

1

2,776,934

HYDROGENATION OF SULFUR-CONTAMINATED OLEFINS

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No Drawing. Application November 27, 1951, Serial No. 258,503

1 Claim. (Cl. 196--78)

The present invention relates to hydrogenation of olefinic hydrocarbons and is particularly concerned with the conversion of such olefinic hydrocarbons in a gasoline or naphtha charge stock, to thereby improve the quality of such stock and without substantial adverse effect on other hydrocarbons present in the charge.

Previously known processes for hydrogenation of olefins in the gasoline boiling range include the production of hydrocarbons for use as a high octane blending agent in aviation gasoline, and the hydrogenation of cracked naphthas. These known processes were carried out either over sulfur-resistant catalysts at high pressures (in the order of 3000 p. s. i. g.) or over sulfur-sensitive nickel catalysts at relatively low pressure (as up to about 200 p. s. i. g.). In the latter case the catalyst became rapidly deactivated requiring frequent regeneration, and even with such regeneration the useful life of the catalyst was of comparatively short duration. While high pressures are considered to favor hydrogenation, such advantage is largely offset by the increased complexity and cost of high pressure operation.

In catalytic hydrogenation of olefins carried out at low pressure and at moderate temperatures, metallic catalysts have been employed, particularly those comprising elements from Group VIII of the Periodic Table, which elements are extremely sensitive to the presence of various catalyst poisons, particularly sulfur compounds usually present in petroleum products. In carrying out hydrogenation in the presence of these catalysts, therefore, the hydrocarbon charge must be practically sulfur-free.

In accordance with the present invention the hydrogenation of olefins in about the gasoline boiling range, and of charge stocks containing the same, is effected in the presence of platinum catalyst under selected operating conditions, particularly temperatures of at least 750° F., such that the catalyst is not susceptible to material deactivation by the presence of sulfur compounds in the charge. The process can be effectively carried out, moreover, without resort to elevated pressures.

Typical operations for the conversions of olefinic hydrocarbon charge over platinum catalyst by the present process, include temperatures in the range of about 750-1000° F., space velocity of from about 0.2 to 10.0 volumes of oil per hour per volume of catalyst, with the addition of at least one mol and up to 10 or more mols hydrogen per mol of oil charged. While atmospheric pressure can be employed, slightly higher pressures as up to about 100 pounds per square inch may be used, if desired, without adverse effect.

Under the above conditions of operation, olefinic compounds present in the charge are selectively hydrogenated, without accompanying undesired hydrogenation of any aromatics which may be present. A portion of the olefins present in the initial charge may also be partly isomerized to branch chain compounds thereby further improving the octane value of the product.

The catalyst utilized comprises 0.05 to about 2.0

2

weight percent platinum, preferably not more than about 1% thereof on a base or carrier that displays little or no tendency to promote cracking or polymerization reactions and which has a comparatively high surface area over which the platinum is distributed. If selective hydrogenation of the olefins is desired with little or no isomerization of the base should be substantially inactive, and may be composed of magnesia. Catalysts having a moderate isomerization activity are exemplified by alumina which has been treated with a compound of an element of groups Ia and IIa of the periodic table (hereinafter referred to as alkali and alkali earth metal), preferably a magnesium compound, to impregnate the alumina with 0.1 to 2.0% alkali or alkali earth metal oxide, prior to the incorporation of the platinum. Such impregnation reduces any cracking promoting activity of the base. Another form of specially treated alumina as a support for platinum, which has proved successful in the process of the invention, is activated alumina which has been given a mild acid leaching, as with acetic acid. Such acid treatment improves the isomerization activity of the catalyst without undesirably increasing activity in promoting cracking of hydrocarbons thereby. Bases composed of silica-alumina are known to promote cracking and polymerization reactions; these may be employed in the present process however, if specially treated to inactivate or reduce cracking activity, as for instance by heat or steam treatment at temperatures above 1200° F. and short of temperatures at which the surface area of the base is caused to be reduced to less than about 20 square meters per gram. While the isomerization function of these silica-alumina bases is thus largely retained, acid-treated alumina is preferred in the present process. Instead of platinum there may be employed other noble metals of the platinum family, particularly palladium, but not necessarily with equal result; generally such other metal should be used in higher proportions than the platinum, as up to about 5% by weight of the carrier.

Impregnated alumina carriers are prepared by incorporating 0.1 to 2.0% alkali earth oxide in gamma alumina or in an activated alumina of commerce. Larger amounts of the alkali earth oxide may be employed, as up to about 5% by weight of the supports but no particular advantage has been found for the increased earth oxide content. The impregnation of the support is effected by dipping the alumina in an aqueous solution of a soluble alkali earth metal salt of sufficient concentration to deposit the required quantity of oxide in the support. Such impregnation may be effected at ordinary or elevated temperatures and is best carried out in several stages of treatment, the treating solution from each stage being withdrawn and replaced by fresh solution. It may be that the wet treatment with the aqueous salt solution, particularly in the case of magnesium salts, in itself has an effect on modifying the characteristics of the alumina in addition to the properties conferred by the presence of the magnesia or other alkali earth oxide in the ultimate catalyst.

