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CATALYST FOR HYDROCARBON CONVERSIONS

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This invention relates to catalytic compositions effective in catalytic processes for converting hydrocarbons. More particularly, the invention relates to new and improved inexpensive catalytic compositions, their preparation, and to processes for using the new catalysts, such as processes for removing nonhydrocarbons from mixtures thereof with hydrocarbons and for converting heavy hydrocarbons to relatively low boiling hydrocarbons. The invention also relates to the conversion of petroleum residues to cracking stock and subsequently cracking the converted residues.

Gas oils and petroleum residues frequently contain relatively large quantities of sulfur, as organic sulfur compounds, and nitrogen, as organic nitrogen compounds. Unless the nonhydrocarbons are removed such petroleum fractions are of little value, e.g., as fuel or as stock for conversion processes such as cracking, since deleterious effects are observed and inferior products are obtained. For example, rapid catalyst deactivation is observed in the cracking of gas oils containing appreciable quantities of sulfur compounds, and the gasoline obtained from the process contains sulfur compounds which are deleterious and have an adverse effect on lead susceptibility. Also, processes for converting heavy hydrocarbon materials, such as residues from petroleum cracking operations, reduced heavy crude oil, still tars, and the like, which contain substantial quantities of nonhydrocarbons are of little value for the same reasons. Processes for desulfurizing petroleum fractions, including processes for converting residues to more valuable lower boiling products, have been described. Such processes generally involve contacting the hydrocarbon material containing nonhydrocarbons with hydrogen and a cracking or hydrogenation catalyst at high temperature and high pressure, the pressure usually being of a magnitude of about 3000 p.s.i.g. or higher. These processes generally require special, expensive catalysts, and suffer from one or more other drawbacks, such as poor yields of the desired liquid products, poor quality of the products produced, excessive coke formation resulting in plugged equipment, degradation of the charge material, excessive production of dry gas, are inefficient for their intended purpose, and other difficulties.

An especially serious drawback of processes heretofore used is the degradation of the relatively high boiling products of the process so that they are unsuitable, or at least less suitable, for use in recycling to the process. By "degradation" is meant the conversion of a portion of the relatively high boiling materials of the charge stock to other relatively high boiling materials which, when again used in the process such as by recycling, are converted to coke. "Degradation" also includes concentrating such high boiling materials, which are converted to coke on reuse, in the recycle fraction. The Ramsbottom carbon residue method (ASTM D524–42) of evaluating the coke forming tendencies of both the charge stock and recycle stock of the process provides a measure of the degradation of the relatively high boiling materials. Thus, when the Ramsbottom carbon residue of the recycle stock from the process is greater than the Ramsbottom carbon residue of the charge stock, the recycle stock has been degraded and its reuse in the process results in the formation of relatively large quantities of coke. Conversely, when the Ramsbottom carbon residue of the recycle stock is less than the Ramsbottom carbon residue of the charge stock, the materials of the recycle stock have been upgraded and their reuse in the subsequent process results in a decrease in coke formation. Upgrading the recycle stock permits recycling to substantial extinction to form relatively low boiling hydrocarbons as the sole product of the process.

An object of the present invention is to provide new and improved inexpensive catalytic compositions effective for converting hydrocarbons and for removing nonhydrocarbons from hydrocarbons. Another object is to provide a process for converting heavy hydrocarbon materials to relatively low boiling hydrocarbon products. A particular object is to provide a process for converting residual oils to cracking stock in good wields, using inexpensive catalysts, in which only negligible quantities of coke and dry gas are formed. A further object is to provide a process for producing gasoline from petroleum residues in which the hydrocarbons of the residue are substantially completely converted to hydrocarbons boiling in the gasoline range.

GENERAL

New catalytic compositions have been discovered which give improved results in converting hydrocarbons and in removing nonhydrocarbons from hydrocarbons. The new catalytic compositions comprise coprecipitated cobalt molybdate-alumina containing a minor quantity of zinc oxide. If desired, cadmium oxide can be substituted for the zinc oxide in whole or in part. It is essential that certain steps be performed in the preparation of the catalyst, and that the defined components be within certain limits as hereinafter described.

