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HYDROCRACKING PROCESS WITH PRECONDITIONED ZEOLITE CATALYST

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FIG. 1

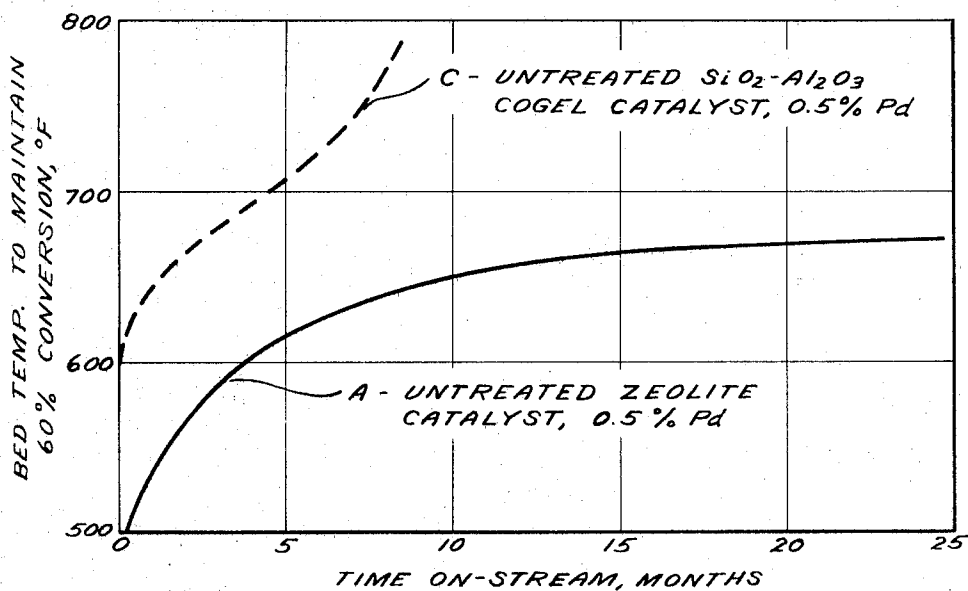
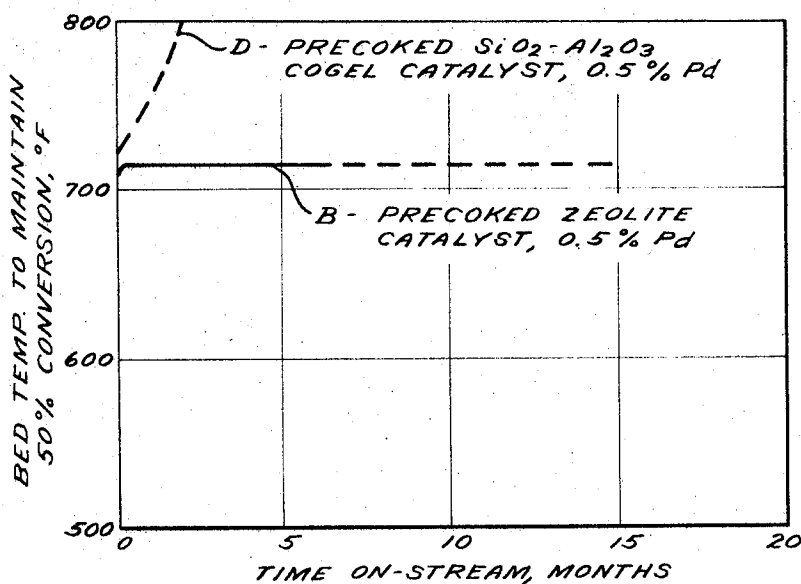


FIG. 2

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HYDROCRACKING PROCESS WITH PRECONDITIONED ZEOLITE CATALYST

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ABSTRACT OF THE DISCLOSURE

A process is disclosed for the catalytic hydrocracking of hydrocarbons using zeolite catalysts which have been preconditioned by accelerated coking with a hydrocarbon feedstock at elevated temperatures. The accelerated coking step partially deactivates the catalyst but is found to precondition it so that its deactivation rate during hydrocracking is substantially nil, thereby enabling the catalyst to be used at relatively high hydrocracking temperatures conducive to the production of high-quality gasoline products over extremely long run lengths without catalyst regeneration.

BRIEF SUMMARY OF THE INVENTION

The invention relates to catalytic hydrocracking, and more particularly is concerned with hydrocracking mineral oil feedstocks using zeolite hydrocracking catalysts which have been preconditioned by accelerated coking in such manner as to take maximum advantage of certain unique characteristics of the zeolite type catalysts. The accelerated coking procedure consists in subjecting the catalyst to contact with a mineral oil feedstock at elevated temperatures of e.g., 650° to 1100° F. and preferably at relatively low hydrogen partial pressures, lower than the hydrogen partial pressure to be employed in the subsequent hydrocracking step. By this procedure, a minor proportion of coke, e.g., 6–15% by weight, is deposited upon the catalyst, with resultant lowering of the absolute activity thereof. The precoked catalyst is then employed for hydrocracking the same or other mineral oil feedstocks at relatively high temperatures of e.g., 650–850° F., and at relatively high hydrogen partial pressures correlated with temperature so as to maintain a substantially steady-state activity, whereby long run lengths of, e.g., six months to two years or more can be maintained at constant conversion levels with little or no temperature increase. The precoking procedure not only permits the rapid attainment of a substantially steady-state activity of the catalyst, but, as a result of the relatively higher hydrocracking temperatures employed with the precoked catalysts, a more aromatic, high-octane gasoline product is obtained, the quality of which does not vary substantially over the run period.

