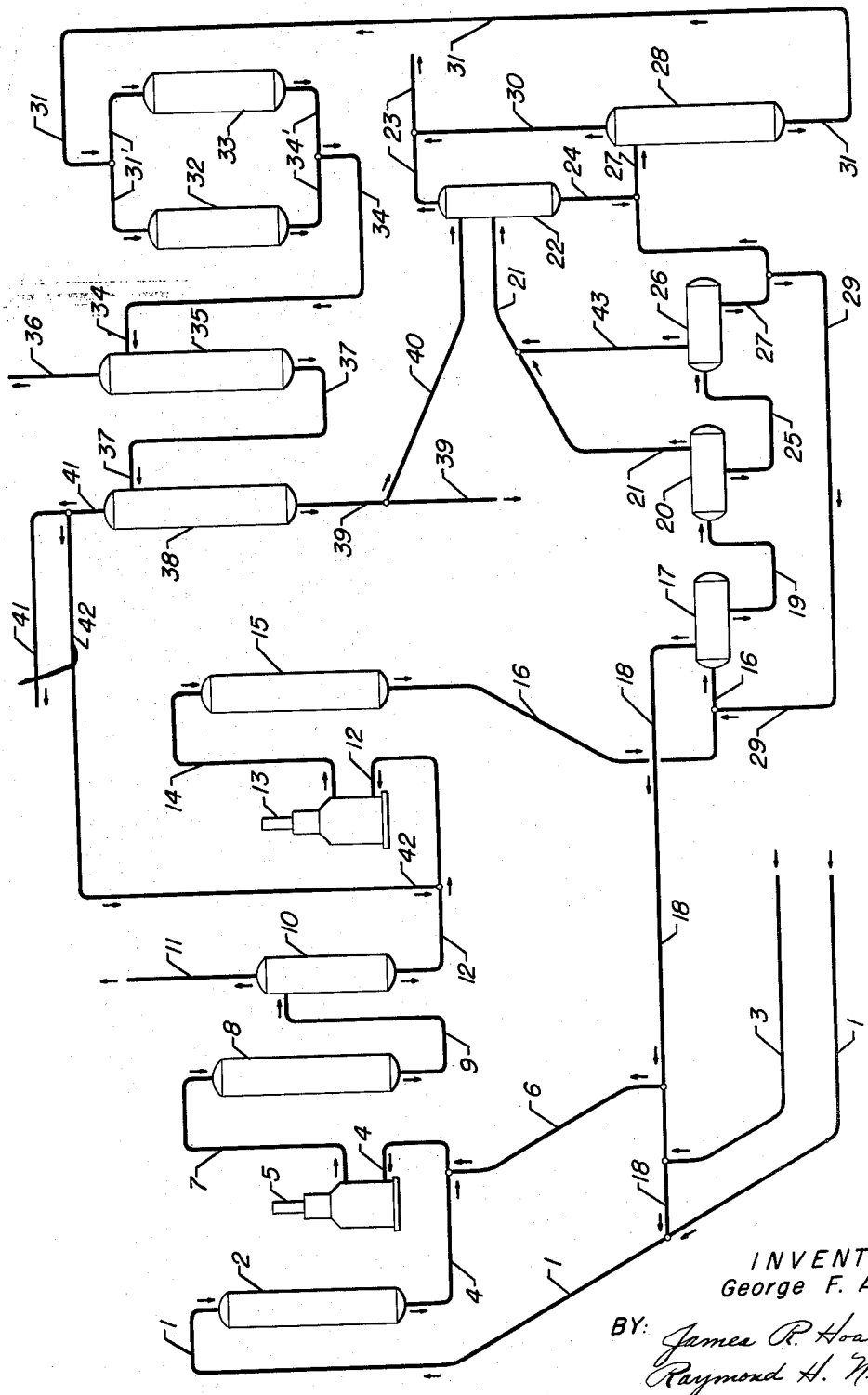
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TREATMENT OF ALKYL-SUBSTITUTED AROMATIC COMPOUNDS

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TREATMENT OF ALKYL-SUBSTITUTED AROMATIC COMPOUNDS

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This application is a continuation-in-part of my co-pending application Serial No. 132,285, filed August 18, 1961, and now abandoned.

This invention relates to a process for the treatment of alkyl-substituted aromatic compounds and substantially to a method for treating alkyl-substituted aromatic hydrocarbons. More specifically, the invention is concerned with a process for obtaining aromatic hydrocarbons from feed stocks comprising olefin-containing alkyl-substituted aromatic hydrocarbons which have overcome prior treatment to remove various contaminants therefrom.

Certain processes which are utilized in the petroleum industry, and particularly in refining operations, whereby hydrocarbonaceous compounds are subjected to reforming involve the use of catalytic compositions of matter. Among these processes are the reforming of gasoline boiling range hydrocarbons, hydrodealkylation of alkylaromatic compounds, the hydrogenation of aromatic compounds to form cyclic paraffins, the hydrocracking of high boiling materials to form lower boiling materials which possess more useful properties, isomerization of paraffins to form isomers thereof, alkylation of aromatic compounds, etc. The starting materials or feed stocks of these various processes may contain certain contaminants among which are organic sulfur, organic nitrogen and organic oxygen compounds. For example, the sulfur may be present in the form of organic sulfides which may be destroyed during the process and thereafter react with the catalyst whereby, in the event that the catalyst is an oxide of a metal, sulfides are formed and water vapor is released. This reaction will continue until the catalyst has lost its activity due to the conversion of sulfides and also to the deposition of coke or other hydrocarbonaceous material on the surface of the catalyst. When the catalyst activity has reached such a low degree of activity that commercial operation is no longer feasible, the plant must then be shut down while the catalyst is either regenerated or replaced by fresh catalyst. The replacement or regeneration of the catalyst is a serious disadvantage in the operation of the particular process and if many of these regenerations or replacements are necessary the economic capabilities of the processes will be greatly reduced and said processes may, in time, become commercially unattractive to operate. In addition, the contaminants will also affect the product quality of the desired reaction product and said product may have to undergo a costly series of steps of purification before the product may be utilized for a particular purpose.