Although the catalyst is above described as containing coprecipitated cobalt molybdate-alumina, it is realized that this catalytic component may consist in whole or in part of a combination of the oxides of the metals thereof, namely, cobalt oxide, molybdic oxide and alumina, and it is convenient to describe the proportion of components present in the composition in terms of such oxides. As hereinafter described, it is preferred to employ a quantity of cobalt oxide less than that which is stoichiometrically required to form cobalt molybdate, and hence it is believed that at least a portion of the metals are present as the oxides. It is also realized that the zinc or cadmium may be present, at least in part, as the molybdate, especially when such metal is present during coprecipitation of the cobalt molybdate and alumina, as hereinafter described.

The reactions involved in the conversion of hydrocarbons in accordance with the invention depend upon the charge stock employed and the reaction conditions used therewith. Thus, when operating with a gas oil to remove nonhydrocarbons, the overall process can be designated as "hydrorefining" and the principal reactions are the conversion of sulfur compounds to hydrogen sulfide and the conversions of nitrogen compounds to form ammonia, which products are readily removed from the hydrocarbon fraction. When operating with a petroleum residue, the reactions are principally the conversion of nonhydrocarbons as above described, and lowering the boiling points of a portion of the hydrocarbons by hydrogenation, e.g., of aromatic to naphthenes, by cracking, e.g., by cleavage of carbon-carbon bonds or by the splitting out of sulfur and/or nitrogen and/or oxygen atoms as hydrogen sulfide, ammonia or water, respectively. Hence the overall process is conveniently designated "hydrocracking," which term includes hydrorefining. Metal contaminants commonly present in such fractions, e.g.,

nickel and vanadium, are also removed in the process.

It has been found that by subjecting a petroleum residue to the hydrorefining process of the invention, the entire liquid effluent can immediately be passed to catalytic cracking and good results obtained therewith. To convert the residue to cracking stock, it is not necessary to cause a substantial amount of cracking, since the high boiling residue, when treated in accordance with the present process, gives good results in subsequent cracking operations.

The new catalytic compositions of the present invention may be prepared by general techniques heretofore known. It is of primary importance that the limits on the ranges of concentration for each ingredient be observed. It is preferred, however, to employ a catalyst prepared by the method as hereinafter described.

THE CATALYST

As above stated, the catalytic compositions of the present invention comprise coprecipitated cobalt molybdate-alumina with a minor quantity of zinc oxide. Cadmium oxide can be substituted for the zinc oxide. The composition of the catalyst of the invention is conveniently defined in terms of the oxides of the metals of the catalyst, namely, molybdic oxide, cobalt oxide, alumina and zinc oxide, i.e., the quantities of the several metals present are stated in terms of the oxides thereof. The quantity of molybdic oxide must be in the range of from 5 to 20% by weight. The mole ratio of cobalt oxide to molybdic oxide must be within the range of from 0.2 to 1, and is preferably in the range of from 0.5 to 0.7. The quantity of cobalt oxide can therefore be from about 0.53 to 10.5% by weight. The amount of zinc oxide to employ must be within the range of from 0.2 to 5% by weight of the composition. The balance of the composition is composed of alumina.

When a quantity of zinc oxide below or above the stated range is used, the efficiency of the catalyst for sulfur removal and the other desired reactions of the process is adversely affected. The quantities of cobalt oxide and molybdic oxide must also be within the stated ranges to secure the advantages of the invention and to prevent undesired reactions. When less than the stated quantity of either cobalt oxide or molybdic oxide is used, the removal of nonhydrocarbons is deleteriously affected. It has also been found that, when the catalytic components are within the stated ranges therefor, the catalyst is not appreciably deactivated by the presence of metals, such as vanadium, in the charge stocks.

To illustrate a preferred catalytic composition of the invention, coprecipitated cobalt molybdate-alumina containing 3.1 weight percent cobalt oxide, 9.4 weight percent molybdic oxide, 86.2 weight percent alumina and 1.3 weight percent zinc oxide, the mole ratio of cobalt oxide to molybdic oxide being 0.63, gives excellent results.

