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METHOD OF STARTING UP A HYDROCRACKING PROCESS

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ABSTRACT OF THE DISCLOSURE

Start-up method comprises contacting the hydrocracking catalyst with a hydrogen-containing gas at a pressure between about 0 and about 2,500 p.s.i.g. and a temperature between about 400° F. and about 850° F.; cooling the catalyst to minimize conversion of hydrocarbons; contacting the catalyst with a first preliminary hydrocarbon feedstock having low concentrations of nitrogen, sulfur and aromatics in a manner that will not deleteriously affect the catalyst; increasing the temperature in the reaction zone to obtain conversion of the first preliminary hydrocarbon feedstock to lower-boiling hydrocarbons; stopping the flow of the first preliminary hydrocarbon feedstock; and contacting the catalyst with a principal petroleum hydrocarbon feedstock. The hydrocracking catalyst comprises a hydrogenation component on a co-catalytic support. The preferred support comprises ultrastable, large-pore crystalline aluminosilicate material suspended in a porous matrix of amorphous silica-alumina. The preferred hydrogenation component comprises a mixture of cobalt oxide and molybdenum trioxide.

CROSS-REFERENCES TO RELATED APPLICATIONS

This is a continuation-in-part application of co-pending U.S. patent application Ser. No. 685,327, which was filed on Nov. 24, 1967, and is now abandoned, and which, in turn, was a continuation-in-part application of U.S. patent application Ser. No. 572,224, which was filed on Aug. 15, 1966, and is now abandoned.

BACKGROUND OF THE INVENTION

This invention relates to the catalytic conversion of petroleum hydrocarbon feedstocks. More particularly, it relates to a method of starting up a single-stage process for the hydrocracking of petroleum hydrocarbon feedstocks.

Hydrocracking is a general term which is applied to petroleum refining processes wherein hydrocarbon feedstocks which have relatively high molecular weights are converted to lower-molecular-weight hydrocarbons at elevated temperature and pressure in the presence of a hydrocracking catalyst and a hydrogen-containing gas. Hydrogen is consumed in the conversion of organic nitrogen and sulfur to ammonia and hydrogen sulfide, respectively, in the hydrocracking of high-molecular-weight compounds into lower-molecular-weight compounds, and

in the saturation of olefins and other unsaturated compounds. In hydrocracking processes, hydrocarbon feedstocks, such as gas oils that boil in the range of about 350° F., to about 1,000° F., typically, catalytic cycle oils boiling between about 350° F. and 850° F., are converted to lower-molecular-weight products, such as gasoline-boiling range products and light distillates.

Typical hydrocarbon feedstocks contain nitrogen compounds in amounts such that the nitrogen present is greater than 20 parts per million. The nitrogen tends to reduce the activity of the catalyst used in the hydrocracking reaction. Such reduction in catalytic activity results in inefficient operation and poor product distribution and yields. As the nitrogen content increases, high reaction temperatures are required to maintain a given conversion level. Generally, the nitrogen content of a hydrocarbon feedstock can be reduced by subjecting that feedstock to a feed-preparation treatment. In such instance, the nitrogen compounds are converted into ammonia. In addition, sulfur is converted into hydrogen sulfide.

Generally, low-temperature hydrocracking processes for maximizing gasoline-boiling-range products employ two processing stages. In the first stage, the feed-preparation stage, the feedstock is hydrotreated to remove nitrogen and sulfur that are typically found in the usual refinery feedstocks. In the second stage, the hydrocracking stage, the pretreated hydrocarbon stream is converted to lower-boiling products.

There are also one-stage hydrocracking processes. In a one-stage process, the denitrogenation and desulfurization occur in the first part of the catalyst bed or in the first reactor. Therefore, denitrogenation, desulfurization, and hydrocracking may be performed by the same catalyst in a one-stage process. But two different catalysts may be used; the first catalyst, for the denitrogenation and desulfurization; the second catalyst, for the hydrocracking. However, ammonia and hydrogen sulfide formed from the denitrogenation and desulfurization, respectively, are passed over the second catalyst along with the hydrocarbons that are to be hydrocracked by the second catalyst. No separation step occurs between the first catalyst bed and the second catalyst bed, whereby the ammonia and hydrogen sulfide are separated from the hydrocarbons.

During the initial operation of a hydrocracking process, the catalyst, in general, provides a very high initial catalyst activity. This is true both in the case of a fresh hydrocracking catalyst and in the case of a used catalyst which has been regenerated. The very high initial activity of the catalyst can lead to overcracking and excessive gas production. Therefore, efficient hydrocracking during the initial operation of a hydrocracking run can be more easily achieved, if the initial high activity of the hydrocracking catalyst can be reduced without deleteriously affecting the steady-state activity of the catalyst.

It has been found unexpectedly that the reduction of this initial high activity of the catalyst can be achieved without accompanying damage being done to the steady-state activity of the catalyst by first reducing the hydrogenation component of the hydrocracking catalyst and then bringing the reduced catalyst on stream at relatively low temperatures in the presence of a petroleum hydrocarbon feedstock having low nitrogen, sulfur, and aromatics contents.

