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PROCESS FOR SELECTIVELY HYDROGENATING PETROLEUM CUTS OF THE GASOLINE RANGE IN SEVERAL STEPS

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ABSTRACT OF THE DISCLOSURE

A feedstock of the gasoline range is selectively hydrogenated in three steps; a first step in liquid phase with a Group VIII metal catalyst, a second step in gaseous phase with a molybdenum or tungstn catalyst on a carrier of low surface and a third step with a molybdenum or tungsten catalyst on a carrier of high surface.

This invention relates to the selective hydrogenation in thre successive catalytic steps of feedstocks comprising aromatic, diolefinic and olefinic hydrocarbons together with sulfur compounds.

Many processes are known for selectively hydrogenating feedstocks containing aromatic hydrocarbons, diolefins, olefins and sulfur compounds. These processes have for object the removal of undesirable components by hydrogenation of diolefins and olefins and hydrodesulfurization. They further result in an easy separation of the aromatic components of the feedstock.

The single step catalytic processes, in which both hydrogenation and desulfurization take place, are no longer used since at the temperature required for the desulfurization of the feedstock the unstable compounds are polymerized. The resulting gums are detrimental to a good operation of the process.

Processes are known which comprise several catalytic steps, for example two or thre steps, these steps consisting in the successive hydrogenation and desulfurization of the feedstock. However, the already known processes suffer from disadvantages. When the olefins of the feedstock are hydrogenated by means of conventional hydrogenation catalysts, the hydrogenation of a portion of the aromatic components of the feedstock cannot be avoided.

This hydrogenation results in a loss of final product of more than 10% when the process is used to obtain aromatic hydrocarbons. When conventional hydrogenation catalysts are used in the first step of the process and the unstable compounds, such as diolefins, have not been completely hydrogenated, it is difficult in the gaseous phase to avoid the formation of polymerized compounds which spoil and quickly deactivate the catalyst.

It is an object of this invention to provide a selective hydrogenation process comprising at least three steps, each of which involves the use of a catalyst whose components, active metal and carrier, if any, are so selected as to avoid the above disadvantages.

This invention relates to a process for selectively hydrogenating a feedstock boiling in the gasoline range and containing aromatic hydrocarbons, diolefins, olefins and sulfur compounds, said process comprising the following steps of (1) reacting in a first reaction zone, the feedstock in liquid phase, with hydrogen in contact with a hydrogenation catalyst consisting of a metal from Group VIII of the periodic classification, (2) reacting in a second reaction zone, the effluent from the first reaction zone, in gaseous phase, with hydrogen in the presence of a catalyst comprising at least one metal selected from molybdenum and tungsten and a carrier, the surface of the catalyst being from 20 to 90 m.²/g., (3) reacting in a third reaction zone, the effluent from the second reaction zone in gaseous phase, with hydrogen in the presence of a catalyst comprising at least one metal selected from molybdenum and tungsten on a carrier the surface of catalyst being from 120 to 500 m.²/g.

The feedstock of the gasoline type is defined as a charge at least 80% of which distills from 30 to 220° C. In this process, the preferred charges have a high content of aromatic components. The process may be used, for example, for treating gasolines obtained by cracking, such as thermal cracking, catalytic cracking or steam cracking, of naphtha or gas-oil, or by coking of distillates.

The operating conditions are as follows:

The first step is carried out in liquid phase, which means that, at the outlet from the first reaction zone, at least 50% by weight of the initial feedstock is again in liquid phase; the remaining portion, if any, was vaporized in the reaction zone. The vaporization is produced by the high amount of heat released by the hydrogenation reaction. The temperature in the reaction zone may vary from 50 to 200° C.; preferably, this temperature is lower than 200° C., even at the outlet ofthe reaction zone so as to avoid any excess polymerization. The liquid charge is preferably fed to the reaction zone at a temperature of from 50 to 120° C. The pressure should be high enough for maintaining at least the major part of the liquid charge in the liquid phase; it usually ranges from 5 to 60 kg./cm.² and preferably from 20 to 45 kg./cm.².

