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2,903,413

HYDROGENATION OF A HYDROCARBON OIL FEED FOR USE IN A CATALYTIC CRACKING PROCESS TO PRODUCE GASOLINE

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This invention relates to a highly active catalyst for the hydrogenation and upgrading of petroleum fractions such as virgin gas-oils, catalytic cycle stocks, naphthas, and the like, especially those stocks containing appreciable amounts of aromatics and/or olefins. More particularly, the invention relates to the use of certain minor amounts of cobalt and nickel incorporated into or deposited upon acidic type supports, such as silica-alumina, silica-magnesia and silica-alumina-zirconia, as the catalyst for upgrading petroleum fractions.

According to this invention, it has been found that a catalyst containing from about 2.0 to 5.0 wt. percent of cobalt and 0.5 to 5.0 weight percent of nickel, supported on a cracking catalyst base, is highly effective in the conversion or upgrading of certain petroleum fractions by hydrogenation at temperatures of about 700° to 800° F. to yield products of increased gravity, decreased unsaturation and enhanced susceptibility to cracking to produce higher yields of motor fuels.

A primary object of the invention is to provide a new catalyst composition and process for the upgrading of petroleum fractions.

Another object of the invention is to provide a cobalt-nickel catalyst supported on a cracking catalyst base which has increased efficiency for the hydrogenation of certain petroleum fractions.

A further object of the invention is to provide a catalyst containing from about 2.0 to 5.0 wt. percent of cobalt and 0.5 to 5.0 weight percent of nickel, supported on a silica-alumina base, in a particular manner for use in the hydrogenation of virgin gas oils, lubricating oils such as bright stocks, catalytic cycle stocks and naphthas at conditions such as 700–800° F., 700 p.s.i.g., a LVHSV of about 1.5, and a hydrogen-to-hydrocarbon mol ratio of about 5.0, preferably at a hydrogen-to-hydrocarbon ratio of 4.0 or above, whereby products of enhanced properties are obtained, especially with respect to further processing to produce motor fuels.

A further object of this invention is to provide a process for hydrogenating hydrocarbons as a preliminary to subjecting same to catalytic cracking whereby increased yields of high grade fuels are obtained.

These and additional objects of the invention will appear or be described as the invention is set forth herein.

It is known in the art that selected mixtures of the oxides of certain group VIII metals of the periodic table, that is, oxides of iron, cobalt and nickel, when present on a supporting material in amounts of about 10% to 20% by weight, are useful in converting gas-oil to high anti-knock gasoline at temperatures ranging from 600 to 850° F., in the presence of hydrogen and under a wide range of pressures. Also, molybdenum and tungsten, in the form of their oxides or sulfides, are referred to as promoters for the hydrogenation of carbonaceous materials under a wide range of conditions. Cobalt and chromium oxides are often referred to in discussions on prior art catalysts, but because of their low activity they are not generally useful at temperatures below 750° F.

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where upgrading of a heavier hydrocarbon containing aromatics and olefins is the primary purpose. Similarly, it is generally preferred to use such catalysts, or the metals iron, cobalt and nickel, supported on silica-alumina bases, for the hydrogenation of mineral oils and other carbonaceous substances at high pressures, particularly pressures above 300 atmospheres, for instance 400 to 800 atmospheres. For these processes, high contents of a metal or metal oxide are generally used, in the order of from 10–25 wt. percent.

In the mild hydrogenation of petroleum stocks such as catalytic cycle stocks, virgin gas-oils and naphthas, the sulfur content is usually substantially reduced and olefins, if present, are substantially completely saturated over catalysts such as cobalt molybdate on alumina or silica-alumina supports. Hydrogenation of aromatics is not achieved to any appreciable extent under the conditions employed, viz., around 750° F. and 700 p.s.i.g.

