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START-UP METHOD FOR AN LPG-REFORMING
PROCESS

John C. Hayes, Palatine, and Roy T. Mitsche, Island Lake,
Ill., assignors to Universal Oil Products Company, Des
Plaines, Ill., a corporation of Delaware
No Drawing. Filed July 13, 1966, Ser. No. 564,720
10 Claims. (Cl. 208—139)

ABSTRACT OF THE DISCLOSURE

Start-up procedure for a naphtha reforming process utilizing a Pt-alumina-crystalline aluminosilicate catalyst, which includes the steps of (1) pressuring the conversion zone with extrinsic hydrogen to an initial level of 75–150 p.s.i.g., (2) heating the conversion zone to a temperature of 775°–825° F., (3) introducing charge stock to the conversion zone, and (4) raising the temperature of the conversion zone at the rate of 5–30° F./hr. to a temperature of 925°–1000° F., whereby the process pressure increases autogenously from said initial level to a final operating level of 400–700 p.s.i.g.

The subject of the present invention is an improved method for the start-up of an LPG-reforming process which utilizes a novel catalyst containing a finely divided crystalline aluminosilicate suspended in an alumina matrix. More exactly, the present invention encompasses a method of start-up of this LPG-reforming process which eliminates certain chronic problems, in the areas of temperature stability and of hydrogen production, which heretofore have plagued start-ups of this process when conventional start-up procedures were employed. The conception of this invention was facilitated by the discovery that there is a pronounced hydrogen production versus temperature dependance for this type of catalyst which becomes evident in a temperature range that heretofore had been tough to be a range in which severe catalyst deactivation would occur if the catalyst was subjected to it during start-up. In essence, then, the present invention provides a method for starting-up this type of LPG-reforming process, which involves a carefully controlled temperature adjustment procedure, and which results in the avoidance of temperature runaway conditions and of substantially all unbalanced hydrogen consumption during start-up.

Ordinarily, as is well known in the art, the requirements for an optimum process for transforming low octane stocks into high octane stocks, at minimum loss to undesirable products, involves a specially tailored catalytic environment designed to promote upgrading reactions for paraffins and naphthenes which are the components of gasolines and naphthas that have the highest octane-improving potential. For paraffins the upgrading reactions are: isomerization, dehydrogenation to olefins, dehydrocyclization to aromatics, and hydrocracking to lower molecular weight paraffins. Of these, the dehydrocyclization reaction shows the maximum gain in the octane number and is, consequently, preferred. For naphthenes, the principal upgrading reactions involve dehydrogenation and ring isomerization of naphthenes to aromatics; but, the improvement in octane number is not as dramatic here as in the case of dehydrocyclization of paraffins since the clear research octane numbers of most naphthenes is in the range of 65 to 80. Accordingly, catalytic reforming operations are designed to provide an optimum mix of these aforementioned reactions, generally employing for this purpose a multi-purpose catalytic composite having at least a metallic dehydrogenation component and an acid-acting component.

It is not, however, to be assumed that the achievement and control of this optimum mix of upgrading reactions is without its problem areas. These, as is true with any complex set of reaction mechanisms, are injected into the picture by the uncontrollable side phenomena that stem from a myriad of factors which color and complicate the actual operations of a reforming process. Foremost among these complicating factors are those associated with undesired side reactions. Examples of these side reactions are: demethylation of hydrocarbons to produce methane, ring opening of naphthenes to give straight chain hydrocarbons, excessive hydrocracking to yield undesired light gases, condensation of aromatics and other components to form carbonaceous deposits on the catalyst, acid catalyzed polymerization of olefins and other highly reactive components to yield high molecular weight reactants that can undergo further dehydrogenation and thus contribute to the carbonaceous deposits on the catalyst, etc.

Accordingly, a successful reforming operation minimizes the effects of these complicating factors by a judicious selection of the catalytic environment and process variables for the particular charge stock of interest. But, adding an additional dimension of complexity to the solution of this problem is the interdependence of the set of desired reactions and the set of undesired reactions such that selection of the proper conditions to minimize one effect may have, and indeed most likely does, a marked effect on the set of desired reactions.