As an example of the problems attendant to the removal of contaminating influences from hydrocarbon feed stocks the removal of sulfur will be used as an illustration. As is known in the prior art there are various types of treating methods which are proposed or utilized for eliminating sulfur compounds from the various feed stocks. For example, it is known in the prior art to convert mercaptans which possess particularly objectionable odors to less odorous disulfides by sweetening processes such as the doctor treatment. However, the disadvantage which is found in this process is that the total sulfur content of the feed stock is not reduced and, in the event that the particular process leads to the preparation of gasoline fractions the disulfides are objectionable inasmuch as they

are as deleterious in their effects on octane number and lead susceptibility as were the original mercaptans. Another type of treatment which is utilized as a sweetening process is the extraction of sulfur containing compounds with an alkaline reagent. However, the use of an alkaline reagent will not remove any thiophenes which may be present in the feed stock. While sulfuric acid may be used to remove sulfur compounds a disadvantage in this process lies in the fact that said acid cannot be utilized if the olefinic content of the feed stock is relatively high inasmuch as said olefins which are present may tend to polymerize in the presence of sulfuric acid.

Another process which may be used to remove sulfur compounds is the vapor phase catalytic process in the absence of hydrogen whereby mercaptans or thioethers may be destroyed. However, a disadvantage in this process, like the use of alkaline reagents, is the fact that thiophenes are relatively unaffected and will remain in the feed stock.

In addition to the aforementioned sulfurous compound contaminants, the various feed stocks may also contain nitrogenous compounds as contaminants therein. The removal of nitrogenous compounds present other difficulties inasmuch as the nitrogenous compounds require considerably more severe conditions, especially of temperature, in order to convert the nitrogenous compounds into hydrocarbons and ammonia. In this respect, other problems arise inasmuch as by utilizing higher operating temperatures, that is, above about 500° F. any aromatic hydrocarbons which may be present in the feed stock will have a tendency to become saturated especially as the nitrogen removal process is effected in the presence of added hydrogen. Therefore, it is incumbent, when the desired product comprises aromatic hydrocarbons to effect the removal of the contaminants such as the sulfurous compounds and the nitrogenous compounds in such a manner as to avoid the hydrogenation of the desired aromatic hydrocarbons.

In order to obtain the desired aromatic hydrocarbons, it is therefore necessary to remove contaminants comprising sulfurous compounds, nitrogenous compounds, oxygen-containing compounds and mixtures thereof from the feed stock before submitting the alkyl-substituted aromatic hydrocarbons to a dealkylation process. For example, when the hydrocarbon feed stock is passed over a hydrorefining catalyst it has been found that some of the aromatic rings of the feed stock are partially hydrogenated. A specific example of this is when a feed stock containing alkyl naphthalenes such as 1-methylnaphthalene, 2-methylnaphthalene 1,2-dimethylnaphthalene, etc., is hydrorefined at the usual conditions of temperatures ranging from about 500° to about 750° F. and at a pressure ranging from about 500 to about 800 pounds per square inch, the chemical equilibrium strongly favors the formation of tetrahydromethylnaphthalene. While it might be possible to formulate a hydrorefining catalyst with a low activity which will permit its use at a temperature in the range of from about 800° to about 950° F., (at which temperatures the chemical equilibrium becomes favorable for the preservation of naphthalene structures) it would be less likely that such a catalyst would be effective for the removal of organic nitrogen compounds which may also be present as contaminants. Furthermore any increase in hydrorefining temperatures would add to the corrosion problems of the plant when utilizing feed stocks containing a high sulfur content.

In view of this problem, it is therefore an object of this invention to provide a process whereby olefin-containing alkyl-substituted aromatic hydrocarbon charge stocks containing certain contaminants may be subjected to successive treatments for the removal of the contaminants

and the dealkylation of the alkyl-substituted aromatic hydrocarbons to form aromatic hydrocarbons therefrom.

A further object of this invention is to provide a process whereby olefin-containing alkyl-substituted aromatic hydrocarbon charge stocks containing nitrogenous compounds, sulfurous compounds and mixtures thereof, may be hydrorefined and thereafter subjected to a dealkylation process whereby the desired aromatic hydrocarbons may be obtained in a commercially desirable yield.

In a broad aspect, one embodiment of this invention resides in a process for producing aromatic hydrocarbons from an olefin-containing, alkyl-substituting aromatic hydrocarbon charge stock containing contaminants selected from the group consisting of nitrogenous compounds, sulfurous compounds and mixtures thereof which process comprises reacting said charge stock with hydrogen in a first reaction zone at hydrogenation conditions including a temperature below 500° F., passing the resultant substantially diolefin-free effluent into a second reaction zone and further reacting said effluent with hydrogen in contact with a catalytic composite having hydrogenation-dehydrogenation activity and at reaction conditions including a temperature above 500 F. to convert nitrogenous compounds into hydrocarbons and ammonia without hydrogenating aromatic hydrocarbons, removing ammonia from the resulting second reaction zone effluent, and further reacting the remainder of said second reaction zone effluent with hydrogen in a third reaction zone in contact with a dealkylation catalyst at dealkylation conditions to convert said alkyl-substituted aromatic hydrocarbons to the corresponding aromatic hydrocarbons.

A further embodiment of this invention is found in a process for producing aromatic hydrocarbons from an olefin-containing, alkyl-substituted aromatic hydrocarbon charge stock containing contaminants selected from the group consisting of nitrogenous compounds, sulfurous compounds and mixtures thereof which process comprises reacting said charge stock with hydrogen in contact with a catalyst composite of at least one metallic component from the group of metals of the left hand column of Group VI–B and Group VIII of the Periodic Table, in a first reaction zone at a temperature in the range of from about 300° to about 500° F. and at a pressure in the range of from about 400 to about 800 pounds per square inch, passing the resultant substantially diolefin-free effluent into a second reaction zone and further reacting said effluent with hydrogen in contact with a catalytic composite having hydrogenation-dehydrogenation activity and at a temperature in the range of from about 800° to about 950° F. and at a pressure in the range of from about 400 to about 800 pounds per square inch to convert nitrogenous compounds into hydrocarbons and ammonia without hydrogenating aromatic hydrocarbons, removing ammonia from the resulting second reaction zone effluent, and further reacting the remainder of said second reaction zone effluent with hydrogen in a third reaction zone in contact with a dealkylation catalyst at a temperature in the range of from about 1000° to about 1500° F. and at a pressure in the range of from about 300 to about 1000 pounds per square inch to convert said alkyl-substituted aromatic hydrocarbons to the corresponding aromatic hydrocarbons.

A specific embodiment of this invention is found in a process which produces naphthalene from an olefin-containing methylnaphthalene charge stock containing contaminants selected from the group consisting of nitrogenous, sulfurous compounds and mixtures thereof which process comprises reacting said charge stock with hydrogen in contact with a catalyst comprising molybdenum and cobalt composited on a silica-alumina base in a first reaction zone at a temperature in the range of from about 300° to about 500° F. and at a pressure in the range of from about 400 to about 800 pounds per square inch, passing the resultant substantially diolefin-free effluent into a second reaction zone and further reacting said effluent with hydrogen in contact with a catalyst comprising platinum and combined chlorine composited on an alumina base at a temperature in the range of from about 800° to about 950° F. and at a pressure in the range of from 400 to about 800 pounds per square inch to convert nitrogenous compounds into hydrocarbons and ammonia without hydrogenating said methylnaphthalene, and further reacting the remainder of said second reaction zone effluent with hydrogen in a third reaction zone in contact with a catalyst comprising chromium composited on an alumina base at a temperature in the range of from about 1000° to about 1500° F. and at a pressure in the range of from about 300 to about 1000 pounds per square inch to convert said methylnaphthalene to naphthalene.