CATALYST PREPARATION

It is essential to the successful preparation of the catalytic composition of the invention that cobalt molybdate and alumina be coprecipitated. The zinc oxide, however, can be incorporated in the composition at any stage prior to drying the composition. Coprecipitation of the cobalt molybdate-alumina is conveniently accomplished by adding ammonium molybdate to a solution of a water soluble aluminum salt and a water soluble cobalt salt, such as a solution of aluminum nitrate, aluminum sulfate or sodium aluminate, and cobalt nitrate or cobalt sulfate. If necessary or desirable, a quantity of ammonium hydroxide can be added to insure complete precipitation of the hydroxides. The zinc oxide can be incorporated in the composition at any convenient step in the process prior to drying, such as by impregnating the wet coprecipitate of cobalt molybdate-alumina, prepared as above described, with an aqueous solution of a water soluble salt, such as zinc chloride. The impregnated precipitate is washed, dried and calcined. Preferably, the zinc oxide is incorporated by including a water soluble zinc salt, such as zinc chloride, in the aqueous solution containing water soluble compounds of aluminum and cobalt prior to coprecipitation. Being thus present during the coprecipitation, a catalyst which is remarkably effective is obtained. It is also preferred, in preparing the present catalytic composition, to add a quantity of an oxidizing agent, preferably hydrogen peroxide, to the coprecipitated materials before filtering. It is further preferred to slurry the filtrate with an oxygen containing solvent, such as methanol, prior to drying, since excellent results are obtained when the catalyst is prepared in this manner. This preferred method of preparing the catalyst of the invention is described and claimed in copending United States patent application, Serial Number 549,838, filed November 29, 1955. The concentration of the water soluble metal salt in solution and the quantity of solution used should be such that the desired quantity of metal oxide is obtained in the final catalytic composition.

After use in a hydrocarbon conversion process for a substantial time, the activity of the catalyst may decrease. Substantially the initial activity of the catalyst can be restored by heating, in contact with an oxygen containing atmosphere such as air, to a temperature of from about 840° F. to 932° F.

HYDROCARBON CONVERSION

The catalytic compositions of the present invention are used for upgrading gas oils or residues by a process conveniently referred to as "hydrorefining," and for simultaneously upgrading residues and converting a substantial proportion of hydrocarbons therein to lower molecular weight hydrocarbons, which process is conveniently referred to as "hydrocracking."

When hydrorefining is the principal reaction desired, such as for removing nonhydrocarbons from gas oils or for upgrading residual oils for subsequent use in catalytic cracking, the reaction conditions should be selected, within the ranges hereinafter recited, so that substantial cracking is not observed. Such conditions are relatively mild, i.e., the temperature is in the lower portion of the defined range, the pressure is in the lower portion of the defined range and/or relatively high space velocity is used. When hydrocracking is desired, the temperature selected should be in the upper portion of the defined temperature range, the pressure should be in the upper portion of the defined pressure range and/or a relatively low space rate should be used, as hereinafter recited.

The temperature to employ in hydrocarbon conversions in the process of the invention can vary from about 550° F. to 900° F. and the pressure can vary from about 1000 p.s.i.g. (pounds per square inch gauge) to 2,500 p.s.i.g. The space rate, or liquid hourly space velocity, which is the volume of hydrocarbons contacted per volume of catalyst per hour (v./v./hour) is important and must be maintained within the range of 0.3 to 5. Hydrogen is added and/or recycled in the process of the invention and the mole ratio thereof to the hydrocarbon oil being converted should be within the range of from 5 to 50.

In the process, the sulfur of the organic sulfur compounds is substantially converted to hydrogen sulfide. The nitrogen of organic nitrogen compounds and the oxygen of organic oxygen compounds, if any, are converted to ammonia and water, respectivey. Hydrogen sulfide, ammonia, and water can readily be removed from the effluent reaction mixture, such as by means known to the art. It is advantageous to recycle a portion of the hydrogen sulfide, together with hydrogen, to the reaction mixture, since good operation is thereby obtained.

As above mentioned, a particular advantage of the process of the invention is that petroleum bottoms, or residues, can be completely converted to cracking stock. This is accomplished by contacting a residue with the

catalyst of the invention under the defined reaction conditions. The total liquid effluent from this step is then passed to catalytic cracking wherein high selectivity for producing gasoline of good lead susceptibility is obtained. Known cracking catalysts, such as silica-alumina compositions, used under known cracking conditions give good results. The higher boiling materials from the cracking step can be recycled, and thus the original petroleum residue is substantially completely converted to gasoline having a high octane rating. In the cracking step, cracking catalyst known to be effective such as silica-alumina, silica-zirconium, silica-alumina-zirconium, and the like, can be employed. Cracking conditions known to be effective for the cracking of hydrocarbons, such as a temperature in the range of from about 750° F. to 1000° F., a pressure of from atmospheric to 200 p.s.i.g., and a space rate of from about 1 to 3, give good results.

