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HYDROCRACKING OF NITROGEN CONTAINING FEEDSTOCKS

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ABSTRACT OF THE DISCLOSURE

Hydrocarbons containing substantial amounts of organonitrogen compounds are subjected to hydrocracking, hydrofining, hydrogenation and the like in the presence of hydrogen over a catalyst comprising alumina and combinations thereof with silica, zirconia, magnesia and the like, such as aluminosilicates, with or without active metal components, in the presence of controlled minor amounts of water followed by the discontinuance of water addition. Further advantage is realized by cycling water addition and deletion to promote even higher average system activities.

BACKGROUND

Recent years have witnessed a phenomenal growth in the development and application of catalytic hydrocarbon conversion processes including hydrocracking, hydrofining, hydrogenation and combinations of these. By far the greatest part of these efforts have been directed toward methods for hydrocracking gas oils to products boiling in the gasoline range. The best catalysts developed to date for this purpose are those comprising a highly active cracking base, e.g., of the crystalline zeolite type, combined with a highly active hydrogenation component such as palladium or platinum. These catalysts are highly efficient for converting middle distillate oils boiling in the 400–750° F. range to gasoline. Due to the extensive present and prospective use of middle distillate stocks as feed to these gasoline-producing hydrocracking units, and to other economic, geographic and seasonal factors, a need is being felt in the industry to provide additional middle distillate stocks to meet the demand for other products such as turbine and diesel fuels. An obviously desirable source of such additional middle distillate stocks comprises the heavy distillates boiling above about 700° F., which have heretofore been diverted largely to fuel oils because of the lack of an economical method for converting them to lower boiling products.

In the initial investigation of hydrocracking techniques for converting hydrocarbon feeds boiling above 700° F. it became apparent that severe hydrocracking to produce gasoline in a single pass conversion step was impractical, firstly because inordinate amounts of butanes and dry gas were produced, and secondly because the gasoline product was always of undesirably low octane quality. It thus became apparent that for purposes of gasoline production, especially on a once through basis, hydrocracking techniques were of primary value in connection with middle distillate feedstocks, and that the hydrocracking of higher boiling stocks would be economically desirable only if conversion to gasoline could be minimized and the production of middle distillates maximized. A primary objective in the hydrocracking of these heavy feeds was thus the realization of maximum middle distillate/gasoline ratios in the resulting product.

It was then found that the catalysts most useful for converting middle distillates to gasoline were least useful for converting heavy feedstocks selectively to middle distillates in that large amounts of dry gases, butanes and

gasoline were produced by those catalysts. A great many conventional hydrocracking catalysts were tested in an attempt to find one which would convert such feedstocks more selectively to middle distillate products. In all cases it was found that the desired selectivity could be maintained only by operating at very low overall conversion per pass, entailing prohibitively high recycle oil rates. However, upon developing and testing certain catalysts not conventionally regarded as hydrocracking catalysts, substantially more promising results were obtained. Specifically, it was found that by using a type of catalyst commonly employed for catalytic hydrofining composed of nickel and molybdenum oxides and/or sulfides supported on activated alumina, the selectivity of conversion to middle distillate products was excellent even at relatively high conversions, e.g., 40–60 volume-percent per pass. Moreover, for feedstocks containing organic nitrogen, it was found that these catalysts were not only more selective, but sometimes more active (on the basis of a lower temperature required for a given total conversion) than even the most active hydrocracking catalysts based on zeolite cracking bases.

Although those catalysts are particularly attractive for converting relatively high boiling nitrogenous feeds to middle distillates and high quality midbarrel fuels, they also have considerable utility in the conversion of similar feedstocks to high octane gasoline boiling range hydrocarbons. However, as is always the case with chemical conversion systems, there remains considerable room for improvement in numerous limiting process parameters such as catalyst activity, product distribution, catalyst life and the like. For example, it is known that catalyst life can be dramatically increased by lowering reaction temperature. However, such procedures decidedly limit the obtainable conversion per pass requiring greater capital and operating expense due to the requirement of larger reactor sizes and recycle systems. Therefore, a reasonable balance must be drawn between catalyst deactivation rate, reaction temperatures and tolerable conversion levels that enable efficient use of process equipment.

Yet another consideration which limits the effectiveness of these catalyst systems for hydrocarbon conversion, particularly hydrocracking and hydrogenation, is the deleterious effect exhibited on catalyst activity by organonitrogen compounds in the feed. Although some of these catalysts are particularly effective for hydrofining, e.g., denitrogenation and desulfurization, we have observed that their hydrocracking and hydrogenation activity is markedly limited by the presence of even minor amounts of organonitrogen compounds when the concentration of those materials in the feed substantially exceeds 1 p.p.m. nitrogen. The most direct approach to the solution of this problem would appear to be the use of a hydrofining zone upstream of the hydrocracking system or the use of a larger hydrocracking catalyst bed. In these systems, and in other apparent alternative schemes, sufficient precontacting of the nitrogen containing feed with these or other hydrofining catalysts under hydrofining conditions can be effected to reduce the nitrogen content to tolerable levels, e.g., less than about 5 p.p.m. Although such procedures undoubtedly provide an available alternative, they are subject to certain obvious disadvantages. In order to reduce the nitrogen content of the feed to a level sufficient to prevent inhibition of hydrogenation and hydrocracking, provision must be made for rather severe hydrofining treatment upstream of the contacting zone. Pretreatments of this nature are known to involve considerable expense.

Although organonitrogen compounds are known to exhibit several deleterious effects on the preferred midbarrel hydrocracking and hydrogenation catalysts such as those comprising Group VI and Group VIII metal

components on a primarily alumina support, their influence on the activity, selectivity and effective catalyst life of the zeolite based catalyst particularly those containing Group VIII noble metals such as platinum and palladium, is even more dramatic. For example, it is known that with some of the zeolite catalysts primarily employed for gasoline production that the presence of substantially more than 5 parts per million of organonitrogen compounds in the feed determined as elemental nitrogen almost completely inhibits the hydrocracking and hydrogenation activity of those compositions, at least in the upstream sections of the contacting zone, until sufficient contacting has been effected to reduce the organonitrogen content to tolerable levels. As a general rule, the zeolite base catalysts are not particularly effective denitrogenation catalysts and many are permanently inhibited by exposure to substantial amounts of organonitrogen compounds. As a result, it is a matter of almost necessity in the use of such compositions to provide for the almost complete denitrogenation of a selected feedstock prior to hydrogenation or hydrocracking over these catalysts. It is usually necessary to reduce the organonitrogen content of such feeds to a point below about 5 p.p.m. and in many cases, nitrogen levels substantially in excess of 1 p.p.m. cannot be tolerated. Obviously, the expense and process complexities involved in effecting these degrees of denitrogenation are considerable. However, to date they have been considered acceptable in view of the lack of available alternatives and the relative degree of comparative success realized by operating in that manner.