As hereinbefore set forth, the present invention is drawn to a process whereby olefin-containing alkyl-substituted aromatic hydrocarbons which contain contaminants such as sulfurous, nitrogenous and oxygenated compounds as well as mixtures thereof, undergo a treatment for the removal of said contaminants followed by a subsequent dealkylation step to prepare the desired aromatic hydrocarbons. The term "olefin-containing" as used in the present specification and appended claims will refer to olefinic as well as diolefinic hydrocarbons. These monoolefinic and diolefinic hydrocarbons such as ethylene, propene, the butenes, butadiene, styrene, isoprene, dicyclopentadiene, etc., induce the coke-forming characteristics of the feed stock, and when the feed stock is subjected to a hydrorefining step for the purpose of removing sulfur, nitrogen and/or oxygen there is encountered a difficulty of effecting the desired degree of reaction due to the formation of coke and other carbonaceous material. The deposition of coke and other carbonaceous material appears to be an inherent result of the necessity to effect the hydrorefining process at elevated temperatures, generally in excess of about 500° F. Various vessels and other appurtenances of the conversion zone are subjected to heavy coking; this appears as the formation of solid, highly carbonaceous material resulting from a thermal reaction from the unstable or coke-forming compounds within the feed stocks being charged to the unit. In addition, polymerization and co-polymerization reactions of the monoolefins and diolefins are effected within the hydrorefining reaction zone to such an extent that the catalytic composite which is present in the zone becomes shielded from the material being processed. The coke-forming hydrocarbon feed stocks are usually those resulting from prior severe conversion treatments, such as catalytic and thermal cracking. These distillants are available in large quantities and generally require the hydrorefining treatment for the purpose of enhancing the possibilities of further usefulness. As hereinbefore set forth, the utilization of temperatures about 500° F. will favor the formation of a partially hydrogenated aromatic compound such as for example, tetrahydromethylnaphthalene. Therefore it becomes necessary to effect a treating step at a temperature below about 500° F. whereby any diolefins which may be present in the feed stocks are hydrogenated prior to passing the substantially diolefin-free compounds to a second reaction zone.

In the present invention, the aforementioned effluent from the first reaction zone which is substantially diolefin-free is passed to a second reaction zone wherein the effluent is treated with hydrogen at relatively severe operating conditions of temperature and pressure in the presence of a catalytic composition of matter which has a dual functioning activity. In this zone, the contaminants which may include sulfurous compounds, nitrogenous compounds, oxygenated compounds and mixtures thereof are converted into hydrocarbons, ammonia, water and hydrogen sulfide without saturating the alkylaromatic hydrocarbons, and due to the dual function of the catalyst, which in this instance is of a hydrogenation-dehydrogenation activity, may dehydrogenate any alkyl-sub-

stituted aromatic hydrocarbons which may have become partially hydrogenated in the first hydrorefining zone. The ammonia, hydrogen sulfide or water which may have been formed in the second reaction zone is separated from the reactor effluent which, by this time, comprises relatively pure alkyl-substituted aromatic hydrocarbons, by any means known in the art, the aforementioned alkyl-substituted aromatic hydrocarbons then being charged to a third reaction zone wherein said hydrocarbons undergo dealkylation in the presence of a dealkylation catalyst at dealkylation conditions. The terms "aromatic hydrocarbons" and "alkyl-substituted hydrocarbons" as used in the specification and appended claims refer to both monocyclic and polycyclic hydrocarbons, said polycyclic aromatic compounds having a condensed ring structure, examples of which include toluene, m-xylene, o-xylene, p-xylene, ethylbenzene, 1-methyl-naphthalene, 2-methylnaphthalene, 1,2-dimethylnaphthalene, 1,4-dimethylnaphthalene, 1-methylanthracene, 2-methylanthracene, 1,2-dimethylanthracene, etc. It is to be understood that the aforementioned alkyl-substituted aromatic hydrocarbons are only representatives of the class of compounds which may be subjected to dehydrogenation and hydrodealkylation in the process of this invention. The feed stocks which may be used as starting materials in this invention include light cycle oil extracts, coke oven by-products, coal tar crudes, etc. The desired products which comprise benzene, naphthalene, etc., will find a wide variety of uses in the chemical field, said uses being too numerous to enumerate at the present time. However, for example, naphthalene will find a wide demand for use in the production of phthalic anhydride, while benzene having a high technical grade purity is an important starting material for alkylaromatic sulfonates which are useful as detergents and surface active agents.

The feed stocks which contain olefins and diolefins as well as contaminants comprising sulfurous compounds, nitrogenous compounds, oxygen-containing compounds and mixtures thereof are hydrorefined by passage over a hydrorefining catalyst at conditions which include a temperature of less than 500° F. As hereinbefore set forth, this step of the process being effected in the presence of added hydrogen, will permit the saturation of monolefins and diolefins thereby preventing the polymerization of these compounds in the second stage of the process. Due to utilizing operating temperature less than about 500° F. within the first reaction zone substantially no desulfurization or denitrogenation is effected. In fact, traces of hydrogen sulfide in the hydrogen-rich gas stream may react with the olefins to form sulfided hydrocarbons which are then destructively removed in the second reaction zone. By saturating the monolefins and diolefins, it is possible to utilize operating conditions within the second reaction zone so that the sulfurous and nitrogenous compounds are removed without incurring the detrimental polymerization reactions otherwise resulting, were it not that saturation of olefins and diolefins had been effected in the first reaction zone.