In the upgrading of stocks containing considerable amounts of aromatics, such as catalytic cycle stocks, etc., it is often desirable from the standpoint of further processing to substantially hydrogenate the aromatics as well as other components. Hydrogenation of aromatics results in a decrease in density with an attendant volume increase. Also, oxidation stability is generally increased, and if stocks such as catalytic cycle stocks are to be used for furnace oils, cleaner burning characteristics are attained by the substantial hydrogenation of aromatics. The greater the degree of hydrogenation of aromatics attained in petroleum stocks, such as catalytic cycle stocks or virgin material, the more susceptible they will be to subsequent catalytic cracking for the production of gasoline. This is especially true of catalytic cycle stocks. It is therefore desirable to carry out the hydrogenation treatment of these stocks over catalysts which have high activity for the hydrogenation of aromatics as well as activity for desulfurization and for saturation of olefins.

In order to demonstrate the effectiveness of the catalysts of this invention, the following examples of the hydrogenation of a catalytic cycle stock are presented.

EXPERIMENT I

Exactly 25.8 gms. of nickel nitrate and 38.4 gms. of cobalt nitrate were dissolved in 450 ml. of distilled water at room temperature. Into the resulting mixed solution were slurried 195 gms. of silica-alumina cracking catalyst containing 87 wt. percent of SiO₂ and 13 wt. percent of Al₂O₃. After completely mixing the slurry, 27 gms. of ammonium carbonate (in 260 ml. of distilled water) were added to precipitate nickel and cobalt carbonates within the pores of the silica-alumina. The resulting slurry was filtered to remove ammonium salts and was dried in an oven at 212° F. for 24 hours. Then it was decomposed, reduced and activated by heating in a hydrogen stream of 5 cu. ft. of H₂ per hour per 100 milliliters of catalyst. During this time the temperature was gradually increased to 950–1000° F. over a period of 5 hours and held at 950° F.–1000° F. for 15–25 hours. The composite catalyst on analysis contained 2.3 wt. percent of Ni and 3.4 wt. percent of Co on a silica-alumina support consisting of 13 wt. percent of Al₂O₃ and 87 wt. percent of SiO₂.

This catalyst was employed in the hydrogenation of a catalytically cracked cycle stock having the following physical and chemical properties: 30.5° API gravity; S, 0.22 wt. percent; R.I., nD₂₀, 1.4947. This material contained 38.7 percent aromatics and 7.2 percent olefins. The boiling range was 436°–629° F. The reaction was carried out at about 750° F., 700 p.s.i.g., a LVHSV of 1.5, and a hydrogen-to-hydrocarbon mol ratio of 5.0. A product was obtained having the following properties: 36° API gravity; S, 0.01 wt. percent; R.I., nD₂₀, 1.4743;

and olefins, 0.9 vol. percent. The hydrogenation of the olefins and aromatics amounted to 59%. Liquid recovery from this experiment was 100 volume percent of the charge. No gaseous hydrocarbons were produced.

EXPERIMENT II

A conventional cobalt molybdate catalyst containing 3.1 wt. percent of CoO and 9.3 wt. percent of MoO₃ was used to treat the same feed under the same conditions as in Experiment I. The product showed the following properties; 32.2° API gravity; S, 0.05 wt. percent; R.I., *n*D₂₀, 1.4838; and olefins, 0.9 vol. percent. Only 26% of the possible hydrogenation of the olefins and aromatics occurred. No gaseous products were produced in either experiment.

Since the olefins were saturated to an extent of about 90 percent in both cases, it is apparent that the catalyst in Experiment I was much more effective in hydrogenating aromatics than was the catalyst in Experiment II.

EXPERIMENT III

In the hydrogenation of the catalytic cycle stock under the conditions outlined in Example I, and over a catalyst composed of 10 percent nickel and 4 percent cobalt on a silica-alumina support (containing 13 percent alumina), high initial hydrogenation activity is obtained. However, this high activity is accompanied by a considerable degree of hydrocracking to gaseous hydrocarbons resulting in a liquid product yield of only 90 percent. Coke deposition on the catalyst is substantial and rapid deterioration of activity occurs.

EXPERIMENT IV

In the hydrogenation of the same charge stock over a catalyst composed of 0.5 percent nickel and 15 percent cobalt on a silica-alumina support (containing 13 percent alumina), activity is much less than that obtained over the catalyst employed in Experiment I, and results are obtained which are approximately equivalent to those obtained over the cobalt-molybdena catalyst of Experiment II.