We have now discovered a procedure whereby several aspects of such hydrocarbon conversion systems can be markedly improved from the standpoint of performance and economy. This procedure enables the attainment of economically feasible conversion levels and product quality at less severe reactor conditions, e.g., lower reaction temperatures, without the necessity of severe prehydrofining. We have discovered that the addition of controlled amounts of water or water precursors to the hydrocarbon feed counteracts the effect of substantial nitrogen levels and enables the catalyst to effect acceptable conversion levels at reduced temperatures. Several of the advantages of these procedures are readily apparent. Firstly, longer catalyst life can be realized due to the lower reaction temperatures required. Secondly, operating and capital expense involved in upstream hydrofining zones can be reduced due to the tolerance of the described conversion systems to higher concentrations of nitrogen compounds. In addition, the activity of these systems for several forms of hydrocarbon conversion is substantially improved, thereby enabling higher conversions, lower operating temperatures, better control of product distribution, and the like. Particularly dramatic effects are evidenced in hydrocracking activity and hydrogenation, particularly the hydrogenation of aromatic constituents. Consequently, these systems can be operated under conditions which provide markedly superior results in the production of those gasolines and midbarrel fuels and even enable the production of such products from relatively highly aromatic refractory feedstocks under recycle conditions while minimizing the degree of refractory buildup in the recycle stream.

It is therefore one object of this invention to provide an improved hydrocarbon conversion process. It is another object of this invention to provide an improved process for producing middle distillate fuels and/or gasoline. It is yet another object of this invention to provide a method for increasing the activity of hydrocracking systems. Yet another object of this invention is the provision of a method for increasing the tolerance of hydrocracking and hydrogenation systems to organic nitrogen compounds. Still another object of this invention is the provision of improved hydrogenation, hydrocracking and hydrofining methods. Another object of this invention is the provision of a method which enables the reduction of hydrocracking temperatures necessary to obtain prescribed conversion levels.

In accordance with one embodiment of this invention, hydrocarbons containing at least about 5 p.p.m. nitrogen as organonitrogen compounds are subjected to hydrocracking, hydrogenation, hydrofining, or combinations thereof in the presence of hydrogen with a catalyst comprising at least one of the metals, oxides and sulfides of Groups II, IV–B, VI–B, VII–B, and VIII combined with a foraminous oxide support in the presence of a controlled promoting amount of added water or water precursor convertible to water at conditions existing in the hydrocarbon conversion zone followed by discontinuance of water injection.

In accordance with another embodiment of this invention, hydrocarbons containing substantial amounts of organonitrogen compounds are contacted in the presence of hydrogen under hydrocarbon conversion conditions with a catalyst comprising at least one active component selected from the Group II, IV–B, VI–B, VII–B and VIII metals, oxides and suufides combined with a foraminous oxide support in the presence of varying controlled amounts of water provided by cycling the addition and deletion of water from the hydrocarbon conversion zone.

During the investigation of this phenomena water was supplied to a hydrocracking zone at several different sets of operating conditions by several different procedures. In one instance water was admixed with a hydrocarbon phase by humidifying the hydrogen stream to the reactor. In another instance, the same results were effected by adding a water precursor, e.g., n-butanol to the feed. Alcohols of this type are believed to be dehydroxylated to produce water under hydrocracking conditions. In every case, the addition of water by these procedures improved the activity of the system. However, an even more surprising result was observed when the water injection was discontinued. Instead of the catalyst deactivating gradually to its original level as expected, the hydrocracking performance exhibited a transient behavior in a reproducible cycle during which the activity improved still further to a maximum and then slowly declined to the activity exhibited by the system prior to water addition. This transient phenomenon was reversible and repeatable. However, despite all efforts, including periodic water injection, no means could be found whereby the maximum catalyst activity observed could be sustained on a continuous basis.

Although the exact mechanism by which this phenomenon is effected is not understood with certainty, it may be that the presence of water mitigates the inhibiting effect of organic nitrogen compounds by either preventing access of those poisons to the catalyst surface or by increasing the tolerance of the catalyst to those impurities. These suppositions are supported somewhat by observations made during operations on hydrocarbon feedstocks having very low nitrogen concentrations, i.e., below about 1 p.p.m. organic nitrogen. In those systems, the catalyst activity was seen to decline upon water addition as would be expected since it is generally believed that water itself is a catalyst inhibitor. Nevertheless, in view of these observations, it seems reasonable to conclude that the phenomena herein described is at least in part a function of the combined effects of water and nitrogen.

The activity exhibited by these catalyst systems at a given set of process conditions is greater in the absence of either nitrogen or water. Both of these materials are generally considered catalyst inhibitors in otherwise clean systems. However, we have observed that considerable advantage can be realized by the addition of water to hydrocracking zones operating on hydrocarbon mixtures containing substantial amounts of organonitrogen compounds, i.e., 5 p.p.m. or greater.

Those skilled in the art readily recognize that the prehydrofining severity required to reduce the nitrogen

content of hydrocarbon mixtures to levels below 5 p.p.m. is not easily attained and involves considerable expense. The method of this invention offers an alternative to such severe hydrofining procedures. It is possible to drastically reduce the severity and expense of prehydrofining treatments and compensate for the residual nitrogen in the hydrocarbon feed by conducting the conversion in the presence of controlled amounts of water as described. In fact, the advantages of this invention can be realized in the absence of any hydrofining whatever, provided of course that the nature of the feedstock is not such that it completely destroys the activity of the catalyst.