SUMMARY OF THE INVENTION

Briefly, in accordance with the present invention, there is a method of starting up a single-stage process for the hydrocracking of a principal petroleum hydrocarbon feedstock. That feedstock which is the one that the process is intended to hydrocrack will hereinafter be referred to as the principal petroleum hydrocarbon feedstock. The hydrocracking process employs in a hydrocracking reaction zone a catalyst which comprises a hydrogenation component on an acidic cracking component. The method of starting up the hydrocracking process comprises: contacting the catalyst with a hydrogen-containing gas at a pressure within the range between about 0 p.s.i.g. and 2,500 p.s.i.g. and a temperature within the range between about 400° F. and about 850° F. for a period of time sufficient to reduce the hydrogenation component; cooling the catalyst to a temperature which will provide low conversion of a petroleum hydrocarbon feedstock, whereby cracking of hydrocarbons can be controlled more easily; contacting the catalyst with a first preliminary hydrocarbon feedstock having low-concentrations of nitrogen, sulfur, and aromatics for a period of time which is sufficient to permit a hot spot to move slowly through the bed of the catalyst without appreciably affecting the activity and other properties of the catalyst in a deleterious manner, the hot spot not being permitted to exceed a temperature of 850° F., preferably, a temperature of 800° F.; after the hot spot has passed through the catalyst bed, increasing the temperature in the reaction zone to obtain conversion of said preliminary hydrocarbon feedstock to lower-boiling hydrocarbons; stopping the flow of said first preliminary hydrocarbon feedstock; and contacting the catalyst with the principal petroleum hydrocarbon feedstock.

In an embodiment of this method, the catalyst is contacted with a second preliminary hydrocarbon feedstock subsequent to being contacted with the first preliminary feedstock and prior to being contacted with the principal petroleum hydrocarbon feedstock. The second preliminary hydrocarbon feedstock should have concentrations of nitrogen, sulfur, and aromatics, which are intermediate between those of the first preliminary hydrocarbon feedstock and those of the principal petroleum hydrocarbon feedstock. There is no limitation on the amount of time that this second preliminary hydrocarbon feedstock may be used.

DESCRIPTION

The time delay between use of feedstocks should be minimized, so that the catalyst will not be reactivated by the hydrogen in the system. In some embodiments of this invention, liquid product obtained with the first preliminary feedstock is recycled and conversion as high as 100%, based on fresh feed, is obtained.

As mentioned above, the principal petroleum hydrocarbon feedstock is the feedstock which is to be hydrocracked during the hydrocracking run. It is conceivable that such a feedstock may contain relatively large concentrations of nitrogen, which deleteriously affects the hydrocracking catalyst. Such feedstocks may contain as much as 1.0 weight percent nitrogen. In order that a large concentration of nitrogen in the feedstock to be converted by the hydrocracking process will not appreciably poison the catalyst during the start-up of the hydrocracking run, a feedstock containing a lower concentration of nitrogen is employed during the start-up procedure. This latter feedstock is conveniently referred to hereinafter as the first preliminary hydrocarbon feedstock. Advantageously, it should contain no more than 75 parts per million nitrogen. If the nitrogen concentration of the principal feedstock is very high, for example, 200 parts per million, a second preliminary feedstock should be employed also. This second preliminary feedstock should contain a nitrogen concentration intermediate between the nitrogen concentration of the principal feedstock and the first preliminary

hydrocarbon feedstock. The use of several preliminary feedstocks having different nitrogen concentrations, each nitrogen concentration being lower than that of the principal hydrocarbon feedstock, will permit the initially-high-activity catalyst to see a gradual increase in nitrogen concentration, which gradual increase will prevent the catalyst's steady-state activity from being appreciably deleteriously affected.

In accordance with the present invention, the hyrogenation component must be in one of its reduced forms. It is not necessary that the reduction of the hydrogenation component be made completely to the elemental form of the metals in the hydrogenation component. The reduction of the hydrogenation component is accomplished in the present start-up method by contacting the hydrocracking catalyst with a hydrogen-containing gas at a pressure within the range between about 0 p.s.i.g. and 2,500 p.s.i.g. and a temperature within the range between about 400° F. and 850° F. Such contacting of the catalyst with the hydrogen-containing gas should be carried on for a period of time which is sufficient to cause the hydrogenation component of the catalyst to exist in a more reduced form.

The temperature of the reduced catalyst is lowered to a value which will minimize the conversion of any petroleum hydrocarbon feedstock which is subsequently passed over the reduced catalyst. The cracking of that feedstock can be more easily controlled so that overcracking and excessive production of make-gas can be prevented.

The reduced catalyst maintained at the relatively low temperature is contacted first with a first preliminary petroleum hydrocarbon feedstock. This feedstock may be a fraction which boils at a relatively low boiling point, for example, a light virgin gas oil. This low-boiling hydrocarbon fraction should have a relatively low nitrogen concentration, for example, less than 75 parts per million nitrogen. It has been found unexpectedly that this low-boiling, relatively-low nitrogen-containing fraction should also contain a low concentration of aromatics, for example, less than 25 volume percent aromatics.

If the concentration of nitrogen in the principal hydrocarbon feedstock is high, for example, greater than 200 parts per million nitrogen, it is desirable that the reduced hydrocracking catalyst see a second preliminary hydrocarbon feedstock prior to its being subjected to the principal hydrocarbon feedstock. As mentioned above, this second preliminary feedstock should possess a nitrogen concentratoin which is intermediate between the nitrogen concentration of the first preliminary feedstock and the nitrogen concentration of the principal hydrocarbon feedstock. Furthermore, it should possess an aromatics concentration which is intermediate between those of the first preliminary feedstock and the principal hydrocarbon feedstock.

Advantageously, the concentration of sulfur may be handled in the same manner, so that the sulfur concentration which the catalyst sees will be gradually increased.

Advantageously, the reduced catalyst should not be permitted to remain at the high temperatures for any length of time in the presence of any oxygen-containing gas. In view of this, the catalyst should remain in a hydrogen-containing atmosphere.

The present invention will be more easily understood by reference to the following description and examples.

Typical operating conditions that are employed in a hydrocracking reaction zone include a temperature within the range between about 450° F. and about 825° F., a hydrogen partial pressure within the range between about 200 p.s.i.g. and about 3,000 p.s.i.g., a liquid hourly space velocity (LHSV) within the range between about 0.2 and about 5 volumes of hydrocarbon per hour per volume of catalyst, and a hydrogen-to-oil ratio within the range between about 2,000 and about 20,000 standard cubic feet of hydrogen per barrel of hydrocarbon. Preferably, the temperature will range between about 650° F.

and about 800° F.; the hydrogen partial pressure, between about 1,000 p.s.i.g. and about 1,800 p.s.i.g.; the LHSV, between about 0.5 and about 3 volumes of hydrocarbon per hour per volume of catalyst; and the hydrogen-to-oil ratio, between about 8,000 and about 12,000 standard cubic feet of hydrogen per barrel of hydrocarbon. It is desirable that a high hydrogen partial pressure be employed, since a high hydrogen partial pressure will prolong catalyst activity.