Gas oils which can be employed in the process of the invention generally boil within the range of from about 400° F. to 1000° F., and contain relatively large quantities of nonhydrocarbons, such as organic sulfur compounds. Such gas oils usually have a sulfur content of from about 0.5 to 6% by weight (calculated as sulfur). Metallic compounds such as compounds of nickel and vanadium are usually present.

A wide variety of heavy hydrocarbon materials, particularly petroleum residues, which generally have initial boiling points above about 840° F., can be converted in the process of the inventon, such as residues from petroleum cracking operations, reduced heavy crude oil, still tars, and the like. It is preferred to use petroleum residues having a hydrogen to carbon atomic ratio of at least 1.2 and preferably above about 1.4. Good results are obtained when the A.P.I. gravity of the heavy hydrocarbons is below 25, but the process has its greatest utility when the A.P.I. gravity is below about 17. Generally the Ramsbottom carbon residue will be from about 9 to 30, but may be as low as about 4. Metallic compounds such as compounds of nickel and vanadium are frequently present and an advantage of the process of the invention is that the catalyst is not deactivated thereby. It is preferred to use tower bottoms from petroleum operations, including for example the residues from thermal or catalytic cracking operations, or reduced heavy crude oils including crude oils having a high content of sulfur compounds, but other heavy hydrocarbon materials such as Athabasca tar can be used. Mixtures of gas oils and residual oils also give good results.

Entire crude oils, or crude oils which have been topped to remove the gasoline and lower boiling hydrocarbons, can be employed in the present process with good results, and such treated crude oils, or fractions obtained therefrom, are especially suitable in subsequent operations such as thermal or catalytic cracking. For convenience, the hydrocracking process of the invention is herein described using "residual oil" as illustrative of the heavy hydrocarbon materials that can be employed.

EXAMPLES

The following examples illustrate embodiments of the invention, in which "parts" refers to parts by weight unless otherwise specified.

Catalyst preparation

A catalyst of the invention, consisting of 3.1% cobalt oxide (CoO), 9.4% molybdenum oxide (MoO_3), 1.3% zinc oxide (ZnO), and about 86.2% alumina (Al_2O_3), was prepared as follows:

2250 parts of aluminum nitrate ($Al(NO_3)_3 \cdot 9H_2O$), 42.8 parts of cobalt nitrate ($Co(NO_3)_2 \cdot 6H_2O$) and 7.3 parts of zinc chloride ($ZnCl_2$, contained in solution of about 20 parts of hydrochloric acid) were dissolved in about 10,000 parts of hot water. To this solution was added, with stirring 563.4 parts of concentrated (25.3° Bé.) ammonium hydroxide containing in solution 40.6 parts of ammonium molybdate($(NH_4)_6Mo_7O_{24} \cdot 4H_2O$). About 350 parts of concentrated (30%) hydrogen peroxide was added with stirring. With continued stirring, about 720 parts of concentrated ammonium hydroxide was added to increase the pH of the solution to 9 and substantially complete the formation of the hydrogel.

The hydrogel-hydrogen peroxide composite was allowed to stand 1 hour and was then filtered. The separated hydrogel was slurried, by rapid mechanical agitation, with about 3200 parts of absolute methanol. The hydrogel was set by the contacting with methanol. After filtering, the precipitate was reslurried with a like quantity of absolute methanol and filtered. The filtered material was slurried with about 3200 parts water to remove any remaining water soluble salts, and filtered. The separated precipitate was dried by heating at 230° F. for 16 hours. The dried material was pulverized, mixed with water to form a dough and cast into pellets, which were dried for 16 hours at 400° F. and then calcined by heating to 1000° F. over a period of from 4 to 6 hours.

