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TREATMENT OF HYDROCARBONS

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This invention relates to the treatment of hydrocarbons of substantially motor fuel boiling range having low antiknock value such as straight-run gasolines and naphthas from paraffinic and naphthenic crude oils or thermally cracked gasolines to improve their antiknock characteristics. The process is also applicable to low boiling hydrocarbons produced from hydrocarbon materials generally including synthetic oils derived from lignites, coals and shales.

More specifically, the invention has reference to a catalytic reforming process which utilizes operating conditions under which no substantial amount of strictly pyrolytic reactions occur. The catalysts are particularly effective in dehydrogenation and also cyclization reactions, and are of importance because of their refractory nature which enables them to retain their catalytic properties for prolonged periods of time under commercial conditions of use and regeneration.

As a general rule, the antiknock value of a hydrocarbon motor fuel mixture increases not only in proportion to its content of olefinic and branched chain hydrocarbons but also in proportion to its content of aromatic compounds. Various other factors also enter in since experiments on pure compounds have shown that their knock rating is also a function of such factors as the number of carbon atoms in a molecule, the position of the double bonds, the degree of saturation of the straight chain and cyclic hydrocarbons, and the presence of other substances in minor amounts which influence the rate of combustion of the fuel. Although the antiknock value may be increased in part as a result of the loss of hydrogen, various other reactions may also occur such as isomerization involving the formation of branched chain hydrocarbons either saturated or unsaturated and the shifting of double bonds, or cyclization and aromatization involving the formation of hydrocarbons of a cyclic character with or without paraffinic and unsaturated side chains.

In one specific embodiment the invention comprises the reforming treatment of hydrocarbon oils boiling substantially within the motor fuel boiling range and having low antiknock value whereby said hydrocarbons are vaporized and subjected to contact with a catalyst comprising essentially an intimate mixture of specially prepared titania supporting an oxide of chromium, whereby a motor fuel of high antiknock value is obtained.

According to the present invention, hydrocarbon fractions boiling substantially within the motor fuel boiling range are contacted with specific catalysts so as to increase the octane number as the result of various hydrocarbon conversion reactions such as cyclization, isomerization, dehydrogenation, hydrogen transfer, desulfurization, and to a minor extent carbon-to-carbon cleavage reactions. In general, paraffinic and naphthenic hydrocarbons are dehydrogenated to produce olefinic and aromatic hydrocarbons and more or less isomerization takes place with the shifting of double bonds and the branching of less branched chain hydrocarbons.

The catalysts used are supported on a titanium oxide carrier. It is necessary that the carrier for a suitable catalyst be of a refractory material which will not sinter or fuse under the high temperature conditions of use and regeneration when in prolonged service in the reforming of the hydrocarbon oils. It is also necessary that the carrier be adaptable to the activating oxides so as to mutually provide the catalytic surfaces promoting the above mentioned desired reactions. The titanium oxide used as a carrier is preferably in a relatively pure state and may be obtained from rutile, ilmenite, or other titanium-containing material. The manufacture thereof is generally known, particularly in connection with the manufacture of paints where titanium oxide has one of its main uses. Titanium oxide prepared as a paint material is one form of titanium oxide preferably used as a carrier for the activating oxides suitable for the reforming of hydrocarbons. It is also advantageous to use the titanium oxide in a fine particle size, particles of $\frac{1}{10}$ to 1 micron for example having been used with good results.

The oxides of chromium include the trioxide CrO_3, the dioxide CrO_2 and the sesquioxide Cr_2O_3. The last named is readily produced by treating the triosice under reducing conditions as in hydrogen containing gas, or in hydrocarbon vapors at temperatures above 250° C. The Cr_2O_3 also results from calcining CrO_3 to varying degrees depending on temperature, time and presence of other materials. The dioxide has been considered to be an equimolecular mixture of the trioxide and the sequioxide. These oxides may be developed readily on the surfaces and in the pores of the carrier granules by impregnating with solutions of chromic anhydride or nitrate to produce primarily the trioxide which is then reduced to the sesquioxide to furnish the active catalyst for use in the present process.

The catalytic oxide preferably used and the relative amounts of the activating oxides and

carriers vary. If too large an amount of the impregnating components is used, the density of the catalyst is increased and the porosity is decreased with a subsequent reduction of catalytically available surface. In the case of chromium sesquioxide Cr_2O_3, which is one of the preferred activating oxides for the reforming reactions when properly supported, various proportions may be used with good results such as from 2 to 30 weight per cent of chromia with respect to titania. Lower and higher percentages of the chromia may give lower catalytic activity.

In the impregnating step, chromium trioxide may be dissolved in water to form a solution used to deposit the desired amount of chromic oxide on the surface and in the pores of the titanium oxide particles after suitable heating. Subsequently, either in use or before using, the chromium trioxide is reduced to the active sesquioxide at temperatures of approximately 500–700° C. In addition to the catalytically active components impregnated into the catalyst a small proportion of stabilizing agent may also be impregnated into the catalyst particles. It has been found that in the prolonged use of this type of catalyst, there is a gradual dropping off of activity due to a change in form of the active material. It has also been found that this tendency can be counteracted by adding small amounts of compounds leading to the formation of metal oxides, more particularly oxides such as those of magnesium and zinc which form spinels. It is believed that double oxides of this type may be formed with the catalyst components at the high temperatures employed in the process which substantially prevent the change of the chromium sesquioxide catalyst to a more inactive form.