In general, hydrocracking catalysts comprise a hydrogenation component on an acidic cracking component. Various hydrogenation components are available for use in hydrocracking catalysts. Such hydrogenation components possess hydrogenation-dehydrogenation activity and may exist in the elemental form. They may also exist as oxides or sulfides of the elements, or even as mixtures of the oxides and/or sulfides. The metallic members of the hydrogenation component may be selected from the metals of Group VI–B of the Periodic Table, for example, molybdenum and tungsten. They may also be selected from the metals of Group VIII of the Periodic Table, for example, cobalt, nickel, and platinum. The hydrogenation component can be introduced into the selected support, i.e., the acidic cracking component, by impregnating the support with a heat-decomposible compound, or compounds, of the selected dehydrogenation metal or metals. The resultant composite is then calcined.

It has been found that the start-up method described herein may be used advantageously to start up a single-stage process for the hydrocracking of petroleum hydrocarbon feedstocks, which process employs a catalyst comprising a hydrogenation component deposited on a co-catalytic support. The co-catalytic support may comprise a large-pore crystalline aluminosilicate material suspended in a porous matrix of amorphous silica-alumina. The preferred large-pore crystalline aluminosilicate material is ultrastable, large-pore crystalline aluminosilicate material. The preferred hydrogenation component comprises a mixture of cobalt oxide and molybdenum trioxide. The amount of cobalt oxide may vary from about 2 weight percent to about 5 weight percent; the amount of molybdenum trioxide, from about 4 weight percent to about 15 weight percent, based on total catalyst weight. The amount of large-pore crystalline aluminosilicate material may vary from about 5 weight percent to about 50 weight percent, based on the weight of said support.

Certain commercially available, naturally-occurring and synthetic crystalline aluminosilicate zeolitic molecular sieve materials are effective cracking components. In view of this, either naturally-occurring or synthetic molecular sieves may be used in a hydrocracking catalyst. Examples of naturally-occurring molecular sieves are erionite, mordenite, chabazite, faujasite, gmelinite, and the calcium form of analcite. Examples of synthetic crystalline aluminosilicate zeolitic molecular sieves are X-Type, Y-Type, D-Type, L-Type, R-Type, S-Type, and T-Type molecular sieves. The above crystalline aluminosilicate zeolitic molecular sieves can be activated by driving out of the sieves a major portion of the water of hydration that may be found therein. They may be characterized and adequately defined by their X-ray diffraction patterns and composition. Characteristics of both naturally-occurring and synthetic molecular sieves and methods for preparing them have been presented in the chemical art.

Now there has been developed a different kind of aluminosilicate material. This aluminosilicate material has large pores, is very stable, and may be a component of the catalyst employed in this invention. An example of such an aluminosilicate material is Z–14US, which is disclosed and claimed in United States Pat. 3,293,192, assigned to W. R. Grace and Company.

By large-pore crystalline aluminosilicate material is meant an aluminosilicate material which possesses pore diameters that are sufficiently large to permit the entry thereinto of the hydrocarbons to be processed, e.g., benzene and larger molecules, and the exit therefrom of the resulting hydrocarbon products. Therefore, the pores should have pore diameters which exceed 8 angstroms.

Ultrastable, large-pore crystalline aluminosilicate material is characterized by an ultrastable structure as evidenced by the retention of a surface area which is greater than 150 m.^{2}/gm. after calcination at a temperature of 1,725° F. for a period of 2 hours and by the retention of a surface area which is greater than 200 m.^{2}/gm. after treatment with an atmosphere of 25% steam at a temperature of 1,525° F. for 16 hours.

The ultrastable, large-pore crystalline aluminosilicate material exhibits extremely good stability toward wetting, which is defined as that ability of a particular aluminosilicate material to retain surface area or nitrogen-adsorption capacity after contact with water or water vapor. It has been found that ultrastable, large-pore crystalline aluminosilicate material containing about 2 percent sodium (the "soda" form of the ultrastable aluminosilicate material) exhibited a loss in nitrogen-adsorption capacity that is less than 2 percent per wetting, when tested for stability to wetting by subjecting the material to a number of consecutive cycles, each cycle consisting of a wetting and a drying.

The ultrastable, large-pore crystalline aluminosilicate material is characterized by a cubic unit cell dimension that is within the range of about 24.20 angstrom units (A.) to about 24.55 A.

The infrared spectra of dry ultrastable, large-pore crystalline aluminosilicate material always show a prominent band near 3700 cm.$^{-1}$ (3695±5 cm.$^{-1}$), a band near 3750 cm.$^{-1}$ (3745±5 cm.$^{-1}$), and a band near 3625 cm.$^{-1}$ (±10 cm.$^{-1}$). The band near 3750 cm.$^{-1}$ is typically seen in the spectra of all synthetic faujasites. The band near 3625 cm.$^{-1}$ is usually less intense and varies more in apparent frequency and intensity with different levels of hydration. The band near 3700 cm.$^{-1}$ is usually more intense than the 3750 cm.$^{-1}$ band. The band near 3700 cm.$^{-1}$ and the band near 3625 cm.$^{-1}$ appear to be characteristic of the ultrastable aluminosilicate material.

It is believed that a substantial proportion or amount of this ultrastable, large-pore crystalline aluminosilicate material is characterized by the apparently unique, well-defined hydroxyl bands near 3700 cm.$^{-1}$ and near 3625 cm.$^{-1}$. By a substantial proportion is meant a major part of the ultrastable aluminosilicate material, i.e., an amount in excess of 50 weight percent.

