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CRACKING A POISONED HYDROCARBON FEEDSTOCK

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This invention is a method for catalytic cracking of mineral oil hydrocarbon feedstocks containing large amounts of nickel. The cracking employs a catalyst having a considerable immunity to the poisoning effects of nickel. The feedstock generally contains at least a portion of highly nickel-contaminated residual petroleum hydrocarbon and the cracking method may include processing steps for removal of nickel and/or other metal contaminants from the catalyst. These procedures help to improve the catalytic cracking selectivity of the catalyst although they may not serve for significant removal of nickel from the catalyst unless this metal is present in rather large amounts.

One of the most important phases of study in the improvement of catalyst performance in hydrocarbon conversion is in the area of metals poisoning. Although referred to as "metals," these catalyst contaminants may be in the form of free metals or relatively non-volatile metal compounds. It is to be understood that the term "metal" used herein refers to either form. Various petroleum stocks have been known to contain at least traces of many metals, and in addition to those metals naturally present, including some iron, petroleum stocks have a tendency to pick up tramp iron from transportation, storage and processing equipment. In conventional processing these metals in the stock deposit in a relatively non-volatile form on the catalyst during the conversion processes and regeneration of the catalyst to remove coke does not remove these contaminants, which have an adverse effect on cracking results when using conventional cracking catalysts. Iron, nickel, vanadium and copper, for example, markedly alter the selectivity and activity of conventional cracking catalysts if allowed to accumulate, producing a higher yield of coke and hydrogen at the expense of desired products, such as gasoline and butanes. For instance, it has been shown that the yield of butanes, butylenes and gasoline, based on converting 60 volume percent of cracking feed to lighter materials and coke dropped from 58.5 to 49.6 vol. percent when the amount of nickel on a conventional catalyst increased from 55 p.p.m. to 645 p.p.m. and the amount of vanadium increased from 145 p.p.m. to 1480 p.p.m. in a more or less conventional catalytic cracking of a normally liquid feedstock containing some metal contaminated stocks. Since many cracking units are limited by coke burning or gas handling facilities, increased coke or gas yields require a reduction in conversion or throughput to stay within the unit capacity.

Refiners cope with the problem of metal poisoning by adopting several techniques. One technique includes selecting only feedstocks of low metal content or treating the feedstock to minimize its metal content. Another technique requires removing from the hydrocarbon conversion system as much metal as is fed to it per unit time, in order to obtain and retain a total amount of metal in the system below a level where the conversion process is made economically unfeasible by the poisoning effect of the metal. In most conversion processes some metal-containing catalyst is continually lost from the system in the form of fines which leave the system with effluent gases. The replacement of this loss with fresh unpoisoned catalyst reduces the net amount of metal in the system. In addition, the refiner usually will purposely remove

enough poisoned catalyst from the system per unit time so that replacement with unpoisoned or less poisoned catayst will keep the metal level at the desired equilibrium. The removed catalyst may be discarded as a waste material, or, using recently developed techniques, the catalyst may be demetallized and returned to the system.

In this invention the contaminating effects of nickel in a feedstock may be substantially avoided by employing a cracking catalyst more resistant to metals, especially nickel, than conventional cracking catalysts so that metals accumulation on the catalyst has less poisoning effect on the system. In operating with this catalyst the petroleum refiner can employ more highly contaminated feedstocks and may allow more metals to accumulate on the catalyst than on a conventional catalyst, without severe, economically disadvantageous, effects on the product distribution. By providing for a greater metals accumulation, that is, by operating at a higher equilibrium metal level, the inevitable stack loss of catalyst fines allows removal of more metal from the system. Further, less catalyst needs to be purposely discarded or demetallized to keep the proper conversion efficiency with a feedstock of a given metal content.

