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PROCESS FOR HYDROGENATING AROMATIC HYDROCARBONS

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This invention relates to a process for hydrogenating aromatic hydrocarbons to the corresponding naphthenes.

Many hydrocarbon stocks, such as jet fuels, diesel fuels, gas turbine fuels, kerosenes, furnace oils, lubricating oils, and the like, can be upgraded by hydrogenation of the aromatic constituents. For example, furnace oil distillates from cracking processes usually contain a relatively large percentage of aromatic compounds, in addition to having relatively high sulfur and olefin contents. Although the common commercial hydrogen refining processes (i.e., so-called "hydrotreating") result in considerable improvement in the quality of these oils, including removal of sulfur and hydrogenation of olefins, their aromatic contents remain substantially unchanged. Because aromatic compounds in general have poor burning characteristics, conversion of the aromatics in such cracked distillates to the corresponding naphthenes is desirable for further improvement in quality. In the case of jet fuels, it is desirable to convert aromatic compounds to the corresponding naphthenes because of the higher heat of combustion of the saturated compounds.

The industry has recognized the desirability of hydrogenating the aromatic compounds in the enumerated stocks, and such hydrogenation is frequently effected by using a catalyst consisting of a hydrogenating component on an acidic support. However, hydrogenation efficiency in such a process is lowered by side reactions such as isomerization and cracking.

This invention is concerned with an improved process for hydrogenation of aromatic hydrocarbons which reduces cracking and isomerization to a minimum.

Accordingly, it is an object of the invention to provide an improved process for hydrogenating aromatic hydrocarbon feed stocks without appreciable cracking and isomerization. Another object is to provide an improved process for hydrogenating feed streams of substantially pure aromatic hydrocarbons. Other objects of the inveniton will become apparent to one skilled in the art upon consideration of the accompanying disclosure.

A broad aspect of the invention comprises contacting a hydrocarbon feed stock containing a substantial proportion of aromatics in admixture with hydrogen and with a nitrogen compound which yields NH_3 under the conditions of the process with a catalyst consisting essentially of a porous support of the silica-alumina type having deposited thereon or being impregnated with a hydrogenating component of the group consisting of the oxides and sulfides of the metals of Group VI–B, metals, oxides, and sulfides of the ferrous metals of Group VIII, and combinations thereof, under hydrogenating conditions including a temperature not above 700° F. and below that at which any substantial cracking occurs so as to effect principally hydrogenation, and recovering the hydrogenated effluent from the contacting.

The process is carried out continuously in well-known types of equipment within the following ranges of operating conditions:

	Broad	Preferred
Temperature, ° F.	500–700	500–650
Pressure, p.s.i.g.	500–5,000	1,000–3,000
H_2, s.c.f./bbl.	500–25,000	4,500–18,500
Aromatic, LHSV	0.1–10.0	0.4–3.0

The active hydrogenating ingredient is selected from

those known to the industry—i.e., the Group VI–B (Lange's Handbook of Chemistry, Eighth Edition, pp. 56–57) oxides and sulfides (Cr, Mo, and W) and the Group VIII ferrous metals, oxides, and sulfides, or mixtures thereof. Usually a Group VI–B oxide or sulfide is used together with a Group VIII ferrous metal, oxide, or sulfide, whereas a Group VIII ferrous metal, oxide, or sulfide is frequently used alone. Exemplary of active hydrogenating ingredients that can be used are nickel, cobalt, nickel oxide-molybdenum oxide (frequently referred to as nickel molybdate), iron sulfide, nickel sulfide, cobalt sulfide, cobalt oxide-molybdenum oxide (frequently referred to as cobalt molybdate), cobalt sulfide-molybdenum sulfide, nickel oxide-tungsten oxide (frequently referred to as nickel tungstate), nickel sulfide-tungsten sulfide, tungsten sulfide, and the like. The active ingredient, or each of the active ingredients if there is more than one, can be present (as metal) to the extent of 0.1 to 25.0 weight percent, preferably 1.0 to 15.0 weight percent, of the support. It is preferred to use a nickel tungstate or a nickel molybdate catalyst, which have been found to be equivalent. Quite frequently the catalyst is sulfided by treating with a material such as carbon disulfide before use. It is also possible to obtain the same effect by operating with a sulfiding material in the feed, or by both presulfiding and operating with a sulfiding material in the feed.