The results obtained by the accelerated coking procedure are to be sharply contrasted with (1) the results obtainable by using the zeolite catalysts without preconditioning, and (2) the results obtainable by using conventional cogel type hydrocracking catalysts which have been precoked in a similar manner. The initial activity of fresh zeolite hydrocracking catalysts (which have not been precoked) is such that low initial hydrocracking temperatures of, e.g., 500–600° F., are necessary to avoid overcracking. An extremely low-octane gasoline product is produced under these conditions, and an on-stream period of several months to two years or more may be required before hydrocracking temperatures can be safely elevated to desirable levels above about 650° F. (assuming that a nitrogen- and sulfur-free feed is used).

All prior experience in catalytic hydrocracking has in-

dicated that as conversion temperatures are increased to compensate for progressive catalyst deactivation, a "snowballing" effect is eventually attained where deactivation progresses geometrically as conversion temperatures increase. It came as a distinct surprise to find that the zeolite type catalysts appear to be a unique exception to this rule, in that they exhibit highest deactivation rates at low temperatures, while at some higher temperature level they attain a deactivation rate which is substantially nil. Prior to my invention, it had been assumed that, in order to achieve acceptable run lengths, it would be necessary to tolerate initial low conversion temperatures with resultant poor product quality over a major part of the run, in order to postpone the anticipated accelerated deactivation during the later high-temperature portion of the run. It was only as experience was gained over long hydrocracking runs using zeolite catalysts that it became apparent that such fears were groundless, for deactivation rates were found actually to decrease with increasing temperatures, at least up to temperature levels of about 750–800° F.

The accelerated coking procedure of this invention is not applicable to conventional cogel type hydrocracking catalysts. The cogel type catalysts conform to the normal expectations of past experience in that their deactivation rates continue to increase with increasing conversion temperatures above about 650° F. The accelerated coking procedure of this invention when applied to a conventional cogel type hydrocracking catalyst not only decreases the absolute activity thereof, but also increases its deactivation rate, necessitating a higher rate of temperature increase to maintain conversion than would be required at lower conversion temperatures without the precoking step.

A major application of the present invention relates to improved "sweet" hydrocracking operations, i.e., hydrocracking processes carried out substantially in the absence of sulfur. For purposes of this invention, "sweet" hydrocracking systems are defined as those wherein the partial pressure of H₂S in the gaseous feed to the hydrocracking zone is less than about 0.3 p.s.i., preferably less than 0.2 p.s.i. As disclosed in U.S. Patent No. 3,132,090, one of the major disadvantages of low-temperature hydrocracking with zeolite catalysts can be overcome by operating in the presence of sulfur, whereby a more aromatic gasoline product can be obtained. However, these "sour" hydrocracking systems require expensive plant alloying in order to avoid corrosion problems. It would be highly desirable to provide a sweet hydrocracking system capable of producing the high-quality products obtained in the sour systems, whereby the hydrocracking reactors, exchangers, etc., could be much more cheaply constructed of low alloy materials, e.g. low-chrome steel. Also, many commercial hydrocracking plants now in operation are designed for relatively high-temperature, sweet operations using conventional cogel type catalysts. The provision of a sweet, high-temperature process for hydrocracking with zeolite catalysts permits the conversion of such units to zeolite hydrocracking plants without sacrificing product quality.

From the foregoing it will be apparent that the principal object of the invention is to provide a method for conditioning zeolite hydrocracking catalysts whereby they may be utilized more efficiently at relatively high temperatures, in the absence of sulfur, to produce an aromatic, high-octane gasoline product. Another object is to provide a hydrocracking process which can be operated over long periods of time at substantially constant temperature levels, to produce a constant quality product. A corollary objective is to eliminate the need for maintaining sour hydrocracking conditions to obtain high quality products, and thus to reduce or eliminate expensive alloying in plant construction. Other objectives will be apparent from the more detailed description which follows.

BRIEF DESCRIPTION OF DRAWINGS

FIGURE 1 is a graph depicting the relative deactivation rates of a conventional cogel type hydrocracking catalyst and a zeolite hydrocracking catalyst, neither catalyst having been subjected to the accelerated coking treatment of the present invention.

FIGURE 2 is a graph depicting the relative deactivation rates of the same catalysts described in connection with FIGURE 1, after they have been subjected to the accelerated coking treatment of this invention.

DETAILED DESCRIPTION

A. Accelerated coking procedure

In general, accelerated coking in accordance with the present invention is carried out by passing a hydrocarbon feedstock through a bed of the catalyst, preferably though not necessarily in admixture with a gaseous diluent, at cracking temperatures adjusted and correlated with the other contacting conditions so as to achieve a more rapid rate of coking than would result under the contemplated hydrocracking conditions. Preferably, low hydrogen partial pressures are utilized, at least 100 p.s.i. and preferably at least about 500 p.s.i. below, the hydrogen partial pressure to be maintained in the subsequent hydrocracking step. It will be understood that coking is "accelerated" by virtue of the relatively high temperatures and/or low hydrogen partial pressures employed, as compared to the coking rates which result under normal hydrocracking conditions. The normal coking of zeolite catalysts which occurs during hydrocracking is relatively slow and progressive and may require several months to reach an equilibrium value. Moreover, the equilibrium coke value which is ultimately reached during hydrocracking is generally lower than can be obtained by accelerated coking. This factor makes it difficult to reach the "plateau" or steady-state hydrocracking temperature levels at which minimum deactivation rates prevail, whereas by accelerated coking the proper coke level can rapidly be attained for immediate hydrocracking at the optimum, plateau temperature levels.