The resulting composition contained 3.1% CoO, 9.4% MoO_3, 1.3% ZnO and 86.2% Al_2O_3, and illustrates a preferred catalytic composition of the invention; this catalyst is designated as "Catalyst A" in the following examples.

The foregoing procedure was repeated except that the incorporation of zinc oxide in the catalyst was omitted. The final composition contained 3.1% CoO, 9.5% MoO_3 and 87.4% Al_2O_3; this catalyst is designated "Catalyst B" in the following examples.

The foregoing procedure was repeated except that cadmium oxide was substituted for zinc oxide by using cadmium nitrate tetrahydrate instead of zinc chloride. The quantities of the catalytic components were: 3.1% CoO, 9.4% MoO_3, 1.3% CdO and 86.2% Al_2O_3; this catalyst is designated as "Catalyst C" in the following examples.

A commercially available catalyst consisting of about 13% cobalt molybdate on alumina is hereinafter designated as "Catalyst D."

Example 1.—A gas oil having a boiling range of from about 678° F. to 920° F. and a relatively high content of organic sulfur compounds was hydrorefined in accordance with the process of the invention. A stream of the charge stock and hydrogen in a mole ratio of hydrogen to hydrocarbons of 20 was passed downwardly through a bed of the indicated catalyst at a space rate of 1 v./v./hour, a temperature of 775° F. and a pressure of 1500 p.s.i.g. The following results, compared to the charge stock, were obtained:

TABLE I

	Charge Stock	Catalyst A	Catalyst B	Catalyst C	Catalyst D
A.P.I. Gravity (60° F.)	22.4	30	30	29.6	30
Viscosity (SUS at 210° F.)	43	36	36	-------	-------
Sulfur Content (Wt. percent as sulfur)	2.2	0.05	0.15	0.05	0.50
Nitrogen Content (Wt. percent as Nitrogen)	0.09	0.008	0.02	0.026	0.036
H/C Atomic Ratio	1.69	1.80	1.73	1.79	1.71

These data show the catalysts of the invention, (Catalyst A and Catalyst C) to be remarkably superior, for removing nonhydrocarbons and for increasing the hydrogen to carbon ratio, to the same catalyst except for the omission of zinc oxide, and to a commercial cobalt molybdate catalyst.

The hydrorefined gas oil is especially suitable for use as the charge stock to catalytic cracking.

The procedure as above described was repeated using the same charge stock and reaction conditions there described, but with different catalysts. The catalysts used combine cobalt molybdate with materials outside the scope of the catalytic composition of the invention. In each instance the process failed, in one or more respects,

to give operable results in accordance with the present invention:

Cobalt molybdate (13%) deposited on bentonite gave a product having 1.00% sulfur.

Cobalt molybdate (13%) deposited on a low surface area alumina gave a product having 0.33% sulfur; with 25% cobalt molybdate, the product had 0.17% sulfur.

Cobalt molybdate (13%) on bauxite gave a product having 0.12% sulfur.

These data show the importance of the presence of the specific components in the catalytic compositions of the invention.

Example 2.—A residual oil prepared by reducing a petroleum crude oil to 10% bottoms was hydrocracked in accordance with the process of the invention. A mixture of the residual oil and hydrogen was contacted with a bed of catalyst as described in Example 1. The reaction conditions and results obtained are shown in following Table II; results obtained with Catalyst B are included for comparison.