A wide variety of hydrocarbon feeds can be employed within the concept of this invention. Similarly, the conditions under which the feed hydrocarbons are reacted and the compositions of the catalysts employed in any specific case can be varied to promote selected reaction mechanisms such as hydrogenation, hydrofining, hydrocracking, and the like. The advantages of this invention can be realized in all of these situations when the feed employed contains a substantial amount of organonitrogen compounds. As a general rule, the hydrocarbon feed employed in these systems will boil above about 200° F. and will include light, medium and heavy naphthas, gas oils, coker distillates, vacuum gas oils, and the like. These systems may be designed for the simple hydrogenation of aromatic feedstock of essentially any molecular weight. However, particular advantage is realized in the hydrogenation of aromatic feedstocks particularly those boiling above about 400° F. and containing in excess of about 5 and usually about 10 to about 200 p.p.m. nitrogen as organonitrogen compounds which we have found to markedly inhibit the aromatics hydrogenation activity of the catalysts encompassed within the scope of this invention. However, the presently most preferred application of this phenomena is in the hydrocracking of raw or partially refined hydrocarbon feeds to produce gasolines and midbarrel fuels. We have observed that the addition of the described controlled water levels to hydrocracking systems dramatically improves the activity thereof and enables much greater control of product distribution than is otherwise possible. The feedstocks employed in such hydrocracking systems boil above about 400° F., usually within the range of about 400 to about 1200° F. Depending upon the degree of prerefining, the organonitrogen content of these feeds can vary substantially. Organonitrogen compounds are usually present in amounts equivalent to about 10 p.p.m. to about 1 weight-percent nitrogen, generally about 10 to about 5,000 p.p.m. nitrogen. However, we have observed that the advantages of operating in the described manner are more apparent when the nitrogen content of the feed is within the range of about 10 to about 600 p.p.m. Consequently, it is presently preferred that feedstocks having nitrogen levels substantially in excess of 1000 p.p.m. be partially hydrofined prior to contacting in the hydrocracking systems operated in accordance with this invention.

Although the sulfur content of the selected feedstock is not presently considered to be a determinative variable with regard to the results observed upon water addition, it is nevertheless a consideration relative to overall catalyst activity. The deactivating effect of excessive sulfur concentrations can be substantially mitigated by the use of sulfactive catalysts, which are generally well known in the art. Similarly, the presence of some sulfur compounds in the feed is often preferred in hydrocracking systems in that these materials tend to sulfide the catalyst maintaining it in the generally more active sulfided state. As a general rule, the raw hydrocarbon feeds may contain organic sulfur concentrations ranging up to about 3 weight-percent sulfur based on the total feed. It is often preferable to substantially reduce this sulfur content to a level below about 100 p.p.m. by prehydrofining. Such desulfurization can be conveniently effected by contacting at conventional hydrofining conditions in the presence of catalysts similar to those herein described. The hydrogen sulfide resulting from the desulfurization of the organic sulfur compounds can be separated prior to introduction of the feed to the hydrocracking zone or can be passed directly over the hydrocracking or hydrogenation catalyst without substantial detriment.

A wide variety of catalysts can be employed within the concept of this invention. Essentially any catalyst comprising an active form of a metal or metal compound of Groups II, VI, VII and VIII of the Periodic Chart supported on a foraminous refractory oxide can be employed in these systems. Since catalysts of this nature are generally well known in the art they need not be described in detail herein. However, brief reference will be made to several of the presently most popular compositions within this class.

The foraminous refractory oxides above referred to can be selected from alumina, silica, magnesia, zirconia and alumina and silica containing clays such as bentonite and attapulgus clay and combinations thereof such as silica, alumina, silica-zirconia and the like. One presently preferred combination of these materials is silica-stabilized alumina containing about 2 to about 30 weight-percent silica. This material in itself is conventional in the art and can be prepared by several procedures such as cogelation or sequential gelation or physical admixture of partially or completely precipitated gels of alumina and silica. It has been observed that the presence of minor amounts of silica in alumina matrices greatly improves the physical properties of the resultant combination. The natural and synthetic crystalline and amorphous aluminosilicate zeolites are also widely employed for the preparation of hydrocarbon conversion catalysts and are applicable to the systems herein described.

Exemplary of these compositions are the aluminum containing ion exchangeable clays, particularly acid extracted clays such as bentonite, montmorillonite, beidellite, halloysite, endelite, kaolinite and the like. The acid extraction of these materials is generally well known in the art and is designed to effect the removal of metals found in the aluminosilicates in their naturally occurring state. Such acid extraction can be effected by contacting the clay with a mildly acidic solution or a strong mineral acid such as nitric, sulfuric, hydrochloric, or phosphoric acids and the like, having a pH of about 4 or above.

A second generally recognized class of amorphous aluminosilicates having the above-described characteristics are the partially degraded crystalline aluminosilicates which have been subjected to acidic and/or thermal environments sufficient to at least partially destroy the characteristic crystalline structure of those materials. As a general rule, there is little economic interest in obtaining starting materials, i.e., aluminosilicates, by this latter procedure since the crystalline aluminosilicates are usually far more expensive than alternative forms of aluminosilicates suitable for use herein. Nevertheless, such materials are suitable for application within the concept of this invention.

Another class of aluminosilicates having the desired characteristics are the silica-alumina cogels. These materials are usually prepared by either coprecipitating silica and alumina from an aqueous solution at soluble salts of silicon and aluminum or by grafting one of these constituents, i.e., either the silica or alumina, onto a previously precipitated alumina or silica gel by acidifying a solution of the water soluble salt of the second component. For example, alumina can be precipitated in the presence of a hydrous silica gel by acidifying a solution of sodium aluminate with a mineral acid such as sulfuric, nitric, and the like. The relative amounts of silica and alumina in the combinations can vary considerably although it is presently preferred that the silica concentration be equivalent to about 10 to about 40 weight-percent of the total silica-alumina combination on a dry weight

basis. The cogels resulting from such coprecipitation or sequential precipitation of separate constituents can then be dried and ion exchanged to replace the undesirable cations with ammonium, hydrogen and/or Group VIII metal-containing cations as previously described.