While the above-mentioned two bands which appear near 3700 cm.$^{-1}$ and near 3625 cm.$^{-1}$, respectively, appear to be characteristic of the ultrastable aluminosilicate material which is a component of the catalytic composition employed in this invention and have not as yet been described in the literature, it is quite possible that they might appear, at a weak intensity, in the infrared spectra of a decationized Y-type or other aluminosilicate material, if that aluminosilicate material were to be subjected to the proper treatment employing the proper conditions.

It is believed that the ultrastable, large-pore crystalline aluminosilicate material of the catalytic composition that is employed in the process of this invention can be identified properly by the hydroxyl infrared bands near 3700 cm.$^{-1}$ and near 3625 cm.$^{-1}$, particularly the former, when considered in conjunction with the characteristic small cubic unit cell dimension. For example, such identification or description will distinguish the ultrastable aluminosilicate material from the "high-silica" faujasites described in the prior art, which "high-silica" faujasites have the small cubic unit cell, but do not exhibit the 3700 cm.$^{-1}$ and 3625 cm.$^{-1}$ infrared bands. Furthermore, while unstable, decationized Y-type aluminosilicate materials may provide hydroxyl infrared bands near 3700 cm.$^{-1}$ and near 3625 cm.$^{-1}$, if such aluminosilicate materials were to receive the proper treatment, they do not exhibit the appropriate smaller cubic unit cell dimension that is char-

acteristic of the ultrastable, large-pore crystalline aluminosilicate material.

Advantageously, embodiments of the catalytic composition of this invention can be prepared as follows. The ultrastable, large-pore crystalline aluminosilicate material, in a finely-divided state, may be added to a hydrogel of silica-alumina and blended therein to form a homogeneous mixture. The hydrogenation components, i.e., the metals of Group VI–B and Group VIII, may be added in the form of heat-decomposible components to this homogeneous mixture. The resulting composition is then thoroughly mixed. The heat-decomposible components may be added in a single solution or in several solutions. The resulting blended composition is then dried to a moisture content ranging between 10 and 40 percent by weight, based on the total weight of the composition. The dried material is then calcined at a temperature between 900° F. and 1,050° F. Alternately, the aluminosilicate material is blended into the hydrosol or a hydrogel and the resultant blend is then dried and formed into the desired shapes, such as pellets. The pellets are washed for removal of soluble salts, dried and/or calcined. Hydrogenation components are impregnated into the catalyst support particles through the use of solutions of suitable salts.

The finished catalyst may contain the ultrastable, large-pore crystalline aluminosilicate material in an amount between about 5 and about 50 weight percent, based on the weight of the support.

To demonstrate the benefits of the present method of starting up a hydrocracking process, the following-described tests were made.

EXAMPLE I

The first test was performed in a multiple-reactor pilot-plant unit. The five reactors in this unit were identical. Each was made of a 1-inch schedule 160 stainless steel pipe. Each had a preheat zone followed by an adiabatic zone. The catalyst bed in each reactor was entirely within the adiabatic zone of that reactor. The bed in each reactor contained 200 cc. of catalyst, which required a length of about 24 inches in the reactor. Consequently, the total catalyst loading in the unit consisted of 1,000 cc. of catalyst and resulted in a catalyst bed having a length of about 10 feet. Each of the 5 identical reactors contained the following loading of catalyst and alumina balls. Starting at the bottom of each reactor were 50 cc. of ¼-inch deactivated alumina balls which served as a catalyst support. Above these alumina balls were 200 cc. of catalyst. Above the catalyst were 200 cc. of ⅛-inch deactivated alumina balls, which served as a preheating section. Conventional recovery equipment was employed to collect the products resulting from the hydrocracking of petroleum hydrocarbon.

Catalyst comprising 2.5 weight percent cobalt oxide and 5 weight percent molybdenum trioxide deposited on a co-catalytic support comprising ultrastable, large-pore crystalline aluminosilicate material suspended in a porous matrix of amorphous silica-alumina was used. The aluminosilicate material was present in an amount of about 14 weight percent of the weight of the support. The silica-alumina contained about 13 weight percent alumina. The amounts of cobalt oxide and molybdenum trioxide were based on total catalyst weight. The catalyst was used in the shape of ⅛" x ⅛" pellets.

After the fresh catalyst had been charged to the unit, the following start-up method was employed. The catalyst was reduced by circulating hydrogen over it at 1,300 p.s.i.g. and 750° F. for about 20 hours. The flow rate of the hydrogen during this reduction period was about 52 standard cubic feet of hydrogen per hour per pound of catalyst. Subsequently, the reduced catalyst was cooled to 625° F. Hydrogen flow was continued over the catalyst, and a light virgin gas oil (LVGO) was introduced into the reaction system as the first preliminary hydrocarbon feedstock at a LHSV of about 0.6 volume of hydrocarbon per hour per volume of catalyst. This LVGO had the properties shown in Table I. It is to be noted that this LVGO possessed an ASTM end point of about 667° F. and contained 69 parts per million nitrogen, 0.16 weight percent sulfur, and about 19 volume percent aromatics.

