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TREATMENT OF HYDROCARBONS

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This is a continuation-in-part of our co-pending application Serial No. 248,777, filed December 31, 1938, now Patent No. 2,267,730, granted December 30, 1941.

This invention relates to a process for treating hydrocarbon mixtures to remove fluorine therefrom. More specifically it relates to the treatment of synthetic hydrocarbons produced in the presence of active fluoride catalysts to remove small amounts of organically combined fluorine present in compounds admixed with the hydrocarbons. The invention is particularly adapted to the treatment of hydrocarbons produced by alkylation of isoparaffinic hydrocarbons with olefinic hydrocarbons using active fluoride catalysts, including hydrogen fluoride or hydrofluoric acid and mixtures comprising essentially hydrogen fluoride and boron fluoride.

The alkylation of branched chain paraffinic hydrocarbons such as isobutane and isopentane with olefinic hydrocarbons to produce saturated liquid hydrocarbons utilizable as gasoline motor fuels with high antiknock properties, is a recent development which is beginning to assume commercial importance. By this means relatively low-boiling isoparaffinic hydrocarbons may be alkylated with low-boiling olefins, thereby converting materials which have relatively low commercial value into hydrocarbons with high antiknock values, said hydrocarbons being particularly useful as components of aviation gasoline.

Active fluoride catalysts including hydrogen fluoride or hydrofluoric acid and mixtures comprising essentially hydrogen fluoride and boron trifluoride are used in the alkylation of isoparaffins by olefins, but it has been found that the resultant alkylation product frequently contains minor quantities of fluorine in combination with some of the hydrocarbon radicals, possibly due to interaction of hydrogen fluoride with olefinic constituents of the reaction mixture. Boron fluoride assists hydrogen fluoride in catalyzing the alkylation of an isoparaffin by ethylene and higher olefins, but in this case also the product contains small quantities of fluorides as do those formed in the presence of hydrogen fluoride from an isoparaffin and an olefin of higher molecular weight than ethylene.

Although the fluorine content of the hydrocarbon product of gasoline boiling range is rarely very high, the presence of fluorine is undesirable both from the standpoint that the combustion products of such a fuel are extremely corrosive, as well as the fact that its antiknock value, generally expressed by the term "octane number,"

is considerably reduced either when the gasoline is used as such, or when a small amount of an anti-detonating agent such as lead tetraethyl is added thereto. Thus it may be shown that the gasoline fractions containing as much as 0.1 by weight of fluorine have inferior antiknock properties particularly as concerns their response to lead tetraethyl as compared to the otherwise same material which contains substantially no fluorine compounds. The present invention offers a method for reducing the fluorine content of the hydrocarbon alkylation product to a point where this adverse effect is no longer substantial.

In one specific embodiment the present invention comprises a process for treating hydrocarbons produced by catalytic alkylation of isoparaffins with olefins in the presence of an active fluoride catalyst, by treating said hydrocarbons with a fluoride of a metal of group II of the periodic table under dehydrofluorinating conditions of temperature and pressure, and recovering the treated hydrocarbons.

According to the present invention the liquid hydrocarbon product containing organic fluorine compounds obtained from alkylation in the presence of a catalyst containing hydrogen fluoride, is contacted with a fluoride of a metal of group II of the periodic table and preferably with a fluoride of a metal of the calcium group generally known as the alkaline earth metals and including calcium, strontium, and barium. Fluorides of other group II metals including magnesium, zinc, cadmium, and mercury are also usable although not necessarily under the same conditions of operation.

This dehydrofluorination treatment in the presence of a group II metal fluoride, including alkaline earth metal fluorides, is carried out at a temperature generally above 100° C. and preferably at about 300° C. when using a liquid space velocity of between about 1 and 5, but under conditions such that substantially no decomposition of the hydrocarbon alkylation product occurs due to cracking or to other undesirable reactions. At higher temperatures, which generally do not exceed 400° C., higher space velocities are employed. The term "space velocity" refers to the volume of liquid hydrocarbon product charged per volume of metal fluoride per hour. The pressure employed during defluorination may be atmospheric, subatmospheric, or superatmospheric, the last named being used mainly in the interest of increasing the plant treating capacity even though the reaction is favored by lower pressures. The catalyst for the present process is utilized