In this step, the liquid feedstock is contacted with a hydrogenation catalyst selected from the metals of the VIIIth group of the periodic chart, for example nickel, cobalt, palladium or platinum. Nickel is preferred, however. The metals are preferably used in the metallic state; carriers may be admixed therewith. The catalysts may be used in fixed or moving bed. Suspended catalysts may also be used, e.g. Raney nickel or cobalt. However, according to a preferred embodiment, they are used with a carrier in fixed bed. The carrier may be any conventional carrier, for example alumina, silica, alumina-silica, magnesia, clay, a zeolite and the like. The preferred carriers, e.g. aluminum or silica, have a low surface acidity. The natural surface acidity of the carrier may be neutralized by adding alkali or earth-alkali metal oxides. The supported catalysts usually comprise from 5 to 50% by weight of active metal. The spatial velocity V.V.H., i.e. the hourly volume rate of the charge per liter of catalyst, may be in the range of from 0.5 to 5 according to the activity of the catalyst and the content of unsaturated compounds of the feedstock. The hydrogen amount introduced into the reaction zone may be varied, so as to obtain a molar ratio of hydrogen to hydrocarbons of, for example, 0.1 to 1.

At the outlet of the first reaction zone, a large fraction of the feedstock is again in the liquid state; it is vaporized by any known means, provided that gum formation be avoided, for example by distilling only 90 to 99% of this liquid.

The gaseous charge is then introduced into the second reaction zone at a temperature of, preferably from 230 to 300° C. The charge and hydrogen are then contacted with a catalyst on a carrier. This catalyst comprises a metal (molybdenum or tungsten) which may be used alone or in admixture with one or several metals of Group VIII, for example cobalt or nickel or a mixture thereof. The active element of the catalyst may be admixed with a carrier of low specific surface, in the range of from about 20 to 90 m.²/g. Alumina, silica magnesia and titanium oxide are examples of these carriers.

Substantially neutral carriers are preferred, i.e. those having a low surface acidity. There will be explained hereinafter what is meant by low acidity of the carrier,

The temperature within the reaction zone is selected from 230 to 360° C. A portion of the charge, either from the first step or from recycling, may be introduced at least at one intermediate point of the catalyst bed, so as to avoid a too high temperature increase resulting from the heat released during the hydrogenation reaction. The pressure within the zone may be from 25 to 60 kg./cm.^{2}. The hydrogen amount is preferably such that the molar ratio of hydrogen to the olefins be in the range of from 5 to 15, and that the hydrogen partial pressure in the catalyst bed be in the range of from 8 to 30 kg./cm.^{2}.

The feedstock spatial velocity (VVH) is preferably from 4 to 20, the volume of charge being calculated as liquid.

The second step catalyst comprises either molybdenum or tungsten or a mixture of the same with at least one Group VIII metal. The following pairs are selected according to a preferred embodiment of this invention: molybdenum-cobalt, molybdenum-nickel, tungsten-cobalt, tungsten-nickel.

The previous catalysts may be used as the oxide, however the sulfided form is preferred. In order to maintain the catalyst at a convenient degree of sulfurization, it is preferred to have a volume ratio of hydrogen sulfide to hydrogen in the range of from 200 to 4000 p.p.m. This may be obtained by recycling hydrogen sulfide from the off-gases of the third step which terminates the feedstock desulfurization.

When the catalyst comprises only molybdenum or tungsten, the content of the active element will be preferably between 6 and 40% by weight of metal expressed as oxide.

When the catalyst comprises at least two metals, the contents of the latter are preferably from 4 to 25% by weight of molybdenum or tungsten as oxide and from 2 to 15% by weight of the Group VIII metal as oxide.