Recently, there has been disclosed a unique type of reforming catalyst which has the singular characteristic of being able to selectively produce LPG (i.e. liquefied petroleum gas—chiefly, C₃ and C₄) and a high octane reformate with minimum loss to methane and ethane. This remarkable selectivity is apparently a consequence of the increase in the acid function of the catalyst which is brought about by the incorporation of a finely divided crystalline aluminosilicate in the alumina matrix associated with the catalyst. This shift of the mix of reaction towards hydrocracking is not without its associated problems—particularly, if it is desired to operate the process in a balanced state wherein the hydrogen consumption reactions are balanced by the hydrogen production reactions in order that the supply of hydrogen in the process is maintained without the necessity of adding an extrinsic source of hydrogen.

As mentioned hereinbefore, in a reforming operation a shift in selectivity of the desired reactions is generally accompanied by perturbation in the set of undesired reactions. This interdependence is manifest in the observations we have made utilizing this new catalyst—particularly, during the start-up period. As will be shown in an example appended to this discussion, these new LPG-reforming catalysts do, indeed, shift the set of desired reactions toward selective hydrocracking; but they also, during start-up of the process, tend to increase the undesired reactions of excessive hydrocracking and demethylation which are strongly exothermic and, if not carefully controlled, can result in a temperature runaway with its attendant detrimental effect on catalyst crystalline structure.

Because of this increase in hydrocracking activity, these LPG-reforming catalysts cause a marked increase in hydrogen consumption relative to a high quality reforming catalyst at the same conditions. This is nowhere more evident than during the start-up period. During this period, an ordinary reforming catalyst will tend to produce enough hydrogen to satisfy hydrogen consumption reactions and to keep the catalyst from deactivating by virtue of carbonaceous deposit formation of the surface of the catalyst. In sharp contrast is the situation encountered when starting-up the previously mentioned LPG-reforming catalysts. These catalysts tend to use all available

hydrogen to satisfy the demand for hydrogen emanating from the selective hydrocracking function of the catalyst. Consequently, as will be shown in an example, it has been found necessary to add hydrogen during the start-up period in order to bring the process into hydrogen balance and to retard the deposition of carbonaceous deposits on the catalyst. It was thought that this lack of ability to stay in hydrogen balance was part of the price that had to be paid for the selective LPG production capability of these novel catalysts. We have now found that this is not the case.

In the past, when adequate extrinsic hydrogen was readily available, a preferred method of starting-up a high quality platinum-containing reforming catalyst, which was designed to operate for significant periods without regeneration, involved, in broad outline, the following procedure. First, the plant was purged with an inert gas in order to remove substantially all free oxygen. Second, the inert gas was removed by purging it with a hydrogen-rich gas at a pressure of about 100 p.s.i.g. to about 200 p.s.i.g. Third, the hydrogen-rich gas was heated and circulated in order to bring the plant up to a temperature of about 650° F. to about 800° F. Fourth, the charge stock, at a temperature corresponding to the plant temperature, was cut in at a rate of from about 25% to about 100% of operational level. Fifth, the temperature of the plant was raised to a level between about 850° F. and 900° F. at which point plant pressure would easily build to operational start-up level of about 300 p.s.i.g. to about 700 p.s.i.g. because of the net hydrogen that was produced in the reaction zone and recycled thereto. Finally, adjustments would be made, if necessary, in the feed rate and process conditions in order to line out the process at the desired output product quality. This method had the dual advantage of avoiding temperature runaway and carbonaceous deposit formation during start-up.

In the utilization of this procedure it was found to be important that the temperature not be raised to operating levels until hydrogen production, as measured by plant pressure, had built to operating levels because of the substantial danger of promoting excessive carbonaceous deposits on the catalyst by subjecting it to high temperatures at low partial pressures of hydrogen. On the other hand, it was not desired to pressure the plant up to operating levels because of the high cost of the necessary hydrogen.

As will be shown in an example, when this start-up procedure is applied to the class of LPG-reforming catalysts mentioned hereinbefore, hydrogen production relative to hydrogen consumption fails to build to self-sustaining levels. Accordingly, it was found necessary to add extrinsic hydrogen in order to reach plant operating pressure. And, even more important, it was found to be necessary to continue to add hydrogen for a significant period of time (i.e. out to an effective catalyst life of about 2 barrels per pound of catalyst) before internal hydrogen production became adequate to sustain the process.

Furthermore, as will be shown in a subsequent example, it was found that even if the start-up procedure was modified so that the process was pressured up to actual operating levels (i.e. in this case 600 p.s.i.g.) with extrinsic hydrogen before the feed was cut in, hydrogen production failed to be self-sustaining and additional hydrogen had to be added to maintain plant pressure.