The foregoing is aptly illustrated by graph A of FIGURE 1, which depicts the bed temperature history of an untreated magnesium-hydrogen Y zeolite hydrocracking catalyst containing 0.5 weight-percent palladium over a two-year commercial hydrocracking run. This run was carried out with minor interruptions and temperature fluctuations not shown, at a pressure of about 1500 p.s.i.g., with space velocities varying between about 1.3 and 1.7 and hydrogen rates varying between about 5,000 and 7,000 s.c.f./b. Hydrocracking temperatures were incrementally increased to maintain 60-70 volume-percent conversion per pass to gasoline. The feed was a substantially sulfur- and nitrogen-free unconverted gas oil (400-850° F. boiling range) from a previous stage of hydrocracking. It will be noted that at the end of the two-year period, the untreated catalyst was only beginning to reach a steady-state activity at about 675° F., where the deactivation rate was only about 0.02° F. per day. In contrast, graph C shows an approximate bed temperature history of a conventional 0.5% palladium-87% silica-13% alumina cogel catalyst when used under the same hydrocracking conditions. In this case, stable hydrocracking temperatures are never reached short of thermal conversion temperatures.

In FIGURE 2, graph B depicts the bed temperature history of a zeolite catalyst identical to that used in the graph A run, but which had been subjected to accelerated precoking with a hydrotreated gas oil feed boiling between about 400-700° F. Coking was continued for 12 hours at 870° F. and 225 p.s.i.g., with unconverted oil and dry gas containing 10-25 mole-percent hydrogen being recycled. This precoked catalyst, when utilized for hydrocracking the same precoking feed at 1500 p.s.i.g., 2.8 LHSV, and with about 6,000 s.c.f./b. of recycle hydrogen containing small amounts of hydrogen sulfide and ammonia, reached an optimum hydrocracking temperature of about 720° F.

within 2-3 days after startup, and the desired 50 percent conversion per pass was continuously maintained for five months thereafter with substantially no incremental temperature increase. In contrast, graph D illustrates the rapid deactivation of the conventional palladium-silica-alumina cogel catalyst when precoked under the same conditions and used for hydrocracking.

It will be understood that results intermediate between those depicted by graphs A and B will be obtained when the zeolite catalysts are subjected to milder accelerated coking procedures than those described in connection with graph B. Severe coking conditions embrace the use of higher temperatures, lower hydrogen partial pressures, longer coking times, and the use of heavier, more aromatic coking feedstocks. Conversely, lower boiling, less aromatic feedstocks, higher hydrogen partial pressures, lower temperatures, and shorter contact times are all factors representing milder coking conditions. In general, it is preferred to correlate and adjust all these conditions so as to deposit on the catalyst between about 2% and 30% by weight of nonvolatile coke over a period of time ranging from about 2 to 6 hours up to 5 to 10 days. However, it will be understood that any degree of coking obtained at an accelerated rate, as compared to the rate at which coke would be deposited in the subsequent hydrocracking step, represents a useful application of the principles of the present invention.

The optimum amount of coke to be deposited on the catalyst will vary somewhat depending upon the particular catalyst, and the hydrocracking conditions under which it is to be utilized. For highly active catalysts, and/or where the catalyst is to be employed at high hydrogen partial pressures, relatively high coke levels of, e.g., 8-30 weight-percent may be desirable, whereas for less active catalysts, or catalysts to be used at relatively low hydrocracking pressures, coke levels in the range of about 2-8 weight-percent may be preferable.

The accelerated coking may be carried out in the presence of a hydrogen recycle gas (which tends to reduce the coking rate), or it may be carried out using an inert diluent gas such as nitrogen, argon, or light hydrocarbon gases such as methane, ethane, etc. Where extremely high coking temperatures are employed, it may be desirable to employ hydrogen in order to moderate the coking reaction and prevent localized over-coking. Conditions generally useful for achieving accelerated coking fall within the following ranges, but are not necessarily limited thereto:

COKING CONDITIONS

	Broad range	Preferred range
Temperature, °F.	550-1,200	750-1,050
Hydrogen partial pressure, p.s.i.	0-2,000	0-400
Total pressure, p.s.i.g.	0-2,500	0-500
Feed rates, v./v./hr.	0.1-50	2-15
Coking time, days	0.1-30	0.5-2
Conversion per pass to products boiling below feed range, vol. percent.	5-100	15-50

The conditions of temperature and pressure are preferably correlated so as to achieve endothermic, dehydrogenating conditions, or at least to avoid exothermic, hydrogen-consuming conditions where a hydrogen-containing recycle gas is employed. Under conditions of high temperatures and/or high hydrogen pressures, the coking feed may be converted largely to light hydrocarbon gases, which may be partially recycled and partially bled from the system for use as fuel gases. Any unconverted oil is normally recycled to extinction.

In one modification of the process, relatively mild coking conditions may be employed, for example tempera-

tures of about 550–750° F. and hydrogen pressures of about 500–1000 p.s.i., whereby desirable commercial products may be produced during the accelerated coking period, e.g., gasoline, propane-butane mixtures (LPG), turbine fuels, diesel fuels, etc. Gasoline is the preferred product during this period, inasmuch as the coking conditions favor the production of aromatic products. In this modification of the process there may be no sharp demarcation between the accelerated coking treatment and the subsequent hydrocracking step, both steps forming a continuous operation characterized by incrementally increasing hydrogen pressures to produce a constant quality product at constant conversion levels over a long run period.

Suitable feedstocks for coking of the catalyst include in general any of the hydrocracking feeds described hereinafter, and more generally may comprise any hydrocarbon feedstock boiling above about 150° F. Specific feeds contemplated in addition to the hydrocracking feedstocks include for example light and heavy naphthas, and the heavy bottoms fraction from naphtha reformates. Preferred feedstocks are aromatic oils containing for example at least about 25 volume-percent aromatic hydrocarbons, having a boiling range between about 400° and 1000° F. Light aliphatic hydrocarbons boiling below about 150° F. are relatively ineffective, while extremely heavy residual oils are generally to be avoided because of their metal content and very heavy asphaltene.

