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MULTISTAGE HYDROGENATIVE REFORMING WITH PLATINUM CONTAINING CATALYSTS

Heinz Heinemann, Swarthmore, and Alex G. Oblad, Springfield, Pa., assignors to Houdry Process Corporation, Wilmington, Del., a corporation of Delaware

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The present invention relates to hydrogenative reforming of gasoline and other naphtha fractions such as for the purpose of obtaining motor fuel of improved octane value or for the production and recovery of aromatics.

Among the principal objects of the present invention is that of providing a convenient and practical process for obtaining improved octane quality motor fuel without accompanying excessive degradation of the charge resulting in loss of gasoline yields.

A further object of the invention is to provide an improved process of reforming a narrow naphtha cut suitable for production of aromatic hydrocarbons such as more particularly benzene and toluene, whereby enhanced yields of aromatics are recovered.

Other objects will be apparent from the description which follows and from the accompanying claims.

It has been previously disclosed in the copending application of Heinz Heinemann and Thomas H. Milliken, Jr., Serial No. 301,796, filed July 30, 1952, and now abandoned, that by the addition of limited quantities of halogen compounds to the reaction zone in catalytic hydrogenative reforming of gasoline and naphtha fractions, higher octane quality products can be obtained over longer periods of continuous operation and at milder operating conditions than otherwise are required; and that for any given octane level of the reformate less severe operating conditions including higher oil throughput are thus made possible.

In a copending patent application of George Alexander Mills for Hydrogenative Reforming of Gasoline and Naphtha, Serial No. 347,837, filed of even date herewith, and now abandoned, novel processes for naphtha reforming are disclosed utilizing a plurality of reaction zones or vessels in series, wherein the initial reaction is effected without halogen addition, and halogen is added to only a subsequent stage. By the described method hydroaromatic naphthenes in the charge are almost quantitatively converted to aromatics without accompanying high degradation of such naphthenes or other components of the charge during the initial reaction stage, permitting the proposed addition of halogen in a later stage to promote isomerization and selective cracking of paraffinic and other non-aromatic components of the charge without adversely affecting the aromatics therein already formed during the initial reaction carried out without such halogen addition.

The process disclosed in the aforesaid patent application of Mills utilizes catalyst composed of a small amount of platinum or other related group VIII noble metal supported on an adsorptive alumina such as activated alumina.

By the present invention a simple and convenient method is provided for utilizing in practice the principles and achieving the advantages set out above. In accordance with the present invention, the naphtha is passed through the entire system comprising a series of reactors or separate reaction zones together with the added halogen, however the catalyst contacted by the charge in one or more of the earlier reaction zones of the series is one which promotes chiefly dehydrogenation, being essentially

non-acidic and not activated by the halogen to promote acid-catalyzed reactions, the effect of the halogen being thus postponed to a subsequent reaction stage or stages wherein the effluent from the previous reaction stage and containing the halogen is contacted with a catalyst capable of promoting acid-catalyzed reactions in the presence of halogen, thus effecting the desired isomerization and selective cracking in such later stage.

The arrangement of the several different types of catalyst in the sequence thus described makes possible recycling of hydrogen-rich gas separated from the final reformate directly to the initial reactor or reaction zone without concern as to the possible presence of halogen in such gas affecting the reaction in such initial stage.

In the preferred practice of the invention, for example, employing a system of three reactors in series, the first reactor will contain catalyst effective principally for promoting dehydrogenation, such as platinum or other noble metal of the platinum family supported on a carrier such as on silica gel, activated carbon or magnesia or on other non-acidic carrier having little or no cracking activity as such or in the presence of halogen. Such catalyst may contain from about 0.05 to 1 or 2% of the platinum or related group VIII noble metal on the carrier; larger amounts of platinum are possible but would be economically unattractive and provide no commensurate advantages. The other reactors of the series will contain the catalyst promoting acid-catalyzed reactions, which may be in the form of about 0.05 to 1.0% and not over 2% Pt (or related noble metal) on an adsorptive alumina such as activated alumina of commerce; such catalyst has the desired promotion effect in the presence of halogen. In some instances it may be preferred to employ the halogen-responsive catalyst only in the last reactor, the other reactors of the series containing platinum on silica or analogous supported noble metal catalyst selective for dehydrogenation. It will be understood that the invention is not limited to any particular number or size of reactors or reaction zones in the series, since in some operations only two of these may be needed and at other times as many as four or more. It is important, however, that the halogen in the charge be made effective in promoting isomerization and selective cracking of remaining components of the charge only after initial dehydrogenation of at least part if not all (up to the equilibrium level) of the hydroaromatic naphthenes present in the original naphtha charged. In this way more severe conversion including more extensive cracking than is otherwise feasible can be resorted to in the subsequent stages of the operation, taking advantage of the presence of aromatics earlier produced by dehydrogenation, to inhibit excessive coke formation.