TABLE II

	Charge Stock	Catalyst A				Catalyst B
Reaction Conditions:						
Temperature (° F.)	----------	800	800	800	810	800
Pressure (p.s.i.g.)	----------	1,500	1,500	2,000	2,000	1,500
Space rate, (v./v./hour)	----------	1	0.5	1	1	1
H_2/oil (mole ratio)	----------	30	18	23	21	27
Recycle gas rate (s.c.f./bbl.)[1]	----------	5,300	3,800	4,930	4,410	3,900
Liquid Product:						
A.P.I. gravity (60° F.)	11.5	19.8	21.4	19.4	19.7	18.5
Ramsbottom carbon (Wt. Percent)	13.6	8.2	6.1	7.1	6.7	8.7
Viscosity (SUS at 210° F.)	1,742	118	71	156	117	144
H/C atomic ratio	1.53	1.59	1.63	1.63	1.59	1.59
Sulfur (Wt. Percent as S)	0.89	0.50	0.29	0.33	0.33	0.6
Nitrogen (Wt. Percent as N)	0.42	0.30	0.25	0.25	0.22	0.36
Nickel (p.p.m. as Ni)	9	3	2	5	2	3
Vanadium (p.p.m. as V)	15	5	3	5	4	5
H_2 consumed (s.c.f./bbl.)		380	650	600	450	420
Product Distribution, Wt. Percent:						
H_2S	----------	0.5	0.7	0.6	0.6	0.3
Dry gas (C_1–C_3)	----------	1	1	1	2	1
Gasoline (C_4–400° F.)	----------	3	4	3	4	4
Gas oil—(400–650° F.)	----------	8	12	7	10	8
(650–840° F.)	----------	11	15	13	13	11
(840–1,000° F.)	10	21	23	29	21	24
Bottoms (above 1,000° F.)	90	56	44	46	50	52
Asphaltenes (Wt. Percent)	9.7	5.7	5.5	5.8	5.6	6.5
Charge Conversion [2]	----------	38	51	49	44	42

[1] S.c.f./bbl.=standard cubic feet per barrel of charge.
[2] Conversion of material boiling above 1,000° F. to materials boiling below 1,000° F.

These data show substantial upgrading, and conversion to cracking stock, of a residual oil by simultaneous hydrorefining and hydrocracking in accordance with the invention. The gas oil obtained is excellent stock for thermal or catalytic cracking. The residue, because of the substantial removal of nonhydrocarbons and the decrease in Ramsbottom carbon value, can be recycled in the process to substantial extinction, or it can be used as fuel if desired. The entire liquid product can also be used as cracking stock, and such use constitutes a preferred embodiment of the invention. The conversion of asphaltenes, which in cracking operations are converted to coke, to hydrocarbons is a substantial advantage of the process.

To illustrate cracking of the hydrorefined residual oil, the entire liquid product, boiling above gasoline, of the run performed at 810° F. as shown in Table II, was admixed with an equal volume of gas oil boiling from about 490° F. to 690° F. to lower the viscosity of the residual oil. The mixture was cracked by contacting with a silica-alumina cracking catalyst at a temperature of 898° F., a space rate of 1.02 v./v./hour, and atmospheric pressure. A total conversion of 53.1% by volume was obtained. Gasoline yield (C_5 to 405° F.) was about 30% by volume. The octane rating of the gasoline was 92.7 (clear) and 97.2 with 1.5 cc. of tetraethyl lead/gallon. The gasoline contained about 0.03 weight percent sulfur (calculated as sulfur). Coke formation was 7.97% by weight.

For comparison a mixture of the same residual oil which had not been hydrorefined, and the same gas oil as above used was cracked under the same cracking conditions with the same cracking catalyst. The coke formation, due to the degradation of hydrocarbons of the residual oil, was 38% greater than above obtained, and the sulfur content of the gasoline fraction was about twice that of the gasoline above obtained.

Example 3.—A residual oil prepared by reducing a crude oil having a high sulfur content to 55% bottoms was hydrocracked in accordance with the process of the invention. A mixture of the residual oil and hydrogen was contacted with a bed of catalyst as described in Example 1. The reaction conditions and results obtained at the two indicated temperatures are shown in following Table III, together with the properties of the charge stock:

TABLE III

	Charge Stock	Catalyst A
Reaction Conditions:		
Temperature (° F.)	----------	800
Pressure (p.s.i.g.)	----------	1500
Space rate (v./v./hour)	----------	1
H_2/oil (mole ratio)	----------	18
Recycle gas rate (s.c.f./bbl)	----------	4740
Liquid Product:		
A.P.I. gravity (60° F.)	17.6	26.1
Ramsbottom carbon (Wt. percent)	5.2	2.9
Viscosity (SUS at 210° F.)	115.4	44.7
H/C atomic ratio	1.61	1.72
Sulfur (Wt. percent as S)	3.93	0.51
Nitrogen (Wt. percent as N)	0.19	0.11
Nickel (p.p.m. as Ni)	14	3
Vanadium (p.p.m. as V)	42	8
H_2 consumed (s.c.f./bbl)	----------	640
Product Distribution Wt. percent:		
H_2S	----------	3.7
Dry gas (C_1–C_3)	----------	1
Gasoline (C_4–400° F.)	----------	3
Gas oil—		
(400–650° F.)	8	22
(650–840° F.)	29	31
(840–1,000° F.)	22	22
Bottoms (above 1,000° F.)	41	17
Asphaltenes (Wt. percent)	6.4	2.4
Charge Conversion [1]	----------	59

[1] Conversion of material boiling above 1,000° F. to materials boiling below 1,000° F.