The invention is described particularly with reference to a silica-alumina support, but any of the known acidic supports can be used to prepare catalysts for the process of the invention. Exemplary of other acidic supports are silica-zirconia, silica-alumina-zirconia, silica-magnesia, silica-alumina-magnesia, silica-thoria, silica-alumina-thoria, alumina-boria, and the like. The support used can optionally be treated with steam to decrease the acidity or with a halogen or halogen acid to increase the acidity.

The compounds which are suitable for introduction into the reaction zone according to the present invention include ammonia, ammonium hydroxide, the primary, secondary, and tertiary alkyl amines, alkanol amines, aryl amines, mixed alkyl aryl amines, alkyl diamines, and aryl diamines. Examples of these compounds are: mono-, di-, and tri-methyl amine; mono-, di-, and tri-ethyl amine; mono-, di-, and tri-ethanol amine; mono-, di-, and triphenyl amine; phenyl-ethyl amine; phenylene diamine, and similar amines. Although only the lower molecular weight amines have been enumerated, the higher molecular weight members of the various homologous series may be used, since they also will be converted to ammonia under the conditions of the hydrogenating process. In addition to the aforementioned compounds, an extremely large number of other nitrogen-containing compounds are suitable, for example, organic nitrates, nitrites, nitriles, nitroso compounds, amides, imides, ammonium salts (such as ammonium acetate), urea and derivatives thereof, cyanates, isocyanates, isocyanides, quaternary ammonium compounds, nitro compounds, pyridine and derivatives thereof such as quinoline, piperidines, oximes, hydroxyl amine, azo compound, or, in general, any nitrogen-containing compound, or mixtures of such compounds, which can be converted to ammonia as one of the products under the conditions of hydrogenation is suitable, provided that such compound, or mixtures of such compounds, will not deposit a solid residue on the catalyst.

It is convenient to express the ratio of nitrogen-containing compound to hydrocarbon feed on the basis of the nitrogen content of the compound used. Sufficient nitrogen-containing compound is used to give 0.005 to 5.0 weight percent, preferably, 0.05 to 3.0 weight percent nitrogen, based on the hydrocarbon feed.

For purposes of illustration the process was applied to a pure feed stock so that the types of reaction obtained could be more clearly defined. The feed stock used was

Tetralin (tetrahydronaphthalene), from which the desired product was Decalin (decahydronaphthalene). The catalyst used contained 3.5 weight percent nickel and 7.7 weight percent molybdenum, and was supported on 10–20 mesh 88 silica-12 alumina. It was prepared by impregnating the support with aqueous ammonium molybdate, calcining at 800° F., impregnating with aqueous nickel nitrate, calcining at 1100° F., treating the product 4 hours at 600° F. and 2000 p.s.i.g. with hydrogen, and then sulfiding 5.5 hours in the presence of hydrogen at the same temperature and pressure with a solution containing 3 volume percent CS_2 in n-hexane. Ten runs were made under the following conditions:

Temperature, ° F.	598–806
Pressure, p.s.i.g.	2000
H_2, s.c.f./bbl.	14,000–17,000
Tetralin, LHSV	0.5

Six of the runs were made without nitrogen in the feed to establish base conditions. Four runs were made with nitrogen in the feed: two with 1000 p.p.m. nitrogen as quinoline, one with 1150 p.p.m. nitrogen as ammonia, and one with 1600 p.p.m. nitrogen as ammonia. Carbon disulfide equivalent to 5000 p.p.m. sulfur was present in all except the runs made with ammonia—i.e., presulfiding alone was used in those runs. The data from these runs were plotted, and the following comparison was taken from the smoothed curves:

Tetralin Converted, wt. Percent	Temp., ° F.		Decalin, wt. Percent		Cracked and Isomerized Products, wt. Percent	
	No N	With N	No N	With N	No N	With N
40	654	693	23.5	32.5	16.5	7.5
60	690	732	25.5	40.0	34.5	20.0