We have now discovered that, if the procedure outlined above is modified, adequate hydrogen production can be attained and sustained without the necessity of continuously adding extrinsic hydrogen to the process during the start-up period. The modification necessary for the method of the present invention encompasses, as will be hereinafter explained in detail, the heating, in a controlled manner, of the charge and hydrogen mixture to a temperature of about 925° F. to about 1000° F. where, as will be demonstrated in an example, a sharp rise in

hydrogen production is encountered without adversely affecting the activity of the catalyst. This unexpected result is in sharp contrast to the teachings of the prior art which would have predicted heavy deposition of carbonaceous deposits on the catalysts with its attendant deactivation of the catalyst—particularly, for the dehydrogenation reactions.

It is, accordingly, an object of the present invention to provide a method for starting-up an LPG-reforming process utilizing a catalyst of the type described herein, which process does not require any extrinsic hydrogen other than the amount initially necessary to charge the plant to a pressure of about 75 p.s.i.g. to about 150 p.s.i.g. A related object is to provide a start-up procedure for an LPG-reforming process that does not require any additional hydrogen to be added after feed cut in and that does not result in excessive carbonaceous deposit formation on the catalyst. Another objective is to avoid the development of runaway conditions in the start-up of an LPG-reforming catalyst of the type disclosed herein.

In a broad embodiment, the present invention relates to a method of start-up of a process for the production of C₃ and C₄ hydrocarbons and of a high octane reformat from a hydrocarbon charge stock, in which process said charge stock and hydrogen are contacted, in a conversion zone, with a catalytic composite containing a finely divided crystalline aluminosilicate suspended in an alumina matrix component having at least one active metallic catalytic component composited therewith, which method comprises: pressurizing the conversion zone with extrinsic hydrogen only to about 75 p.s.i.g. to about 150 p.s.i.g., heating the conversion zone to a temperature of about 775° F. to about 825° F., introducing charge stock to said conversion zone, raising the temperature of the conversion zone at a rate of from about 5° F. to about 30° F. per hour to a temperature of from about 925° F. to about 1000° F. whereby the process pressure rises to the desired operating level of about 400 to about 700 p.s.i.g. without the necessity of adding any additional hydrogen.

Specific embodiments of this invention relate to particular preferred process conditions, concentration of catalytic ingredients, types of charge stock, and various mechanisms of effecting the process. These will be hereinafter discussed in a detailed explanation of the invention which is contained in the description of the elements, conditions, and mechanism that can be employed in the practice of the present invention.

Without limiting the scope and spirit of the appended claims by this explanation, we believe that this unexpected increase in hydrogen production, with no corresponding increase in carbonaceous deposits, is primarily caused by the fact that, for this type of catalyst, the slope of the hydrogen production versus temperature function is much higher than the corresponding slope of the hydrocracking versus temperature function in the temperature range of 925° F. to about 1000° F. Hence, hydrocracking activity, with its attendant hydrogen consumption, remains relatively constant in this temperature range whereas hydrogen production increases greatly. It is to be noted that this is not necessarily the result after the catalyst has been onstream for some time and accumulated significant carbonaceous deposits because these adversely affect the dehydrogenation activity of the catalyst and therefore change the slope of the dehydrogenation versus temperature response curve. But, we have observed this temperature dependence for reasonably carbon-free catalyst and this is precisely the situation of interest during start-up.

Before considering in detail the various ramifications of the present invention, it is convenient to define several of the conventions, terms, and phrases used in the specification and in the appended claims. In those instances where temperatures are given with respect to boiling ranges and boiling points, it is understood that they have reference to those which are obtained through the use of

standard ASTM distillation methods. The phrase "gasoline boiling range" as used herein refers to a temperature range having an upper limit of about 400° F. to about 425° F. The term "naptha" refers to a selected fraction of a gasoline boiling range distillate and will generally have an initial boiling point of from about 150° F. to about 250° F. and an end boiling point within the range of about 350° F. to about 425° F. The phrase "hydrocarbon fraction or distillate" is intended to refer to a portion of a petroleum crude oil, the mixture of hydrocarbons, of a coal tar distillate, of a shale oil, etc., that boils within a given temperature range. All weight percents of elements reported herein are calculated on an elemental basis even though the element may be present in a combined form. The phrase "platinum group metallic component" embraces all the members of Group VIII of the Periodic Table having an atomic weight greater than 100 as well as compounds, and mixtures of any of these. The "liquid hourly space velocity" (LHSV) is defined to be the equivalent liquid volume of the reference fluid flowing over the bed of catalyst per hour divided by the volume of catalyst disposed within the reaction zone. The expression "in hydrogen balance" when used in reference to a reforming operation refers to the situation when hydrogen consumption is balanced against hydrogen production with a slight excess of hydrogen being produced which is generally the major component of the "excess recycle gas."