Following the accelerated coking treatment, the catalyst may if desired be subjected to a stripping operation with hydrogen at elevated temperatures in order to remove volatile and/or readily hydrogenatable hydrocarbonaceous deposits, thus leaving a relatively stable, nonvolatile coke residue on the catalyst. If the stripping step is not employed, it may be found that the catalyst will tend to regain activity during the initial hydrocracking period, necessitating a gradual decrease in hydrocracking temperatures until a stable coke level is reached. Such an operation is not precluded herein, but may be undesirable from process stability and control standpoints.

In order to determine the exact severity of the coking procedure to be employed, it may be desirable to conduct several experimental precoking test runs, followed by activity testing under the particular hydrocracking conditions to be utilized. By this means the optimum degree of precoking may be readily established, and hydrocracking initiated substantially immediately at the desired steady-state temperature level. The optimum "steady state" temperature level may be defined as the temperature at which the desired conversion level can be maintained for several days, e.g., at least 1–2 months, by adjusting the hydrocracking temperature an average of no more than about plus-or-minus 0.1° F. per day. However, any degree of precoking sufficient to elevate the hydrocracking temperature to a level at which deactivation rates are lower than those which would be attained in the same time under normal hydrocracking conditions is a useful application of the present invention. Optimum steady-state temperature levels for the zeolite catalysts of this invention are normally attained somewhere in the 625°–800° F. range.

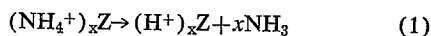
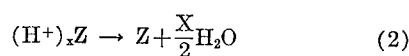
It should not be concluded from the foregoing that the relative deactivating effect of coke on the catalyst is a simple function of the amount deposited. Coke deposited under severe coking conditions and/or from highly aromatic coking feedstocks has a relatively greater deactivating effect than the same amount of coke deposited under relatively milder conditions, and/or from less aromatic feedstocks. To achieve the most stable and effective type of coke deposit, the coking should be carried out with aromatic feedstocks and/or under severe, dehydrogenating conditions conducive to the synthesis of condensed aromatic nuclei. Coke deposited under mild conditions, and/or from relatively nonaromatic feeds, tends to be less effective for the present purposes in that

it is more readily hydrogenated and volatilized during hydrocracking, with resultant recovery of some measure of the original fresh catalyst activity. It is for this reason that it is very difficult to achieve the results desired herein by the normal deposition of coke under conventional hydrocracking conditions.

B. Hydrocracking catalysts

Operative catalysts for use herein comprise in general any crystalline zeolite cracking base upon which is deposited a minor proportion of a Group VIII metal hydrogenating component. The zeolite cracking bases are sometimes referred to in the art as molecular sieves, and are composed usually of silica, alumina and one or more exchangeable cations such as sodium, hydrogen, magnesium, calcium, rare earth metals, etc. They are further characterized by crystal pores of relatively uniform diameter between about 4 and 14 Å. It is preferred to employ zeolites having a relatively high SiO₂/Al₂O₃ mole-ratio, between about 3.0 and 12, and even more preferably between about 4 and 8. Suitable zeolites found in nature include for example mordenite, stilbite, heulandite, ferrierite, dachiardite, chabazite, erionite, and faujasite. Suitable synthetic molecular sieve zeolites include for examples those of the B, X, Y and L crystal types, or synthetic forms of the natural zeolites noted above, especially synthetic mordenite. The preferred zeolites are those having crystal pore diameters between about 8–12 Å., wherein the SiO₂/Al₂O₃ mole-ratio is about 3–6 and the average crystal size is less than about 10 microns along the major dimension. A prime example of a zeolite falling in this preferred group is the synthetic Y molecular sieve.

The naturally occurring molecular sieve zeolites are normally found in a sodium form, an alkaline earth metal form, or mixed forms. The synthetic molecular sieves normally are prepared first in the sodium form. In any case, for use as a cracking base it is preferred that most or all of the original zeolitic monovalent metals be ion-exchanged out with a polyvalent metal, and/or with an ammonium salt followed by heating to decompose the zeolitic ammonium ions, leaving in their place hydrogen ions and/or exchange sites which have actually been decationized by further removal of water:



Mixed polyvalent metal-hydrogen zeolites may be prepared by ion exchanging first with an ammonium salt, then partially back-exchanging with a polyvalent metal salt and then calcining. In some cases, as in the case of synthetic mordenite, the hydrogen forms can be prepared by direct acid treatment of the alkali metal sieves. Hydrogen or "decationized" Y sieve zeolites of this nature are more particularly described in U.S. Patent No. 3,130,006.

There is some uncertainty as to whether the heating of the ammonium zeolites produces a hydrogen zeolite or a truly decationized zeolite, but it is clear that, (a) hydrogen zeolites are formed upon initial thermal decomposition of the ammonium zeolite, and (b) if true decationization does occur upon further heating of the hydrogen zeolites, the decationized zeolites also possess desirable catalytic activity. Both of these forms, and the mixed forms, are designated herein as being "metal-cation-deficient." The preferred cracking bases are those which are at least about 10%, and preferably at least 20%, metal-cation-deficient, based on the initial ion-exchange capacity. A specifically desirable and stable class of zeolites are those wherein at least about 20% of the ion-exchange capacity is satisfied by hydrogen ions, and at least about 10% by polyvalent metal ions such as magnesium, calcium, zinc, rare earth metals, etc.