Cracking of heavier hydrocarbon feedstocks to produce hydrocarbons of preferred octane rating boiling in the gasoline range is widely practiced and conventionally uses a solid oxide catalyst to give end products of fairly uniform composition. The catalysts which have received the widest acceptance today are usually activated or calcined predominantly silica or silica-based, e.g. silica-magnesia, silica-zirconia, silica-alumina, etc., compositions in a state of slight hydration and containing small amounts of acidic oxide promoters in many instances. These oxides or more-or-less homogeneous oxide mixture compositions sometimes may also contain small amounts of other inorganic materials, but current practice in catalytic cracking leans more toward the exclusion from the silica materials of foreign constituents such as alkaline metal salts which may cause sintering of the catalyst surface on regeneration and a drop in catalytic activity. For this reason, the use of wholly or partially synthetic gel catalysts, which are more uniform and less damaged by high temperatures in treatment and regeneration, is often preferable. Such homogeneous catalysts, however, are sensitive to the poisoning effects of nickel in the feedstock, while the catalyst used in this invention is almost insensitive to the effect of nickel at moderate levels. The catalyst comprises a synthetic alumina gel precipitated on or mixed with a silica-alumina substrate.

The substrate is a solid inorganic oxide mixture, generally a clay or a synthetic silica-alumina gel. The substrate usually contains at least about 40% silica and often is predominantly silica. Preferably the substrate contains alumina, generally in an amount of at least about 5 to 30% and the combined silica and alumina content is at least about 85 or 90% of the substrate, the remainder, if any, generally comprising other inorganic oxides, such as those found originally in the clay, or added for additional promoting effects. The substrate may be derived from one of the clays conventionally used in catalytic cracking, such as halloysite or dehydrated halloysite (kaolinite) or bentonite. In most cases it is desirable to treat the clay with mineral acid for purposes of activation or at least for iron removal. The substrate may also be a completely synthetic-gel oxide material, which may be silica-based and ordinarily contains a substantial amount of a gel or gelatinous precipitate comprising a major portion of silica and at least one other material, such as alumina, magnesia, zirconia, etc.

The substrate is in the form of recognizable particles. While the size range of the particles is not of the utmost

significance, the particles are greater than colloidal in size, that is, they are larger than the micelles, the submicronic particles which make up a colloid. The substrate particles may be characterized by their lack of electric charge and the fact that they do not disperse to form a colloid when placed in an aqueous medium, and even if severely agitated, do not form a true, stable, colloidal suspension but rather settle, on standing, to leave a supernatant liquid. Also, particles suitable for forming the substrate do not grow by accretion or inorganic polymerization with each other. The silica-based gel substrate is generally prepared for alumina deposition by being washed, dried, if desired, and sized. Although there usually is no need for calcination before alumina addition, this may be performed and the substrate will usually exhibit cracking activity upon calcination.

Hydrated alumina gel can be mixed with the substrate particles to form the catalyst. Alternatively the alumina gel can be prepared in the presence of the substrate particles. Preferably the hydrated gel is formed by reacting ammonia with an aqueous solution of an aluminum salt after which the alumina hydrate or alumina hydrate-substrate slurry is washed and the hydrate concentrated as by settling and the aqueous material filtered off. The aluminum salt is generally a sulfate, such as $Al_2(SO_4)_3$ or $NH_4Al(SO_4)_2$. The solution may contain a concentration of about 5 to 20% aluminum salt and the ammonia will generally be added as ammonia water until the desired amount of alumina hydrate is precipitated. During the formation of the alumina hydrate the pH is generally controlled to produce certain characteristics in the alumina hydrate. For example, a catalyst formed from a substrate plus alumina precipitated at a pH greater than 10 has good resistance to nickel, preferably, however, the catalyst is prepared by precipitation of hydrous alumina in the presence of the substrate, at a pH of about 5 to 9. These conditions serve to give a catalyst having the precipitated alumina substantially entirely in the amorphous form as determinable by standard monochromatic X-ray diffraction using a tungsten target. Preferably this hydrated alumina gel is formed at a pH of about 7 to 7.5. Precipitation of alumina from an aqueous solution of an alkali aluminate by addition of an acid may also be employed. Also, the hydrous alumina may be precipitated by hydrolysis from alcohol solutions of aluminum alkoxides although the use of inorganic salts is preferred. The alumina produced in the presence of the substrate and at the pH conditions described, is, upon calcination, mostly amorphous, as distinguished from alumina precipitated at higher pH's, which is crystalline in its form. Generally, about 3 to 100 parts of the hydrous synthetic alumina (dry basis), preferably 10 to 25 parts of alumina, are coated on 100 parts of substrate (dry basis). Thus the finished catalyst contains about 3 to 50% of synthetic alumina on the substrate, preferably about 9 to 20% and the total alumina content of the catalyst is between about 20 and 65 percent, preferably around 25 to 50% dry basis. For example, about 10 to 20 parts synthetic alumina hydrate gel may be added to or mixed with about 100 parts of an acid-treated clay containing about 20% alumina to give a catalyst having a total alumina (natural and synthetic) content of about 27 to 33%. After precipitation the alumina hydrate-substrate slurry is washed and the hydrate concentrated as by settling, and the aqueous material is filtered off, after which the catalyst precursor is thoroughly washed to remove sulfate or other interfering anions.