The hydrorefining catalyst which is utilized in the first reaction zone comprises at least one metallic component selected from the group consisting of the metals of the left hand column of Group VI and Group VIII of the Periodic Table and compounds thereof. Thus, the catalyst will comprise at least one metallic component selected from the group consisting of chromium molybdenum, tungsten, iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium, platinum, and mixtures of two or more, etc. The preferred catalytic composite, for utilization in the first reaction zone of the process of the present invention, comprises molybdenum and at least one metallic component selected from the iron group of Group VIII of the Periodic Table. The molybdenum component will generally be in the greater concentration, that is, from about 4.0% to about 30.0% by weight, while the iron group metallic component will be present in an amount within the range of from about 1.0% to about 6.0% by weight, such concentrations being calculated on the basis of the elemental meta. An essential feature of the catalytic component is that the catalytically active metallic components, of the type hereinabove set forth, be composited with a non-acidic carrier material. Generally speaking, catalytically active metallic components are composited with any suitable refractory inorganic oxide material including alumina, silica, zirconia, thoria, boria, titania, hafnia, mixtures of two or more, etc. Similarly, other components are often combined with the metallic components of the carrier material; these components including members of the halogen family, particularly fluorine and/or chlorine. However, these components, as well as some of the various refractory inorganic oxides hereinabove set forth, impart a particular acid-acting function to the catalytic composite, which function is not desirable in the process of this invention. For example, a carrier material comprising a component of alumina and silica, will possess sufficient hydrocracking activity to affect detrimentally the attainment of the specific object of the present invention. Therefore, it is an essential feature that the catalytically active components be composited with a non-acidic refractory inorganic oxide carrier material, the term being specifically intended to preclude the utilization of members of the halogen family and other components which might impart an acid-acting function to the catalytic composite. Therefore, a particularly preferred carrier material for utilization in manufacturing the catalyst employed in the process of the present invention comprises alumina in its many anhydrous forms, or as alumium hydroxide. Although any suitable means may be employed for the manufacture of the catalytic composite, a convenient means involves the use of impregnating techniques on a preformed alumina carrier material. For example, a catalyst consisting essentially of about 2.2% by weight of cobalt and about 5.7% by weight of molybdenum calculated as the elements thereof, may be prepared by impregnating alumina particles of any suitable size and/or shape, with a single impregnating solution of suitable water-soluble compounds of cobalt and molybdenum. A double impregnation technique may be effected whereby the molybdenum component is first composited, the thus impregnated carrier material being subjected to high temperature calcination, followed by a second impregnating procedure in which the cobalt component is composited. Suitable water-soluble compounds, for use in preparing the impregnating solution, include molybdic acid, ammonium molybdate, cobalt chloride hexahydrate, nickel nitrate hexahydrate, etc. Following the impregnation, the catalyst is dried at a temperature within the range of from about 200° to about 400° F. and thereafter subjected to a calcination procedure in an atmosphere of air, at an elevated temperature of from about 500° to about 1000° F. Following the calcination of the impregnated carrier material, the composite may be treated in any manner designed to cause the metallic components to exist in a particularly desired form. Thus, the composite may be treated so as to convert the metallic components substantially to the form of oxides, sulfides, sulfates, etc.

The substantially diolefin-free feed stock is withdrawn from the hydrorefining zone or first reaction zone and passed to a second reaction zone wherein the feed is treated with hydrogen in the presence of a catalytic composition of matter which has a dual functioning activity. This duel functioning catalyst will possess both hydrogenation and dehydrogenation activities. In addition, the feed stock is treated at rather severe operating conditions of temperature, said conditions including a temperature in the excess of 500° F., and preferably at a temperature in the range of from about 800° to about 950° F. In addition, pressures ranging from about 300 to

about 1000 pounds per square inch and preferably from about 400 to about 800 pounds per square inch will be utilized. The purpose of the catalytic composition of matter which possesses a dual functioning activity will permit the removal of the contaminants such as the nitrogenous compounds and sulfurous compounds by converting said compounds into hydrocarbons, ammonia and hydrogen sulfide while effecting the dehydrogenation of any partially saturated aromatic compounds which may be present. In addition, the catalyst, due to the particular nature thereof, will not permit the saturation of any aromatic hydrocarbons or alkyl-substituted aromatic hydrocarbons which may be present even in the presence of added hydrogen. By thus converting any partially saturated aromatic or alkyl-substituted aromatic hydrocarbons which may be present, the partial destruction of any polycyclic aromatic compounds to the single ring aromatic hydrocarbon is avoided. Examples of effective catalytic compositions of matter which possess the dual function of hydrogenation-dehydrogenation activity include chromia composited on alumina, platinum composited on alumina, molybdenum composited on alumina, tungsten composited on alumina, the oxides of magnesium, copper, zinc, cadmium, vanadium tantalum, etc., composited on alumina, a noble metal of Group VIII of the Periodic Table composited on a solid carrier such as alumina, etc. Specific examples of catalytic composites which possess the dual function of hydrogenation-dehyrogenation activity include a catalyst composed of 0.75% platinum by weight and 0.90% chlorine by weight composited on alumina; 0.375% platinum by weight and 0.90% chlorine by weight composited on alumina; 0.75% palladium by weight and 0.90% chlorine by weight composited on alumina; 0.375% palladium by weight and 0.90% chlorine by weight composited on alumina. It is to be understood that these catalysts are only representatives of the class of catalysts possessing hydrogenation-dehydrogenation activity which may be utilized in the second stage of the present process, and that said process is not necessarily limited thereto.

The reactor effluent is withdrawn from the second reaction zone and passed to a stripper wherein any ammonia and/or hydrogen sulfide which has been formed in the second reaction zone is separated from the feed stock, after which the feed stock and added hydrogen, after being heated to the desired reaction temperature, are passed to a third reaction zone in which the hydrodealkylation of the alkyl-substituted aromatic hydrocarbons is effected in a catalytic-type operation. The catalysts which are utilized in the hydrodealkylation reaction may contain a noble metal of Group VIII of the Periodic Table such as platinum, palladium, rhodium, ruthenium, osmium, or iridium composited on a suitable refractory oxide. In addition the catalyst may contain other metals such as cesium, vanadium, chromium, tungsten, etc., composited on a suitable refractory oxide. It is also contemplated that combinations of the latter classes of metallic components may be utilized with themselves or with a noble metal of Group VIII of the Periodic Table. Suitable refractory oxides which may be used include alumina, particularly alumina containing a relatively high surface area such as gamma-alumina, eta-alumina and theta-alumina, silica-zirconia, silica-alumina, alumina-boria, silica-zirconia-alumina, etc. A particularly effective hydrodealkylation catalyst comprises chromia impregnated on high surface area alumina, said metal being present in the finished catalytic composite in an amount of from about 15 to about 20% by weight or more calculated as the elemental metal.

The catalysts which are to be utilized in the hydrodealkylation reaction may be prepared in any manner well known in the art. One such type of preparation is to dry the desired refractory oxide base such as a high surface area alumina in order to reduce the volatile content of said base to a minimum. The dried base is then pilled to a desired crushing strength and calcined at a relatively high temperature of from about 1000° to about 1300° F. Following this the base is impregnated with the metal in any manner, one such application being to impregnate the base with a solution of a metal such as chromium following which the composite is dried and oxidized at a relatively high temperature of from about 1200° to about 1400° F. for a period of about three hours.