The essential active metals employed herein as hydrogenation components are those of Group VI–B and/or

Group VIII, i.e., iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium and platinum, chromium, molybdenum, tungsten, uranium, or mixtures thereof. The noble metals are preferred and particularly palladium and platinum. In addition to these metals, other promoters may also be employed in conjunction therewith, including the metals of Group VII-B, e.g., manganese.

The amount of hydrogenating metal in the catalyst can vary within wide ranges. Broadly speaking, any amount between about 0.05% and 20% by weight may be used. In the case of the noble metals, it is normally preferred to use about 0.05% to 2% by weight. The preferred method of adding the hydrogenating metal is by ion exchange. This is accomplished by digesting the zeolite, preferably in its ammonium form, with an aqueous solution of a suitable compound of the desired metal wherein the metal is present in a cationic form, as described for example in U.S. Patent No. 3,236,762.

Following addition of the hydrogenating metal, the resulting catalyst powder is then filtered off, dried, pelleted with added lubricants, binders, or the like if desired, and calcined in air at temperatures of, e.g., 700–1200° F. in order to activate the catalyst and decompose zeolitic ammonium ions. Alternatively, the zeolite component may first be pelleted, followed by addition of the hydrogenating component and activation by calcining. The calcining step converts the catalyst to an oxidized form, and it is important to observe that prior to the accelerated coking treatment this oxidized form of the catalyst should first be subjected to reduction with hydrogen at e.g., 500–1000° F. for a sufficient length of time, normally about 1–40 hours, to remove substantially all labile oxygen as water. If the oxidized catalyst is directly subjected to precoking, undesirable deactivation involving agglomeration of the hydrogenating metal may occur. Catalysts deactivated in this manner do not give the desired results, as will be shown hereinafter.

The foregoing catalysts may be employed in undiluted form, or the powdered zeolite catalyst may be mixed and copelleted with other relatively less active adjuvants, diluents or binders such as activated alumina, silica gel, coprecipitated silica-alumina cogel, magnesia, activated clays and the like in proportions ranging between about 5% and 50% by weight. These adjuvants may be employed as such, or they may contain a minor proportion of an added hydrogenating metal, e.g., a Group VI-B and/or Group VIII metal.

C. Hydrocracking feedstocks

Feedstocks which may be employed herein include in general any hydrocarbon material boiling above the boiling range of the desired product. For purposes of gasoline production, the primary feedstocks comprise straight-run gas oils, coker distillate gas oils, deasphalted crude oils, cycle oils derived from catalytic or thermal cracking operations and the like. These feedstocks may be derived from petroleum crude oils, shale oils, tar sand oils, coal hydrogenation products and the like. Specifically it is preferred to use feedstocks boiling between about 400° and 900° F., having an API gravity of about 20 to 35°, and containing at least about 20% by volume of acid soluble components (aromatics plus olefins). The process of this invention may also be used for converting naphthas and/or light gas oils boiling up to about 600° F. to propane-butane mixtures, commonly referred to in the art as liquefied petroleum gas (LPG).

The process is of maximum benefit in connection with the hydrocracking of feeds which are substantially free of sulfur, and especially nitrogen. Preferably such feeds should contain less than about 500 p.p.m. of sulfur and less than about 100 p.p.m. of nitrogen, such for example as may be achieved by prehydrofining. Sulfur compounds, and to an even greater extent, nitrogen compounds, lead to higher steady-state hydrocracking temperature levels,

but even in such cases these steady-state temperature levels are more rapidly attained by virtue of the accelerated coking procedure.

D. Hydrocracking conditions

Operative hydrocracking conditions contemplated herein fall within the following ranges:

	Broad range	Preferred range
Temperature, ° F.	550-850	650-776
Pressure, p.s.i.g.	500-4,000	750-2,500
LHSV.	0.2-30	1-10
H ₂ /oil ratios, M s.c.f./b.	0.5-20	4-12

The above conditions are suitably adjusted and correlated to give the desired conversion per pass to products boiling below the initial boiling point of the feed. Normally, conversion levels in the range of about 20–90 volume-percent, preferably 30–80 volume-percent, are desirable to obtain a suitable balance between process economics and a desirable product distribution.

If it is found upon reaching the desired conversion temperature (i.e., the temperature at which the desired conversion level is attained), that such temperature level is not sufficiently high to give the desired product quality, hydrogen pressures may be reduced and/or temperatures increased temporarily in order to induce additional accelerated coking of the catalyst. This procedure may be repeated until a point is reached at which the desired conversion level can be maintained at the desired temperature level. This desired temperature level will normally correspond substantially to the steady-state activity temperature of the catalysts, and can be maintained within plus-or-minus 20° F. thereof for periods of at least about 4–6 months, with average daily temperature adjustments of no more than about plus-or-minus 0.1° F., normally about 0.01–0.04° F. This condition can be maintained either in once-through operation with no recycle of unconverted oil, or in operations where total recycle of unconverted oil is maintained.

Total run lengths obtainable in the practice of this invention are at present indeterminate. The available data such as that illustrated by graphs A and B of the attached drawings suggest an infinite run length, i.e. a process in which the catalyst would never require regeneration. Several years of experimental and commercial use of the zeolite catalysts of this invention for hydrocracking at 1500 p.s.i.g. have failed to produce a catalyst which actually required regeneration from an economic standpoint, except where deactivation occurred as a result of some process upset. Obviously however, deactivation can occur fairly rapidly at low hydrogen partial pressures, at extremely high temperatures, high feed rates, or when hydrocracking refractory feeds such as residual oils. However, under the preferred hydrocracking conditions described herein, it is clear that run lengths of at least about four months and normally at least one year are readily obtainable.