The hydrocarbon stocks that can be converted in accordance with the process of the present invention comprise hydrocarbon fractions containing naphthenes and paraffins. The preferred stocks are those consisting essentially of naphthenes and paraffins although in some cases aromatic and/or olefins may also be present. This preferred class includes straight run gasoline, natural gasolines, and the like. On the other hand, it frequently is advantageous to charge thermally or catalytically cracked gasolines or higher boiling fractions thereof to the conversion process of the present invention. Mixtures of straight run and cracked gasoline can also be used. The gasoline charge stock may be a full boiling range gasoline having an initial boiling point of from about 50° F. to about 100° F. and an end boiling point within the range of from about 325 to 425° F., or may be a selected fraction thereof which usually will be a higher boiling fraction commonly referred to as a naphtha. It is also possible to charge to the process of the present invention pure hydrocarbons or a mixture of hydrocarbons, usually paraffins or naphthenes, which it is desired to convert to aromatics and LPG. As will be demonstrated in an example appended to the present discussion, the process of the present invention is particularly applicable to the conversion of hydrocarbons to LPG.

The recently developed catalysts employed in this invention consist essentially of a component comprising a finely divided crystalline aluminosilicate dispersed in an alumina matrix and at least one metallic catalytic component composited therewith. The dual-function catalysts having halogen and a metal possessing hydrogenation-dehydrogenation activity are the preferred catalytic ingredients to be composited with the alumina matrix component and form the preferred catalyst employed in the process of this invention. Especially preferable ingredients are at least one halogen selected from the group consisting of chlorine and fluorine and metals selected from Group VIII of the Periodic Table (platinum group metals being the most preferred). One specific catalyst has been found to be particularly effective, contains up to 0.75 wt. percent platinum and up to about 1.0 wt. percent chloride, these ingredients being composited with an alumina component comprising an alumina matrix having less than about 20 wt. percent crystalline aluminosilicate dispersed therein.

The crystalline aluminosilicates are composed of SiO_4 and AlO_4 tetrahedra, a silicon or aluminum atom being

centered around 4 oxygen atoms in the tetrahedra and the oxygens being shared with other surrounding tetrahedra. These aluminosilicates are geometrically arranged to form a pore structure having sufficiently large pore mouths to permit the reactant molecules to pass into said pore structure. Preferably the aluminosilicates employed in the catalyst support have pore mouths of from about 5 up to about 15 Angstroms in cross-sectional diameter. The aluminosilicates are treated to improve their catalytic activity by techniques such as ion-exchange with suitable cations and thermal treatment. Ordinarily, the aluminosilicates are synthetically prepared in the alkali metal form (usually sodium) and there is one monovalent alkali metal cation associated with each aluminum-centered tetrahedra (to maintain electrical neutrality). The aluminosilicates may be ion-exchanged with polyvalent cations such as calcium, magnesium, beryllium, rare earths, etc., to replace a substantial amount of the monovalent cations. This causes one polyvalent cation to be associated with more than one aluminum-centered tetrahedra and if these tetrahedra are spread sufficiently far apart (due to the presence of silicon-centered tetrahedra), areas of local electrical charge will be formed which aid in promoting catalytic reactions. Another technique to improve the catalytic activity of the aluminosilicates is to ion-exchange with ammonium ions followed by thermal treatment, preferably above 300° C. to convert the crystalline aluminosilicate to the hydrogen form.

There are numerous types of crystalline aluminosilicates, both synthetic and natural occurring. It is preferable that the pore mouths of the crystalline aluminosilicates have a cross-sectional diameter of from about 5 to about 15 Angstrom units. Among the preferable crystalline aluminosilicates that are suitable are the hydrogen and/or polyvalent forms of faujasite, and mordenite, especially preferable is the hydrogen form of mordenite.