The gas effluent from the second step is fed to a third reaction zone, preferably at a temperature of from 300 to 350° C., and contacts a catalyst comprising a metal, either molybdenum or tungsten, alone or admixed with one or several metals of Group VIII. The preferred catalysts are the catalyst pairs mentioned above, i.e. Co-Mo, Ni-Mo, Co-W, Ni-W. The metals are incorporated to a carrier of a rather large specific surface, i.e. from about 120 to 500 m.^{2}/g. This carrier may be, for example, a transition alumina, eta alumina, alumina-silica. Slightly acidic carriers are preferred, as explained hereinafter. The reaction temperature within the third reaction zone may be in the range of from 300 to 390° C.; the total pressure may be, for example, in the range of from 10 to 60 kg./cm.^{2}, preferably from 30 to 50 kg./cm.^{2}.

The feedstock spatial velocity (VVH) is preferably from 0.5 to 5 liters of feed per liter of catalyst and per hour, these volumes being calculated as liquid.

The hydrogen amount is such that the hydrogen partial pressure within the catalyst bed is preferably from 8 to 25 kg./cm.^{2} and the molar ratio of hydrogen to the olefins remains between 5 and 15.

The third step catalysts may be used as oxides, irrespective of the number of different metals contained therein. A sulfurized catalyst is, however, preferred; in that case, the amount of hydrogen sulfide is preferably so selected as to have a ratio by volume of hydrogen sulfide to hydrogen between 200 and 4,000 p.p.m. When the catalyst contains only one metal (molybdenum or tungsten), the preferred amount thereof is from 5 to 35% by weight expressed as oxide.

When the catalyst contains at least one pair of metals such as hereinbefore defined, the content of molybdenum or tungsten expressed as oxide is preferably from 5 to 30% by weight and the content of Group VIII metal, expressed as oxide is preferably from 1 to 6% by weight.

The metal content is expressed as the weight of corresponding oxide since these metals are usually incorporated to carriers as metal compounds which may be converted to metal oxides by heating before being reduced or sulfided if desired.

The acidity of the carriers used in the process may be determined by the heat of adsorption of ammonia thereon at a pressure of 10^{-4} mm. Hg. The heat of adsorption ΔH may be expressed as follows:

$$\Delta H = \frac{\text{Heat released in calories per gram of carrier}}{\text{Ammonia adsorption in millimoles of } NH_3 \text{ per gram of carrier}}$$

These two determinations may be carried out by microgravimetry and differential thermal analysis at the temperature at which the catalyst must be used.

When ΔH is lower than 0.04 (carriers of the second step), the carrier may be considered as substantially neutral or slightly acidic. When ΔH is between 0.04 and 0.1 (carriers of the third step), the carrier may be considered as slightly acidic.

EXAMPLE 1

The feedstock is a steam-cracking gasoline having the following compostion:

Paraffins and naphthenes: 27% by volume
Mono-olefins: 8.6% by volume
Diolefins and cycloolefins: 10:4% by volume
Aromatic and alkenylaromatic compounds: 54% by volume
Total sulfur: 160 p.p.m.

The operating conditions are the following:

First step

Inlet temperature: 80° C.
Outlet temperature: 180° C.

The catalyst consists of nickel deposited on alumina; it contains 12.5% of nickel expressed as oxide sp. surf. 70 m.^{2}/g.

Pressure: 30 kg./cm.^{2}
VVH: 2
Molar ratio of hydrogen to hydrocarbons: 0.3

Second step

Inlet temperature: 280° C.
Outlet temperature: 320° C.
Total pressure: 43 kg./cm.^{2}
H_2 partial pressure: 15 kg./cm.^{2}
Hydrogen sulfide/hydrogen: 1,000 p.p.m. by volume
Hydrogen/olefins: 10 (molar ratio)
VVH: 6
Catalyst:cobalt: 5.7% by weight expressed as CoO (0.076, mole of oxide per 100 g. of catalyst)
molybdenum: 5.7% by weight expressed as MoO_3 (0.040 mole of oxide per 100 g. of catalyst)
carrier: alumina

Thus 100 grams of catalyst contain 0.116 mole of metal oxide; the catalyst has a specific surface of 70 m.^{2}/g.