TABLE I.—PROPERTIES OF VARIOUS FEEDSTOCKS

Feedstock	LCCO	LVGO	70% LCCO/ 30% LVGO
ASTM Distillation (D-86), ° F.:			
IBP	383	425	399
5% rec. at			
10%	467	495	475
20%	492	514	497
30%	505	527	510
40%	518	537	523
50%	530	549	535
60%	544	561	549
70%	559	576	564
80%	578	597	583
90%	601	626	608
95%			
E.P.	637	667	649
Gravity, ° API	25.6	34.4	28.1
Viscosity, centistokes:			
100° F.			3.50
210° F.			1.31
Chemical composition:			
Carbon, wt. percent	88.47	86.59	87.75
Hydrogen, wt. percent	11.11	13.24	11.89
Sulfur, wt. percent	0.40	0.16	0.35
Nitrogen, p.p.m.	190	69	150
Chlorine, p.p.m.	0.2	0.5	
Molecular wt.	197	224	207
Refractive index at 20° C.	1.5132	1.4734	1.5014

Upon introduction of this LVGO into the reaction system, a hot spot formed immediately. This hot spot constituting a 60° F. temperature rise, moved slowly through the catalyst bed. Approximately 48 hours were required for this hot spot to pass completely through the total catalyst. In this particular test, as the hot spot passed through the bed the conversion was high and little recycle oil was produced. As the hot spot disappeared from the catalyst bed, the conversion of this LVGO dropped considerably. The rate of the fresh feed was increased to a LHSV of 1.0 volume of hydrocarbon per hour per volume of catalyst and the recycle oil which was then formed was introduced into the reaction system and adjusted to provide a throughput ratio of about 1.3. Reactor temperatures were adjusted to values which would furnish 100% conversion of the LVGO to material boiling below 360° F. The run was continued with the LVGO at a throughput rate of 1.3 for about 24 hours.

At this point, the first preliminary feedstock, the LVGO, was changed to a second preliminary feedstock. This second preliminary feedstock comprised a blend of the above LVGO and a light catalytic cycle oil (LCCO). The blend contained 30% LCCO and 70% LVGO. Properties of the LCCO used in this blend are presented in Table I. This second preliminary feedstock contained 105 parts per million nitrogen, 0.23 weight percent sulfur, and about 27.5 volume percent aromatics. This second preliminary feedstock was processed for 16 hours. Then the flow of this second preliminary feedstock was stopped and the principal feedstock was introduced into the reaction system. This principal feedstock was another blend of the LCCO and the LVGO. It contained 70% LCCO and 30% LVGO. The properties of this latter blend are also presented in Table I. It had an ASTM end point of about 649° F. and it contained 150 parts per million nitrogen, 0.35 weight percent sulfur and about 39 volume percent aromatics. This principal feedstock was processed for a period of time in excess of 90 days. The following operating conditions were employed: a total pressure of about 1,300 p.s.i.g.; a hydrogen partial pressure of about 1,200 p.s.i.g. at the reactor inlet; a LHSV of about 1.0 volume of fresh feed per hour per volume of catalyst; a throughput ratio of about 1.3 volumes of total hydrocarbons per volume of fresh feedstock; a hydrogen recycle rate of about 9,000 standard

cubic feet of hydrogen per barrel of total hydrocarbons; and a temperature required for 100 percent conversion of the fresh feedstock.

The activity of the catalyst for hydrocracking petroleum hydrocarbons may be conveniently expressed as the average catalyst temperature required to produce 100 percent conversion of the fresh feedstock to material boiling below 360° F. After 15 days on stream, the catalyst required an average temperature of 718° F.; after 20 days on stream, about 720° F.; and after 90 days on stream, about 740° F.

The following yield data were obtained with the principal feedstock at 4 days on stream:

TABLE II

Yield data

Component:	Yield, wt. percent of total hydrocarbon product
C_1+C_2's	0.60
C_3	3.51
i-C_4	7.12
n-C_4	4.56
i-C_5	10.18
n-C_5	1.09
C_6-180° F.	13.45
Heavy naphtha	59.49
	100.00

EXAMPLE II

A second test was made in a bench-scale pilot-plant unit. Fresh catalyst was charged to the unit. This unit had one reactor, which had an I.D. of ⅝ inch. A second batch of the catalyst used in Example I was charged to this reactor in the form of 14-to-20-mesh material. The catalyst charge consisted of 20 cc. and provided a 4-inch bed in the reactor. Hydrocarbon products were recovered through the use of a conventional bench-scale recovery equipment and techniques.

After the catalyst was charged to the unit, the catalyst was reduced by circulating once-through hydrogen over it for about 2 hours at a pressure of about 1,250 p.s.i.g. and a temperature of about 750° F. The flow rate of hydrogen was about 82 standard cubic feet of hydrogen per hour per pound of catalyst. The reduced catalyst was cooled to a temperature of about 650° F. Hydrogen flow was maintained. The LCCO considered in Example I was introduced into the hydrocracking reaction zone at a LHSV of 1.25 and a once-through hydrogen rate of about 9,000 standard cubic feet of hydrogen per barrel of hydrocarbons. The properties of this LCCO are presented in Table I. This LCCO possessed an ASTM end point of about 637° F., and contained 190 parts per million nitrogen, 0.40 weight percent sulfur and about 47 volume percent aromatics. The hot spot which was produced was permitted to slowly pass through the catalyst bed. Reactor temperatures were adjusted to values which furnished about 77% conversion of the LCCO to material boiling below 360° F. Hence, in this run the first preliminary hydrocarbon feedstock was this LCCO. After this LCCO had been processed for about 15 days, the flow of this preliminary feedstock was stopped, and the principal hydrocarbon feedstock was introduced into the hydrocracking reaction zone. As in Example I, the principal hydrocarbon feedstock was a blend of LCCO (70%) and LVGO (30%). It was processed for a period of about 5 days. Operating conditions similar to those used in Example I were employed.

Again, catalyst activity was determined from the average catalyst temperature required to produce 100 percent conversion of the feedstock to material boiling below 360° F. After 15 days on stream, the catalyst required an average temperature of about 740° F.; after 20 days on stream, an average temperature of about 741° F.