Repeating the run of Table III at a space rate of 0.5 v./v./hour, the sulfur content was reduced to 0.24, nickel to 1 p.p.m. and vanadium to 2 p.p.m.

In accordance with the invention, the entire liquid effluent from the above hydrocracking is advantageously subjected to catalytic cracking. Thus, contacting the liquid effluent with a silica-alumina cracking catalyst at a temperature of about 895° F., a space rate of about 1 v./v./hour and a conversion of about 57 volume percent is obtained, whereas a conversion of about 59 volume percent is obtained with the same material not hydrocracked. However coke and gasoline formation observed with hydrocracked material is about 6.6% by weight and 37.5% by volume, which compares with about 13.4% by weight and 31.1% by volume, respectively, obtained with the same material without prior hydrocracking. Hence the selectivity of the process for producing gasoline is greatly enhanced in accordance with the present invention. Also, the octane number and lead susceptibility are substantially enhanced by the hydrocracking operation performed prior to cracking. For example, the octane number of the gasoline produced according to the invention is increased from about 90.7 to 95.8 by the addition of 1.5 ml. of tetraethyl lead, as compared to an increase of from 90.0 to 93.8 by the same addition to the gasoline obtained by cracking the same material without the prior hydrocracking.

The foregoing examples illustrate embodiments of the invention. When other catalysts and/or reaction conditions within the limits herein described are used, results substantially equivalent to those of the examples are obtained. Also, within the operable reaction conditions of the process, the hydrocarbon contacting with the catalyst is performed as a liquid phase operation, but it is realized that a portion of the hydrocarbons, such as when operating with a relatively low boiling gas oil, may be present in gas phase, and good results are obtained therewith.

The invention claimed is:

1. A catalyst composition effective for removing nonhydrocarbons from mixtures thereof with hydrocarbons and for lowering the boiling points of a portion of the hydrocarbons which consists essentially of cobalt molybdate in amount to provide from 5% to 20% by weight of molybdenum calculated as molybdic oxide and from 0.53% to 10.5% by weight of cobalt calculated as cobalt oxide, from 0.2% to 5% by weight of a promoter selected from the group consisting of zinc oxide and cadmium oxide, and the balance alumina.

2. The composition of claim 1 in which the ratio of cobalt oxide to molybdic oxide is in the range of from 0.2/1 to 1/1.

3. The composition of claim 3 in which the promoter is zinc oxide.

4. A process for removing nonhydrocarbons from mixtures thereof with a petroleum fraction and for lowering the boiling points of a portion of the petroleum fraction which comprises contacting a petroleum fraction selected from the group consisting of gas oils and petroleum residues containing nonhydrocarbons, at a temperature of from about 550° F. to 900° F., a pressure of from about 1000 to 2500 p.s.i.g. and a space rate of from 0.3 to 5, and in the presence of added hydrogen, with a catalyst consisting essentially of cobalt molybdate in amount to provide from 5% to 20% by weight of molybdenum calculated as molybdic oxide and from 0.53% to 10.5% by weight of cobalt calculated as cobalt oxide, from 0.2% to 5% by weight of a promoter selected from the group consisting of zinc oxide and cadmium oxide, and the balance alumina.

5. The process according to claim 4 in which the ratio of cobalt oxide to molybdic oxide in the catalyst is in the range of from 0.2/1 to 1/1.

6. The process according to claim 5 in which the promoter is zinc oxide.

7. A catalyst composition for removing nonhydrocarbons from mixtures thereof with a petroleum fraction and for lowering the boiling points of a portion of the petroleum fraction which consists of cobalt molybdate in amount to provide about 3.1% by weight of cobalt calculated as CoO and about 9.4% by weight of molybdenum calculated as MoO_3, about 1.3% by weight of ZnO and the balance alumina.

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