The presently preferred aluminosilicates are the crystalline species having SiO_2/Al_2O_3 ratios of at least about 2. This class includes both synthetic and naturally occurring zeolites. Illustrative of the synthetic zeolites are Zeolite X, U.S. 2,882,244; Zeolite Y, U.S. 3,130,007; Zeolite A, U.S. 2,882,243; Zeolite L, Belgian 575,117; Zeolite D, Canadian 611,981; Zeolite R, U.S. 3,030,181; Zeolite S, U.S. 3,054,657; Zeolite T, U.S. 2,950,952, Zeolite Z, Canadian 614,995; Zeolite E, Canadian 636,931; Zeolite F, U.S. 2,995,358; Zeolite O, U.S. 3,140,252; Zeolite B, U.S. 3,008,803; Zeolite H, U.S. 3,010,789; Zeolite J, U.S. 3,011,869; Zeolite W, U.S. 3,012,853; Zeolite KG, U.S. 3,056,654. Illustrative of the naturally occurring crystalline aluminosilicates which can be suitably treated by the methods herein described are levynite, dachiardite, erionite, faujasite, analcite, paulingite, noselite, ferrierite, haylandite, scolecite, stilbite, clinoptilolite, harmotome, phillipsite, brewsterite, flakite, datolite, chabazite, gmelinite, cancrinite, leucite, lazurite, scolacite, mesolite, ptilolite, mordenite, nephenline, natrolite, and sodalite. The natural and synthetic faujasite-type crystalline aluminosilicate zeolites, e.g., Zeolites X and Y, are presently particularly preferred.

When these catalysts are prepared in whole or in part from zeolitic aluminosilicates, it is often desirable to substantially reduce the alkali metal content of the aluminosilicate during some stage of the catalyst preparation and convert the zeolite into an acidic form. Consequently, the alkali metals which are present both in natural and synthetic aluminosilicates in their original state are preferably removed during some stage of the catalyst preparation by ion exchange. Any one of numerous procedures can be employed for this purpose. Probably the most convenient procedures include ion exchange with aqueous solutions of ammonium or hydrogen or soluble salts of metal cations of Groups II, VII and VIII of the Periodic Chart. As a general rule, the alkali metal content of the aluminosilicates should be reduced to less than 5 weight-percent preferably less than about 2 weight-percent determined as a corresponding oxide. This objective can be realized by continuing the exchange with the cations above mentioned until the desired reduction in alkali metal content has been achieved. When exchange with the noted metal cations is employed, the resultant concentration of the respective metal in the final composition will usually be within the range of about 0.2 to about 5 weight-percent determined as the elemental metal. These metals can also be added to the aluminosilicate or other foraminous oxides by impregnating the support with an aqueous solution of a water soluble thermally decomposable salt of the desired metal. The Group VI–B metals can also be added by this procedure. Illustrative of suitable water soluble thermally decomposable compounds are the nitrates, sulfates, carbonates and halides of calcium, magnesium, molybdenum, tungsten, manganese, rhenium, nickel, cobalt, platinum, palladium and the like.

Catalysts presently particularly preferred for the production of midbarrel fuels comprise composites of nickel and/or cobalt metals, oxides and sulfides and one or more of molybdenum and tungsten metals, oxides and sulfides combined with an alumina support.

The aluminas presently preferred are high surface area amorphous materials having relatively low cracking activities corresponding to Cat-A indices below 25. However, higher activities can be tolerated when higher relative gasoline production is desired. It is also preferred that the alumina support be stabilized by combination with a minor amount of amorphous silica gel. Silica can be present in concentrations of up to about 40 weight-percent based on the combined weight of silica and alumina. Presently preferred compositions have silica concentrations within a range of about 3 to about 25 weight-percent.

The presently preferred midbarrel catalyst compositions contain about 0.5 to about 10 weight-percent nickel and/or cobalt metals, oxides or sulfides determined as the corresponding oxides, and about 4 to about 30 weight-percent of molybdenum and/or tungsten metals, oxides or sulfides based on the corresponding oxides. Combinations of nickel and molybdenum sulfides are particularly preferred. Such compositions are normally prepared by impregnating the selected alumina carrier with an aqueous solution or solutions of soluble salts of the respective metals followed by draining, drying and calcining in air at temperatures of 800° to about 1200° F. The calcined catalysts are preferably presulfided prior to contact with a feedstock as by reaction with a gaseous mixture of hydrogen and hydrogen sulfide, carbon disulfide, elemental sulfur and the like.

The preferred carrier for these midbarrel fuel catalysts is activated alumina gel containing a minor proportion of coprecipitated silica gel. The silica content should not exceed about 40 percent by weight. Higher silica contents tend to decrease cracking selectivity to midbarrel fuels. The preferred silica content is between about 3 and 25 percent by weight. The preferred supports comprise at least about 60 weight-percent alumina, the remainder being silica, magnesia, aluminosilicates, and the like. Prior to impregnation, the carrier is preferably formed into pellets of about 1/32 to 1/4 inch diameter (by extrusion or die-compression). Alternatively, the catalyst may be employed in a powder form.

Particularly preferred catalyst compositions are prepared by impregnation with the stabilized impregnating solutions discussed in U.S. Pats. 3,232,887 and 3,287,280. By these procedures the selected support is contacted with a solution of the desired metal salts containing stabilizing amounts of phosphate ions introduced by the addition of an acid of phosphorus, e.g., phosphoric acid, phosphorous acid and the like. Phosphorus concentrations in the final catalyst are at least about 0.2 weight-percent, usually within a range of about 0.5 to about 8 weight percent, preferably about 2 to about 5 weight-percent based on the free metal.

Hydrocracking conditions generally considered to be most desirable include reaction temperatures within a range of 500 to about 900° F., preferably 550 to 850° F., reactor pressures of at least about 500 p.s.i.g., preferably 1000 to about 5000 p.s.i.g., and liquid hourly space velocities (LHSV) of about 0.1 to about 10, preferably 0.3 to about 5. The free hydrogen content in the reaction zone should be equivalent to at least about 500, generally about 500 to about 20,000 and preferably about 1000 to about 15,000 standard cubic feet per barrel of reactor charge.