In operation of the invention the usual operating conditions customarily employed may be utilized. For instance in reforming of gasoline and naphtha for production of improved motor fuel such conditions include temperature in the range of about 875–975° F., preferably at 900–950° F.; pressures of about 400–700 p.s.i.g. and space rates above 1 and preferably of about 2 to 4 volumes of naphtha per hour per volume of catalyst; hydrogen in the form of recycled hydrogen-rich gas is passed into the initial reaction zone at the rate of at least 5 and preferably in the order of 10 or more volumes of such gas per volume of naphtha charged to such zone. In some instances, as will hereinafter appear, lower pressures and lower temperatures than those set out above may be employed in the later reaction stage or stages.

With respect to the amount of halogen to be added with the charge when operating in accordance with the present invention, it can be stated generally that the practical limitations heretofore imposed in connection with the operations described in the previous application Serial

No. 301,796 do not strictly apply, since possible loss of high octane products by cracking of aromatics-forming naphthenes is largely avoided by the previous dehydrogenation of such naphthenes over the dehydrogenation catalyst employed in the initial reaction stage. Moreover, limited cracking may be tolerated or even be advantageous in the subsequent reaction stages, so that the amount of halogen employed may be quite high as compared with the limits set out in said previously filed application. The addition of more than about 0.5% halogen to the charge is not advised, since at such high halogen levels the extent of cracking may be excessive and the loss of liquid yield accordingly may be disproportionate to the octane advantage thereby gained. While the effect of the halogen addition may be evidenced even at rates as low as 1.0 part per million of naphtha charged, for practical benefits there should be used at least 0.001 percent halogen by weight; for most operations concerned with upgrading of gasoline over catalyst composed of up to 1% Pt (or Pd) on activated alumina, the preferred amount of added halogen will be in the range of 0.005 to 0.1 percent by weight of the original gasoline charge.

The halogen may be added as free halogen gas or vapor, as hydrohalide, or as compounds capable of releasing free halogen or hydrohalide. Examples of suitable halogens and halogen compounds include chloroform, carbon tetrachloride, free chlorine, iodine and other free halogen gases and vapors, hydrogen chloride and hydrogen bromide vapors. Convenient compounds giving highly successful results are the alkyl halides, for example t-butyl chloride and n-butyl iodide.

No outstanding differences have been observed among the various halogen compounds, except for an appreciable tendency of the fluorides to increase the relative extent of cracking and in the case of iodine and iodides there is a tendency at least initially to obtain somewhat higher yields of liquid products at certain octane levels.

The principal effect of adding halogen to an intermediate reaction zone when processing a typical gasoline fraction such as a C_7+ distillate or one boiling within the range of say about 200–400° F., appears to be largely that of permitting higher conversion of naphthenes to aromatics by initially effecting dehydrogenation of the naphthenes rather than cracking so that more selective cracking as well as isomerization and dehydrocyclization of higher acyclic components of the charge can be subsequently effected, particularly of those paraffins of eight carbon atoms and higher, to give aromatics and normally liquid lower branched chain compounds of high octane quality.

The operation described has also beneficial advantages in other reforming operations, such as the treatment of a narrow naphtha cut of suitable boiling range for the recovery of aromatic hydrocarbons; such a cut may be, for instance, one boiling over the range of about 180–230° F. utilized for production of benzene and toluene. When such naphtha fraction is treated in the presence of added halogen with catalyst such as platinum on activated alumina, alkylated C_5 naphthenes in the charge, such as methylcyclopentane and its homologues, are converted to aromatics by dehydroisomerization. On the other hand the presence of halogen in a reaction zone containing such catalyst would also tend to further the reverse reaction according to the equilibrium formula:

$$\underset{\text{Methylcyclopentane}}{(\text{MCP})} \rightleftarrows \underset{\text{Cyclohexane}}{(\text{CH})}$$

At about 800° F. the mass action constant K (isomerization) is equal to 0.111 and there is present about 0.9 mol fraction of MCP in the mixture, somewhat more as temperature is increased. By removing the cyclohexane initially present in the charge through dehydrogenation to benzene, larger quantities of the total naphthenes are thus converted to aromatics.