The titanium oxide carrier may be impregnated with the activating oxides before it is formed into granules or it may be impregnated after forming into particles. Thus the titanium oxide may be mixed with a lubricant and formed into pellets in a pilling machine, and subsequently heated in air at a temperature of approximately 500° C. to decompose and remove the lubricant. The pelleted material is then impregnated with solutions of the metal compounds which are to be decomposed to produce the activating metal oxides. The titanium oxide carrier may also be shaped into particles by other methods such as extrusion or pressing with subsequent granulation and the particles thus formed impregnated similarly as above. The activating oxides or compounds from which they are produced may also be incorporated into the carrier before it is shaped into particles in which case the heating and calcination after shaping into particles removes any lubricant which may be employed and may also convert the impregnated material into the desired active form for reaction.

The catalyst particles are suitable employed in beds and the hydrocarbons to be treated are vaporized and contacted with the catalyst beds at regulated temperature, pressure and time conditions. The temperature of the catalyst bed is so regulated as to compensate for the endothermic and exothermic conditions occurring during the reaction and reactivation periods. While in use there is a deposition of carbonaceous material upon the catalytic surfaces as a result of secondary reactions. This gradually reduces the catalytic reaction and when the reaction has dropped off materially, the catalyst is regenerated by the oxidation of the carbonaceous materials using an oxygen-containing gas. The temperature is regulated during the burning of these deposits as before indicated so as to avoid heating the catalyst to unnecessarily high temperatures which may gradually reduce its activity. Various means such as regulating the oxygen concentration in the gases and the volume of said gases or removing heat by heat-absorbing means are the more common methods employed.

The hydrocarbon oil fraction which is to be processed is vaporized and subjected to contact with the above catalyst at a temperature of the order of 450–700° C. and under a pressure from substantially atmospheric to approximately 500 pounds or more per square inch. The rate at which the hydrocarbon vapors are passed over the catalyst may vary from approximately 0.1 to 40 volumes of liquid charge per hour per volume of catalyst space in the reactor.

The titanium oxide supported catalyst is not restricted to use as particles in a granular mass since the catalyst can be used as a finely divided powder and contacted with the vapor or disposed in a stream of the hydrocarbon oil to be reformed, and processed under suitable conditions of temperature, pressure and contact time to produce large yields of the desired high antiknock gasoline. The powdered catalyst may then be separated from the high antiknock gasoline and from the adhering oil by various procedures and the separated catalyst is then regenerated by removing hydrocarbonaceous deposits by solvent treatment and/or heating in the presence of air or oxygen-containing gases in order to remove the deposited material. The regenerated catalyst is then used either alone or in mixture with fresh catalyst suspended in the hydrocarbon oil or vapors processed.

The following specific example is given to illustrate the process, a method of catalyst preparation also being given. The process should not be considered as limited to the example nor to the particular catalyst preparation since these are given merely as illustrations of the novelty and utility of the invention.

The titanium dioxide carrier for the catalyst of the following example is a very finely divided titanium dioxide of approximately 99% purity and having an average particle size between 1 and $\frac{1}{10}$ microns. The dry carrier is mixed with a small amount of a hydrogenated vegetable oil lubricant to facilitate pelleting and is formed into $\frac{1}{8}$ by $\frac{1}{8}$ inch cylindrical pellets. The pellets are calcined at a temperature of approximately 500° C. to remove the lubricant. After cooling, the pellets are impregnated with a solution of chromic acid in sufficient proportion and concentration to give ultimately a catalyst having the approximate composition of 8% Cr_2O_3 and 92% TiO_2. The impregnated pills are then dried and calcined at a temperature of approximately 500° C.

A Mid-Continent straight-run naphtha having an end-point of approximately 205° C. and an octane number of 41 was vaporized and preheated to a temperature of approximately 575° C. and contacted with the above described chromium sesquioxide-titania catalyst disposed in a reactor at substantially atmospheric pressure using a liquid space velocity of approximately 1.49. Smaller and higher space velocities may be employed without materially affecting the character of the product. The treated vapors were then condensed and 205° C. end-point gaso-

line and gas separated from the products. The recovered motor fuel corresponded to 87 volume per cent of the naphtha charged to the process and had an octane number of 67 by the motor method.

I claim as my invention:

1. A process for treating hydrocarbons of approximately motor fuel boiling range to increase the antiknock value thereof which comprises subjecting said hydrocarbons at a temperature from about 450 to about 700° C. and at a pressure from about atmospheric to about 500 pounds per square inch to contact with a catalytic material comprising essentially a major proportion of titanium oxide supporting a minor proportion of chromium oxide.

2. A process for increasing the antiknock value of hydrocarbons boiling in the gasoline range which comprises subjecting the hydrocarbons to reforming conditions in the presence of a chromium oxide dehydrogenating catalyst supported on a relatively pure titanium oxide of an average particle size of about $\frac{1}{10}$ to 1 microns.

3. A process for increasing the antiknock value of hydrocarbons boiling in the gasoline range which comprises subjecting the hydrocarbons to reforming conditions in the presence of a catalyst comprising a major proportion of titanium oxide supporting a minor proportion of chromium oxide.

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