Hydrogenation and hydrofining, e.g., denitrogenation and desulfurization can be effected at these same conditions and in fact, are effected under hydrocracking conditions when there are constituents in the feed subject to hydrogenation and/or hydrofining. However, it is sometimes desirable to effect denitrogenation, desulfurization and/or hydrogenation in the absence of substantial degrees of hydrocracking. In those instances, it is desirable to contact the feed under somewhat milder conditions of reduced temperature and pressure, e.g., pressures of about 100 to about 1200 p.s.i.g. Catalyst compositions also determine the relative degrees of hydrocracking and hydrogenation and can be selected to favor one over the other as desired.

The equivalent water concentration in the reaction zone should be sufficient to promote the activity of the catalyst as evidenced by higher conversion levels at otherwise identical conditions. We have found that the most dramatic improvement in catalyst activity is effected at equivalent water concentrations in excess of about 0.1 weight-percent, generally about 0.2 to about 5 weight-percent and

preferably about 0.2 to about 2 weight-percent. Depending upon the characteristics of the particular systems such as reaction conditions and the selected catalyst and the organonitrogen content of the selected feedstock, the preferred water level in the reaction zone may vary considerably from about 0.1 to about 5 weight-percent. A constant improvement in activity can be realized by maintaining a predetermined controlled water concentration in the reaction zone. We have observed that the rate of the increase in catalyst activity is related to the maximum equivalent water concentration in the reaction zone, certain reaction parameters such as liquid hourly space velocity and mixing characteristics and of course the duration of water injection into the reaction zone. Therefore, it is possible when employing the cyclic water injection procedure previously described, to extend the cycle length during which these beneficial effects are realized by operating at the higher water concentrations and/or lower liquid hourly space velocities.

An essential aspect of this procedure is that the prescribed controlled water concentration be provided in the reaction zone. This can be accomplished by the addition of either free water or a water precursor to the hydrocarbon feed, to one or more of the streams entering the reactor, or directly to the reactor. Exemplary of readily available water precursors are the organic alcohols. Presently preferred due to their availability and cost are those having from about 2 to about 12 carbon atoms and one to about five hydroxyl groups per molecule.

Although it is presently preferred that the water concentrations be maintained only in the hydrocracking zone, it is within the scope of this invention to provide for the addition of water to process systems upstream of the hydrocracking zone. The most apparent alternative in this regard is the addition of water or water precursor to the hydrocarbon feed entering a hydrofining stage immediately preceding the hydrocracking zone. This mode of operation is particularly convenient in integral hydrofining-hydrocracking systems employing catalysts similar to those herein described in both hydrofining and hydrocracking zones. Nevertheless, it is not necessary to introduce water into the hydrofining zone to take advantage of the results herein described. For example, in a single stage hydrofining-hydrocracking system, the water or water precursor can be injected alone or in combination with recycle hydrogen or hydrocracker recycle oil at an intermediate point in the reaction zone. However, procedures employing this approach will generally involve the use of two or more reactors in one or more stages. The distinction between stages is conventionally characterized by the separation, or partial separation, of intermediate products such as ammonia and hydrogen sulfide from the first stage product prior to introduction of the hydrocarbon phase to the second stage. As a consequence, these systems can involve the use of a single reaction zone in which conditions are controlled such that hydrofining occurs in the first portion of the catalyst bed while hydrocracking is effected in the terminal portion of the catalyst bed. In the alternative, a single stage process can be employed using two or more reactors in which the upstream reactors are controlled so as to effect primarily hydrofining while the downstream reactors are operated to promote hydrocracking. In these more complex plural reactor systems the advantages of this invention can be realized by injection of water or suitable water precursors to one or more of the hydrocracking stages whether or not some hydrofining occurs in each respective stage.

Particular advantage can be obtained when employing multizone hydrocracking systems wherein the organic nitrogen content of the hydrocarbon phase is gradually reduced upon sequential passage through the several hydrocracking zones. As the nitrogen content of the hydrocarbon phase is reduced to a level below 5 p.p.m., the beneficial effects realized by water addition are mitigated. In fact, at nitrogen levels substantially below 5 p.p.m., particularly 1 p.p.m. or less, the addition of water is detrimental rather than beneficial due to its inherent catalyst inhibiting characteristics. Consequently, it is presently preferred to maintain the described water levels in the hydrocracking zones in which the nitrogen level in the feed is substantially above 5 p.p.m. while avoiding water addition and/or substantial carryover to the terminal hydrocracking zones or stages or otherwise reducing the water content of the hydrocarbon phase therein when the organic nitrogen content falls substantially below 5 p.p.m. nitrogen. By this procedure, the advantages of this invention can be most efficiently realized while preventing any deleterious effects attributable to the presence of water in the absence of substantial nitrogen concentrations.

As pointed out in the examples hereinafter detailed, the activity of the catalyst immediately subsequent to addition of water or water precursor gradually approaches an increased equilibrium level and remains at that level in the absence of significant catalyst deactivation as long as the water level is maintained at the same concentration. However, when water addition is discontinued after the catalyst has reached this equilibrium activity, the hydrocarbon conversion activity of the system increases still further reaching a maximum and then gradually declines to the original activity of the system prior to water addition. In view of these observations, it is possible to control the catalyst activity in several ways. For example, the concentration of water in the hydrocracking zone can be maintained at a predetermined constant level throughout the run duration. However, in that mode of operation, the activity of the catalyst will reach an equilibrium intermediate level and continue at that level subject only to gradual catalyst deactivation usually observed in such systems. An alternative procedure that provides substantially higher average catalyst activities involves periodic water addition. By this procedure, a predetermined water concentration is maintained until the catalyst approaches equilibrium. Water addition is then discontinued to increase the catalyst activity even further. Effective utilization of this procedure must take into account the amount of water added, the time required for the catalyst to approach its equilibrium activity and the cycle time of the catalyst activity increase and decrease subsequent to the discontinuance of water addition. The duration of the several cycles involved in this transient behavior can be readily ascertained by simply adding water to the conversion zone in the precsribed amounts and observing either the increased conversion realized at otherwise identical operating conditions or by reducing reaction temperature sufficiently to maintain a constant conversion level until the catalyst activity has equilibrated at its higher intermediate value. The time required for the completion of this response will vary somewhat with water concentration and with the prevailing liquid hourly space velocity. Nevertheless, the cycle time for the first step of the procedure can be readily ascertained for any given set of operating conditions by the procedure described.