The foregoing data illustrate a number of facts which are significant. Even though the addition of N compounds requires somewhat higher operating temperatures to obtain the same conversion—at which more product loss to byproducts would be expected—the yield of hydrogenated product is increased by 38 and 57 percent, respectively, at the two conversion levels shown. It should be noted that a temperature of 693° F. with nitrogen in the feed is about as high as one would operate within the scope of the invention because of the higher conversion of aromatics to cracked and isomerized products rather than to naphthenes. At a temperature of 732° F. there is a higher yield of Decalin but there is also a substantial increase in the formation of cracked and isomerized products which is to be avoided. Consequently, hydrogenation temperature would be generally maintained below 700° F. and at a level at which there would be less than 8 to 10 percent conversion of the feed to cracked and isomerized products.

The invention is applicable to any hydrocarbon feed stock which contains about 5 to 100 weight percent aromatics.

Certain modifications of the invention will become apparent to those skilled in the art and the illustrative details disclosed are not to be construed as imposing unnecessary limitations on the invention.

I claim:

1. A process for hydrogenating an aromatic hydrocarbon feed which comprises the steps of:

(a) contacting said feed in a hydrogenating zone with a catalyst consisting essentially of a porous support selected from the group consisting of silica, alumina, magnesia, thoria, zirconia, and combinations thereof impregnated with a hydrogenating component selected from the group consisting of the oxides and sulfides of the metals of Group VI–B, the metals, oxides, and sulfides of the Group VIII ferrous metals, and combinations thereof, in admixture with hydrogen under hydrogenating conditions including a temperature not more than about 700° F. which avoids substantial cracking of the feed;

(b) incorporating in the reaction mixture in the hydrogenating zone of step (a) a nitrogen compound which supplies ammonia therein at an N concentration in the range of 0.05 to 3.0 weight percent based upon the weight of said feed;

(c) recovering a hydrogenated effluent from the zone of step (a).

2. The process of claim 1 wherein said nitrogen compound is an amine.

3. The process of claim 1 wherein said nitrogen compound is NH_3.

4. The process of claim 1 wherein said nitrogen compound is quinoline.

5. The process of claim 1 wherein said catalyst consists essentially of the oxides of nickel and molybdenum on silica-alumina.

6. The process of claim 1 wherein said catalyst consists essentially of the sulfides of nickel and molybdenum on silica-alumina.

7. A process for hydrogenating an aromatic hydrocarbon which comprises the steps of:

(a) passing a stream of said hydrocarbon into a hydrogenating zone in admixture with hydrogen;

(b) maintaining in the zone of step (a) a volatile nitrogen compound which supplies NH_3 in the reaction mixture, said compound being in a concentration (calculated as N) in the range of 0.05 to 3 weight percent of the hydrocarbon feed;

(c) contacting the reactant mixture in said zone with a hydrogenating catalyst consisting essentially of silica-alumina and a hydrogenating component selected from the group consisting of the oxides and sulfides of the metals of Group VI–B, the metals, oxides, and sulfides of the ferrous metals of Group VIII, and combinations thereof, under hydrogenating conditions so as to hydrogenate said hydrocarbon;

(d) maintaining hydrogenating temperature in said zone not above 700° F. and below that at which any substantial cracking occurs so as to effect principally hydrogenation; and

(e) recovering an effluent stream from said zone comprising hydrogenated hydrocarbon as the principal conversion product.

8. The process of claim 7 wherein the hydrocarbon feed is principally Tetralin and the product is principally Decalin.

9. The process of claim 7 wherein the hydrocarbon feed is a cracked distillate containing a substantial concentration of aromatics and a substantial proportion of said aromatics is converted to the corresponding naphthenes.

10. The process of claim 7 wherein said hydrocarbon feed is an oil boiling below about 600° F. and contains at least 5 weight percent of aromatics and a substantial proportion of said aromatics is converted to the corresponding naphthenes.

11. The process of claim 7 wherein said hydrocarbon feed is a jet fuel containing a substantial proportion of aromatics and a substantial proportion of said aromatics is converted to the corresponding naphthenes.

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