The reaction conditions under which the hydrodealkylation of the alkyl-substituted aromatic hydrocarbon is effected may vary over a relatively wide range and it is not intended that the present process be unduly limited to the operating conditions hereinafter set forth. The hydrodealkylation zone is usually maintained at a temperature in the range of from about 1000° to about 1500° F., preferably at a temperature ranging from about 1250° to about 1450° F. and under an imposed pressure in the range of from about 300 to about 1000 pounds per square inch, preferably in a range of from about 500 to about 600 pounds per square inch. The liquid hourly space velocity, which is defined as the volume of liquid hydrocarbon charge per volume of catalyst per hour, will generally lie within the range of from about 0.1 to about 10.0 and preferably within a range of from about 0.5 to about 5.0. Furthermore, the hydrogen/hydrocarbon ratio should be in the range of from about 5 to about 30. In addition to charging the feed stock to the third reaction zone a hydrogen stream consisting of a portion of the recycled hydrogen is also continuously charged thereto, the other portion of said recycle hydrogen being passed back to the first and second reaction zones. The reactor effluent from the dealkylation zone is withdrawn and passed to a high pressure separator or flash drum which is maintained at a pressure in the range of from about 500 to about 600 pounds per square inch. In this separator the hydrogen-rich gaseous phase which has a purity in excess of 50% is separated and recycled to the hydrodealkylation zone and to the dehydrogenation zone. The liquid hydrocarbon fraction comprising both mononuclear and polynuclear aromatic hydrocarbons as well as the unreacted corresponding alkylaromatic hydrocarbons along with a small percentage of some light hydrocarbons such as methane, ethane, propane, etc., and also some dissolved hydrogen is withdrawn as bottoms and passed to a second separator or flash drum which is maintained at a considerably lower pressure. It is contemplated that the second separator or flash drum may be maintained at a pressure in the range of from about 50 to about 150 pounds per square inch in the event that a third separator or flash drum is used. However, if only two separators or flash drums are to be used the second separation zone is maintained at approximately atmospheric pressure. In this second separation zone or flash drum the light gaseous hydrocarbons are withdrawn and passed to a gas absorber wherein any desired aromatic hydrocarbon or unreacted alkylaromatic hydrocarbon which is flashed overhead with the light hydrocarbons are absorbed in the absorber oil and passed to a stripper, while the light gaseous hydrocarbons such as methane, ethane and propane are recovered and passed to storage for subsequent use as fuel. The liquid hydrocarbon fraction from the last flash drum is withdrawn, a portion of this fraction being passed to clay towers or treaters wherein said fraction is treated to remove any impurities so that the desired product can pass the acid wash color specifications and bromine index specifications. From the clay treaters the fraction is passed to a fractionating zone wherein the desired aromatic hydrocarbon either mononuclear or polynuclear in character is separated, withdrawn from the fractionator and passed to storage while any unreacted alkylaromatic hydrocarbon is recycled to the hydrodealkylation zone to

form a portion of the feed stock. Alternatively a portion of the liquid hydrocarbon fraction from the last flash drum may be first fractionated to recover the desired aromatic hydrocarbons such as benzene or naphthalene and then passed to the clay towers or treaters for removal of any impurities which may be present. A second portion of the liquid hydrocarbon fraction from the last flash drum is recycled, one part of this fraction being admixed with the reactor effluent prior to entry into said high pressure separator or flash drum. By recycling a portion of the liquid hydrocarbon fraction from the low pressure separator the light hydrocarbons of the type hereinbefore set forth are absorbed in said liquid hydrocarbon fraction, thereby permitting the hydrocarbon rich gaseous fraction which is separated in the high pressure flash drum to be of a relatively high degree of purity, that is, over 50% (the degree of purity being defined as the mole ratio of hydrogen to hydrogen plus impurities). By utilizing a hydrogen stream possessing a relatively high degree of purity, the possibility of catalyst deactivation in the dealkylation zone and in the dehydrogenation zone due to the deposition of coke or other heavy carbonaceous material upon the catalytically active centers and surfaces of the catalyst is substantially reduced. Furthermore by eliminating the decomposition of methane to form free carbon the elimination of massive carbon formation on the walls of the reactor and other pieces of apparatus, in the spaces surrounding the catalyst as well as on the catalyst particles themselves, thereby rendering the catalyst inoperative and necessitating frequent shut-downs for decoking of the catalyst or changing the catalyst entirely will be avoided.

Yet another portion of the recycled liquid hydrocarbon fraction from the last flash drum is admixed with the reactor effluent prior to the removal of the reactor effluent from the hydrodealkylation zone thereby acting as a quench for the effluent and lowering the temperature thereof, this step being taken to reduce any metallurgical problems which may arise in the outlet system. Alternatively if so desired, the quench may comprise a portion of the desired aromatic hydrocarbons which have been recovered from a fractionation step which occurs subsequent to removal of the liquid hydrocarbon fraction from the last flash drum and prior to the treating of the aromatics in clay towers to remove any impurities. Inasmuch as the dealkylation of alkylaromatic hydrocarbons such as toluene, the xylenes, methylnaphthalene, etc., is strongly exothermic, the temperature must of necessity be controlled within a desired range in order to remove the large amount of reaction heat which might build up and have a tendency to destroy the desired product by hydrocracking the benzene or naphthalene. By recycling a portion of the liquid hydrocarbon fraction from the last flash drum, or a portion of the aromatic hydrocarbons recovered from a fractionation step after removal of the liquid hydrocarbon fraction from said last flash drum to the hydrodealkylation zone this tendency is minimized due to the fact that the reaction temperature is controlled within the desired range hereinbefore set forth.