After the catalyst has equilibrated at the intermediate activity level, water addition can be discontinued and the increase in catalyst activity can be observed in a manner similar to that above described until the activity preceding water addition is reestablished. The data obtained by this procedure for any system will enable the most effective utilization of the observed phenomenon by directing the control of intermittent water addition depending upon the cycle time of the selected system. For example, it may be desirable to allow the catalyst activity to approach its original value subsequent to the discontinuance of water addition before reintroducing water to the hydrocracking zone. However, it is not necessary to defer the reintroduction of water to that point. On the contrary, additional advantage can be obtained by reintroducing water to the system when the declining catalyst activity approaches the intermediate equilibrium value established during continuous water addition. By this procedure the activity of

the catalyst can be maintained at its equilibrium level or above by intermittently adding water or a selected water precursor.

As previously observed, the cycle time required to traverse the complete cycle of this transient catalyst activity response depends on the characteristics of the catalyst employed, the hydrocarbon feedstock, the nitrogen content in the hydrocracking zone, the water level employed and the liquid hourly space velocity. However, as a general rule, when operating within the conditions above referred to, the time required to complete a cycle of this transient response is within a range of about 30 minutes to about 100 hours. This range is of course narrowed considerably for narrower ranges of operating conditions. For example, if the preferred liquid hourly space velocity is between about 0.3 to about 5, and the maximum water level is within a range of about 0.2 to about 2 weight-percent, the observed cycle time will usually be within the range of about 1 to about 60 hours. Consequently, it is presently preferred to continue water addition to the hydrocracking zone until the conversion level is stabilized which usually necessitates continuance of water addition for at least about 10 minutes, preferably from about 1 to about 100 hours. The supply of added water to the reactor is then preferably discontinued for a period sufficient to enable the activity of the catalyst to pass through its maximum and decline to approximately its equilibrium value which involves periods of at least about 2 hours, usually about 1 to about 100 hours.

The effectiveness of this procedure is demonstrated by the following examples which are intended only to be illustrative of the concept of this invention and not limiting thereof.

Example 1

The hydrocarbon feed employed in this example had the following characteristics:

TABLE 1

Boiling range, by D–1160, ° F.	555–1016
Composition, by Univ. Hi Pass, weight percent:	
Total saturates	35.0
Total aromatics	35.2
Sulfur, Wickbold, UTM–350, weight percent	1.54
Nitrogen, total, weight percent	0.387

This feed was partially hydrofined by contacting with a catalyst containing 3 weight-percent NiO, 18 weight-percent MoO_3, 3 percent P, 3 percent SiO_2 and 73 percent alumina. Operating conditions in the hydrofining zone included a reactor temperature of 740° F., a liquid hourly space velocity of 1.0, a total reactor pressure of 2500 p.s.i.g. and a hydrogen feed rate of 8000 s.c.f./bbl. feed. The product was then flashed to remove ammonia and hydrogen sulfide and passed to the hydrocracking zone. The decribed hydrofining procedures were sufficient to reduce the organic nitrogen content of the reactor charge to the hydrocracking zone to 50 p.p.m. and the organic sulfur content to 40 p.p.m.

Hydrocracking conditions included a total reactor pressure of 2500 p.s.i.g., a liqiud hourly space velocity of 0.5 LHSV and a dry hydrogen feed rate of 8000 s.c.f./bbl. at an overall 40 percent conversion per pass. The above described catalyst was also employed in the hydrocracking zone. Water was provided in the reaction zone by the addition of n-butanol to the hydrocarbon feed in amounts equivalent to 1.0 weight-percent water based on hydrocarbon.

Prior to water addition the reaction temperature was maintained at 740° F. for a total of 11 days. This temperature was sufficient to provide a constant conversion per pass of 40 percent to products boiling below the initial boiling point of the feed. Water injection was then commenced and continued for a period of 168 hours. Immediately after water addition the catalyst activity increased as evidenced by a drop in temperature requirement needed to maintain the desired conversion per pass. This gradual increase in catalyst activity continued for 24 hours and then equilibrated at a level of 40 percent conversion per pass at 736° F. The introduction of water was discontinued after 168 hours. The catalyst activity again began to increase and continued to increase for a period of 12 hours at which time the maximum catalyst activity was obtained. The activity of the catalyst at this point was sufficient to obtain the same conversion per pass observed prior to water introduction at a reaction temperature of 710° F., 34° F. below the original reaction temperature. However, after this point the activity began to decline and continued its decline gradually for about 24 hours until the system equilibrated at a conversion level of 40 percent conversion per pass at 744° F. These conditions were identical to those observed before water addition. No significant variation in product quality or distribution was observed at any time throughout the cycle.

From these observations it is readily apparent that substantial advantage can be achieved by the described procedures. These results were apparently the result of the influence of water in mitigating the inhibiting effect of nitrogen on both hydrogenation and hydrocracking activity. The aromatics hydrogenation activity of the illustrated system increased along with the hydrocracking activity as evidenced by the proportionately higher aromatics conversion rate which is known to necessitate hydrogenation.

Example 2

The catalyst employed in this example comprised a refractory oxide base consisting of 20 weight-percent stabilized zeolite Y, 65 weight-percent Harshaw alumina and 15 weight-percent peptized catapal alumina. The active metal components were nickel and tungsten present in amounts equivalent to 4.1 weight-percent NiO and 22.8 weight-percent WO_3 based on the total dry weight of the active metal components and refractory oxide. The resulting composition had an apparent bulk density of 0.957 grams/cc. and a surface area of 248 meters per gram. The catalyst was sulfided by contacting with a 10% mixture of hydrogen sulfide in hydrogen sufficient to convert substantially all of the metal oxides to the corresponding sulfides.

The feed employed in this operation had the following characteristics:

TABLE 2

Boiling point range, by D–1160, ° F.	580–986
Composition, by Univ. High Pass, wt. percent:	
Total Saturates	45.1
Total Aromatics	27.7
Sulfur, X-ray, wt. percent	2.91
Nitrogen, total, wt. percent	0.082
API gravity, D–287	22.3

Conversion was effected in a recycle system in which the above-described feed was passed into admixture with a recycle stream and the combination was then introduced into a hydrocracking zone in which the described catalyst was retained in a fixed bed. The product from the reaction zone was admixed with water (during those periods in which water injection was employed) and the combination was flashed to produce a vapor phase comprising primarily hydrogen, water vapor, and hydrocarbons having 3 carbon atoms per molecule or less. This vapor phase was employed as hydrogen recycle to the hydrocracking zone with hydrogen makeup being added as required to maintain the desired hydrogen levels in the reactor. The water concentration in the hydrogen recycle stream was determined by the saturation level of water in the vapor phase and was equivalent approximately 0.1 weight-percent water based on total hydrocarbon feed to the hydrocracking zone.