This catalyst is sulfided by pretreating with a mixture of H_2S and H_2.

The carrier, when subjected to the acidity test, shows a ΔH of 0.03.

Third step

Inlet temperature: 320° C.
Outlet temperature: 340° C.
Total pressure: 43 kg./cm.^{2}
Hydrogen partial pressure: 14 kg./cm.^{2}
VVH: 1
Hydrogen sulfide/hydrogen (by volume): 1,200 p.p.m.
Catalyst:
cobalt: 2.2.% by weight as CoO
molybdenum: 12.2% by weight as MoO_3
carrier: alumina of ΔH 0.07
The catalyst has a specific surface of 300 m.^{2}/g.

This catalyst is sulfided by pretreating with a mixture of H_2S and H_2. The characteristics of the feedstock before and after treatment are given hereinafter in Table 1 with those of the feedstock of comparative Example 2.

COMPARATIVE EXAMPLE 1A

The same feedstock as in Example 1 is subjected to a three-step hydrogenation: the first step is the same as in Example 1; however, in the second step, the catalyst is 1% platinum on alumina. The specific surface is 220 m.²/g. and platinum is used in the metal form. In the third step, the catalyst is the same molybdenum-cobalt catalyst as in Example 1 (300 m.²/g.), the CoO and MoO_3 content being respectively 2.2% and 12.2%. This catalyst was presulfided as in Example 1. The properties of the feedstock and the product are given in Table I.

TABLE 1

Composition	Feed stock	Product of— Ex. 1	Ex. 1A
Paraffins plus naphthenes, percent by vol	27	47	52
Monoolefins, percent by vol	8.6	0	0
Diolefins plus cycloolefins, percent by vol	10.4	0	0
Aromatics plus alkenylaromatics, percent by vol	54	53	48
Specific gravity, g./cm.³	0.793	0.785	0.778
Bromine number, g. Br²/100 g	66	<1	<1
M.A. V., mg. M.A./g	74	0	0
Gums (existing), mg./100 ml	30	2	2
Gums (potential), mg/100 ml	7,740	3	3.2
Total sulfur, p.p.m	20	4	4

In this table, the bromine number is determined according to ASTM method D1159–61. By M.A.V.,there is meant "maleic anhydride value" determined according to DOP method 326–58. The tests used for determining the amounts of existing and potential gums are ASTM D381–61 and ASTM D873 respectively.

This table shows (bromine number and MAV) that the olefin hydrogenation rate is substantially the same in the two processes; however the composition of the products is changed.

In Example 1, the loss of aromatic components by hydrogenation is only 1 unit; it is six in comparative Example 1A. The yield increase is about 10% according to this invention, as compared to the prior process, the quality of the product being similar.

COMPARATIVE EXAMPLE 1B

The same feedstock as in Example 1 is hydrogenated in three steps. The operating conditions and the catalysts are the same as in Example 1, except that, in the second step (catalyst Mo-Co), there is too high specific surface (220 m.²/g.). The resulting product contains 51% by volume of aromatics and alkenyl aromatics, in comparison with 53% in Example 1.

COMPARATIVE EXAMPLE 1C

The same feedstock as in Example 1 is subjected to a three steps hydrogenation treatment. The operating conditions and catalysts are those of Example 1; however, in the second step the ratio by volume of hydrogen sulfide to hydrogen is 100. The resulting product contains 51.5% by volume of aromatics and alkenylaromatics; it also contains 100 mg. of gums per 100 ml., instead of 2 mg./100 ml. in Example 1.