The substrate particles will generally be provided in a fluidizable particle size and thus the resulting coated material will be fluidizable. Alternatively the coated substrate may be formed to macro-shape by pelleting, extrusion, etc., dried, and generally the catalyst is calcined before use. The physical form of the catalyst varies with the type of manipulative process to which it will be exposed. In fluid processing, gases are used to convey the catalyst between reaction and regeneration zones and to keep it in the form of a dense turbulent bed which has no definite upper interface between the dense (solid) phase and the suspended (gaseous) phase mixture of catalyst and gas. This type of processing requires the catalyst to be in the form of a fine powder, generally in a size range of about 20 to 150 microns or less.

Cracking is ordinarily effected to produce gasoline as the most valuable product and is generally conducted at temperatures of about 750 to 1100° F., preferably about 850 to 950° F., at pressures up to about 200 p.s.i.g., preferably about atmospheric to 100 p.s.i.g., and without substantial addition of free hydrogen to the system. In cracking, the feedstock is usually a mineral oil or petroleum hydrocarbon fraction such as straight run or recycle gas oil or other normally liquid hydrocarbon boiling above the gasoline range. For typical operations, the catalytic cracking of the hydrocarbon feed would normally result in a conversion of about 50–60 percent of the feedstock into a product boiling in the gasoline boiling range.

In this invention, the hydrocarbon petroleum oil utilized as feedstock for the conversion process contains poisoning metal; that is, nickel and in most cases vanadium and perhaps other metals mentioned above. More than one-third part per million of nickel (0.3 p.p.m. measured as NiO) with or without one-half part or more per million vanadium (0.5 p.p.m. measured as V_2O_5) may be in the feedstock and may result from blending a residual feedstock component containing perhaps as much as about 500 or even 1000 p.p.m. metal with a relatively unpoisoned stock of any desired type normally utilized in catalytic conversion operations. The process of this invention is of greatest value in converting feedstocks such as residual and heavy distillate stocks, that is, atmospheric tower bottoms and materials derived therefrom. Such stocks, when blended with relatively unpoisoned stocks, may contain more than about one p.p.m. nickel, with or without vanadium, and the total nickel in the feed may range up to about 5 or 15 p.p.m.

The catalyst is generally used as a fluidized bed, preferably containing at least 40% of particles smaller than 200 mesh, that is, smaller than 74 microns. Preferably at least about 25% of the catalyst particles are in the 40–80 micron range.

Catalytic conversion systems also include regeneration procedures in which the catalyst is periodically contacted with free oxygen-containing gas in order to restore or maintain the activity of the catalyst by removing carbon. Conventionally, fluid catalyst regenerators process about 5–60 tons of catalyst per minute, using about 2000 to 2800 standard cubic feet of air per ton of catalyst. The average residence time for a quantum of catalyst is often about 3–10 minutes. The regeneration rate is generally designed to keep the catalyst in the reactor at a carbon level up to about 1.2% and regenerated catalyst usually has a carbon content of about 0.2 to 0.5%.

As mentioned, this invention usually employs a feedstock more heavily contaminated with nickel than conventional hydrocarbon feeds and employs a nickel resistant catalyst. In accordance with this invention, the use of a semi-synthetic alumina-on-halloysite or kaolin clay catalyst containing about 10 to 65% alumina to crack a feedstock containing more than about one p.p.m. nickel is operable economically with a catalyst having an equilibrium nickel content about two or three times as high as normally causes a severe penalty in cracking activity or selectivity. This level frequently may be "automatically" maintained by the ordinary additions of fresh catalyst to replace fines unpreventably lost in the process, as mentioned above. The catalysts employed in this invention have a further significant advantage in that procedures which have been developed for vanadium removal from a

poisoned cracking catalyst may be applied to these catalysts when the vanadium level is sufficiently high, to give an improvement in subsequent cracking. Some nickel also may be removed in some of these procedures especially when extra high nickel levels are encountered. Such metals removal gives an improvement in subsequent cracking.