It is not possible to state at this time whether the ultimate run lengths obtainable with the precoked catalysts of this invention are shorter or longer than the ultimate run lengths obtainable without precoking. But in any event, where run lengths of six months or more are obtainable there is a diminishing return from any further extension of such run which tends to be outweighed by the benefits obtained herein of obtaining a constant, high-quality product over the entire run length. Hence, the use of the precoked catalysts of this invention is advantageous even if total run lengths are thereby somewhat shortened, which is by no means certain.

The following examples are cited to illustrate the in-

vention and certain of its critical novel aspects, but are not to be construed as limiting in scope:

EXAMPLE I

To investigate the effect of differing degrees of accelerated coking of a zeolite hydrocracking catalyst, an extended hydrocracking run was carried out wherein pressures were periodically reduced in varying degrees to accelerate coking. Following each low-pressure coking period, the pressure was raised to the normal 1500 p.s.i.g. hydrocracking pressure in order to test activity. The catalyst was essentially a hydrogen Y zeolite containing 0.5 weight-percent palladium, the zeolite component analyzing about 73% SiO₂, 25% Al₂O₃ and 1.5% Na₂O. This catalyst was ground and copelleted with an equal weight of activated alumina containing a minor proportion of impregnated nickel. Throughout the run, the liquid hourly space velocity was maintained at about 1.5, and hydrogen ratios at about 8,000 s.c.f./b. The feed employed throughout the run was an essentially sulfur- and nitrogen-free unconverted oil derived from a previous stage of hydrocracking, having an API gravity of 30.4°, a boiling range of about 400°–750° F., and containing about 46.5 weight-percent aromatics. The significant conditions and results of the run were as follows:

TABLE I

Run period	Accelerated coking				Testing at 1,500 p.s.i.g.			
	Cat. age, hrs.	Temp., ° F.	Pressure, p.s.i.g.	Time, hrs.	Cat. age, hrs.	Temp., ° F.	Conversion to 400° F. E.P.	ADTA, ¹ ° F.
A.....		Fresh catalyst						
B.....	782	746–920	500	125	34	559	50	0.5
C.....	1,016	645–943	300	79	940	700	50	–4.5
D.....	1,108	943	300	30	1,100	750	10–25	(?)
		940–942	100	32				
					1,220	719	50	–2.5
E.....	1,246	Feed out—hydrogen reduction at—						
		Temp., ° F.	Time, hrs.					
		700	6					
		750	6					
		800	6					
		850	6					
		900	24		1,320	700	50	~1

¹ Average daily temperature adjustment required to maintain conversion.

² Conversion was rising rapidly.

Comparing the results shown in run periods B and C with those of run period A, it is apparent that the accelerated coking at low pressures significantly reduced activity of the catalyst. Although initial hydrocracking temperatures in run periods B and C were in the desired range the catalyst was in both cases rapidly regaining activity, indicating that insufficient coking had occurred to achieve stable hydrocracking temperatures in the desired range of about 700–720° F. In run period D this objective was achieved as a result of the more severe coking at 100 p.s.i.g. The hydrocracking temperature of 719° F. in run D does not however represent the exact steady-state activity of the catalyst, as evidenced by the negative ADTA of –2.5° F. In order to accelerate the attainment of a steady-state activity, the catalyst was subjected to the hydrogen reduction treatment in run period E to more rapidly remove volatilizable coke deposits. The resulting hydrocracking temperature of 700° F. for 50% conversion, with a slight positive ADTA figure, shows that the steady-state activity of the catalyst is intermediate between the 700° F. and 719° F. temperatures of run periods D and E.

To illustrate the desirable improvement in gasoline quality obtained at higher hydrocracking temperatures, the gasoline products obtained at various temperatures

in the above run were tested for knock rating with the following results:

TABLE 2

Hydrocracking temp., ° F.	Knock ratings, F-1+3 ml. TEL	
	C ₇ -400° F. gasoline	C ₅ -C ₈ gasoline
560.....	73.8	98.7
620.....	¹ (81)	99.9
700.....	92.3	101

¹ Interpolated data.

From the foregoing it is clear that both the light and heavy gasoline fractions are of higher quality when produced at higher hydrocracking temperatures.

EXAMPLE 2

In another accelerated coking-hydrocracking run, a zeolite hydrocracking catalyst was precoked for 8 hours at 850° F., 300 p.s.i.g., and 1.47 LHSV, using 2500 s.c.f./b. of recycle gas containing 55 mole-percent hydrogen. The coking feedstock was a hydrofined gas oil boiling between about 385–700° F., containing 37.9 weight-percent aromatics. Unconverted oil boiling above the gasoline range was recycled. The catalyst was a copelleted mixture of 80 weight-percent of a Y zeolite containing 0.5 weight-percent palladium, and 20 weight-per-

cent of an activated alumina binder. The zeolite component had a SiO₂/Al₂O₃ mole ratio of about 4.7, about 35% of the zeolitic ion exchange capacity thereof being satisfied by magnesium ions (3 weight-percent MgO), about 10% by sodium ions, and the remainder by hydrogen ions.

Following this accelerated coking treatment, the catalyst was employed for hydrocracking the same feed at 1500 p.s.i.g., 2.91 LHSV, with about 6,000 s.c.f./b. of hydrogen. Over a period of 24 hours, 60 volume-percent conversion to 400° F. end-point products was obtained at a substantially constant temperature of 682° F. Upon reducing space velocity to 2.18, 80 volume-percent conversion to gasoline was obtained at a substantially constant temperature of 683.8° F. over a 12 hour period.