EXAMPLE III

A third test was made in a bench-scale pilot-plant unit employing a reactor having an I.D. of ⅞ inch and using another portion of the same catalyst. The catalyst charge consisted of 50 cc. and provided a 6-inch bed in the reactor. After the catalyst was charged to the unit, the catalyst was reduced by circulating once-through hydrogen over it for about 4 hours at a pressure of about 1,250 p.s.i.g. and a temperature of about 750° F. The flow rate of hydrogen was about 52 standard cubic feet of hydrogen per hour per pound of catalyst. The reduced catalyst was cooled to a temperature of about 650° F. Hydrogen flow was maintained. The principal hydrocarbon feedstock used in Example I was introduced into the hydrocracking reaction zone. The hot spot, which resulted from the introduction of feedstock into the reaction zone, was permitted to move slowly through the catalyst bed. After the hot spot had passed through the bed and recycle oil was introduced into the reaction system, the reactor temperatures were adjusted to values which would furnish 100% conversion of the fresh principal hydrocarbon feedstock to material boiling below about 360° F. This principal hydrocarbon feedstock was processed over the catalyst for a period of time in excess of 90 days. In this particular test, the principal hydrocarbon feedstock was used as the sole feedstock. Operating conditions were similar to those used in Examples I and II.

As in the prior examples, catalyst activity was determined from the average catalyst temperature required to produce 100% conversion of the feedstock to material boiling below 360° F. After 15 days on stream, the catalyst required an average temperature of about 729° F.; after 20 days on stream, an average temperature of about 730° F.; and after 90 days on stream, an average temperature of about 743° F.

In addition, the following yield data were obtained at 4 days on stream:

TABLE III

Yield data

Component:	Yield, wt. percent of total hydrocarbon product
C_1+C_2's	0.71
C_3	4.32
i-C_4	7.79
n-C_4	5.15
i-C_5	10.76
n-C_5	1.10
C_6-180° F.	13.50
Heavy naphtha	56.67
	100.00

The results obtained from the above three tests clearly show that the test which employed the start-up procedure of the present invention, i.e., the test in Example I, provided 100% conversion of the principal hydrocarbon feedstock at an average catalyst temperature which was appreciably lower than the average temperatures needed in the other runs. The results of these tests also show that as the feedstock which the fresh catalyst first saw contained larger amounts of nitrogen, sulfur, and aromatics, a larger average temperature was required to produce 100% conversion of the principal hydrocarbon feedstock to material boiling below 360° F., that is, the catalyst possessed a lower activity.

In addition, the results also indicate that the yields furnished by the catalyst subjected to the start-up procedure of the present invention employing two preliminary hydrocarbon feedstocks, depicted in Example I, produced at least 2% more heavy naphtha and less light gases than those catalysts which were subjected to the other start-up procedures.

EXAMPLE IV

The disclosed start-up procedure was used in two additional experimental tests performed in the multiple-reactor pilot plant discussed in Example I. The catalyst in the first of these two runs contained 13 weight percent ultrastable, large-pore crystalline aluminosilicate material, based on the weight of the support; the catalyst in the second run contained 35 weight percent ultrastable, large-pore crystalline aluminosilicate material. A third test was performed in the same multiple-reactor pilot plant. This latter run employed a catalyst containing the 13 weight percent ultrastable, large-pore crystalline aluminosilicate material and a start-up procedure that was somewhat different from the procedure disclosed herein.

The two feedstocks used in the runs described in this example were quite similar in composition to the LVGO the LCCO-LVGO blend employed in the preceding examples. The properties of the feedstocks employed in this example are presented in Table IV.

TABLE IV.—PROPERTIES OF ADDITIONAL FEEDSTOCKS

	Feedstock	
	X	Y
Feed type	LVGO	70% LCCO-30% LVGO blend
Gravity, ° API	34.4	27.5
ASTM distillation, ° F.:		
IBP	425	398
10% rec. at	945	
30	527	519
50	549	546
70	576	563
90	626	614
Max	667	632
Sulfur, wt. percent	0.16	0.26
Nitrogen, p.p.m	67	160
Molecular weight	232	205
Refractive index, n_D^{20}	1.4734	1.5026
Molecular type (mass spec.), vol. percent:		
Aromatics	23.1	42.2
Paraffins	32.5	23.5
Naphthenes	44.4	34.3

The two catalysts that were employed in this example contained oxides of cobalt and molybdenum deposited upon a co-catalytic support comprising ultrastable, large-pore crystalline aluminosilicate material suspended in a matrix of amorphous silica-alumina. The silica-alumina employed in this support was a low-alumina silica-alumina and contained about 13 weight percent alumina. The one catalyst, identified hereinafter as Catalyst A, contained about 13 weight percent ultrastable, large-pore crystalline aluminosilicate material. The second catalyst, identified hereinafter as Catalyst B, contained 35 weight percent ultrastable, large-pore crystalline aluminosilicate material. The results of inspections performed on these two catalysts are presented in Table V.

TABLE V.—CATALYSTS INSPECTIONS

Catalyst	A	B
Aluminosilicate material content, wt. percent	13	35
Pill size, inches	1/8 x 1/8	1/8 x 1/8
Surface area, $m.^2/g.$	362	407
Crushing strength, lbs.	15	25
Abrasion loss, wt. percent	7.5	0.5
Apparent bulk density, lbs./ft.^{3}	38.7	43.1
CoO content, wt. percent (volatile-free)	2.44	2.52
MoO content, wt. percent (volatile-free)	4.77	9.46
Volatile, wt. percent	6.28	2.71
Sodium content, wt. percent	0.071	0.40
Support properties:		
Surface area, $m.^2/g.$	599	636
Sodium content, wt. percent	0.06	0.31
"d" IRA	196	200+
Carbon factor	0.23	0.15

As mentioned above in this example, two different start-up procedures were employed. The first start-up procedure, identified hereinafter as start-up procedure 1, was different from the start-up procedure disclosed herein. The second start-up procedure, identified hereinafter as start-up procedure 2, was an embodiment of the disclosed procedure employing one preliminary feedstock and a principal feedstock.