Typical operating conditions as applied to aromatics production, include temperatures of about 900 to 950° F. at space rates of about 2 to 4, the pressures being somewhat lower than those employed in upgrading motor fuels and may be in the range of about 200 to 300 pounds per square inch gauge; 3 to 5 mols of hydrogen-rich gas are added or recycled to the reforming operation.

As in the usual systems for either gasoline or aromatics production, suitable means are provided for reheating of the hydrocarbon effluent between conversion zones to compensate temperature loss by the previous endothermic reaction or to bring the charge to desired operating temperature for the stage to which it is being charged.

In practice of the present invention whether for upgrading of gasoline or production of aromatics, one is not limited to employing the same operating conditions in the several reactors of the series. It has been observed, in general, that higher yields of reformate are favored at lower pressures, but operation at such lower pressures may be contra-indicated because of the tendency of increased coke formation. Such increased coke formation at the lower pressure may be overcome to some extent by lower temperature. On the other hand, increased temperatures favor dehydrogenation. These effects of changes in operating variables can be beneficially utilized and add to the overall flexibility of the present process. Since the reaction desired in the early stage is largely dehydrogenation and the catalyst employed is highly selective for such reaction, the favorable effect on such reaction of high temperature within the described operating range can be used to advantage, operating at the higher pressures in the described range to reduce coking tendency. In the later stage or stages applied to the already dehydrogenated material, the pressure can be reduced to obtain improved yields of reformed products, excessive coking being avoided by reduction in temperature. Thus for upgrading motor fuel, the naphtha fraction may be contacted with the Pt on SiO_2 or related catalyst at temperatures of 900–975° F. under a pressure of 600–700 pounds per square inch gauge, and the subsequent stage of treatment over Pt/Al_2O_3 catalyst at 825 to 900° F. under a pressure of 300–500 pounds per square inch gauge. Hydrogen or recycled hydrogen-rich gas as well as halogen is added to the initial charge as above described, but the latter has no significant effect on the reactions until such later stage of treatment over the Pt/Al_2O_3 catalyst.

The dehydrogenating catalyst employed in the primary reforming step is prepared by impregnation of the named carriers with a solution of a soluble salt or complex of the noble metal in an amount to furnish the required quantity of the metal on the carrier, followed by drying. The dried material so impregnated may then be subjected to calcination or reduction to decompose the salt or complex of the noble metal or such decomposition may be carried out after loading the catalyst in the hydrocarbon conversion reactor, wherein it will be subjected to a stream of hydrogen-containing gas during initial pressurizing of the reactor.

The catalyst employed in the later isomerizing step may be prepared in substantially the same manner as that above described except for selection of the carrier. In this instance there can be employed an adsorptive alumina, such as precipitated alumina or activated alumina of commerce. To obtain good distribution of the platinum in the carrier it may be found advantageous to treat the alumina with acid prior to impregnation with the solution of the platinum salt or complex, for which purpose there may be employed volatilizable or decomposable acids such as aqueous HCl or acetic acid. Among the noble metal solutions that can be employed in the preparation of either type of catalyst there may be named for example aqueous solutions of chloroplatinic acid, palladium chloride, and such solutions of amino or ammonium nitrito complexes of these metals.

Example I

The catalyst in a series of reactors is distributed so that 40% of the total catalyst contacted by the naphtha is used in the initial reaction stage and consists of 0.5% Pt on silica gel; the remaining 60% of the total catalyst, which is employed in the subsequent reactors of the series is composed of 0.5% Pt on acetic acid leached activated alumina.

A heavy East Texas naphtha is charged to this system and the reaction carried out over the Pt on silica catalyst is operated at 950° F., while that over the Pt on alumina catalyst is operated at 875° F. To the initial naphtha charge as fed to the first reactor of the series there is added 0.005% Cl as tertiary butyl chloride; and recycled hydrogen-rich gas, separated from the final reformate, is added to the charge at a recycle ratio of 10 mols gas per mol of naphtha. The pressure in all of the reactors is maintained at 600 pounds per square inch and the naphtha is fed to the system at an overall space rate of 3 volumes naphtha per hour per volume of the total catalyst.

There is obtained a yield of C_5+ gasoline corresponding to 81% of the naphtha charged, which gasoline has an octane rating of 91 F_1 clear.