The catalyst used to obtain the degree of upgrading noted is one containing 2.0 to 5.0 wt. percent of cobalt and 0.5 to 5.0 weight percent of nickel, supported on a cracking catalyst base. Concentrations of nickel higher than 5.0 wt. percent will result in excessive hydrocracking and coke deposition upon the catalyst. Although the role of the cobalt is not definitely known, it is believed to act as a stabilizer for the nickel and thus decreases the rate of catalyst degeneration. This leads to increased catalyst life and longer on-stream periods between regenerations. It has been found that the cobalt in the catalyst compositions of this invention does not show X-ray diffraction lines, and therefore the cobalt must be present either as amorphous cobalt, cobalt oxide or as a complex or compound formation with the acidic support. If concentrations of cobalt over about 5.0 wt. percent are used, the function of the nickel would be masked by cobalt. These conclusions are supported in part by Experiments III and IV.

As a further illustration of the advantage gained by employing the preferred nickel-cobalt-on-silica-alumina catalyst, the products obtained in Experiments I and II were catalytically cracked in order to determine the amount of gasoline available from each. A similar evaluation was carried out on the initial cycle stock charged in Experiments I and II.

The hydrogenated products obtained from Experiments I and II were compared with untreated cycle stock, by determining the amount of gasoline produced when subjected to fixed-bed catalytic cracking, under standard operating conditions and with a specific cracking catalyst, in a laboratory experimental unit. The catalyst used for these tests was a commercial, natural silica-alumina (alumina content, 17 percent) cracking catalyst in pellet form

(3/16" diam. by 3/16" long). The operating conditions were:

Temp.: 800° F. (reactor), 810° F. (preheat)

Press.: Atmospheric

Catalyst volume: 200 ml.

Charge rate: 300 ml./hr.

Cycle time: 10 minutes on stream

Upon completion of the cracking test, during which the amount and the specific gravity of the effluent gas were determined, the liquid product was flushed from the reactor and exit lines, and distilled in a micro-distillation column to determine the amount of 420° F. end-point gasoline produced. The amount of gasoline produced was taken as an indication of the degree to which the cycle stock had been up-graded by the hydrogenation procedure.

The catalyst was removed from the reactor and the amount of carbonaceous material deposited thereon was determined by combustion. From these measurements, the distribution of cracked products was obtained, and the efficacy of the improvement by hydrogenation was determined.

Results of these tests are shown in the Table I.

Table I

	Conv., vol. per- cent	Gas (vol. per- cent)	Carbon (Wt. per- cent)	Gas (Wt. per- cent)
Cycle Stock	4.0	31.2	4.6	5.8
Hydrogenated Product (Exp. II) w./CoMo ₃ on alumina	47.7	36.7	3.6	6.6
Hydrogenated Product (Exp. I) w./ Ni-Co on silica-alumina	56.8	46.9	3.3	6.3

The experiments show that by hydrogenating olefin-containing stocks at about 700° to 800° F. and using a LVHSV of about 1.5 with a hydrogen-to-hydrocarbon ratio of about 4.0:1 to 5.0:1, products having increased API gravity, decreased olefin content and other improved qualities are obtained. The process and catalyst may be used to form improved hydrogenated products such as heating oils, lubricating oils and the like by hydrogenation alone. In general, cycle stocks having API gravities of about 18° to 32°, sulfur contents in the order of 1.25 to 0.10 weight percent, containing about 2.0 to 10% of olefins by volume, and having about 30% to 55% by volume of aromatics may be benefited by the present method of hydrogenation to give API gravity increases of 3 to 7 degrees, around 90 percent or greater sulfur removal and substantial removal of olefins and reduction of the aromatic content. Some examples of light and heavy cycle stocks that may be used are listed in Table II.