Acid treatment of alumina is preferably carried out with organic carboxylic acid; or inorganic acids may be employed, such as hydrochloric, care being taken to subsequently remove all halide by washing or otherwise. The amount and concentration of acid ordinarily is such that under the treating conditions not more than 10% and preferably not more than about 5% of the alumina is leached out thereby. Following acid treatment, the alumina is generally washed with water to remove soluble materials and dried, the extent of the water washing depending upon whether or not it is necessary to wash the product free of the anion of the particular acid or acid-reacting salt employed. The dried alumina is then

calcined to remove combined water and volatiles, and is impregnated with the dehydrogenating metal component.

The calcined alumina support, whether impregnated or acid treated as above described, is then dipped in an aqueous solution of a decomposable compound of the noble metal of sufficient concentration to provide the desired quantity of metal in the finished catalyst and then heated or otherwise treated to effect conversion of the metal compound to the free metal, or to an oxide thereof reducible to a free metal. Suitable treating solutions include, for example, aqueous solutions of chloropalladic and chloroplatinic acid of suitable concentration to deposit the required quantity of noble metal in the carrier. Transformation of the deposited noble metal compound to free metal may be effected by heating alone or by treatment at elevated temperature with a reducing gas, such as hydrogen.

The alumina support may be in the form of irregular lumps or granules of desired size range, but is preferably in the form of bodies of more regular shape and size, such as spherical beads, or tablets or pellets of cylindrical or other shape. It is preferred that the alumina be not heated to temperatures sufficiently high to effect transformation thereof to so-called "alpha" form.

Coke formation in the hydrogenation process is quite low, so that the process can be operated continuously over comparatively long on-stream periods without necessitating regeneration of the catalyst.

The preparation of preferred catalysts is illustrated in the following examples.

Example I

Commercial activated alumina tablets (Harshaw) were treated with about 5 times their volume of a 20% aqueous solution of $MgCl_2$, passed over the tablets at the rate of about 25 milliliters solution per liter of tablets per minute. The first fifth of the effluent was discarded and the remainder recycled twice over the tablets. The thus treated tablets were then washed in water until free of chloride ion and dried overnight at 180° F. By this treatment any residual alkali metal ion present in the original commercial alumina is considerably reduced in quantity.

An aqueous solution comprising 26.7 grams of chloroplatinic acid (H_2PtCl_6) per liter was then poured over the dried tablets, employing the stated solution in an amount furnishing 24.8 grams of chloroplatinic acid per kilogram of the tablets. The mixture was let stand for ½ hour and excess liquid drained. The thus wetted tablets were then dried in an oven at 180° F. overnight and subsequently treated in a muffle furnace at 1050° for 2 hours to drive off HCl, followed by an additional 2 hour heat treatment in flowing air at the same temperature.

The catalyst thus prepared contained by weight of total catalyst, 0.56% MgO and 0.55% Pt (on 105° C. dry basis).

Example II

Commercial activated alumina pellets (Harshaw) were treated with 10% acetic acid solution for one hour, decanted, and the treatment repeated for another hour with fresh acid of the same concentration, an amount of acid being employed just sufficient to cover the pellets. The treated pellets were then washed a number of times with water, dried at 200° F. and calcined in air at 900° F. The calcined pellets were then dipped for ½ hour in a chloroplatinic acid solution of sufficient strength to give about 0.6% platinum on the finished catalyst. The impregnated catalyst was then dried at 200° F. and calcined at 1050° F. in air for 2 hours. On

analysis the finished catalyst was found to contain 0.5% by weight of platinum.

Example III

A mixture of hexenes in a hydrogen stream was passed at atmospheric pressure over catalyst prepared as described in Example I, at a temperature of 752° F. and at a space velocity of 0.2 volumes per hour per volume of catalyst. The charge contained 4 mols hydrogen per mol of hydrocarbon.

The effluent conversion product was analyzed by chromatographic adsorption in silica gel. The content of the several types of hydrocarbons in the feed as compared with that in the conversion product is shown below:

	Feed, Wt. Percent	Product, Wt. Percent
Aromatics	0	8.0
Olefins	90.7	2.3
Paraffins and Naphthenes	9.3	89.7

The extent of selective conversion of olefins will be appreciated from the comparatively low olefin content of the product. The aromatics formed in the operation apparently resulted in part from dehydrogenation of naphthenes in the charge and to some extent by paraffin or olefin dehydroaromatization.

The catalyst of the type described in Example II, under similar conditions of operation, obtains results substantially similar to that reported above.

The process is applicable to the treatment of gasoline and naphtha fractions containing an appreciable quantity of olefins, such as gasoline obtained in thermal cracking or from upgrading processes involving dehydrogenation. The process is also applicable to such gasolines of appreciable to high aromatic content, such as catalytically cracked gasoline, since under the selected conditions of operation, such aromatic compounds are not hydrogenated. Another important application of the invention is for the hydrogenation of the codimer obtained by the polymerization of isobutylene with other C_4 olefins for production of iso-octanes (hydrocodimer) useful as high quality blending agents in aviation and motor fuel.

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 claim.

I claim:

The method of hydrogenating sulfur-contaminated olefins boiling in the range of gasoline and naphtha which comprises contacting such an olefin with molar excess of hydrogen at a pressure not in excess of 100 pounds per square inch and at a temperature from above 750° F. to about 1000° F., in the presence of a catalyst comprised of 0.05 to 2.0% platinum supported on a carrier consisting of activated alumina which has been impregnated with magnesia.

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