The concentration of crystalline aluminosilicate in the alumina matrix is preferably less than about 20 wt. percent of the alumina although in some cases greater concentrations may also be suitable. We especially prefer concentrations of aluminosilicate of about 10 wt. percent or less. The preferable concentration of Group VIII metal depends to a large extent on the metal. When employing platinum group metals such as platinum, the concentration on the catalyst is preferably from about 0.05 up to about 5 wt. percent whereas in the case of non-noble metals such as nickel, preferable concentration ranges are from about 1 up to as much as 40 wt. percent. The halogen content of the catalyst is less critical since the crystalline aluminosilicate provides a similar type of catalytic activity. Chlorine is the preferred halogen and may be present in the catalyst in concentrations up to as high as 3.0 wt. percent although lower values of from 0.2 up to about 1.0 wt. percent are preferred.

Hydrocarbons may be converted in accordance with out process using fluidized, fluidized-fixed bed processes, suspensoid, moving bed or batch type of processes. However, we prefer fixed bed processes primarily because operations of this type tend to minimize attrition losses of the relatively expensive catalyst. One fixed-bed system of utilizing the process comprises preheating hydrogen-rich gas and hydrocarbon charge stock to conversion temperature and passing the same through a plurality of substantially adiabatic conversion zones containing a catalyst of the type described herein. The effluent from the reactor system passes, after cooling, to a high pressure separating zone. In this zone a liquid phase separates from a gaseous phase. The gaseous phase is rich in hydrogen and at least a portion of it is recycled to the conversion zones and another portion is, usually, recovered as excess recycle gas. The liquid phase is passed to a debutanizer column in which light ends are taken overhead and a C_5+ product is recovered as a bottoms fraction.

In starting-up a process of the type described above, using the method of the present invention, it is first nec-

essary to purge all of the oxygen from the system. This can be done using any suitable inert gas such as nitrogen. The inert gas is then displaced with a hydrogen-rich gas and the system is pressured up to about 75 p.s.i.g. to about 150 p.s.i.g. Then the hydrogen-rich gas is disconnected from the system; and heating and circulating of the gas through the system is commenced. When the system has reached a temperature of from about 775° F. to about 825° F., the feed is introduced in amount of from about 25% to about 100% of the full rate of flow. The temperature of the conversion zone is then raised at a rate of from about 5° F. to about 30° F. per hour to a final operating temperature of about 925° F. to about 1000° F., at which point the pressure of the process will easily rise to an operating level of about 400 p.s.i.g. to about 700 p.s.i.g. Once adequate hydrogen production is attained the feed rate can be adjusted to obtain an operating liquid hourly space velocity of from about 0.5 to about 5. Then depending on the amount of excess recycle gas, and the desired octane number of the C₅+ product, the temperature of the system can be adjusted to achieve final operating temperature in the range of 850° F. to about 1100° F. In addition, the recycle hydrogen rate can be set to yield an operating hydrogen to oil mol ratio of about 2 to about 20.

It is to be kept in mind that the exact selection of the particular setting of all of the variables of this start-up method are at least partially dependent on the physical and/or chemical characteristics of the charge stock being subjected to the present process and, as such, have to be individually determined for each particular type of input stream.

The following examples are given to illustrate further the method of the present invention, and to indicate the benefits to be afforded through the utilization thereof. It is understood that the examples are given for the sole purpose of illustration, and are not considered to limit the generally broad scope and spirit of the appended claims.

The method of catalyst preparation employed in the following examples is intended to be illustrative of a preferred method of preparation and is not to be construed to be an essential limitation of the present invention inasmuch as similar results are observed with catalysts of the same composition which have been prepared according to any of the methods of the prior art.

Example I

This example demonstrates that there is a significant temperature control problem associated with the start-up of the LPG-reforming catalyst of the type discussed herein relative to a typical high quality reforming catalyst.

High purity aluminum metal was digested in hydrochloric acid to produce a sol having a weight ratio of Al/Cl of about 1.40 and a specific gravity at 60° F. of 1.4030. Two liters of this sol were blended with 150.6 cc. of concentrated hydrochloric acid, and the specific gravity of the resultant solution was adjusted with water to a value of 1.3450. The Al/Cl ratio at this point was 1.15. This solution was then aged for three days.

An aqueous solution containing 28% by weight of hexamethylenetetramine (HMT) was then prepared and a 700 cc. portion of this HMT solution was added to a 700 cc. portion of the aluminum sol. About 20 grams of the hydrogen form of mordenite, in the form of a fine powder, was added to the resulting solution and thoroughly dispersed therein.