A number of procedures have been developed by which vanadium and other poisoning metals may be removed from cracking catalysts, as described, for example, in copending applications Serial No. 767,794, filed October 17, 1958; 849,119, filed October 28, 1959, now abandoned; 19,313, filed April 1, 1960, now abandoned; 39,810, filed June 30, 1960; 53,623, filed September 2, 1960; 54,405, now Patent No. 2,122,510, filed September 7, 1960; 55,160, filed September 12, 1960; 55,703, filed September 13, 1960; 55,838, filed September 14, 1960, now abandoned; 67,518, filed November 7, 1960; 95,101, filed March 13, 1961, now abandoned; 115,617, filed June 8, 1961; and 167,903 filed January 22, 1962; 169,588, filed January 27, 1962, now Patent No. 3,122,511, all of which are hereby incorporated by reference. It has been found, for example, that a chlorination treatment can convert iron and vanadium to easily removable forms. It has also been found that a basic aqueous wash containing ammonium ions is suitable for removal of vanadium poisons as reported in copending application Serial No. 39,810. Also, as pointed out in copending applications Serial Nos. 19,313, and 55,160, a preliminary treatment of the catalyst with molecular oxygen-containing gas is of value in improving the vanadium removed by subsequent procedures. The withdrawal of catalyst from the cracking system can be on a continuous or intermittent basis and ordinarily the catalyst will not be allowed to accumulate more than about 5000 to 7500 p.p.m. of poisoning metal, but the extent of permissible accumulation varies with the type of catalyst. Subjecting the poisoned catalyst sample to magnetic flux may be found desirable to remove any tramp iron particles which may have become mixed with the catalyst.

Treatment of the regenerated catalyst with molecular oxygen-containing gas is frequently employed to improve the removal of vanadium from the poisoned catalyst. This treatment is preferably performed at a temperature at least about 50° F. higher than the regeneration temperature, that is, the average temperature at which the major portion of carbon is removed from the catalyst. The temperature of treatment with molecular oxygen-containing gas will generally be in the range of about 1000 to 1800° F. but below a temperature where the catalyst undergoes any substantial deleterious change in its physical or chemical characteristics, preferably a temperature of about 1150 to 1350° or even as high as 1600° F. The duration of the oxygen treatment and the amount of vanadium prepared by the treatment for subsequent removal is dependent upon the temperature and the characteristics of the equipment used. If any significant amount of carbon is present in the catalyst at the start of this high-temperature treatment, the essential oxygen contact is that continued after carbon removal, which may vary from the short time necessary to produce an observable effect in the later treatment, say, a quarter of an hour to a time just long enough not to damage the catalyst. In any event, after carbon removal, the oxygen treatment of the essentially carbon-free catalyst is at least long enough to convert a substantial amount of vanadium to a higher valence state, as evidenced by a significant increase, say at least about 10%, preferably at least about 100%, in the vanadium removal in subsequent stages of the process. This increase is over and above that which would have been obtained by the other metals removal steps without the oxygen treatment. The maximum practical time of treatment will vary from about 4 to 24 hours, depending on the type of equipment used. The oxygen-containing gas used in the treatment contains molecular oxygen as the essential active ingredient and there is little significant consumption of oxygen in the treatment. The gas may be oxygen, or a mixture of oxygen with inert gas, such as air or oxygen-enriched air, containing at least about 1%, preferably at least about 10% O_2. The partial pressure of oxygen in the treating gas may range widely, for example, from about 0.1 to 30 atmospheres, but usually the total gas pressure will not exceed about 25 atmospheres.

The catalyst may pass directly from the oxygen treatment to a vanadium removal treatment. Such treatment may be a basic aqueous wash such as described in copending patent applications Serial Nos. 767,794 and 39,810. Alternatively vanadium may be removed by a vapor treatment as described in copending applications Serial Nos. 849,199 or 115,617, filed June 8, 1961.

Vanadium may be removed from the catalyst after the high temperature treatment with molecular oxygen-containing gas by washing it with a basic aqueous solution. The pH is frequently greater than about 7.5 and preferably the solution contains ammonium ions which may be NH_4+ ions or organic-substituted NH_4+ ions such as methyl ammonium and quaternary hydrocarbon radicals ammoniums. This aqueous wash solution can be prepared by addition of a dry reagent or a concentrated solution of the reagent to water, preferably distilled or deionized water. Ammonia or methylamine gas may be dissolved directly in water.

