be used in the hydrocarbon conversion and regeneration processes. The drying process can be performed at atmospheric, subatmospheric, or superatmospheric pressure.

We have found in accordance with the invention that the effect of treating a permanently deactivated silica-alumina catalyst with a solution of boric acid varies depending upon the amount of boria deposited on the catalyst. Thus the present invention offers a means of obtaining different types of reactivation. We have

found when maximum gasoline production is desired, it is preferable to accomplish the reactivation by treating the permanently deactivated catalyst with a solution of boric acid in an amount equivalent to that necessary to produce a reactivated catalyst containing between about 4 and 8 per cent by weight of boria. In certain cases it is desirable to reduce the production of coke and gas to the minimum while at the same time obtaining a reasonable yield of gasoline. We have found, for example, that by reactivating a permanently deactivated cracking catalyst with a solution of boric acid in an amount equivalent to that necessary to produce a reactivated catalyst containing between about 8 and about 12 per cent by weight of boria, a catalyst is obtained which produces when employed in the cracking operation a somewhat lower yield of gasoline than when a catalyst containing between about 4 and 8 per cent by weight of boria is used, but the production of gas and coke is at an exceptionally low level. In other words, when a reactivated catalyst contains between about 8 and about 12 per cent by weight of boria, the use of the catalyst in a catalytic cracking process results in an operation involving very little conversion of the charge material to relatively useless products. Less than 4 per cent of boria deposited on a permanently deactivated catalyst produces a catalyst having a greater activity than the permanently deactivated catalyst but optimum activity is obtained at about 4 to 8 per cent. Depositing more than 12 per cent of boria on the catalyst is generally undesired because better results are obtained with less boria. In many cases, the yield of gasoline obtained by the use of a catalyst containing more than 12 per cent boria in a cracking process is not substantially better than the yield obtained by the permanently deactivated catalyst. When as much as 12 per cent or more of boria is deposited on the permanently deactivated catalyst, however, the production of gas and coke is reduced to a very low value. In accordance with the preferred embodiment of our invention, however, we deposit not more than about 12 per cent by weight of boria on the catalyst.

The invention also involves the surprising discovery that the yield of gasoline increases while the yield of gas plus coke simultaneously decreases, so long as the boria deposit on the catalyst is not greater than about 6 per cent by weight of the catalyst.

The following examples will serve to illustrate the practice of the invention. The gas plus coke yields given in certain of the examples were determined by the difference between the oil charged and the total liquid recovery, as we have found this to be a simple and accurate way to compare the gas and coke producing properties of catalysts. The deviation from the actual yields is small, of the order of one or two per cent greater, and the deviation is substantially constant from one run to another.

Example I

197.3 parts by weight of permanently deactivated silica-alumina catalyst containing about 12 per cent by weight of alumina was treated as described below. The catalyst had been deactivated by being used in a commercial fixed-bed unit for about 18 months. This catalyst was a commercial material prepared by co-precipitating hydrous silica and alumina gels containing sodium, drying the combined gels, base exchanging the

dried gels with ammonium hydroxide, pelleting and calcining. This catalyst was calcined in preparation for reactivation by heating the body of catalyst to about 1000° F. in 6 hours and main-

results for a fresh and a permanently deactivated catalyst of the type used in Example I and for re-activated catalysts containing various percentages of boria deposit on the catalyst.

Catalyst	Treating Agent	Boria Deposit, Wt. Per Cent	Yields, Wt. Per Cent	
			Gasoline	Gas + Coke
Fresh Catalyst.....	-----	0	30.1	13.1
Permanently Deactivated Catalyst.....	-----	0	21.4	9.7
Reactivated Catalyst.....	2.5% aqueous solution of H_3BO_3	1.0	24.6	9.6
Do.....	8.1% aqueous solution of H_3BO_3	3.3	26.7	8.2
Do.....	13.0% aqueous solution of H_3BO_3	5.5	28.8	7.6
Do.....	14.7% aqueous solution of H_3BO_3 at 76° C.....	5.8	29.9	8.4
Do.....	18.4% aqueous solution of H_3BO_3 at 95° C.....	7.4	29.0	7.5
Do.....	21.4% aqueous solution of H_3BO_3 at 90° C.....	9.1	25.9	6.8
Do.....	23.8% aqueous solution of H_3BO_3 at 95° C.....	11.4	23.7	4.4

taining this temperature for about 10 additional hours. During this time a stream of air was passed over the catalyst. When the catalyst had cooled to room temperature it was subjected to a vacuum of 8 mm. of mercury for about 20 minutes. There was then added a quantity of a 13.0 per cent aqueous solution of boric acid sufficient to cover the catalyst, and this was allowed to stand for about 5 minutes under the vacuum conditions, and then the pressure was raised to atmospheric and the material allowed to stand for another 10 minutes. The excess boric acid solution was allowed to drain off. The catalyst was weighed and found to have increased to 355 parts indicating that 157.7 parts by weight of boric acid solution had been adsorbed. Upon calculation from the concentration of the solution it was found that the 197.3 parts of permanently deactivated catalyst had adsorbed 11.53 parts calculated as B_2O_3 .