Table II

PHYSICAL AND CHEMICAL PROPERTIES OF EXAMPLE FEED STOCKS

Cycle Stock type	°API	S (wt. Percent)	Olefins (Vol. Percent)	Aro- matics (Vol. Percent)	RI <i>n</i> D ₂₀
1. Light	29.5	0.39	5.3	40.1	1.5011
2. Heavy	23.8	0.66	3.0	38.0	1.5248
3. Light	30.5	0.22	7.2	38.7	1.4947
4. Light	25.3	0.49	6.2	50.2	1.5179
5. Heavy	20.8	1.03	2.2	45.6	1.5373

These results also demonstrate that the hydrogenation of cycle stock over a Ni—CO-on-silica-alumina catalyst yielded a product which, upon subsequent cracking, gave 46.9 volume percent gasoline, as compared with only 31.2 volume percent obtained in cracking the untreated cycle stock under the same conditions. Hydrogenation of the cycle stock with a well-known cobalt molybdate catalyst gave a product which yielded only 36.7 volume percent gasoline as compared with the 46.9 percent obtained from

the hydrogenated product resulting from the use of the catalyst of our invention. It is seen, too, that both the carbon and gas made were less in cracking the hydrogenated product obtained with the nickel-cobalt-on-silica-alumina catalyst. Thus, the carbon from this hydrogenated product was only 3.3 percent as compared to the 4.6 percent carbon obtained in the cracking of the original stock even though conversion by cracking was increased as much as from 42.0 to 56.8 percent.

Accordingly, the invention is directed to the discovery of a particular catalyst composition which brings about these enhanced results and the hydrogenation process used therewith. The invention also resides in an improved catalytic cracking process wherein the improvement lies in hydrogenation of the hydrocarbon using the nickel-cobalt-silica-alumina catalyst composition prior to the cracking step. In general, the conditions used in the cracking step are well known in the art and are described by R. V. Shankland in "Advances in Catalysis," Academic Press, vol. VI (1954). The cracking conditions useful are as follows:

Temperature ----- 800-1000° F.
 Pressure ----- Substantially atmospheric.
 Space velocity ----- 0.5 to 5.0 v./hr./v.
 Catalyst/oil ratio ----- 1.5-30.

The various known fixed, moving and fluid bed techniques of cracking may be used. In the fixed-bed process the process period is usually about 10 minutes duration.

The acidic-type supports used in the preparation of the catalysts of this invention include those compositions which in general have found use in the catalytic cracking of hydrocarbons. These materials generally have a microporous structure with surface areas of 100 square meters/gm. or above, and in many cases have surface areas in excess of 300 square meters per gram. The preferred acidic-type commercial cracking catalysts used as supports in accordance with this invention contain a major portion, that is, about 75 to 90 weight percent of silica, and a minor portion, that is, about 25 to 10 weight percent, of alumina, magnesia or alumina-zirconia. Compositions coming within this definition include supports containing about 87-83 weight percent of silica with about 13-17 weight percent of alumina, magnesia or alumina-zirconia. Where zirconia is present about 1-5 weight percent is used. For the species silica-alumina, weight percentages of 87 silica to 13 alumina and 83 silica to 17 alumina give consistent results. Other supports may include silica-alumina compositions containing from 5-50 weight percent alumina, silica-alumina-zirconia compositions containing around 5-10 percent alumina and 5-10 percent zirconia, and silica-magnesia supports with around 15-35 percent magnesia. Similarly, activated clays such as those derived from montmorillonite or halloysite may be employed. Activated aluminas, containing only small amounts of silica to impart acidic properties, may be employed although their activity may be somewhat less. Included in this category are H-41-type aluminas produced by the Alumina Company of America, and activated and purified bauxites.

In preparing the catalysts of this invention, the acidic-type support is impregnated with an aqueous solution of a water-soluble cobalt salt, such as cobalt acetate, cobalt chlorate, cobalt chloride, cobalt nitrate, cobalt iodide and cobalt sulfate, and simultaneously or subsequently impregnated with a water-soluble salt of nickel such as the acetate, bromide, chloride, iodide, nitrate, and sulfate. Before the impregnation, the acidic support may be given a pretreatment with mineral acids such as hydrochloric acid or hydrofluoric acid. In accordance with this invention, sufficient amounts of the cobalt and nickel compounds are incorporated in the catalyst to give, after calcination and reduction, a catalyst composition containing from about 2.0 to 5.0 wt. percent of cobalt, referring to the entire catalyst mass, and from 0.5 to 5.0 weight

percent of nickel, also referring to the total catalyst mass. After impregnation of the acidic support with one or both of the metal salts, the solid material is separated from the excess aqueous solution, dried in an oven at 100° C. for 8-24 hours, and then decomposed and activated, preferably in a stream of hydrogen, by gradually heating to 950-1000° F. over a period of 4-8 hours, and preferably conditioning in hydrogen at 950-1000° F. for several hours. If the catalyst is to be used in a fixed-bed operation, it is generally desirable to pellet, extrude, or otherwise form the catalyst before activation.