in the form of powder, granules, or particles of definite size and shape formed by mechanical means. A preferred catalyst is obtained by mixing about 95% by weight of a fluoride of a group II metal or a mixture of such fluorides with about 5% by weight of powdered graphite and forming the mixture into pellets by a pelleting machine. Before being used in the process, the catalyst is generally dried and calcined, preferably in a dry substantially inert gas as hydrogen, nitrogen, or air, with or without small amounts of anhydrous hydrogen fluoride at a temperature in the approximate range of the treating temperature.

The different catalysts which may be produced by compositing different fluorides of group II metals as well as different proportions of the various fluorides are not necessarily equivalent in their action in catalyzing the removal of fluorine from alkylation products produced in the presence of a catalyst containing hydrogen fluoride.

We have found that alkyl fluorides as such or dissolved in hydrocarbons, including those produced by alkylation in the presence of active fluoride catalysts, are converted into substantial amounts of olefins and hydrogen fluoride by contact under the above indicated treating conditions with a fluoride or mixture of fluorides of group II metals. In order to prevent substantial recombination of hydrogen fluoride with said olefins, the product recovered from the metal fluoride treatment is quickly treated further to remove hydrogen fluoride. For example, the mixture containing the olefin and hydrogen fluoride is passed over solid granular sodium fluoride or potassium fluoride either of which forms with hydrogen fluoride an addition compound of the type $\text{NaF}\cdot\text{HF}$. The olefin so liberated in the paraffinic alkylation product usually represents only a very small proportion of the total defluorinated product. If desired, hydrogen fluoride may be recovered from the double salt by heating and it may then be utilized further as catalyst for the hydrocarbon alkylation reaction. Other means of removing hydrogen fluoride from the resulting mixture of paraffinic and olefinic hydrocarbons and hydrogen fluoride include washing the treated product with water, a solution containing an alkali, or a solution containing a salt which will react with hydrogen fluoride to produce an insoluble or non-volatile fluoride.

The process of this invention is also utilizable for converting alkyl fluorides into hydrogen fluoride and olefins or for converting a mixture of alkyl fluorides into hydrogen fluoride and a mixture of olefins.

The following example is given to show results obtainable in the operation of the process, but it should not be considered to unduly limit the broad scope of the invention.

A substantially butane-free hydrocarbon product formed by alkylation of isobutane with isobutene at 25° C. in the presence of anhydrous hydrogen fluoride and containing 0.13% by weight of fluorine, is passed under atmospheric pressure through a nickel tube containing a pelleted composite of 95% by weight of calcium fluoride and 5% by weight of graphite maintained at 300° C. When the alkylation product containing fluorine is charged at an hourly liquid space velocity of 2, a treated hydrocarbon product is obtained equivalent to 97% by volume of the hydrocarbon fraction treated and containing 0.01% by weight of fluorine.

The character of the present invention and

particularly its practical value are evident from the preceding specification and example given, although neither section is intended to unduly limit its generally broad scope.

We claim as our invention:

1. A process for treating a hydrocarbon mixture containing as an impurity a relatively small percentage of organically combined fluorine to remove fluorine therefrom which comprises contacting said mixture with a fluoride of a metal of group II of the periodic table under dehydrofluorinating conditions of temperature and pressure, and recovering the treated hydrocarbons.

2. A process for treating a hydrocarbon mixture containing as an impurity a relatively small percentage of alkyl fluorides to remove fluorine therefrom which comprises contacting said mixture with a fluoride of a metal of group II of the periodic table under dehydrofluorinating conditions of temperature and pressure, and recovering the treated hydrocarbons.

3. A process for treating a hydrocarbon mixture containing as an impurity a relatively small percentage of organically combined fluorine and produced by catalytic alkylation of an isoparaffinic hydrocarbon with an olefinic hydrocarbon in the presence of an active fluoride catalyst which comprises, treating said mixture with a fluoride of a metal of group II of the periodic table under dehydrofluorinating conditions of temperature and pressure, and recovering the treated hydrocarbons.