The amount of ammonium ion in the solution is sufficient to give the desired vanadium removal and will often be in the range of about 1 to 25 or more pounds per ton of catalyst treated. Five to fifteen pounds is the preferred ammonium range but the use of more than about 10 pounds does not appear to increase vanadium removal unless it increases pH. The temperature of the wash solution does not appear to be significant in the amount of vanadium removed, but may vary within wide limits. The solution may be at room temperature or below, or may be higher. Temperatures above 215° F. require pressurized equipment the cost of which does not appear to be justified. The temperature, of course, should not be so high and the contact should not be so long as to seriously harm the catalyst. The time of contact also may vary within wide limits, so long as thorough contact between the catalyst and the wash solution is assured. Very short contact times, for example, about a minute, are satisfactory, while the time of washing may last 2 to 5 hours or longer.

After the ammonium wash the catalyst slurry can be filtered to give a cake which may be reslurried with water or rinsed in other ways, such as, for example, by a water wash on the filter, and the rinsing may be repeated, if desired, several times. A repetition of the ammonium wash without other treatments seems to have little effect on vanadium removal if the first washing has been properly conducted but repetition of the basic aqueous ammonium wash after a repeated high temperature oxygen treatment usually does serve to further diminish the vanadium content of the catalyst.

Alternatively, after the high temperature treatment with oxygen-containing gas, treatment of a metals contaminated synthetic catalyst with a chlorinating agent at a moderately elevated temperature is under some conditions of value in removing vanadium and iron contaminants from the catalyst as volatile chlorides. This treatment is described in copending applications Serial Nos. 849,199; 54,532 filed September 7, 1960, now abandoned; 55,703; 67,518 and 83,921 filed January 23, 1961. Generally, the major proportion of these volatile chlorides is removed during contact with the chlorinating vapor and where the volatile chlorides are insufficiently removed, a purge with an inert gas such as nitrogen at an elevated temperature may be applied to the chlorinated catalyst. The basic aqueous ammonium wash may be used as a substitute or complement to such a purge.

A conversion to volatile vanadium chloride after the

high temperature oxygen treatment preferably makes use of vapor phase promoted chlorination at a moderately elevated temperature, up to about 700° or even 1000° F., wherein the catalyst composition and structure is not materially harmed by the treatment and a substantial amount of the poisoning metals content is converted to chlorides. The chlorination takes place at a temperature of at least about 300° F., preferably about 550 to 650° F. with optimum results usually being obtained near 600° F. The chlorinating agent is essentially anhydrous, that is, if changed to the liquid state no separate aqueous phase would be observed in the reagent.

The chlorinating reagent is a vapor which contains chlorine or sometimes HCl, in combination wtih a promoter, preferably a carbon or sulfur compound, for example, a chlorine substituted light hydrocarbon, such as carbon tetrachloride, which may be used as such or formed in-situ by the use of, for example, a vapor mixture of chlorine gas with low molecular weight hydrocarbons such as methane, n-pentane, etc.

The stoichiometric amount of chlorine required to convert iron, nickel and vanadium to their most highly chlorinated compounds is the minimum amount of chlorine ordinarily used and may be derived from free chlorine, combined chlorine or the mixture of chlorine with a chlorine compound promoter described above. However, since the stoichiometric amount of chlorine frequently is in a neighborhood of only 0.001 g./g. of catalyst, a much larger amount of chlorine, say about 1–10 percent active chlorinating agent based on the weight of the catalyst is generally used. The amount of chlorinating agent required is increased if any significant amount of water is present on the catalyst so that substantially anhydrous conditions preferably are maintained as regards the catalyst as well as the clorinating agent. The promoter is generally used in the amount of about 1–5 or 10 percent or more, preferably about 2–3 percent, based on the weight of the catalyst for good metals removal; however, even if less than this amount is used, a considerable improvement in metals conversion is obtained over that which is possible at the same temperature using chlorine alone. The amount of promoter may vary depending upon the manipulative aspects of the chlorination step, for example, a batch treatment may sometimes require more promoter than in a continuous treatment for the same degree of eeffctiveness and resuls. The chlorine and promoter may be supplied individually or as a mixture to a poisoned catalyst. Such a mixture may contain about 0.1 to 50 parts chlorine per part of promoter, preferably about 1–10 parts per part of promoter. A chlorinating gas comprising about 1–30 weight percent chlorine, based on the catalyst, together with one percent or more S_2Cl_2 gives good results. Preferably, such a gas provides 1–10 percent Cl_2 and about 1.5 percent S_2Cl_2, based on the catalyst. A "saturated" mixture of CCL_4 and Cl_2 or HCl can be made by bubbling chlorine or hydrogen chloride gas at room temperature through a vessel containing CCl_4; such a mixture generally contains about 1 part CCl_4:5–10 parts Cl_2 or HCl.