As an alternate method of preparation, the support may be impregnated with a suitable salt solution of nickel and cobalt, and the metals fixed thereon as insoluble compounds by precipitation within the pores of the catalyst through the addition of a suitable precipitant. Thus the support may be impregnated with the nitrates of the metals and the metals co-precipitated as carbonates by the addition of ammonium carbonate. The resulting material is then freed of excess solution, dried, and activated in the usual manner. Similarly, the metals may be precipitated as insoluble compounds in the presence of, or the compounds may be added to, a slurry of an undried support, after which the composite catalyst is filtered, dried and activated.

These catalysts may be used to promote the hydrogenation reaction in fixed beds, in movable beds, or as a fluid powder suspended in a vapor stream of the reactants. The fixed-bed catalysts may be positioned in tubes mounted in the convection section of a furnace, or they may be positioned in a single bed or a plurality of beds in vertical towers or chambers. When using the moving-bed technique, the catalysts may be charged to the top of the tower or tube either continuously or intermittently, the spent catalyst being withdrawn from the base for recycle, regeneration, etc., at substantially the same rate. The powdered catalyst may be fed to a rapidly moving stream or vaporized oil and hydrogen, separated therefrom after the reaction is complete, and separately regenerated by contact with oxygen while suspended in flue gas. Any of these specific catalytic processing techniques or their equivalents may be used in carrying out the invention.

In the hydrogenation of stocks containing considerable amounts of sulfur over the active catalysts of our invention, some loss in activity occurs with time on stream with the result that conversion gradually decreases. The extent of loss in activity will be dependent upon the amount of sulfur in the charge and upon the degree of severity employed in the hydrogenation operation. Hydrogen-to-hydrocarbon mole ratios of 4 or above are usually employed to maintain high activity for longer periods of time.

In order to restore maximum activity, the catalyst may be regenerated in a conventional manner by burning off accumulated poisons with air, followed by reduction with hydrogen, after which charging of the hydrocarbon stock can be resumed. In another method, the activity may be fully regained for numerous cycles simply by employing intermittent charging of the cycle stock or other hydrocarbon material while maintaining a continuous flow of hydrogen. In this manner, the catalyst activity is restored by intermittent treatment with hydrogen alone.

What is claimed:

1. The process of producing gasoline from petroleum fractions which comprises hydrogenating said petroleum fractions at temperatures of about 700° to 800° F. using a space velocity of about 1.5 and a hydrogen-to-hydrocarbon ratio of about 4.0/1 in the presence of a catalyst consisting of about 3.4 weight percent of cobalt, 2.3 weight percent of nickel on a support containing from about 75 to 90 weight percent of silica and from about 25 to 10 weight percent of alumina, separating the hydrogenated products and subjecting the hydrogenated products to catalytic cracking in the presence of a silica-

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alumina cracking catalyst containing about 17 weight percent of alumina at temperatures of about 800° to 1000° F. using substantially atmospheric pressures, a space velocity of about 0.5 to 5.0 and a catalyst-to-hydrogenated product ratio of about 1.5 to 30 and recovering increased yields of gasoline.

2. The process in accordance with claim 1 in which the hydrogenation reaction is conducted at a temperature of about 750° F. and a pressure of about 700 p.s.i.g.

3. The process in accordance with claim 1 in which

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the petroleum fraction is a catalytically cracked cycle stock leaving an API gravity of about 18 to 32°, a sulfur content of about 0.10 to 1.25 weight percent, an olefin content of about 2.0 to 10.0 volume percent and an aromatic content of about 30 to 55 volume percent.

References Cited in the file of this patent

UNITED STATES PATENTS

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,903,413

September 8, 1959

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It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 4, Table 1, under the heading "Conv., vol. percent", first item, for "4.0" read -- 42.0 --; column 6, line 69, for "about 4.0/l" read -- about 5.0/l --.

Signed and sealed this 1st day of March 1960.

(SEAL)

Attest:

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