4. A process for treating a hydrocarbon mixture containing as an impurity a relatively small percentage of organically combined fluorine which comprises, contacting said mixture with a fluoride of an alkaline earth metal under dehydrofluorinating conditions of temperature and pressure and recovering the treated hydrocarbons.

5. A process for treating a hydrocarbon mixture containing as an impurity a relatively small percentage of organically combined fluorine and produced by catalytic alkylation of an isoparaffinic hydrocarbon with an olefinic hydrocarbon in the presence of an active fluoride catalyst which comprises, contacting said mixture with calcium fluoride under dehydrofluorinating conditions of temperature and pressure, and recovering the treated hydrocarbons.

6. A process for treating a hydrocarbon mixture containing as an impurity a relatively small percentage of organically combined fluorine and produced by catalytic alkylation of an isoparaffinic hydrocarbon with an olefinic hydrocarbon in the presence of an active fluoride catalyst which comprises, contacting said mixture with strontium fluoride under dehydrofluorinating conditions of temperature and pressure, and recovering the treated hydrocarbons.

7. A process for treating a hydrocarbon mixture containing as an impurity a relatively small percentage of organically combined fluorine and produced by catalytic alkylation of an isoparaffinic hydrocarbon with an olefinic hydrocarbon in the presence of an active fluoride catalyst which comprises, contacting said mixture with barium fluoride under dehydrofluorinating conditions of temperature and pressure, and recovering the treated hydrocarbons.

8. A process for treating a hydrocarbon mixture containing as an impurity a relatively small percentage of organically combined fluorine and produced by catalytic alkylation of an isoparaffinic hydrocarbon with an olefinic hydrocarbon

in the presence of an active fluoride catalyst containing hydrogen fluoride which comprises, contacting said mixture with a fluoride of a metal of group II of the periodic table at a temperature of from about 100° to about 400° C., and recovering the treated hydrocarbons.

9. A process for treating a hydrocarbon mixture containing as an impurity a relatively small percentage of organically combined fluorine and produced by catalytic alkylation of an isoparaffinic hydrocarbon with an olefinic hydrocarbon in the presence of an active fluoride catalyst containing hydrogen fluoride which comprises, contacting said mixture with a fluoride of an alkaline earth metal at a temperature of from about 100° to about 400° C., and recovering the treated hydrocarbons.

10. A process for treating a hydrocarbon mixture containing as an impurity a relatively small percentage of organically combined fluorine and produced by catalytic alkylation of an isoparaffinic hydrocarbon with an olefinic hydrocarbon in the presence of an active fluoride catalyst containing hydrogen fluoride which comprises, contacting said mixture with calcium fluoride at a temperature of from about 100° to about 400° C., and recovering the treated hydrocarbons.

11. A process for treating a hydrocarbon mixture containing as an impurity a relatively small percentage of organically combined fluorine and produced by catalytic alkylation of an isoparaffinic hydrocarbon with an olefinic hydrocarbon in the presence of an active fluoride catalyst con-

taining hydrogen fluoride which comprises contacting said mixture with strontium fluoride at a temperature of from about 100° to about 400° C., and recovering the treated hydrocarbons.

12. A process for treating a hydrocarbon mixture containing as an impurity a relatively small percentage of organically combined fluorine and produced by catalytic alkylation of an isoparaffinic hydrocarbon with an olefinic hydrocarbon in the presence of an active fluoride catalyst containing hydrogen fluoride which comprises, contacting said mixture with barium fluoride at a temperature of from about 100° to about 400° C., and recovering the treated hydrocarbons.

13. A process for treating a hydrocarbon mixture containing as an impurity a relatively small percentage of organically combined fluorine to remove fluorine therefrom which comprises contacting said mixture with a substantially anhydrous fluoride of a metal of group II of the periodic table at a temperature of from about 100° to about 400° C., and recovering the treated hydrocarbons.

14. A process for treating a hydrocarbon mixture containing as an impurity a relatively small percentage of alkyl fluorides to remove fluorine therefrom which comprises contacting said mixture with a substantially anhydrous fluoride of a metal of group II of the periodic table at a temperature of from about 100° to about 400° C., and recovering the treated hydrocarbons.

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