Conveniently, a pressure of about 0–100 or more p.s.i.g., preferably about 0–15 p.s.i.g. may be maintained in chlorination. The chlorination may take about 5 to 120 minutes, more usually about 20 to 60 minutes, but shorter or longer reaction periods may be possible or needed, for instance, depending on the linear velocity of the chlorinating and purging vapors.

Vapor phase chlorination may be employed without a promoter to provide for vanadium removal by a later aqueous wash treatment from a synthetic or semi-synthetic catalyst as described in copending applications Serial Nos. 55,838 and 167,903. The aqueous medium may be a water solution of a vanadium chelating agent or a water solution of a reducing agent. The unpromoted chlorination is conducted at more or less the same conditions as the chlorination procedure described above but the chlorinating agent consists essentially of chlorine gas itself. Such chlorination is preceded by sulfidation of the catalyst by exposure to a sulfiding vapor at elevated temperatures. The sulfiding step can be performed by contacting the poisoned catalyst with elemental sulfur vapors, or more conveniently by contacting the poisoned catalyst with a volatile sulfide, such as H_2S, CS_2 or a mercaptan. This step also serves to aid later removal of nickel when such removal is feasible.

The contact with the sulfur-containing vapor can be performed at a pressure from atmospheric to about 1000 p.s.i.g. and an elevated temperature generally in the range of about 750 to 1600° F., preferably about 1000 to 1200° F. The preferred upper pressure limit is about 15 p.s.i.g. Other treating conditions can include a sulfur-containing vapor partial pressure of about 0.1 to 30 p.s.i.g. or more, preferably about 0.5–15 p.s.i.g Hydrogen sulfide is the preferred sulfiding agent. The sulfiding gas may contain about 10 to 100 mole percent H_2S, preferably at least about 80 mole percent H_2S. Pressures below atmospheric can be obtained either by using a partial vacuum or by diluting the vapor with gas such as nitrogen or hydrogen. The time of contact may vary on the basis of the temperature and pressure chosen and other factors such as the amount of metal to be removed. The sulfiding may run, for, say, up to about 24 hours or more depending on these conditions and the severity of the poisoning. Usually about 1–6 hours is a sufficient time. Temperatures of about 900 to 1200° F. and pressures approximating 1 atmosphere or less seem near optimum for sulfiding and this treatment often continues for at least 1 or 2 hours but the time, of course, can depend upon the nature of the treating system, e.g. batch or continuous, as well as the rate of diffusion within the catalyst matrix.

It has been found that sulfidation also causes formation of a characteristic sulfur-vanadium compound on the catalyst surface and that when the catalyst, simultaneously with or subsequent to, the sulfidation is subjected to severe agitation such as is caused by exposure to ultrasonic vibrations, particles of this compound may be pruned from the catalyst surface and may be removed by elutriation with a gas from the catalyst mass.

In practicing this invention at the refinery, a portion of the poisoned catalyst is removed from the hydrocarbon conversion system after being regenerated, is given a high temperature treatment with an oxygen-containing gas at a temperature and for the length of time found to be sufficient to increase vanadium removal without damaging the catalyst, and then the catalyst is washed with the aqueous ammonia solution. The treated catalyst, usually after calcination at about 1050° F. but not so limited can be returned to the unit, for example, to the regenerator. The amount of metal removed in practicing the procedures outlined or the proportions of each which are removed may be varied by proper choice of treating conditions. It may prove necessary, in the case of very severely poisoned catalysts, to repeat the treatment to reduce the metals to an acceptable level.