The treated catalyst was then dried for about 19 hours at about 250° to 260° F. followed by a calcining treatment comprising raising the temperature to about 1000° F. in about 6 hours and maintaining this temperature for an additional 10 hours. The catalyst was again weighed and found to comprise 208.9 parts by weight, showing that it now contained 11.6 parts or 5.5 per cent of boria deposit.

Following the deposition of boria the reactivated catalytic material was tested by passing one volume of 37.4° A. P. I. gravity Pennsylvania gas oil, boiling over the range from 458° to 676° F. in one hour, through a tube containing one volume of catalyst at 841° F. The gasoline yield in weight per cent of charge was found to be 28.8 per cent and the gas plus coke yield 7.6 per cent. When the untreated permanently deactivated catalyst was tested for cracking activity in the manner described above, a gasoline yield of 21.4 per cent and a gas plus coke yield of 9.7 per cent were obtained. Thus, there was a substantial reactivation by the herein described treating process.

Example II

A series of runs were made in which the permanently deactivated catalyst of the type used in Example I was reactivated with various percentages of boria deposited on the catalyst. The impregnation procedure for this series of runs was similar to that described in Example I. However, when impregnating with solutions containing above about 13 per cent of boric acid, it was necessary to use an impregnating temperature of about 75° to 95° C. instead of room temperature because of the limited solubility of boric acid in water. The following table shows conversion

When the above data are plotted in a graph, it can be seen that optimum yields of gasoline are obtained when the boria deposit is maintained between about 4 and 8 per cent, the peak of the curve being at about 6 per cent. The data show that the yield of gas plus coke is exceptionally low when the boria deposit is between about 8 and 12 per cent, the yield at 11.4 per cent boria deposit being only 4.4 per cent. The data show further that up to about 6 per cent of boria deposit, the yield of gasoline is increased while the yield of gas plus coke is simultaneously decreased.

Example III

This example illustrates the reactivation of the permanently deactivated catalyst described in Example I but using alcoholic solutions of boric acid as the reactivating agent. Following a procedure similar to that described in Example I but using a 22.7 per cent methanol solution of boric acid, a deposition of 4.5 per cent B_2O_3 was effected. When this catalyst was tested under conditions similar to those described in Example I, yields of 27.0 per cent gasoline and 6.8 per cent gas plus coke were obtained. When a 22.0 per cent ethanol solution of boric acid was employed as the impregnating agent, a deposition of 1.7 per cent B_2O_3 was effected. This catalyst gave a 25.3 per cent yield of gasoline and a 6.5 per cent yield of gas plus coke.

Example IV

This example illustrates the reactivation of the permanently deactivated catalyst described in Example I but using a 15.2 per cent glycerin solution of boric acid as the impregnating agent. When this agent was used, a deposition of 6.6 per cent of B_2O_3 was effected. When the catalyst was tested under conditions similar to those described in Example I, yields of 25.7 per cent gasoline and 5.4 per cent gas plus coke were obtained.

It will be understood that the foregoing examples are merely illustrative of the invention and that advantageous results can be obtained by treating others of the class of silica-alumina catalysts by the procedures described. The catalysts to be reactivated in accordance with the invention can be treated in the form in which they were employed in use, such as pellets, granules, beads, powder, and the like. For example, the silica-alumina catalyst available commercially in the form of beads can be reactivated effectively by the present process.

Throughout this specification we have referred to permanently deactivated catalysts. This description has come to be applied to catalysts that have lost any of their initial activity and that

cannot be restored to their initial activity by regeneration. The term "spent catalysts" is sometimes used to mean the same thing as "permanently deactivated catalysts," but a spent catalyst is more properly a catalyst that has been permanently deactivated to a stage such that it is no longer usable in commercial operations. The term "permanently deactivated catalysts" properly includes not only spent catalysts but also catalysts that have lost only a part of their initial activity. As previously pointed out, the present reactivation treatment may be employed to maintain the activity of a catalyst. For example, in fixed-bed operations the catalyst may be treated as herein described long before the activity of the catalyst has fallen to a point where replacement of the catalyst is normally indicated. The invention is particularly advantageous, however, in reactivating a catalyst which has lost at least 25 per cent of its initial activity.

Our invention may be applied to the reactivation of catalysts used in moving-bed type operations as well as fluid-type catalytic cracking processes. However, our invention is particularly advantageous when applied to fixed-bed operations in that the catalyst can be reactivated without removing the catalyst from the cracking chamber.

It will be understood that where catalyst surfaces are referred to herein the interior or pore surfaces as well as the exterior surfaces of the catalyst are intended.