The mordenite used was analyzed and found to have the following composition: 11.6% by weight Al₂O₃, 87.7% by weight SiO₂, 0.21% by weight Na, and between 0.01% to 0.04% by weight of Ca.

The resultant solution was separately passed through a vibrating dropping head and dropped in discrete particles into a forming oil maintained at 95° C. The rate of vibration and the volumetric flow of alumina sol was set

to produce finished spherical particles of about 1/16 inch in diameter. The dropped particles were then aged in oil at 95° C. for 21 hours and then separated from the oil and aged in a 2% NH₃ solution at 95° C. for 3 hours. The aged spherical particles were then water washed at 95° C. for 4 hours to remove neutralization salts. The particles were then oven dried and calcined at 600° C. for 4 hours.

About 350 cc. of the resulting particles were placed in a vessel. An impregnating solution containing chloroplatinic acid and hydrochloric acid was added to the vessel and the resultant mixture was heated until all of the solution evaporated. The resultant particles were then oxidized to produce a finished product having a wt. percent platinum content of 0.75, a wt. percent chloride content of 1.00, and a wt. percent mordenite content of about 10.0. A portion of the resultant particles was then prerduced and presulfided in such a manner that 0.12 wt. percent sulfur was incorporated therewith. In the subsequent discussion the sulfur-less portion is designated as catalyst A and the sulfur-containing portion as catalyst B.

A third catalyst was prepared in exactly the same manner as catalyst B above except for the inclusion of the mordenite in the alumina, and contained a 0.90% by weight of chloride, about 0.10% by weight of sulfur and about 0.75% by weight of platinum. This catalyst is designated as catalyst C in the subsequent discussion and is representative of a high quality reforming catalyst.

Catalysts A, B, and C were then separately subjected to an identical high stress start-up evaluation test. This consisted of charging a light naphtha having: an initial boiling point of 255° F., an end boiling point of 380° F., a 59.3° API specific gravity at 60° F., a paraffin content of 81% by volume, a naphthene content of 16% by volume, and an aromatic content of 3% by volume, to a block-type, isothermal reactor. This reactor was part of a plant which also included a high pressure separating zone, a debutanizer fractionating column, a recycle separator gas compressor, a charge pump and miscellaneous equipment. In this plant the charge stock and a recycle hydrogen stream passed through the reactor, through cooling means, into a separating zone, in which a gas phase separated from a liquid phase. A portion of the gas phase was recycled to the reactor zone to supply hydrogen there-to and another portion was recovered as excess recycle gas. The liquid phase from the separating zone was introduced into the debutanizer column and an overhead fraction recovered along with the C₅+ bottom fraction.

The start-up procedure was designed to detect, among other things, any tendency for catalyst runaway; consequently, it was made at conditions that were quite severe. This procedure involved: pressurizing the plant with hydrogen to 500 p.s.i.g., heating the plant to a temperature of about 896° F., and then introducing the charge stock at a rate which corresponded to a space velocity of 2.0 and a hydrogen to charge stock mole ratio of about 10.0.

The peak temperature observed at oil cut in was then recorded. For catalyst B it was 966° F. For catalyst C it was 902° F. and for catalyst A, a temperature runaway developed in which the temperature rose rapidly to 970° F. with no sign of cresting; consequently the plant was shut down.

Here, then, is ample evidence of the substantial start-up temperature control problem that can very easily develop with these mordenite-containing LPG-reforming catalyst (i.e., catalyst A and B) as compared to a high quality reforming catalyst (i.e., catalyst C). These results highlight the unique nature of these mordenite-containing catalysts.

Example II

This example shows the substantial hydrogen balancing problem encountered when an LPG-reforming catalyst, of the type previously discussed, is started-up using the normal start-up procedure for a high quality reforming catalyst.

An LPG-reforming catalyst was manufactured in exactly the same manner as delineated for catalyst B in Example I. The finished catalyst contained 0.83 wt. percent platinum, 0.76 wt. percent chloride, 0.11 wt. percent sulfur and about 4.6 wt. percent of the hydrogen form mordenite type aluminosilicate.

A block type of reactor was loaded with 100 cc. of this catalyst. The flow scheme employed in this example was exactly the same as that outlined in Example I. The charge stock was a light Kuwait naphtha having an initial boiling point of 172° F., an end boiling point of 362° F., a 62.0° API specific gravity at 60° F., a paraffin content of 75% by volume, a naphthene content of 16.0% by volume, and an aromatic content of about 9.0% by volume.