The following examples of the method of this invention are to be considered illustrative only and not limiting The test cracking procedures reported were performed using conventional evaluation techniques. The feedstock employed in the test cracking was a petroleum hydrocarbon East Texas gas oil fraction having the following approximate characteristics:

IBP	° F.	490–510
10%	° F.	530–550
50%	° F.	580–600
90%	° F.	650–670
EP	° F.	690–710
Gravity (API)	° F.	33–35
Viscosity (SUS at 100° F.)		40–45
Aniline point	° F.	170–175

Pour point	° F.	35–40
Sulfur	percent	0.3
Nickel oxide	p.p.m.	<0.1

A catalyst was made by slurrying a commercially obtained synthetic silica-alumina catalyst (sample 53) in a solution of aluminum sulfate and ammonium hydroxide was added to the solution to precipitate alumina hydrate gel while holding the pH below 7. Excess liquid was drained from the slurry and the substrate-hydrate mixture was washed with deionized water, dried and calcined to produce sample 63. An alumina hydrate gel was precipitated at a pH of about 10, concentrated, washed and added to a portion of sample 53 according to the procedure of U.S. Patent 2,935,463. The mixture was mulled, dried and calcined to produce sample 12. A portion (54) of the catalyst base 53, a portion (67) of catalyst 63 and a portion (21) of catalyst 12 were each artificially poisoned with nickel by absorption of a solution of a nickel chelate of ammonium ethylene diamine tetraacetate. Table I gives the results of test cracking using each of these catalysts. Figures in this table also show the test-cracking results obtained using a chelate-poisoned (sample 26) and unpoisoned (sample 68) catalyst containing a high alumina content, but manufactured by conventional procedures, that is, simultaneous precipitation of silica and alumina from a solution.

Table I

Sample	53	54	68	26	63	67	12	21
Percent Al_2O_3	24.6	24.6	50.6	50.6	36.8	36.8	35.4	35.4
P.p.m. NiO	------	481	------	620	------	489	------	540
Test Cracking:								
Relative Activity	41.0	32.5	79.7	59.5	59.5	56.0	36.0	32.2
Distillate + Loss	36.2	31.8	50.5	43.7	43.7	42.0	33.9	31.7
Gas Factor	0.96	1.22	0.87	1.07	0.80	0.93	1.21	1.09
Coke Factor	0.96	1.20	0.82	1.15	0.70	0.86	1.12	1.06
Gas Gravity	1.31	1.13	1.35	1.13	1.38	1.24	1.21	1.20
Activity Decline:								
Percent	------	20.7	------	25.4	------	5.88	------	10.5
Percent per 100 p.p.m. NiO	------	4.32	------	4.10	------	1.20	------	1.96

These figures show the severe effects of nickel poison on other catalysts, whether of conventional or very high alumina content, while those prepared by the addition of alumina hydrate to a substrate suffer very little from nickel poisoning.

A crude oil containing large amounts of nickel and vanadium contaminants is fractionated to produce a 650° F.+ boiling residual fraction. The residual fraction (atmospheric reduced crude) is solvent deasphalted to produce a gas oil containing about 1 p.p.m. nickel and 3 p.p.m. vanadium. This feedstock is sent to a catalytic cracker at a temperature of about 900 to 925° F. and a pressure of about 5–15 p.s.i.g. under fluidizing conditions. The catalyst is one derived from halloysite clay by acid activation and impregnation with about 23 parts synthetic alumina gel to 100 parts clay. The catalyst contains about 51 weight percent Al_2O_3 and has a bulk density of about 0.805 gm./cc. The cracked products are introduced to a fractionator where approximately 60% gasoline and other low boiling components are removed. The residue, including gas-oil fractions, is recycled to the cracker for further processing. A portion of the silica-alumina catalyst is continuously removed from the cracking reactor and brought to a regenerator. Average residence time in the regenerator is about 5 minutes at a temperature of about 1100° F. before catalyst is returned to the cracking reactor at a carbon level of about 0.4%.