EXAMPLE 2

Example 1 is repeated except that the second step is carried out with a sulfided molybdenum catalyst deposited on an alumina carrier. The specific surface is 70 m.²/g. The content of molybdenum expressed as MoO_3 is 16.6% by weight, i.e. 0.116 mole of oxide.

The following results are obtained:

Composition	Charge	Product
Paraffins plus naphthenes, percent by vol	27	45.4
Monoolefins, percent by vol	8.6	1.1
Diolefins plus cycloolefins, percent by vol	10.4	
Aromatics plus alkenylaromatics, percent by vol	54	53.5
Specific gravity, g./cm.³	0.793	0.7855
Bromine number, g. Br₂/100 g	66	1.8
M.A.V., mg. M.A./g	74	0
Gums (existing), mg./100 ml	30	2
Gums (potential), mg./100 ml	7,740	3
Total sulfur, p.p.m	20	5

A comparison of these results with those of Example 1 shows that the process may be successfully carried out with a molybdenum catalyst in the second step: although the removal of undesired compounds such as olefins and sulfur is not so complete, the yield of aromatic components is better (loss of 0.5 unit only).

What we claim as our invention is:

1. A process for selectively hydrogenating a feedstock boiling in the gasoline range, containing aromatic hydrocarbons, olefins, diolefins and sulfur compounds, which comprises:
   (a) a first step of reacting said feedstock in the liquid phase with hydrogen in the presence of a hydrogenation catalyst comprising a metal from Group VIII,
   (b) a second step of reacting the product from the first step, in gaseous phase, with hydrogen in the presence of a catalyst comprising at least one supported metal selected from the group consisting of molybdenum and tungsten said catalyst having a specific surface of from 20 to 90 m.²/g.
   (c) a third step of reacting the product from the second step, in gaseous phase, with hydrogen in the presence of a catalyst comprising at least one supported metal selected from the group consisting of molybdenum and tungsten said catalyst having a specific surface of from 120 to 500 m.²/g.

2. A process according to claim 1, wherein the third step catalyst is in the form of a sulfide.

3. A process according to claim 1, wherein the second step catalyst is in the form of a sulfide.

4. A process according to claim 2, where hydrogen sulfide is fed to the third reaction zone in an amount corresponding to a ratio of hydrogen sulfide to hydrogen in the range of from 200 to 4,000 p.p.m. by volume.

5. A process according to claim 3, wherein hydrogen sulfide is fed to the second reaction zone in an amount corresponding to a ratio of hydrogen sulfide to hydrogen in the range of from 200 to 4,000 p.p.m. by volume.

6. A process according to claim 1, wherein the catalyst of the second step comprises a metal selected from the group consisting of molybdenum and tungsten and a metal of group VIII.

7. A process according to claim 1, wherein the catalyst of the third step comprises a metal selected from the group consisting of molybdenum and tungsten and a metal of Group VIII.

8. A process according to claim 6, wherein the metal from group VIII is selected from the group consisting of nickel and cobalt.

9. A process according to claim 7, wherein the metal from Group VIII is selected from the group consisting of nickel and cobalt.

10. A process according to claim 8, wherein the catalyst of the second step comprises from 4 to 25% by weight of molybdenum or tungsten compound expressed as oxide and from 2 to 15% by weight of nickel or cobalt compound expressed as oxide.

11. A process according to claim 9, wherein the catalyst of the third step comprises from 4 to 25% by weight of molybdenum or tungsten compound expressed as oxide and from 2 to 15% by weight of nickel or cobalt compound expressed as oxide.

12. A process according to claim 1, wherein the catalyst of the first step consists of a metal from Group VIII in the metal form.

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HERBERT LEVINE, Primary Examiner

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CERTIFICATE OF CORRECTION

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Inventor(s) YVES JACQUIN ET AL.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, Heading: Insert under Foreign Application Priority Data: -- July 27, 1970, France E.N. 70/27.704 --.

Signed and sealed this 22nd day of May 1973.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents

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