While the foregoing discussion has referred only to boric acid as the impregnating agent for boria, it should be understood that any compound yielding boron oxide on decomposition may be used. For example, an organic or inorganic boron compounds such as an alkyl boric acid, an aryl boric acid, boron chloride, or an alkali metal borate may be used. The decomposable boron compound can be applied in the form of a vapor, liquid, or solution. Decomposition may be accomplished by heating or with the use of a hydrolyzing agent. Naturally, the treatment applied to the permanently deactivated catalyst, particularly in fixed-bed operations, may vary depending upon the type of compound used to deposit the boria on the catalyst surface.

Obviously many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. The method of reactivating a calcined permanently deactivated silica-alumina cracking catalyst consisting essentially of silica and alumina and comprising a major proportion of silica and a minor proportion of alumina which has been permanently deactivated in use, which comprises impregnating the surface of said catalyst with a fluid compound yielding boria upon thermal decomposition in an amount sufficient to produce a reactivated catalyst, and thermally decomposing said impregnant compound into boria.

2. A method in accordance with claim 1 in which the compound yielding boria upon decomposition is a solution of boric acid.

3. A method in accordance with claim 2 in which the solution of boric acid is an aqueous solution.

4. The method of reactivating a calcined permanently deactivated synthetic silica-alumina cracking catalyst consisting essentially of silica

and alumina and comprising a major proportion of silica and a minor proportion of alumina which has been prepared by combining undried alumina hydrogel with silica gel and which has been permanently deactivated in use, which comprises impregnating the surface of said catalyst with a fluid compound yielding boria upon thermal decomposition in an amount sufficient to produce a reactivated catalyst, and thermally decomposing said impregnant compound into boria.

5. The method of reactivating a permanently deactivated synthetic silica-alumina cracking catalyst consisting essentially of silica and alumina and comprising a major proportion of silica and a minor proportion of alumina in the form of a calcined composite of undried silica and alumina hydrogel which has been permanently deactivated in use, which comprises impregnating the surface of said catalyst with a fluid compound yielding boria upon thermal decomposition in an amount sufficient to produce a reactivated catalyst, and thermally decomposing said impregnant compound into boria.

6. A method in accordance with claim 5 in which the compound yielding boria upon decomposition is a solution of boric acid.

7. A method in accordance with claim 6 in which the solution of boric acid is an aqueous solution.

8. The method of reactivating a calcined permanently deactivated synthetic silica-alumina cracking catalyst consisting essentially of silica and alumina and comprising a major proportion of silica and a minor proportion of alumina which has been prepared by combining alumina hydrogel with silica gel and which has been permanently deactivated in use, which comprises impregnating said permanently deactivated catalyst with a solution of boric acid in an amount equivalent to that necessary to produce a reactivated catalyst containing not more than about 12 per cent by weight of boria, heating said catalyst impregnated with said boric acid to decompose said boric acid and produce a catalyst containing not more than about 12 per cent by weight of boria, and calcining the resulting boria-containing catalyst.

9. The method of reactivating a calcined permanently deactivated silica-alumina cracking catalyst consisting essentially of silica and alumina and comprising a major proportion of silica and a minor proportion of alumina which has been prepared by combining alumina hydrogel with silica gel and which has been permanently deactivated in use, which comprises impregnating said permanently deactivated catalyst with an aqueous solution of boric acid in an amount equivalent to that necessary to produce a reactivated catalyst containing between about 4 and 8 per cent by weight of boria, heating said catalyst impregnated with said boric acid to decompose said boric acid and produce a catalyst containing between about 4 and 8 per cent by weight of boria, and calcining the resulting boria-containing catalyst.

10. The method of reactivating a calcined permanently deactivated silica-alumina cracking catalyst consisting essentially of silica and alumina and comprising a major proportion of silica and a minor proportion of alumina which has been permanently deactivated in use, which comprises impregnating the surface of said catalyst with a fluid compound yielding boria upon thermal decomposition in an amount equivalent to that necessary to produce a reactivated catalyst

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containing not more than about 12 per cent by weight of boria, and thermally decomposing said impregnant compound into boria.

11. The method of reactivating a calcined permanently deactivated synthetic silica-alumina cracking catalyst consisting essentially of silica and alumina and comprising a major proportion of silica and a minor proportion of alumina which has been prepared by combining undried alumina hydrogel with silica gel and which has been permanently deactivated in use, which comprises impregnating the surface of said catalyst with a fluid compound yielding boria upon thermal decomposition in an amount equivalent to that necessary to produce a reactivated catalyst containing not more than about 12 per cent by weight of boria, and thermally decomposing said impregnant compound into boria.

12. The method of reactivating a calcined permanently deactivated synthetic silica-alumina cracking catalyst consisting essentially of silica and alumina and comprising a major proportion of silica and a minor proportion of alumina in the form of a calcined composite of undried

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silica and alumina hydrogel which has been permanently deactivated in use, which comprises impregnating the surface of said catalyst with a fluid compound yielding boria upon thermal decomposition in an amount equivalent to that necessary to produce a reactivated catalyst containing not more than about 12 per cent by weight of boria, and thermally decomposing said impregnant compound into boria.

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