About 0.2 pound of virgin catalyst is added to the cracking reactor for each barrel of fresh feed processed to make up for catalyst which is inadvertently lost from the system or which, due to physical deterioration, is discarded from the system. About 10% of the cracking catalyst inventory, poisoned to a metals level of about 1200 p.p.m. nickel and 960 p.p.m. vanadium, is sent each day as a side stream from the regenerator to demetallization. In the demetallization process the catalyst is held in air for about two hours at about 1300° F. and then chlorinated in a chlorination zone with an equimolar mixture of Cl_2 and CCl_4 at about 600° F. After about 1 hour no trace of vanadium chloride can be found in the chlorination effluent and the catalyst is quickly washed with water. A pH of about 3–4 is imparted to this wash medium by chlorine entrained in the catalyst. The demetallization procedure removes about 25% of the vanadium from the catalyst, but no significant amount (2%) of nickel. The demetallized catalyst is returned to the regenerator.

This application is a continuation-in-part of application Serial No. 100,535, filed April 4, 1961.

It is claimed:

1. A method for producing gasoline in a hydrocarbon cracking system consisting essentially of a catalytic cracking zone and a catalyst regeneration zone between which catalyst is cycled, which consists essentially of cracking at elevated temperature in said cracking zone, a hydrocarbon feedstock heavier than gasoline and containing more than about 0.3 p.p.m. nickel impurities, with a calcined catalyst consisting essentially of about 10 to 65% total alumina prepared by the addition of about 3 to 100 parts by weight of a synthetic alumina hydrate gel to 100 parts of a solid silica-alumina substrate having particles greater than colloidal in size.

2. The method of claim 1 in which the cracking is performed under fluidizing conditions.

3. The method of claim 1 in which catalyst contains about 9 to 20% synthetic alumina hydrate gel added to the substrate.

4. The method of claim 1 in which the catalyst contains about 15 to 50% total alumina.

5. The method of claim 1 in which the substrate is an acid-activated clay.

6. The method of claim 1 in which the feedstock contains residual petroleum hydrocarbons.

7. The method of claim 2 in which the normally liquid hydrocarbon feedstock contains at least about 1 p.p.m. nickel impurities.

8. A method for producing gasoline in a hydrocarbon cracking system consisting essentially of a fluidized catalytic cracking zone and a catalyst regeneration zone between which catalyst is cycled, which consists essentially of cracking at elevated temperature in said cracking zone, a hydrocarbon feedstock heavier than gasoline and containing more than about 0.3 p.p.m. nickel impurities with a calcined catalyst containing about 480 to 1200 p.p.m. NiO and consisting essentially of about 10 to 65% total alumina prepared by the addition of about 3 to 100 parts by weight of a synthetic alumina hydrate gel to 100 parts of a solid silica-alumina substrate having particles greater than colloidal in size.

9. The method of claim 1 in which the catalyst consists essentially of about 15 to 50% total alumina prepared by the addition of about 9 to 20 parts by weight of the synthetic alumina hydrate gel to 100 parts of the solid silica-alumina substrate.

10. The method of claim 8 in which the normally liquid hydrocarbon feedstock contains at least about 1 p.p.m. nickel impurities.

11. The method of claim 1 in which the catalyst has an equilibrium nickel content higher than that which would cause a decrease in cracking selectively of a catalyst without added alumina.

12. The method of claim 8 in which the catalyst consists essentially of about 15 to 50% total alumina prepared by the addition of about 9 to 20 parts by weight of the synthetic alumina hydrate gel to 100 parts of the solid silica-alumina substrate.

13. The method of claim 8 in which the normally liquid hydrocarbon feedstock contains at least about 1 p.p.m. nickel impurities.

14. The method of claim 8 in which a portion of catalyst is bled from the cracking system, vanadium is removed from the catalyst and devanadized catalyst is returned to the cracking system.

15. The method of claim 1 in which the normally liquid hydrocarbon feedstock contains at least about 1 p.p.m. nickel impurities.

16. The method of claim 1 in which the substrate is a synthetic silica-alumina gel.

17. The method of claim 3 in which the substrate is a synthetic silica-alumina gel.

18. The method of claim 7 in which the substrate is a synthetic silica-alumina gel.

19. The method of claim 8 in which the substrate is a synthetic silica-alumina gel.

20. The method of claim 14 in which the substrate is a synthetic silica-alumina gel.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,158,565 November 24, 1964

Robert A. Sanford et al.

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

Column 5, line 35, for "to" read -- or --; column 10, line 69, for the claim reference numeral "8" read -- 9 --.

Signed and sealed this 28th day of September 1965.

(SEAL)
Attest:

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