As previously disclosed the hydrodealkylation step of the present process may utilize either two or three separate flash drums for separation of the hydrogen, light hydrocarbons and liquid hydrocarbon fractions. In the event that three flash drums are used the high pressure separator or flash drum will be maintained at a pressure in the range of from about 500 to about 600 pounds per square inch. The hydrogen rich gaseous fraction will be separated from the liquid hydrocarbon fraction in this separator, the hydrogen rich gas fraction being recycled back to the dealkylation zone and/or if so desired, to the hydrorefining zone. The liquid hydrocarbon fraction from the high pressure flash drum is withdrawn and passed to an intermediate pressure separator and is maintained at a pressure in the range of from about 50 to about 150 pounds per square inch. Any light hydrocarbons such as methane, ethane or propane which are flashed off from this separator are taken overhead and passed to a gas absorber. The liquid hydrocarbon fraction from the intermediate pressure separator is then charged to a low pressure separator or flash drum which is maintained at approximately atmospheric pressure. Any light hydrocarbons which may still be entrained in the liquid hydrocarbon fraction are withdrawn and passed to the gas absorber in combination with the light hydrocarbons and entrained aromatic or alkylaromatic hydrocarbons, if any, which have flashed off overhead from the intermediate pressure separator and low pressure separator. The light hydrocarbons are treated as hereinbefore set forth, that is, by being withdrawn from the absorber and passed to storage for utilization as fuel while the aromatic hydrocarbons and alkylaromatic hydrocarbons are passed to a stripper and recovered. The liquid hydrocarbon fraction from the low pressure separator is withdrawn and treated in a manner similar to that hereinbefore set forth, that is, one portion going to the clay treater for treatment, subsequent fractionation and recovery of the desired product, or alternatively to fractionation, then clay treatment; the second portion being recycled for use as a quench for the reactor effluent prior to the withdrawal of the effluent from the dealkylation zone while the third portion is admixed with the reactor effluent subsequent to withdrawal from the dealkylation zone and prior to entry into the high pressure separator. It is also contemplated within the scope of this invention that a fourth portion of the recycle liquid may be charged to the inlet of the dealkylation zone for use as a control of any temperature rise which might occur.

The process of the present invention may be understood more clearly through reference to the accompanying drawing. It is to be understood that the drawing, as well as the explanation thereof, is given for the purpose of illustration and is not intended to limit the process of the present invention to the particular flow so illustrated. For the sake of simplicity and clarity, various valves, heaters, condensers and other appurtenances have been eliminated from the drawing; only those vessels and connecting lines which are necessary for a complete understanding of the process are herein indicated. Referring now to the drawing, a hydrocarbon feed stock containing contaminants such as nitrogenous compounds, sulfurous compounds and oxygenated compounds as well as olefins and diolefins is charged through line **1** to a first reaction zone **2**. In this reaction zone the hydrocarbon feed stock comprising alkyl-substituted aromatic compounds is hydrorefined in the presence of a hydrorefining catalyst of the type hereinbefore set forth in greater detail, the hydrorefining conditions including a temperature of less than 500° F. and an imposed pressure of from about 400 to about 800 pounds per square inch and in the presence of added hydrogen which may be added through make-up line **3**, the hydrogen being admixed with the feed stock in line **1** before entrance into reaction zone **2**. The reactor effluent comprising substantially diolefin-free hydrocarbon feed stocks is withdrawn from reactor **2** through line **4** and passed to heater **5**. In addition, if so desired, an additional amount of hydrogen may be admixed with the reactor effluent in line **4** by means of line **6**. In heater **5**, the substantially diolefin-free feed stocks which may still contain contaminants of the type hereinbefore set forth is heated to the desired temperature, that is, above about 500° F. and preferably to a temperature of between 800 and 950° F. The charge stock is then passed through line **7** to the second reaction zone **8** which contains a dual function catalyst possessing hydrogenation-dehydrogenation activity. After treatment in this reaction zone, whereby the contaminants are formed into hydrocarbons, ammonia and hydrogen sulfide as well as dehydro-

genating any partially saturated alkyl-substituted aromatic hydrocarbons the reactor effluent is withdrawn through line **9** and passed to stripper **10**. In stripper **10**, the thus formed ammonia and hydrogen sulfide is removed through line **11**. The stripper effluent comprising alkyl-substituted aromatic hydrocarbons substantially free of contaminants, the term "contaminants" including, for purposes of this invention olefins, is withdrawn from stripper **10** through line **12** and passed to heater **13**. In heater **13**, the alkylaromatic hydrocarbon is heated to the desired reaction temperature required for hydrodealkylation, that is, a temperature of from about 1000° to about 1500° F. and preferably from a temperature of about 1250° F. to about 1450° F. The heated alkyl-substituted aromatic hydrocarbons are withdrawn from heater **13** through line **14** and passed to a third reaction zone **15**. This reaction zone in which the hydrodealkylation of the alkyl-substituted aromatic hydrocarbons is effected will contain a hydrodealkylation catalyst of the type hereinbefore set forth. The effluent from third reaction or hydrodealkylation zone **15** is withdrawn through line **16** and passed to high pressure separator **17**. This high pressure separator or flash drum is maintained at a pressure in the range of from about 500 to about 600 pounds per square inch. In this separator, the hydrogen rich gaseous phase is separated and withdrawn through line **18**, thereafter being recycled to form a portion of the added hydrogen which is admixed with the hydrocarbon feed stock in line **1** before entry into hydrorefiner **2**. In addition, as hereinbefore set forth, a portion of this hydrogen rich recycle gas may pass through line **6** and be admixed with the reactor effluent from hydrorefiner **2**, said admixture being effected in line **4**. The liquid hydrocarbon fraction from high pressure separator **17** is withdrawn through line **19** into intermediate pressure separator **20**. This second separator or flash drum is maintained at a lower pressure than is the first separator, the pressure being usually in the range of from about 50 to about 150 pounds per square inch. In the second separator, the light gaseous hydrocarbons are withdrawn and passed through line **21** to a gas absorber **22**. In gas absorber **22**, the light gaseous hydrocarbons such as methane, ethane, etc., may be recovered and passed through line **23** to storage for a subsequent use as fuel, while any desired aromatic hydrocarbon or unreacted aromatic hydrocarbon is withdrawn through line **24**. The liquid hydrocarbon fraction which is separated from the light gaseous hydrocarbons in the intermediate pressure separator **20** is withdrawn through line **25** and passed to a low pressure separator **26**. This low pressure separator is maintained at approximately atmospheric pressure. The liquid hydrocarbon fraction from the last separator or flash drum is withdrawn through line **27** to a stripper **28**. The gaseous fraction from separator **26** is withdrawn through line **43** and admixed with the gaseous products in line **21** before said gaseous products pass into absorber **22**. A portion of the liquid hydrocarbon fraction is separated from the main stream and recycled through line **29** to admix with the total reactor effluent in line **16** from the hydrodealkylation zone **15**, prior to the step of charging the reactor effluent to high pressure separator **17**. In stripper **28**, any gaseous hydrocarbons which may still be entrained in the liquid hydrocarbon fraction are stripped and withdrawn through line **30**, where they are admixed with the light gaseous hydrocarbons which were withdrawn from gas absorber **22** through line **23**. The stripped liquid hydrocarbon fraction is withdrawn from stripper **28** through line **31** and passed to clay treaters **32** and **33** through lines **31** and **31'**. In these clay towers or treaters the liquid hydrocarbon fraction is treated to remove any impurities in order that the aromatic hydrocarbons, either monocyclic or polycyclic in nature, will meet acid wash color and bromine index specifications. The treated fraction is withdrawn from the clay towers or treaters **32** and **33** through lines **34** and **34'** and passed to a fractionation tower **35** wherein the desired aromatic hydrocarbons, either monocyclic or polycyclic in nature, are separated. The desired aromatic hydrocarbons are withdrawn through line **36** and passed to storage. The unreacted alkylaromatic hydrocarbons are withdrawn as bottoms from fractionator **35** through line **37** and passed to a second fractionating zone **38**. The heavy aromatics are withdrawn from fractionation zone **38** through line **39**, a portion of said heavy aromatics being recycled to absorber **22** through line **40**. The unreacted alkyl-substituted aromatic hydrocarbons such as toluene, xylene, methylnaphthalene, etc., are withdrawn overhead through line **41**, a portion of said overhead being utilized as recycle liquid and is passed through line **42** for admixture with the feed stock from stripper **10**, said admixture taking place in line **12** before passage into heater **13**