The process was started-up using a conventional start-up procedure for a high quality reforming operation. This procedure essentially involved: purging the plant with nitrogen in order to remove oxygen, pressurizing the plant with a hydrogen-rich gas to about 100 p.s.i.g., heating and circulating the hydrogen gas to a temperature of about 700° F., introducing the charge stock, heating the admitted charge stock and hydrogen to a temperature of about 900° F. At this point the LHSV was 2.0 and the recycle gas to charge stock mol ratio was 6.0.

Based on previous experience with typical platinum-containing reforming catalyst, it was expected that the process would, at this point, have produced sufficient excess hydrogen such that the plant pressure would have risen to desired operating level—in this case 600 p.s.i.g. But this was not the case. Plant pressure remained low; consequently, it was necessary to add extrinsic hydrogen in order to reach 600 p.s.i.g. Furthermore, it was necessary to continue to add extrinsic hydrogen out to a catalyst life of 1.75 barrels per pound of catalyst in order to maintain plant pressure at the desired level.

This hydrogen imbalance was caused by the extensive hydrocracking that is a singular characteristic of this type of catalyst. This hydrocracking activity is manifest in the following Table I which shows the average yield structure obtained with the catalyst of the present example versus what would be obtained for a good reforming catalyst at similar conditions (i.e., catalyst C of Example I).

TABLE I.—COMPARISON OF AVERAGE YIELD STRUCTURE

	4.5% Mordenite Catalyst	Catalyst C
C ₁ +C ₂ , wt. percent.....	8.3	8.9
C ₃ +C ₄ , wt. percent.....	27.5	16.3
C ₅ +, wt. percent.....	63.9	74.1

It is to be emphasized that the reasons hydrogen was added in order to make plant pressure, before increasing the plant temperature above 900° F., were essentially: accumulated experience with platinum-containing reforming catalysts which indicated that there would be a substantial decline in activity of the reforming catalyst if it were subjected to temperatures above 900° F. at low partial pressure or hydrogen, and the danger of a temperature runaway at these conditions as illustrated in Example I. This expected decline in activity would be characterized by the formation of carbonaceous deposits on the catalysts and inability to make hydrogen via the dehydrogenation mechanisms.

Example III

This example demonstrates the substantial improvement in start-up hydrogen production that is an extraordinary feature of the present invention.

The catalysts employed in this example were manufactured in accordance with the method delineated for cata-

lyst B in Example I with the result that they had the following weight percent composition:

(a) Catalyst D—0.60 platinum, 0.75 chloride, 0.50 sulfur, and 10.2 hydrogen form mordenite;

(b) Catalyst E—0.60 platinum, 0.75 chloride, 0.30 sulfur, and 10.2 hydrogen form mordenite;

(c) Catalyst F—0.64 platinum, 0.82 chloride, 0.12 sulfur, and 9.9 hydrogen form mordenite;

(d) Catalyst G—0.60 platinum, 0.75 chloride, 0.08 sulfur, and 10.2 hydrogen form mordenite.

The charge stock and flow scheme employed in this example were the same as reported in Example II.

With the exception of catalyst F all of these catalysts were started-up using the method of the present invention which involved the following specific steps:

(a) Purging oxygen from the plant with nitrogen;

(b) Pressurizing the plant with hydrogen to 100 p.s.i.g.;

(c) Heating and circulating the hydrogen until a temperature of 797° F. was attained for catalyst D, 800.6° F. for catalyst E, and 815° F. for catalyst G;

(d) Introducing the charge stock at an LHSV of 1.5 and a recycle gas to charge stock mol ratio of 8.0; and

(e) Raising the plant temperature at a rate between 9° F. and 18° F. per hour.

The results for catalyst D, E, and G are shown in Table II:

TABLE II.—PLANT PRESSURE VERSUS PLANT TEMPERATURE

Hours on Stream	Catalyst D		Catalyst E		Catalyst G	
	Temp., ° F.	Pressure	Temp., ° F.	Pressure	Temp., ° F.	Pressure
Feed cut in.....	797.0	100	800.6	100	815.0	100
1.....	816.8	130	815.0	125	809.6	130
2.....	833.0	170	834.8	160	824.0	160
3.....	833.0	180	851.0	200	845.6	180
4.....	867.2	195	870.8	220	865.4	210
5.....	887.0	225	892.4	245	887.0	250
6.....	896.0	240	905.0	280	905.0	280
7.....	915.8	265	924.8	300	914.0	280
8.....	932.0	300	941.0	350	937.4	350
9.....	950.0	355	950.0	350	962.6	440
10.....	968.0	400	975.2	375	964.4	500
11.....	971.6	460	982.4	460	978.8	555
12.....	968.0	510	1002.2	540	975.2	600
13.....	977.0	550	987.8	580	-----	-----
14.....	986.0	575	986.0	600	-----	-----
15.....	984.2	600	-----	-----	-----	-----

