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[54] CHLORIDE ADDITION DURING HYDROGENATION

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[58] **Field of Search** 208/143, 144; 260/683.9

[56] **References Cited**

UNITED STATES PATENTS

3,085,971	4/1963	Mooi et al.	208/143
3,125,511	3/1964	Tupman et al.	208/143
3,144,404	8/1964	Tyson	208/143
3,422,001	1/1969	Kouwenhoven et al.	208/143
3,457,162	7/1969	Riedl et al.	208/143

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[57] ABSTRACT

A process for hydrogenation of an unsaturated hydrocarbon feedstock at an elevated temperature and pressure in a hydrogenation zone by (a) contacting the feedstock, in the presence of hydrogen, with a hydrogenating catalyst containing at least one noble metal on an alumina support and containing no essentially irreversibly sulfided metal (such as nickel, cobalt, or molybdenum), and (b) adding a chloride to the hydrogenation zone and reacting the chloride with the catalyst in an amount sufficient to increase hydrogenation activity of the catalyst.

7 Claims, No Drawings

CHLORIDE ADDITION DURING HYDROGENATION

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to the hydrogenation of unsaturated hydrocarbons by means of a noble metal catalyst.

2. Prior Art

The hydrogenation of unsaturated hydrocarbons and hydrocarbon mixtures by bringing them together with hydrogen into contact with a noble metal catalyst or a catalyst-containing group VI or group VIII metals is a well-known art. The hydrogenation of unsaturated hydrocarbons is carried out at elevated temperatures and pressures, generally within the range of about 400°–900° F., and 200–5,000 p.s.i.g., respectively. More usually, the hydrogenation is carried out at temperatures between about 550° and 700° F. and pressures between about 500 and 2,000 p.s.i.g.

The hydrogenation of aromatics by means of the aforementioned catalyst is applied to the products of the petroleum industry for several purposes. For example, hydrogenation is used for the preparation of cyclohexane from crude benzene, for the improvement of smoke point of kerosene, for increase in the specific combustion heat of fuels for jet engines, as well as for improvement of lubricating oil properties.

It is particularly desirable at the present time to improve existing hydrogenation processes which are used to upgrade kerosene feedstocks to high grade jet fuel. One of the basic criteria used to determine the suitability of a fuel for use as a jet fuel is the smoke point of the fuel. With a high aromatics content, the fuel will have a relatively low smoke point and will be deemed unsatisfactory as a jet fuel. By hydrogenation, aromatics present in kerosene distillates can be converted to naphthenes to raise the smoke point of kerosene distillate and thereby obtain a satisfactory jet fuel. The hydrogenation process upgrades the kerosene distillate in other respects also; but the conversion of aromatics to naphthenes is usually of primary importance. The term kerosene is used herein to mean a hydrocarbon mixture boiling within the range 250° to 600° F.

In the past, reforming catalysts have been treated with halide compounds to improve the hydrocracking activity of the reforming catalyst. See, for example, U.S. Pat. No. 2,742,382. The reforming reaction is basically different from a hydrogenation reaction in that reforming is conducted at higher temperatures than hydrogenation, and reforming basically involves dehydrogenation of hydrocarbons, whereas hydrogenation, of course, basically involves hydrogenation of hydrocarbons.

Based on the prior art, one would not expect that the addition of chloride to the hydrogenation catalyst during a hydrogenation reaction would be desirable. U.S. Pat. No. 2,642,384, for example, teaches that it is advantageous to add chloride when reforming hydrocarbons, i.e., converting naphthenes to aromatics, etc. U.S. Pat. No. 3,642,384 teaches that the chloride addition is advantageous in that it tends to raise the hydrocracking activity of the reforming catalyst. Chloride addition is also known to increase the activity of reforming catalysts for dehydrocyclization of paraffins. However, hydrocracking and dehydrocyclization basically are not desired in a hydrogenation reaction. As pointed out in U.S. Pat. No. 3,269,938, selectivity of a hydrogenation catalyst is interfered with by concomitant reactions such as hydrocracking. The hydrocracking reaction is undesirable according to U.S. Pat. No. 3,269,938 because it leads to lower yield of the desired hydrogenation product.

Thus, it can be seen from the prior art that, although catalysts have been subjected to treatment with halogens before, the purpose has been in general to promote the acidic character of the catalyst so that the catalyst would perform better in hydrocracking reactions.

U.S. Pat. No. 3,422,001 discloses that if hydrogen chloride treatment of a sulfided catalyst is carried out during the sulfiding step, or applied when the hydrogenation metal component is already present in sulfide form, then the hydrogenation activity of the sulfided catalyst is increased by the hydrogen chloride treatment and under the usual hydrogenation conditions, undesirable side reactions such as cracking do not occur to a higher degree than without the hydrogen chloride treatment. U.S. Pat. No. 3,422,001 is directed to sulfided catalysts such as sulfided nickel or cobalt or molybdenum or tungsten. The aforementioned metals form relatively stable sulfide compounds on the catalyst such as nickel sulfide or cobalt sulfide.