Example II

For comparison with the above run, the same naphtha charge reformed under the same conditions except that the catalyst in all of the reactors consists of 0.5% Pt on acetic acid leached activated alumina (the same catalyst as used in only the latter reactors of Example I above), gives the following yields of C_5+ gasoline depending on temperature over a range of 915–940° F.:

Yield C_5+ gasoline, vol. percent:	Octane F_1 clear
81	88
79.5	91
79.0	92

It will be appreciated from the foregoing that by using the halogen-responsive catalyst only in the latter reaction stages (Example I) improved yield octane relations of the reformed gasoline are obtained.

Example III

The run described in Example I is repeated with the exception that a pressure of 600 pounds per square inch is maintained in the initial reaction stage carried out over Pt on silica and a lower pressure of 400 pounds per square inch is maintained in the reaction zone employing the halogen responsive Pt on alumina catalyst. A yield of 81 volume percent of C_5+ gasoline of 93 F_1, clear octane rating is obtained.

The term "halogen" when employed in the present specification and the accompanying claims is intended to include not only free halogen as such but also such compounds as are capable of releasing free halogen or hydrogen halide in the catalytic reaction zone under the operating conditions employed. The amounts and percentages of halogen are stated in terms of the elemental content (e.g. Cl).

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.

What is claimed is:

1. The method of hydrogenative reforming of hydrocarbon charge boiling in the range of naphtha which comprises initially dehydrogenating components of such charge by passing a hydrogen-rich recycle gas and such a charge stock together with from 0.005 to 0.1% by weight halogen in the form of hydrohalide through a primary reaction zone maintained under hydrogenative reforming conditions including a pressure of from 600 to 700 pounds per square inch gauge, a temperature of from about 900 to about 975° F., there being at least 5 volumes of hydrogen per volume of gaseous naphtha, said primary reaction zone containing supported platinum, the support for said catalyst being incapable of promoting acid-catalyzed reactions in the presence of such hydrohalide, whereby said primary reaction zone dehydrogenates components of said naphtha with minimized cracking of said naphtha; and thereafter passing the effluent from said primary reaction zone into a secondary reaction zone maintained at hydrogenative reforming conditions including temperature of 825–900° F. and pressure of 300–500 pounds per square inch and containing catalyst comprising a small amount of platinum supported on an alumina carrier capable of being activated by halogen to promote acid-catalyzed reactions, thereby effecting isomerization and selective cracking of non-aromatic components of the effluent introduced into said secondary reaction zone; separating hydrogen-rich gas from the reformate discharged from the secondary reaction zone, and recycling such gas directly to the primary reaction zone.

2. The method according to claim 1 wherein the catalyst in said primary reaction zone consists predominantly of silica gel and a minor amount of platinum supported thereon.

3. A method of obtaining yield-octane characteristics better than obtained from comparable upgrading over a single kind of catalyst during the upgrading of naphtha of the gasoline boiling range in two stages, comprising: preparing a first stage catalyst by the impregnation of silica gel with sufficient chloroplatinic acid to provide, after reduction with hydrogen, about 0.5% platinum; preparing a second stage catalyst by subjecting activated alumina to a leaching with acetic acid and thereafter impregnating the acetic acid leached activated alumina with sufficient chloroplatinic acid to provide, after reduction with hydrogen, a catalyst consisting predominantly of alumina and containing about 0.5% platinum and about 0.5% chloride; restricting the quantity of platinum on silica catalyst in said first stage to about 40% of the total catalyst; restricting the quantity of platinum on alumina catalyst in said second stage to about 60% of the total catalyst; controlling the space rate of the two stage upgrading to provide about 3 volumes of liquid naphtha per hour per volume of total catalyst; preparing a mixture of the naphtha and sufficient tertiary butyl chloride to provide about 0.005% by weight chloride; passing the vapors of such mixture together with about 10 mols of hydrogen-rich recycle gas per mol of naphtha at a pressure of about 600 pounds per square inch gauge over said first stage catalyst at about 950° F. for a first stage upgrading of the naphtha; passing the effluent from the first stage upgrading through a second stage upgrading at a temperature of about 875° F. at a pressure significantly less than in said first stage and at a pressure not greater than about 400 pounds per square inch over said second stage catalyst; recovering a high yield of high octane naphtha of the gasoline boiling range from the effluent from such second stage upgrading; and recovering a portion of the gaseous effluent from such second stage upgrading and recycling such portion directly to the first stage as said hydrogen-rich recycle gas; whereby the effect of the tertiary butyl chloride is controlled to be of no significance in the first stage treatment over the catalyst comprising the silica gel carrier but whereby the effect of the tertiary butyl chloride cooperates with the alumina carrier in the second stage treatment to enhance the isomerization activity of the second stage catalyst.

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