As can be seen from Table II, as temperature was raised past 925° F., an unexpected increase in hydrogen production relative to hydrogen consumption took place as measured by plant pressure. This data indicates an unexpected sharp dependence of rate of hydrogen production on temperature in the range of 925° F. to about 1000° F. for these mordenite-containing catalysts; and this discovery constitutes an essential feature of the present invention. These runs were then continued for a substantial period of time and they were completely self-sustaining in hydrogen production. In addition, no unusual catalyst deactivation was observed.

To further characterize this hydrogen production versus temperature effect, a run was made using catalyst F in which the same start-up procedure as outlined above was followed except the plant was prepressurized to 600 p.s.i.g. The temperature was brought up, in the same fashion as the runs reported in Table II, to a level of 977° F.; but it was found necessary to continuously add hydrogen in order to maintain plant pressure at 600 p.s.i.g. This run then indicates that it is necessary to start the temperature adjustment procedure at low pressures in order to attain hydrogen balance. This low pressure start-up then is an additional feature of the present invention which is highly desirable since it conserves valuable hydrogen.

This example, then demonstrates it is possible to start-up these mordenite-containing reforming catalysts without encountering the temperature runaway problems il-

illustrated in Example I and the hydrogen balancing problem illustrated in Example II.

We claim as our invention:

1. A method for starting-up a process for the production of C₃ and C₄ hydrocarbons and of a high octane reformat from a hydrocarbon charge stock in which process said charge stock and hydrogen are contacted, in a conversion zone, with a catalytic composite containing a finely divided crystalline aluminosilicate suspended in an alumina matrix component, having at least one catalytically active platinum group metallic component composited therewith, which method comprises: pressurizing the conversion zone with extrinsic hydrogen to a level of about 75 p.s.i.g. to about 150 p.s.i.g., heating the conversion zone to a temperature of about 775° F. to about 825° F., introducing the charge stock to said conversion zone, raising the temperature of the conversion zone at a rate of from about 5° F. to about 30° F. per hour to a temperature of from about 925° F. to about 1000° F., whereby the process pressure rises to the desired operating level of about 400 to about 700 p.s.i.g. without adding additional extrinsic hydrogen subsequent to said charge stock introduction step.

2. The method of claim 1 further characterized in that said crystalline aluminosilicate is in the hydrogen form.

3. The method of claim 1 further characterized in that said crystalline aluminosilicate is a mordenite type and said catalytically active platinum group metallic component is selected from the group consisting of platinum, palladium, and compounds thereof.

4. The method of claim 3 further characterized in that said mordenite is present in the alumina matrix in a concentration of less than 20% by weight of said matrix, and said platinum is present in a concentration of from about 0.05% to about 5.0% by weight of the catalytic composite.

5. The method of claim 1 further characterized in that

said hydrocarbon charge stock boils within the gasoline range.

6. The method of claim 1 further characterized in that said process is performed at operating conditions which include an LHSV of from about 0.5 to about 5.0, a temperature of from about 850° F. to about 1100° F., a pressure of from about 400 p.s.i.g. to about 700 p.s.i.g., and a hydrogen to oil mol ratio of from about 2 to about 20.

7. The method of claim 1 further characterized in that said catalytic composite also contains a halogen component selected from the group consisting of chlorine and fluorine which is present in a concentration from about .05% to about 2.0% by weight of the catalytic composite.

8. The method of claim 1 further characterized in that the total effluent from said conversion zone is passed to a separating zone in which a hydrogen-rich gas separates from a liquid phase and the hydrogen-rich gas is recycled to said conversion zone in order to furnish necessary hydrogen thereto.

9. The method of claim 1 further characterized in that said charge stock is a light naphtha having an initial boiling point greater than 150° F. and an end boiling point less than 400° F.

10. The method of claim 1 further characterized in that said conversion zone is substantially free of oxygen before the start-up method is initiated.

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HERBERT LEVINE, *Primary Examiner*.