As pointed out in U.S. Pat. No. 3,054,833, nickel, for example, reacts with hydrogen sulfide to form nickel sulfide and the reaction is only partially reversible. On the other hand, platinum reacts somewhat with hydrogen sulfide to form platinum sulfide, but this reaction is readily reversible, so that, particularly in a hydrogen atmosphere, the platinum sulfide will revert to the unsulfided form. Platinum sulfide also tends to revert to the unsulfided form at the relatively high temperatures under which hydrogenation is effected. Other noble metals, as, for example, palladium, iridium, rhodium, ruthenium, etc., are believed to be similar to platinum in this respect; that is, they are present, in a hydrogenation catalyst operating under hydrogenation conditions, mostly in an unsulfided state in contrast to the sulfided state of nickel, cobalt, etc., as in U.S. Pat. 3,422,001.

U.S. Pat. No. 3,422,001 further teaches that, if the hydrogen chloride treatment is performed in a stage of the catalyst preparation when the metals are not present as the sulfide, little or no effect of the hydrogen chloride treatment on the hydrogenating activity of the catalyst is obtained.

Thus, it is seen that the prior art basically teaches that halogens are added to reforming catalysts to increase the hydrocracking and cyclization activity of the catalyst. However, hydrocracking and cyclization are basically not desired during a hydrogenation reaction. The prior art teaches that hydrogenation chloride treatment can improve hydrogenation activity of a hydrogenation catalyst only if the hydrogenation chloride treatment is carried out with respect to a sulfided catalyst. The sulfided catalyst is formed by sulfiding a hydrogenation catalyst containing nonnoble metals, such as nickel or cobalt. The noble metal hydrogenation catalysts exist primarily in the unsulfided state under hydrogenation conditions, particularly in the case of the noble metal platinum, as platinum tends to exist in the unsulfided state under the elevated temperatures and high hydrogen partial pressure used for hydrogenating hydrocarbons.

SUMMARY OF THE INVENTION

According to the present invention, a process is provided for hydrogenation of an unsaturated hydrocarbon feedstock at an elevated temperature and pressure in a hydrogenation zone by: (a) contacting the feedstock in the presence of hydrogen with a hydrogenating catalyst comprising at least one noble metal and alumina and containing essentially no metals from group VI or group VIII (excepting noble metals), and (b) adding a chloride to the hydrogenation zone and reacting the chloride with the catalyst in an amount sufficient to increase hydrogenation activity of the catalyst.

A particularly preferred catalyst for use in the process of the present invention is a catalyst comprising platinum and alumina.

We have found that it is particularly desirable to increase the chloride content of a noble metal hydrogenation catalyst by adding a chloride compound or compounds to the hydrogenation zone while the hydrogenation reaction is being carried out. The process of the present invention is particularly advantageously applied to reactions such as the hydrogenation of aromatics to form naphthenes and is particularly advantageously applied to the hydrogenation of unsaturated hydrocarbon feedstocks to form improved jet fuels. Thus, the process of the present invention is advantageously applied to the hydrogenation of a kerosene distillate or heavy gasoline distillate to form a jet fuel of greatly improved smoke point, as, for example, a smoke point of 20 mm. or higher.

In the operation of the process of the present invention, the chloride compound may be added to the feedstock to the hydrogenation zone or it may be added directly to the hydrogenation zone. The chloride compound can be added continuously, but usually it is more preferable to add the halide compound intermittently as needed to achieve satisfactory hydrogenation, for example, to hydrogenate a kerosene feedstock to a smoke point of 20 mm. or better. Analytical data on the hydrogenation zone and the product from the hydrogenation zone can be used to gauge the requirement for chloride and, in certain instances, it is advantageous to periodically remove a portion of the hydrogenation catalyst from the hydrogenation zone, using a catalyst sampler so that the catalyst may be analyzed for chloride content.

An important feature of the present invention is that the chloride is added to the catalyst during hydrogenation service rather than to the catalyst when the catalyst is being manufactured. Numerous chloride compounds are satisfactory for introduction to the hydrogenation zone together with the feed, or for introduction to the hydrogenation zone in some other manner. For example, propylene dichloride can be used. In most instances there is at least some water present in the feed to the hydrogenation zone. The water will tend to remove or cause chloride to be lost or stripped from the hydrogenation catalyst. However, the process of the present invention requires the addition of chloride to the catalyst in the hydrogenation zone while the hydrogenation reaction is in progress. Therefore, loss of some of the chloride during the hydrogenation operation is compensated for by the addition of new chloride. Furthermore, chloride addition in accordance with the present invention has the advantage that in some instances a slight amount of water is desired in the feed to improve the selectivity of the hydrogenation catalyst for certain hydrogenation reactions catalyzed by the platinum-alumina chloride catalysts, and the chloride added during operation pursuant to the present invention will maintain or allow an increase in chloride content of the hydrogenation catalyst even though water is present in the feed to the hydrogenation zone.