At this point the hydrocracking run was modified by adding thiophene and t-butylamine to the feed in amounts sufficient to provide about 108 mole-p.p.m. of H₂S and 190 mole-p.p.m. of NH₃ in the recycle gas. At 2.9 LHSV, the temperature required to achieve 60 volume-percent conversion was 723.6° F., which rose slowly to 730° F. over a period of 10 days, after which the temperature remained constant at 730° F. for an additional 10 days (ADTA=0).

The significant results of the foregoing run are compared in the following table with the results obtained in a similar run using the same catalyst in a fresh uncoked condition, employing essentially the same hydrocracking conditions and the same feed to which had been added 304 p.p.m. of sulfur as thiophene:

Hydrocracking conditions—Precoked catalyst			Gasoline yields and quality			
Temp, ° F.	Conversion, vol. percent	ADTA, ° F.	C ₅ -C ₆		C ₇ -400° F.	
			Vol. percent feed	F-1 Oct. 3 ml. TEL	Vol. percent feed	F-1 Oct. 3 ml. TEL
682-----	60	Negl.	35.8	99.5	56.0	88.6
684-----	80	Negl.	40.5	99.6	49.0	91.0
723.6-----	60	0.4	26.5	99.4	72.5	89.3
730-----	60	0	31.1	99.9	67.0	91.4
Fresh catalyst						
528-----	60	1	26.6	99.2	82.0	76.9

The foregoing data clearly shows the the precoked catalyst gives a much higher quality C₇-400° F. gasoline than is obtainable with the fresh catalyst, even when the latter is used under H₂S-sour conditions. The light gasoline quality is also slightly improved. While the total liquid yields obtainable with the fresh catalyst are higher than those obtained with the coked catalyst, this apparent disadvantage largely disappears if the results are compared on an after-reforming basis, i.e., after the respective C₇-400° F., gasolines are reformed to the same optimum octane level and blended back with the respective hydrocracked light gasolines to give a 10 RVP, 100 octane blend.

EXAMPLE 3

This example demonstrates that the results achieved herein by accelerated coking deactivation cannot be achieved by other known methods of partial deactivation, specifically by partially agglomerating the hydrogenating metal component of the catalyst.

A hydrogen Y zeolite catalyst containing 0.5 weight-percent palladium had a fresh activity such that 50 volume-percent conversion of a 400°-850° F. boiling range gas oil containing about 0.5 weight-percent sulfur was obtainable at 618° F., 1500 p.s.i.g. and 1.5 LHSV. This catalyst was subjected to artificial coking using an 800° F. end-point East Texas gas oil at 200 p.s.i.g. and 800° F. in a dry nitrogen atmosphere for 12 hours. The catalyst was then stripped with dry nitrogen at 200 p.s.i.g. and 800° F. for 8 hours, after which it was subjected to oxidative regeneration in the presence of 2.3 p.s.i.a. of water vapor at 200 p.s.i.g. and about 850° F. maximum temperature. Regeneration of the catalyst in the presence of water vapor is known to bring about agglomeration of palladium, but does remove substantially all coke.

The catalyst regenerated as above described was then tested for hydrocracking activity, using an 850° F. end-point gas oil feed, under the same conditions used for testing the fresh catalyst. The initial temperature required for 50 volume-percent conversion was 668° F., which increased to 695° F. after 32 hours. The ADTA required to maintain conversion was thus about 20° F. This example hence demonstrates that deactivation by partially agglomerating the palladium component can produce a catalyst initially operative at the herein desired relatively high temperatures, but such catalyst continues to deactivate at such a rapid rate that its use is impractical.

EXAMPLE 4

Another known method for partially deactivating zeolite catalysts consists in partially destroying crystallinity and surface area by hydrothermal degradation, but this method likewise does not give a catalyst of stable activity, as indicated by the following experiment:

A low-sodium (0.23 weight-percent Na₂O) hydrogen Y zeolite catalyst containing 0.5 weight-percent palladium had a fresh activity such that 50 volume-percent conversion of a 430-850° F. hydrofined gas oil was obtainable

at 502° F., 1500 p.s.i.g., 1.5 LHSV and 8000 s.c.f./b. of hydrogen. A portion of this fresh catalyst was allowed to become fully hydrated by adsorption of atmospheric moisture to a water content of about 20 weight-percent. The hydrated catalyst was then recalcined for 16 hours at 900° F., causing a drop in surface area from 867 m.²/g.

to 25 m.²/g. The resulting catalyst was again activity tested using the same feed and hydrocracking conditions. The initial temperature required for obtaining 50 volume-percent conversion was 736° F., which increased to 750° F. over a period of 8 hours. Thus, although the zeolite catalysts may be treated to destroy sufficient surface area to permit initial operation in the desired temperature range, the resulting deactivation rate (ADTA at least about 20° F.) is such as to render this technique completely impractical.

In addition it was noted that the hydrothermally degraded catalyst gave a very poor quality light gasoline product, the ratio of isobutane/n-butane being 1.3 and of isopentane/n-pentane 1.6. In contrast, the coked catalyst used in Example 2 gave a 1.7 ratio of isobutane/n-butane, and a 9.5 ratio of isopentane/n-pentane.

The results of this example, and of Example 3, clearly show that other known means for partially deactivating zeolite catalysts are not the equivalent of the accelerated coking technique of this invention.

Additional modifications and improvements utilizing the discoveries of the present invention can be readily anticipated by those skilled in the art from the foregoing disclosure, and such modifications and improvements are intended to be included within the scope and purview of the invention as defined by the following claims.