The following example is given to illustrate the process of the present invention which, however, is not intended to limit the generally broad scope of the present invention in strict accordance therewith.

Example I

A feed stock comprising coke oven light oil is hydrorefined by passing the charge stock at a liquid hourly space velocity of 3 over a hydrorefining catalyst comprising a composite containing 2.2% by weight of cobalt and 5.7% by weight of molybdenum impregnated on alumina. The catalyst is prepared by impregnating 1/8" x 1/8" cylindrical alumina pills with a single impregnating solution containing sufficient molybdic acid (85% by weight of molybdenum oxide) and cobalt nitrate hexahydrate whereby the final catalytic composite will contain the aforementioned 2.2% by weight of cobalt and 5.7% by weight of molybdenum, calculated as the elements thereof. Following the calcination of the alumina pills, the composite is dried at a temperature of about 200° F. and is calcined at an elevated temperature of about 900° F. in an atmosphere of air. Following the calcination procedure, the temperature is decreased to about 750° F. and the catalyst is treated at this temperature with a mixture of hydrogen and hydrogen sulfide for the purpose of converting the cobalt and molybdenum components to the sulfides thereof.

The feed stock comprising, as hereinbefore set forth, a coke oven light oil is heated to a temperature of about 375° F. and contacted with the catalyst under an imposed pressure of from about 400 to about 800 pounds per square inch in a circulated stream of hydrogen at a rate ranging from about 300 to about 1500 cubic feet per barrel.

The effluent from this reactor, which is substantially diolefin-free, is passed to a second reaction zone which contains a dual function catalyst, said catalyst possessing a hydrogenation-dehydrogenation activity. An example of the catalyst used in this step comprises a composite in which alumina spheres which have been dried at a temperature of about 400° F. and thereafter calcined at a temperature ranging from about 950° F. to about 1265° F. until the volatile matter content of the alumina spheres has been decreased to a level of below 2% by weight are commingled in a rotating evaporator with water, hydrochloric acid and sufficient chloroplatinic acid to yield a catalyst which will contain 0.75% by weight of platinum calculated as the element. Following the impregnation of the alumina spheres, the spheres are subjected to high temperature calcination after being dried, said calcination or oxidation being effected at a temperature of about 550° F. for a period of one hour and thereafter increased to a temperature of about 932° F. for an additional period of two hours. The catalyst thus prepared is fluoride-free and contains 0.75% by weight of platinum and 0.9% by weight of chloride, calculated as the element. The catalyst then is heated to a temperature of about 900° F. and is contacted with a continuously circulating stream of about 95% hydrogen. After a period of about 1.5 hours, the hydrogen circulation is stopped, residual hydrogen is

purged from the vessel with nitrogen and the temperature of the catalyst is decreased to about 100° F. Following this, hydrogen sulfide is introduced in an amount sufficient to yield a final catalyst having absorbed therein 0.10% by weight of sulfur which is believed to exist as a mono-layer on the surface of the reduced platinum.

The diolefin-free charge stock from the first reaction zone, as hereinbefore set forth, is passed to the second reaction zone which contains a catalyst prepared according to the above paragraph, said feed stock being charged to the reactor at a liquid hourly space velocity of about 3. The reactor is maintained at a temperature in the range of from about 800° to about 950° F. and is under imposed pressure of from 400 to about 800 pounds per square inch. In addition, hydrogen is charged thereto at a rate in the range of from about 1000 to about 3000 cubic feet per barrel.

After passage over the catalyst and in the presence of the added hydrogen, the reactor effluent is passed to a stripper wherein any ammonia and hydrogen sulfide which are formed during the refining step are taken as overhead, while the liquid hydrocarbon fraction comprising alkyl-aromatic hydrocarbons and particularly toluene, the xylenes, etc., along with any hydrocarbons which may have formed during the purification step are taken as bottoms and, after passing through a heat exchange apparatus, are charged to a hydrodealkylation reactor. This hydrodealkylation reactor contains a catalyst comprising about 16% by weight of chromia composited on alumina.

This catalyst is prepared by drying alumina powder containing 38.8% volatile matter for a period of about 4 hours at temperatures ranging from about 600° to about 850° F., the volatile content of the dried base being reduced to about 16%. Following this, the dried base is lubricated with 5% by weight of polyvinyl alcohol and pilled, the size of said pills being ⅛". These catalyst base pills are then calcined for a period of about 1.5 hours at 950° F. and for an additional 3 hours at 1200° F. The calcined base is then impregnated with a chromic acid solution and the resulting composite is dried for a period of about 3 hours at 300° F., followed by oxidation for 1.5 hours at 800° F. The finished catalysts will contain 17.6% by weight of chromia.

The alkyl-substituted aromatic hydrocarbons are subjected to hydrodealkylation at a temperature of about 1250° F. and an imposed pressure of between 500 to 600 pounds per square inch in the presence of hydrogen, said feed stock being charged to the hydrodealkylation reactor at a liquid hourly space velocity of 1. After passage through the reaction zone the reactor effluent is withdrawn and passed to a high pressure separator wherein the gaseous hydrogen rich fraction is separated and recycled while the liquid hydrocarbon fraction is passed to a second separation zone having a lower pressure. In this zone, the normally gaseous hydrocarbons are removed while the liquid hydrocarbon fraction is passed through clay treaters and to a fractionation zone. In the fractionation zone, the desired benzene is recovered while the unreacted toluene and xylenes are recycled to form a portion of the feed stock entering the feed stream at a point prior to the hydrodealkylation reactor.