Start-up procedure 1 comprised the following: the catalyst was reduced with hydrogen at 730° F. and 1,300 p.s.i.g. for 16 hours. Hydrogen was circulated at a rate of 40 standard cubic feet per hour per pound of catalyst. Then the temperature was reduced to 630° F. and Feedstock Y was introduced into the reactor zone at 630° F. and an initial LHSV of about 0.5 volume of hydrocarbons per hour per volume of catalyst and an initial hydrogen recycle rate of about 23,000 standard cubic feet of hydrogen per barrel of hydrocarbons. Gradually over the next 5 hours, the oil rate was increased to a LHSV of about 1 volume of hydrocarbons per hour per volume of catalyst with a corresponding decrease in hydrogen recycle rate to about 12,000 standard cubic feet of hydrogen per barrel of hydrocarbons. During the next 12 hours, a controlled hot spot traveled through the catalyst bed. After 22 hours on stream, recycle oil was introduced into the unit to provide a throughput ratio of 1.3 volumes of total hydrocarbons per volume of fresh feed hydrocarbons and the recycle hydrogen rate was reduced to about 9,000 standard cubic feet of hydrogen per barrel of hydrocarbons. The temperature was adjusted to maintain 100% conversion of fresh feed to 360° F.-end-point naphtha and lighter material.

Start-up procedure 2 comprised the following: the catalyst was reduced with hydrogen at 730° F. and 1,300 p.s.i.g. for 16 hours. Hydrogen was circulated at a rate of 40 standard cubic feet per hour per pound of catalyst. Then the temperature was reduced to 530° F. and a preliminary feedstock, Feedstock X, was introduced into the reactor zone at 530° F. and an initial LHSV of about 0.4 volume of hydrocarbons per hour per volume of catalyst and an initial hydrogen recycle rate of about 29,000 standard cubic feet of hydrogen per barrel of hydrocarbons. Gradually over the next 3 hours, the oil rate was increased to a LHSV of about 1 volume of hydrocarbons per hour per volume of catalyst with a corresponding decrease in hydrogen recycle rate to about 12,000 standard cubic feet of hydrogen per barrel of hydrocarbons. During these 3 hours, a controlled hot spot travelled through the catalyst bed. After 4 hours on stream, recycle oil was introduced into the unit to provide a throughput ratio of 1.3 volumes of total hydrocarbons per volume of fresh feed hydrocarbons and the recycle hydrogen rate was reduced to about 9,000 standard cubic feet of hydrogen per barrel of hydrocarbons. The temperature was adjusted to maintain an 80 to 90 percent conversion of this fresh feed to 360° F.-end-point naphtha and lighter material. This operation was continued for 48 hours. Then introduction of Feedstock X into the reactor zone was stopped and Feedstock Y was introduced into the reactor zone. The temperature was adjusted to maintain 100% conversion of fresh Feedstock Y to 360° F.-end-point naphtha and lighter material.

After the start-up procedure was completed in each test, the operating conditions included a total pressure of about 1,300 p.s.i.g.; a fresh-feed LHSV of about 1.0 volume of hydrocarbons per hour per volume of catalyst; a fresh-feed weight hourly space velocity of about 1.39 pounds of hydrocarbons per hour per pound of catalyst; a hydrogen recycle rate of about 9,000 standard cubic feet of hydrogen per barrel of total hydrocarbon feed; a hydrogen recycle purity of about 95 volume percent; and a throughput ratio of about 1.3 volumes of total hydrocarbons per volume of fresh-feed hydrocarbons.

In test 1 of this example, a first sample of Catalyst A was used to convert Feedstock Y after the catalyst had been subjected to start-up procedure 1. In test 2 of this example, a second sample of Catalyst A was used to convert Feedstock Y after the catalyst had been subjected to the start-up procedure 2. In test 3 of this example, Catalyst B was used to convert Feedstock Y after the catalyst had been subjected to start-up procedure 2. The activities of the catalysts are expressed as a ratio of the activity of a particular catalyst relative to the activity of Catalyst A

in test 1. The activity decline rate observed for each of these three tests is expressed as the rate at which the temperature must be increased to maintain the selected constant conversion. The decline rate values were calculated for the same periods of time on oil. The results obtained from these three tests are presented in Table VI.

TABLE VI.—TEST DATA

Catalyst	Start-up procedure	Activity at 7 days	Activity decline rate, ° F./day
A	1	1.00	2.0
A	2	1.17	0.8
B	2	2.20	1.2

These results show that start-up procedure 2 provides improved hydrocracking performance. Higher catalytic activity and lower activity decline rate are obtained when the catalyst is subjected to start-up procedure 2, an embodiment of the present invention, prior to its use as a hydrocracking catalyst. Furthermore, the results show that the use of start-up procedure 2 in a run employing a catalyst containing a substantial quantity of the ultrastable, large-pore crystalline aluminosilicate material provides subsequent satisfactory hydrocracking performance.

The above examples are presented for purposes of illustration only and are not intended to limit the scope of the present invention.

The method of starting up a hydrocracking process disclosed herein is readily adaptable to either a single-stage hydrocracking process or a multiple-stage hydrocracking process.

What is claimed is:

1. A method of starting up a process for the hydrocracking of a principal petroleum hydrocarbon feedstock, which process employs in a hydrocracking reaction zone a hydrocracking catalyst comprising a hydrogenation component deposited on a solid acidic cracking component, which method comprises: contacting said catalyst with a hydrogen-containing gas at a pressure within the range between about 0 p.s.i.g. and 2,500 p.s.i.g. and a temperature within the range between about 400° F. and about 850° F. for a period of time sufficient to reduce said hydrogenation component; cooling said catalyst to a temperature which will provide low conversion of a hydrocarbon feedstock, whereby cracking of hydrocarbons can be controlled more easily; contacting said catalyst with a first preliminary hydrocarbon feedstock having low concentrations of nitrogen, sulfur, and aromatics for a period of time which is sufficient to permit a hot spot to move slowly through the bed of said catalyst without appreciably affecting the activity and other properties of the catalyst in a deleterious manner, said hot spot having a maximum temperature of 850° F.; after said hot spot has passed through the bed of said catalyst, increasing the temperature in said reaction zone to obtain conversion of said first preliminary hydrocarbon feedstock to lower-boiling hydrocarbons; stopping the flow of said first preliminary hydrocarbon feedstock; and contacting said catalyst with said principal petroleum hydrocarbon feedstock.