The process of the present invention is preferably applied to hydrogenation of feedstocks containing a relatively small amount of sulfur as, for example, less than 0.5 weight percent sulfur. It is particularly advantageous to carry out the process of the present invention substantially in the absence of sulfur compounds as, for example, in the case of hydrogenation of feedstock containing less than about 0.01 percent sulfur by weight, and still more preferably, less than 10 parts per million sulfur by weight.

Also, in accordance with the present invention, chloride is added to the hydrogenation catalyst during the hydrogenation reaction. Thus, the present invention is to be distinguished from hydrogenation processes using fluorided catalysts and, particularly, the present invention is to be distinguished from processes using catalysts having 10 weight percent fluoride or more for hydrogenation in the presence of substantial amounts of sulfur, such as in U.S. Pat. No. 3,435,085.

EXAMPLE

A kerosene feedstock having an ASTM D-86 boiling range of about 300° to 490° F. was first hydrotreated to clean up the feed, that is, to reduce sulfur and nitrogen compounds present in the kerosene feedstock. The hydrotreated kerosene feedstock had a smoke point of 9 mm. and was a particularly difficult stock for hydrogenation as it contained 60.1 percent aromatics even after hydrotreating. The naphthene and paraffin content of the kerosene feedstock was 23.2 and 16.7 percent, respectively.

Hydrogenation of the kerosene feedstock was carried out over a platinum-on-alumina catalyst which contained about 0.3 weight percent chloride, 0.75 weight percent platinum and the balance alumina. The catalyst had previously been used in reforming service at very high temperatures (about 925° F.). Operating conditions used in the hydrogenation of the kerosene feedstock included an average catalyst temperature of 630° F., pressure of 685 p.s.i.g., liquid hourly space velocity (LHSV) of 1.05, gas rate in standard cubic feet of hydrogen per barrel of feed of 10,000, and hydrogen partial pressure in the hydrogenation reactor of about 600 p.s.i.a. The hydrogen consumption was about 1,200 standard cubic feet per barrel of feed. Table I tabulates the very advantageous results obtained by adding chloride to the hydrogenation catalyst during hydrogenation operation.

TABLE I

	Aniline Point	Aromatics	Smoke Point
Kerosene Feedstock	60° F.	≈60 %	≈9 mm.
Base Period (before C1 addition)	122	≈22	≈18
Add 0.3wt. % C1	125	≈16	≈20
Add 2nd. increment of 0.3 wt. % Cl	131	≈11	≈32

As can be seen from table I above, the addition of chloride greatly improves the hydrogenation of the kerosene feedstock. The smoke point of the kerosene feedstock was raised from about 9 mm. to 18 mm. by the basic hydrogenation reaction, but the first 0.3 weight percent increment of chloride gave an unexpected further improvement of 2 mm. and the second increment surprisingly gave a still further improvement to raise the smoke point up to about 22 mm. The chloride content was thus increased from the initial approximately 0.3 weight percent to about 0.9 weight percent by the addition of chloride to the hydrogenation zone catalyst by admixture of a chloride compound with the kerosene feedstock. As can be seen from table I, the aromatics were reduced more than 50 percent by the addition of 0.6 weight percent chloride to the hydrogenation catalyst during hydrogenation operation.

Although various specific embodiments of the invention have been described, it is to be understood that they are meant to be illustrative only and not limiting. Certain features may be changed without departing from the spirit or essence of the invention. It is apparent that the present invention has broad application to hydrogenation of unsaturated hydrocarbons, using a noble metal-containing catalyst to which chloride has been added during the hydrogenation reaction. Accordingly, the invention is not to be construed as limited to the specific embodiments illustrated, but only as defined in the appended claims.

We claim:

1. A process for hydrogenation of an unsaturated hydrocarbon feedstock in a hydrogenation zone which comprises:
   a. contacting the feedstock, at elevated temperature and pressure and in the presence of hydrogen, with a hydrogenating catalyst consisting essentially of at least one noble metal and alumina; and
   b. adding a chloride to the hydrogenation zone and reacting the chloride with the catalyst in an amount sufficient to increase hydrogenation activity of the catalyst and to maintain at least about 0.3 weight percent chloride on the catalyst.

2. A process in accordance with claim 1 wherein the catalyst comprises platinum and alumina.

3. A process in accordance with claim 1 wherein the chloride is continuously introduced to the hydrogenation zone in admixture with the unsaturated hydrocarbon feedstock.

4. A process in accordance with claim 1 wherein the chloride is intermittently introduced to the hydrogenation zone as the catalyst exhibits decreased hydrogenation activity.

5. A process in accordance with claim 1 wherein sufficient chloride is added to the hydrogenation zone to maintain at least about 0.9 weight percent chloride on the hydrogenation catalyst.

6. A process in accordance with claim **1** wherein the feedstock to the hydrogenation zone contains less than 0.5 weight percent sulfur.

7. A process in accordance with claim **1** wherein the feedstock to the hydrogenation zone contains less than 0.01 weight percent sulfur.

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