I claim:

1. In the catalytic hydrocracking of hydrocarbons wherein a crystalline zeolite catalyst containing a minor proportion of Group VIII and/or Group VI-B metal hydrogenating component is utilized at elevated temperatures and pressures, a method of preconditioning said catalyst whereby more stable hydrocracking temperatures can be maintained, which comprises subjecting said catalyst to accelerated precoking by contact with a hydrocarbon feedstock at a hydrogen partial pressure at least 100 p.s.i. below the hydrogen partial pressure utilized during said hydrocracking step, and at elevated temperatures at least as high as the initial temperature in said hydrocracking, so as to effect deposition of at least about 2 weight-percent of nonvolatile coke thereon with resultant substantial partial deactivation thereof.

2. A method as defined in claim 1 wherein said accelerated coking is carried out at a hydrogen partial pressure at least about 500 p.s.i. below the hydrogen partial pressure utilized in said hydrocracking step.

3. A method as defined in claim 1 wherein said catalyst is composed of a Y zeolite wherein the zeolitic cations are predominately hydrogen ions and/or polyvalent metal ions, and wherein said hydrogenating component comprises a Group VIII noble metal.

4. A method as defined in claim 1 wherein said accelerated coking step is completed in a period of time less than about 10 days, to deposit between about 8 percent and 30 percent by weight of nonvolatile coke on said catalyst.

5. A method as defined in claim 1 wherein said accelerated coking step is carried out at a temperature between about 550° and 1200° F. and at a hydrogen partial pressure below about 400 p.s.i.g.

6. A method as defined in claim 1 wherein the feedstock employed in said accelerated coking step is a mineral oil containing at least about 25 volume-percent of aromatic hydrocarbons, and boiling in the range of about 400°–1000° F.

7. A method for hydrocracking a hydrocarbon feedstock to produce therefrom lower boiling hydrocarbons, which comprises contacting said feedstock plus added hydrogen with a hydrocracking catalyst comprising a crystalline zeolite cracking base upon which is deposited a minor proportion of a Group VI-B and/or Group VIII metal hydrogenating component at elevated temperatures and pressures correlated to give a substantial conversion to lower boiling hydrocarbons, said catalyst having been preconditioned prior to said hydrocracking by hydrogen reduction followed by contact with a hydrocarbon pretreatment feedstock at elevated temperatures at least as high as the initial temperature in said hydrocracking and at hydrogen partial pressures at least 100 p.s.i. below the hydrogen partial pressure utilized in said hydrocracking step so as to achieve partial deactivation thereof by the accelerated deposition of at least about 2 weight-percent of nonvolatile coke thereon.

8. A method as defined in claim 7 wherein the severity of said accelerated coking step is controlled to give an optimum degree of deactivation whereby, during at least the first month of said hydrocracking step a substantially constant conversion per pass is maintained at a substantially constant temperature level varying an average of not more than about plus-or-minus 0.1° F. per day.

9. A method as defined in claim 8 wherein said hydrocracking step is continued for a period of at least four months with no more than about a 20° F. temperature increase over that period.

10. A method as defined in claim 7 wherein said preconditioning step is carried out at a hydrogen partial pressure at least about 500 p.s.i. lower than the hydrogen partial pressure maintained in said hydrocracking step.

11. A method as defined in claim 7 wherein said catalyst is composed of a Y zeolite wherein the zeolitic cations are predominately hydrogen ions and/or polyvalent metal ions, and wherein said hydrogenating component is a Group VIII noble metal.

12. A method as defined in claim 7 wherein said preconditioning step is completed in a period of time less than about 10 days, to deposit between about 8% and 30% by weight of nonvolatile coke on said catalyst.

13. A method as defined in claim 7 wherein said preconditioning step is carried out at a temperature between about 750° and 1050° F., and a hydrogen partial pressure between about 0 and 400 p.s.i., and wherein said hydrocracking step is carried out at a temperature between about 650° and 775° F. and a pressure between about 750 and 2500 p.s.i.g.

14. A method as defined in claim 7 wherein said pre-

conditioning step is carried out under dehydrogenating endothermic conditions.

15. A method as defined in claim 7 wherein said pretreatment feedstock is substantially more aromatic in character than said hydrocracking feedstock.

16. A method for the production of a substantially aromatic, high-quality gasoline by catalytic hydrocracking at relatively constant temperatures between about 650° and 775° F. over a substantial run period of at least about 4 months utilizing a Group VIII metal-promoted zeolite hydrocracking catalyst, which comprises:

(1) subjecting said catalyst to an accelerated precoking treatment by contact with a hydrocarbon feedstock at a hydrogen partial pressure at least 100 p.s.i. lower than that employed in the hereinafter-defined hydrocracking step, and at elevated coking temperatures at least as high as the initial temperature in said hydrocracking to achieve an optimum degree of partial deactivation predetermined to result in a substantially steady-state temperature level between about 650° and 775° F. in the subsequent hydrocracking step; and

(2) contacting a gas oil feedstock plus added hydrogen with the precoked catalyst from step 1 at a pressure between about 750 and 2500 p.s.i.g., and at a substantially constant hydrocracking temperature between about 650° and 775° F. over an extended run length of at least one month while maintaining a substantially constant conversion to high-quality gasoline products.

17. A method as defined in claim 16 wherein the severity of said accelerated precoking step is controlled to give a degree of deactivation such that during at least the first month of said hydrocracking run a substantially constant conversion per pass is maintained at a temperature level varying an average of not more than about plus-or-minus 0.1° F. per day.

18. A method as defined in claim 16 wherein said hydrocracking run is continued for a period of at least about four months with no more than about a 20° F. temperature increase over that period.

19. A method as defined in claim 16 wherein said accelerated precoking step is carried out at a hydrogen partial pressure at least about 400 p.s.i. lower than the hydrogen partial pressure maintained in said hydrocracking step.

20. A method as defined in claim 16 wherein said hydrocracking step is carried out substantially in the absence of sulfur.

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