The liquid hydrocarbon phase from the separation stage was treated by caustic scrubbing and fractionation to recover an overhead product having an end boiling point of 545° F. ASTM and a recycle product boiling above 545° F. which was continuously recycled to the hydrocracking zone.

The hydrocracking stage was continuously operated at a pressure of 1990 p.s.i.g., a liquid hourly space velocity of 1.5 and a hydrogen concentration equivalent to 7000 standard cubic feet of hydrogen per barrel of total feed. Reactor temperature was varied as required to maintain a 50% conversion level per pass to products boiling below 545° F. By this means the effect of water in the reaction zone was determined as a function of the temperature required to maintain the established conversion level of 50% per pass.

The run was initiated and continued for a period of 9 days (216 hours) with water injection at a rate equivalent to 0.1 weight-percent based on total reactor charge. Water injection via saturation of the hydrogen recycle stream was then discontinued by omitting water introduction into the reactor product as previously described. Within 3 hours following the discontinuance of water injection the equivalent catalyst activity had increased to a point at which 50% conversion per pass could be maintained at a temperature of 714° F. After reaching this maximum activity the catalyst began to deactivate and continued deactivation gradually for a period of about 33 hours after which time a temperature of 733° F. was required to maintain the same conversion level. Water injection was commenced after 11 days into the run (252 hours) after which time the catalyst activity began to gradually increase and reached an activity after an additional 48 hours sufficient to maintain 50% conversion per pass at a temperature of 722° F. The total system lined out at that temperature (722° F.) indicating a gradual catalyst deactivation during the 4 day test period equivalent to a daily temperature increase requirement (TIR) of 0.714° F. Obviously the gradual catalyst deactivation indicated by the noted temperature increase requirement tended to normalize the effect of water addition and deletion. Consequently, it becomes apparent that the differences in reaction temperature required to maintain 50% conversion would have been even greater than those determined in this operation were it not for the gradual catalyst deactivation observed. Nevertheless, the unusual cycle of catalyst activity resulting from the removal of water from a hydrocracking system was apparent from these observations. The catalyst activity first increased by an amount equivalent to a reaction temperature difference of 5° F. and then gradually decreased by an amount equivalent to about 19° F. Activity then gradually increased to the pre-run activity after reintroduction of 0.1 weight-percent water (taking TIR into account). These results are summarized in Table 3.

TABLE 3

Run length, hrs.	Water level, wt. percent	Reactor temp., ° F.[1]
216	0.1	719
219		714
252		733
312	0.1	722

[1] Required to maintain 50% conversion per pass to 545° F. minus product in view of catalyst deactivation equivalent to a daily TIR at 0.7° F.

If desired, reactor temperature can be varied while cycling water addition and deletion to maintain a constant conversion level. The markedly reduced reaction temperatures required to accomplish this result are known to greatly reduce catalyst deactivation rate and consequently extend the run length obtainable before regeneration is necessitated. Conversely, reaction conditions can be maintained constant while cycling water addition as described to vary the overall conversion level. Depending upon the downstream systems necessary to post-treat the hydrocracker effluent one or the other of these procedures may be preferred. In most situations it is desirable to maintain a constant conversion level in view of the complexities involved in modifying the operation of downstream fractionation and recycle systems. Consequently, in most situations it may be simpler to vary reaction temperature as a function of water addition and conversion level in order to maintain a constant conversion level at all times. In any event, considerable improvement in hydrocarbon conversion can be achieved by either of these procedures or other alternatives readily apparent to one skilled in the art in view of the aforegoing disclosure in the appended claims.

We claim:

1. The method of contacting hydrocarbons containing at least about 5 p.p.m. organically bound nitrogen at conditions of temperature, pressure and in the presence of hydrogen sufficient to effect at least one of hydrogenation and hydrocracking of said hydrocarbons upon contact with a hydrogenation active catalyst comprising a catalytically active amount of at least one active component selected from the Group II, IV–B, VI–B, VII–B and VIII metals, oxides and sulfides and a foraminous refractory oxide which comprises contacting said hydrocarbons in the presence of a controlled amount of water, or water precursor convertible to water under the conditions at which said hydrocarbons are contacted, sufficient to provide a water concentration based on said hydrocarbons of at least about 0.1 weight-percent, and the concentration of said water and/or water precursor is subsequently reduced.

2. The method of claim 1 wherein said water concentration is about 0.1 to about 5 weight percent and said water and/or precursor is added to said hydrocarbons and said addition of said water and/or water precursor is discontinued and is subsequently recommenced after the water concentration of said hydrocarbons has substantially diminished.

3. The method of claim 1 wherein the concentration of said water or water precursor is maintained until the conversion rate of said hydrocarbons over said catalyst becomes substantially constant, said concentration is subsequently reduced and the cycle of water level reduction and increase is periodically repeated.

4. The method of claim 1 wherein the level of said water and/or water precursor is maintained for a period of at least about 10 minutes and is then reduced for a period of at least about two hours.

5. The method of claim 1 wherein said hydrocarbons boil substantially above 200° F. and contain about 5 to about 1000 parts per million nitrogen as organonitrogen compounds, and said foraminous refractory oxide is selected from alumina, silica, zirconia, magnesia and combinations thereof.

6. The method of claim 1 wherein said hydrocarbons are contacted with said catalyst at a temperature of about 400° to about 900° F. in the presence of at least about 500 s.c.f. of hydrogen per barrel of said hydrocarbon, said water concentration is within the range of about 0.2 to about 2 weight-percent, said refractory oxide is primarily alumina, and the level of said water and/or water precursor is maintained for a period of at least about 10 minutes.

7. The method of claim 1 wherein said refractory oxide comprises at least one of alumina, silica-alumina, silica-magnesia, and aluminosilicates, said hydrocarbon boils primarily above 400° F. and contains at least about 10 p.p.m. nitrogen as organonitrogen compounds.