I claim as my invention:

1. A process for producing aromatic hydrocarbons from an olefin-containing, alkyl-substituted aromatic hydrocarbon charge stock containing contaminants selected from the group consisting of nitrogenous compounds, sulfurous compounds and mixtures thereof which process comprises reacting said charge stock with hydrogen in a first reaction zone at hydrogenation conditions including a temperature below 500° F. to hydrogenate diolefins and partially hydrogenate at least a portion of said alkyl-substituted hydrocarbons, passing the resultant substantially diolefin-free effluent into a second reaction zone and further reacting said effluent with hydrogen in contact with a catalytic composite having hydrogenation-dehydrogenation activity at reaction conditions including a temperature above 500° F. to convert nitrogenous compounds into hydrocarbons and ammonia and to dehydrogenate the partially hydrogenated aromatic hydrocarbons formed in said first zone, removing ammonia from the resulting second reaction zone effluent, and further reacting the remainder of said second reaction zone effluent with hydrogen in a third reaction zone in contact with a dealkylation catalyst at dealkylation conditions to convert said alkyl-substituted aromatic hydrocarbons to the corresponding aromatic hydrocarbons.

2. A process for producing aromatic hydrocarbons from an olefin-containing, alkyl-substituted aromatic hydrocarbon charge stock containing contaminants selected from the group consisting of nitrogenous compounds, sulfurous compounds and mixtures thereof which process comprises reacting said charge stock with hydrogen in a first reaction zone at a temperature in the range of from about 300° to about 500° F. and at a pressure in the range of from about 400 to about 800 pounds per square inch to hydrogenate diolefins and partially hydrogenate at least a portion of said alkyl-substituted hydrocarbons, passing the resultant substantially diolefin-free effluent into a second reaction zone and further reacting said effluent with hydrogen in contact with a catalytic composite having hydrogenation-dehydrogenation activity at a temperature in the range of from about 800° to about 950° F. and at a pressure in the range of from about 400 to about 800 pounds per square inch to convert nitrogenous compounds into hydrocarbons and ammonia and to dehydrogenate the partially hydrogenated aromatic hydrocarbons formed in said first zone, removing ammonia from the resulting second reaction zone effluent, and further reacting the remainder of said second reaction zone effluent with hydrogen in a third reaction zone in contact with a dealkylation catalyst at a temperature in the range of from about 1000° to about 1500° F. and at a pressure in the range of from about 300 to about 1000 pounds per square inch to convert said alkyl-substituted aromatic hydrocarbons to the corresponding aromatic hydrocarbons.

3. A process for producing aromatic hydrocarbons from an olefin-containing, alkyl-substituted aromatic hydrocarbon charge stock containing contaminants selected from the group consisting of nitrogenous compounds, sulfurous compounds and mixtures thereof which process comprises reacting said charge stock with hydrogen in contact with a catalytic composite of at least one metallic component from the group of metals of the left hand column of Group VIB and Group VIII of the Periodic Table, in a first reaction zone at a temperature in the range of from about 300° to about 500° F. and at a pressure in the range of from about 400 to about 800 pounds per square inch to hydrogenate diolefins and partially hydrogenate at least a portion of said alkyl-substituted hydrocarbons, passing the resultant substantially diolefin-free effluent into a second reaction zone and further reacting said effluent with hydrogen in contact with a catalytic composite having hydrogenation-dehydrogenation activity at a temperature in the range of from about 800° to about 950° F. and at a pressure in the range of from about 400 to about 800 pounds per square inch to convert nitrogenous compounds into hydrocarbons and ammonia and to dehydrogenate the partially hydrogenated aromatic hydrocarbons formed in said first zone, removing ammonia from the resulting second reaction zone effluent, and further reacting the remainder of said second reaction zone effluent with hydrogen in a third reaction zone in contact with a dealkylation catalyst at a temperature in the range of from about 1000° to about 1500° F. and at a pressure in the range of from about 300 to about 1000 pounds per square inch to convert said alkyl-substituted aromatic hydrocarbons to the corresponding aromatic hydrocarbons.

4. A process for producing aromatic hydrocarbons from an olefin-containing, alkyl-substituted aromatic hydrocarbon charge stock containing contaminants selected from the group consisting of nitrogenous compounds, sulfurous compounds and mixtures thereof which process comprises reacting said charge stock with hydrogen in contact with a catalytic composite of at least one metallic component from the group of metals of the left hand column of Group VIB and Group VIII of the Periodic Table, in a first reaction zone at a temperature in the range of from about 300° to about 500° F. and at a pressure in the range of from about 400 to about 800 pounds per square inch to hydrogenate diolefins and partially hydrogenate at least a portion of said alkyl-substituted hydrocarbons, passing the resultant substantially diolefin-free effluent into a second reaction zone and further reacting said effluent with hydrogen in contact with a catalytic composite containing a noble metal of Group VIII of the Periodic Table at a temperature in the range of from about 800° to about 950° F. and at a pressure in the range of from about 400 to about 800 pounds per square inch to convert nitrogenous compounds into hydrocarbons and ammonia and to dehydrogenate the partially hydrogenated aromatic hydrocarbons formed in said first zone, removing ammonia from the resulting second reaction zone effluent, and further reacting the remainder of said second reaction zone effluent with hydrogen in a third reaction zone in contact with a dealkylation catalyst at a temperature in the range of from about 1000° to about 1500° F. and at a pressure in the range of from about 300 to about 1000 pounds per square inch to convert said alkyl-substituted aromatic hydrocarbons to the corresponding aromatic hydrocarbons.

5. Process of claim 4 wherein said alkyl-substituted aromatic hydrocarbons are selected from the group consisting of toluene, xylenes and methylnaphthalene and the catalyst of said second zone comprises platinum and combined chlorine composited on an alumina base.

6. A process for producing aromatic hydrocarbons from an olefin-containing, alkyl-substituted aromatic hydrocarbon charge stock contaminated with sulfurous compounds which process comprises reacting said charge stock with hydrogen in a first reaction zone at hydrogenation conditions including a temperature below 500° F. to hydrogenate diolefins and partially hydrogenate at least a portion of said alkyl-substituted hydrocarbons, passing the resultant substantially diolefin-free effluent into a second reaction zone and further reacting said effluent with hydrogen in contact with a catalytic composite having hydrogenation-dehydrogenation activity at reaction conditions including a temperature above 500° F. to convert sulfurous compounds into hydrocarbons and hydrogen sulfide and to dehydrogenate the partially hydrogenated aromatic hydrocarbons formed in said first zone, removing hydrogen sulfide from the resulting second reaction zone effluent, and further reacting the remainder of said second reaction zone effluent with hydrogen in a third reaction zone in contact with a dealkylation catalyst at dealkylation conditions to convert said alkyl-substituted aromatic hydrocarbons to the corresponding aromatic hydrocarbons.

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