2. The method of claim 1 wherein said catalyst is contacted with a second preliminary hydrocarbon feedstock subsequent to being contacted with said first preliminary feedstock and prior to being contacted with said principal petroleum hydrocarbon feedstock, said second preliminary hydrocarbon feedstock having concentrations of nitrogen, sulfur, and aromatics intermediate between those of said first preliminary hydrocarbon feedstock and those of said principal petroleum hydrocarbon feedstock.

3. The method of claim 1 wherein said hot spot is permitted to have a maximum temperature of 800° F.

4. The method of claim 1 wherein said contacting said catalyst with a first preliminary hydrocarbon feedstock is carried out at a maximum liquid hourly space velocity of three-fourths of that of the principal hydrocarbon feedstock.

5. The method of claim 1 wherein any liquid product obtained with said first preliminary hydrocarbon feedstock is recycled and combined with said first preliminary hydrocarbon feedstock being introduced into said reaction zone prior to entry of said first preliminary hydrocarbon feedstock into said reaction zone.

6. The method of claim 1 wherein said contacting said catalyst with a hydrogen-containing gas is carried out for a period of time between about 1 hour and about 48 hours.

7. The method of claim 1 wherein said contacting said catalyst with a hydrogen-containing gas is carried out for a period of time within the range between about 1 hour and about 24 hours.

8. The method of claim 1 wherein said cooling said catalyst is performed to obtain a temperature of said catalyst which is greater than 550° F.

9. The method of claim 1 wherein said solid acidic cracking component comprises a large-pore crystalline aluminosilicate material suspended in a porous matrix of silica-alumina, said aluminosilicate material being present in an amount between about 5 and about 50 weight percent, based on the weight of said cracking component.

10. The method of claim 1 wherein said hydrogenation component comprises a mixture of cobalt oxide and molybdenum trioxide, said cobalt oxide being present in an amount between about 2 and about 5 weight percent and said molybdenum trioxide being present in an amount between about 4 and about 15 weight percent, based on the total weight of said catalyst.

11. The method of claim 1 wherein said solid acidic cracking component comprises ultrastable, large-pore crystalline aluminosilicate material suspended in a porous matrix of silica-alumina, said alumino-silicate material being present in an amount between about 5 and about 50 weight percent, based on the weight of said cracking component.

12. The method of claim 9 wherein said catalyst is contacted with a second preliminary hydrocarbon feedstock subsequent to being contacted with said first preliminary feedstock and prior to being contacted with said principal petroleum hydrocarbon feedstock, said second preliminary hydrocarbon feedstock having concentrations of nitrogen, sulfur, and aromatics intermediate between those of said first preliminary hydrocarbon feedstock and those of said principal petroleum hydrocarbon feedstock.

13. The method of claim 11 wherein said hydrogenation component comprises a mixture of cobalt oxide and molybdenum trioxide, said cobalt oxide being present in an amount between about 2 and about 5 weight percent and said molybdenum trioxide being present in an amount between about 4 and about 15 weight percent, based on the total weight of said catalyst.

14. The method of claim 13 wherein said contacting said catalyst with a hydrogen-containing gas is carried out for a period of time between about 1 and about 24 hours.

15. The method of claim 13 wherein said catalyst is contacted with a second preliminary hydrocarbon feedstock subsequent to being contacted with said first preliminary feedstock and prior to being contacted with said principal petroleum hydrocarbon feedstock, said second preliminary hydrocarbon feedstock having concentrations of nitrogen, sulfur, and aromatics, intermediate between those of said first preliminary hydrocarbon feedstock and those of said principal petroleum hydrocarbon feedstock.

16. The method of claim 13 wherein said hot spot is permitted to have a maximum temperature of 800° F.

17. The method of claim 13 wherein any liquid product obtained with said first preliminary hydrocarbon feedstock is recycled and combined with said first preliminary hydrocarbon feedstock being introduced into said reaction zone prior to entry of said first preliminary hydrocarbon feedstock into said reaction zone.

18. The method of claim 13 wherein said contacting said catalyst with a hydrogen-containing gas is carried out for a period of time between about 1 hour and about 48 hours.

19. The method of claim 14 wherein said process is a single-stage process.

20. The method of claim 14 wherein said cooling said catalyst is performed to attain a temperature of said catalyst which is greater than 550° F.

21. The method of claim 20 wherein said hot spot is permitted to have a maximum temperature of 800° F.

22. The method of claim 21 wherein said contacting said catalyst with a first preliminary hydrocarbon feedstock is carried out at a maximum liquid hourly space velocity of three-fourths of that of the principal hydrocarbon feedstock.

23. The method of claim 22 wherein any liquid product obtained with said first preliminary hydrocarbon feedstock is recycled and combined with said first preliminary hydrocarbon feedstock being introduced into said reaction zone prior to entry of said first preliminary hydrocarbon feedstock into said reaction zone.

24. The method of claim 23 wherein said catalyst is contacted with a second preliminary hydrocarbon feedstock subsequent to being contacted with said first preliminary hydrocarbon feedstock and prior to being contacted with said principal petroleum hydrocarbon feedstock, said second preliminary hydrocarbon feedstock having concentrations of nitrogen, sulfur, and aromatics intermediate between those of said first preliminary hydrocarbon feedstock and those of said principal petroleum hydrocarbon feedstock.

25. The method of claim 23 wherein said process is a single-stage process.

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