8. The method of claim 1 wherein said hydrocarbon boils primarily above about 400° F. and contains about 10 to about 600 p.p.m. nitrogen as organonitrogen compounds, said foraminous oxide is selected from alumina, silica-alumina, silica-magnesia and zeolitic aluminosilicates, said active component comprises at least one of the metals, oxides and sulfides of calcium, magnesium,

molybdenum, tungsten, manganese, rhenium, nickel, cobalt, platinum and palladium and said hydrocarbon is contacted with said catalyst at a temperature of about 400° to about 900° F. with at least about 500 s.c.f. of hydrogen per barrel of said hydrocarbon, said water concentration is within the range of about 0.1 to about 5 weight-percent and is maintained by the addition of said water or precursor to said hydrocarbon and said addition is continued for a period of at least about one hour and is discontinued for a period of at least about two hours prior to reintroduction of said water and/or water precursor.

9. The method of claim **8** wherein said refractory oxide comprises at least about 60 weight percent alumina and said active component is selected from molybdenum, tungsten, nickel and cobalt metals, oxides and sulfides.

10. The method of claim **1** wherein said foraminous oxide comprises primarily alumina, said active component comprises at least one of the metals, oxides and sulfides of molybdenum, tungsten, nickel, cobalt, platinum and palladium, said hydrocarbon boils primarily above about 200° F. and contains about 10 to about 600 p.p.m. nitrogen as organonitrogen compounds and is contacted with said catalyst at a temperature of about 400 to about 900° F. and a liquid hourly space velocity of about 0.2 to about 10 with at least about 500 s.c.f. of hydrogen per barrel of said hydrocarbon and said water concentration is about 0.1 to about 2 weight-percent.

11. The method of claim **1** wherein said foraminous oxide is selected from alumina, silica-stabilized alumina, silica-magnesia and zeolitic aluminosilicates, said catalyst further comprises at least about 0.2 weight-percent phosphorus and said water concentration is maintained for a period of at least about 10 minutes.

12. The methor of claim **1** wherein said catalyst comprises at least one of alumina, silica-stabilized alumina, silica-magnesia and aluminosilicates containing a promoting amount of at least one of nickel and cobalt, metals, oxides and sulfides and a promoting amount of at least one of molybdenum and tungsten metals, oxides and sulfides and at least about 0.2 weight-percent phosphorus, and said hydrocarbon is contacted with said catalyst at a temperature of about 500 to about 900° F. in the presence of at least about 500 s.c.f. of hydrogen per barrel of said hydrocarbon sufficient to hydrocrack at least a substantial portion of said hydrocarbon.

13. The method of converting hydrocarbons boiling between about 200 and 1200° F. containing about 10 to about 1000 p.p.m. nitrogen as organonitrogen compounds which comprises contacting said hydrocarbons with a hydrogenation active catalyst comprising a promoting amount of at least one of nickel, cobalt, molybdenum and tungsten metals, oxides and sulfides distended on a refractory oxide support comprising at least one of alumina, silica-alumina, silica-magnesia, and aluminosilicates at a temperature of about 400 to about 900° F., a pressure of at least about 1000 p.s.i.g. at a liquid hourly space velocity of about 0.2 to about 10 in the presence of at least about 1000 s.c.f. of added hydrogen per barrel of said hydrocarbon while controlling the amount of water and/or water precursor in said hydrocarbons at a level sufficient to provide a water concentration based on said hydrocarbons within the range of about 0.1 to about 5 weight-percent, reducing the water concentration of said hydrocarbon and subsequently increasing the concentration of said water and/or water precursor.

14. The method of claim **13** wherein said amount of water is maintained by the addition of said water and/or precursor to said hydrocarbons, said addition being continued for a period of at least about 10 minutes.

15. The method of claim **14** wherein the addition of said water and/or water precursor is continued until the conversion rate of said hydrocarbons over said catalyst becomes substantially stable, said water addition is subsequently discontinued and the cycle of water addition and discontinuance is periodically repeated.

16. The method of claim **13** wherein said catalyst further comprises at least about 0.2 weight-percent phosphorus, said hydrocarbon boils primarily above about 400° F. and is contacted with said catalyst at a temperature of at least about 500° F. and under conditions of pressure and hydrogen concentration sufficient to hydrocrack a substantial proportion of said hydrocarbon.

17. The method of hydrocracking hydrocarbons boiling within a range of about 400 to about 1200° F. and containing about 10 p.p.m. or more of organically bound nitrogen which comprises contacting said hydrocarbons at a temperature of about 500 to about 900° F., a total pressure of at least about 500 p.s.i.g. and a liquid hourly space velocity of about 0.1 to about 10 in the presence of at least about 500 standard cubic feet of hydrogen per barrel of said hydrocarbon with a catalyst containing about 0.5 to about 10 weight-percent of at least one of nickel and cobalt metals, oxides and sulfides based on the corresponding oxide and about 4 to about 30 weight-percent of at least one of molybdenum and tungsten metals, oxides and sulfides based on the corresponding oxide combined with a refractory oxide comprising at least one of alumina and combinations thereof with silica, and said hydrocarbons are combined with at least one of water and water precursors in an amount sufficient to provide about 0.1 to about 5 weight-percent of water in said reaction zone based on the weight of said hydrocarbon for a period at least sufficient to approach an equilibrium water concentration in said reaction zone after which the addition of said water and/or water precursor is discontinued for a period sufficient to approach equilibrium in said reaction zone and said water or water precursor is subsequently reintroduced to said hydrocracking zone.

18. The method of claim **17** wherein said hydrocarbons are combined with at least one of water and water precursors convertible to water at the hydrocracking conditions under which said hydrocarbons are contacted in amounts sufficient to provide an equivalent of about 0.2 to about 2 weight-percent equivalent water in said reaction zone based on the weight of said hydrocarbon for a period of at least about 10 minutes, and the addition of said water is discontinued for a period of at least about two hours prior to reintroduction of said water and/or water precursor.

19. The method of claim **17** wherein the addition of said water and/or water precursor is continued for a period of about 1 to about 100 hours and is then discontinued for a period of about 8 to about 100 hours before repeating the cycle.

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