CRACKING WITH POISON-RESISTANT CATALYST

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This invention is a method for catalytic cracking of mineral oil hydrocarbon feedstocks containing vanadium and nickel. The cracking employs a catalyst having a considerable immunity to the poisoning effects of nickel and the catalyst may be demetalized to remove vanadium.

The feedstock generally contains at least a portion of highly nickel-contaminated residual petroleum hydrocarbon and the cracking method includes processing steps for controlling the level of metal poisons by discarding some portions or demetalizing other portions of the nickel and vanadium contaminated catalyst. These procedures help to improve the catalytic cracking selectivity of the catalyst by keeping catalyst metal contaminants at or below a tolerable level.

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 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. Nickel, vanadium, iron 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, butylene and gasoline, based on converting 60 volume percent of cracking feed to lighter materials and coke dropped from 58.5 to 49.6 volume 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. and 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 process is made economically unfeasible by the poisoning effect of the metal. In most conversion processes some metal-containing catalyst is continuously 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 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.

The present invention provides for procedures where, in the use of moderately high nickel-content feedstocks, the nickel contamination of the catalyst may be controlled by catalyst discard and vanadium contamination of the catalyst may be controlled by subjecting the catalyst to demetalization procedures. Such procedures include contacting the contaminated catalyst with a molecular oxygen-containing gas after conventional regeneration procedures to remove carbonaceous deposits, and subsequently treating the catalyst with a basic aqueous wash containing ammonium ions. 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. The oxide or more or less homogeneous oxide mixture compositions sometimes may also contain small amounts of other inorganic materials, but current practice in catalytic cracking leads 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 particulate material having a coating or deposit of synthetic alumina hydrate on a substrate. The substrate is a solid inorganic oxide mixture, generally a clay or a synthetic silica-alumina gel or a mixture of the two. 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 or 10 to 30% and the combined silica and alumina content is at least about 80 to 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), montmorillonite 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 containing a 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 sub-
microscopic particles which make up a colloid. The sub-
strate particles may be characterized by their lack of elec-
tric 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 super-
natant liquid. All particles suitable for forming the sub-
strate do not grow by accretion or inorganic poly-
erization with each other. The silica-based gel substrate
is generally prepared for alumina deposition by being
washed, dried, if desired, and sized.

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 par-
ticles. 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 Al₂(SO₄)₃
or NH₄Al(SO₄)₂. The solution may contain a concen-
tration of about 5 to 20% aluminum salt and the am-
monia 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, how-
ever, the catalyst is prepared by precipitation of hydrous
alumina in the presence of the substrate, at a pH of about
5 to 9. Preferably this hydrated 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 alu-
mina may be precipitated by hydrolysis from alcohol
solutions of aluminum alkoxides although the use of in-
organic salts is preferred. The alumina produced in the
presence of the substrate and at the pH conditions
described, is, upon calcination, mostly amorphous, as di-
istinguished 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 contained on 100 parts of substrate (dry basis). Thus the finished catalyst contains about 3 to 50% of synthetic alumina on the sub-
strate, preferably about 9 to 20% and the total alumina content of the catalyst is between about 20 and 65 per-
cent, preferably around 25 to 50% dry basis. For ex-
ample, 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 syn-
thetic) 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 inter-
fusing 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 sub-
strate may be formed by macro-shape by pelleting, extru-
sion, 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 ex-
posed. 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 cata-
lyst and gas. This type of processing requires the cata-
lyst 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
temperature between 400°F and 600°F. The optimal temper-
atures for conversion range from 580 to 950°F, at pressures up to about 200 psig, preferably about 100 psig, and without
substantive addition of free hydrogen to the system. In
cracking, the feedstock is usually a mineral oil or petro-
leum hydrocarbon fraction such as straight run or re-
cycle gas oil or other normally liquid or gaseous boil-
ing above the gasoline range. For typical operations, the
hydrocarbon feedstock used as a cracking feed-
stock often contains traces of poisoning metals; the advan-
tageous features of this invention are more fully ex-
plained when the feedstock contains poisoning metal;
that is, nickel and vanadium, and perhaps other metals
mentioned above. More than one-third part per million of
nickel (0.3 p.p.m. measured as NiO) and/or one-half
part or more per million vanadium (0.5 p.p.m. measured
as V₂O₅) may be in the feedstock and may result from
blending a residual feedstock component containing per-
haps as much as about 500 to even 1000 p.p.m. metal
with a relatively unpoisoned stock of any desired type
formally utilized in catalysis. In 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	herfrom. Such stocks, when blended with relatively im-
pure residua, such as coke oven bottoms, may contain more than about one p.p.m. nickel and more than about two p.p.m. vanadium. 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, pref-
erably 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, feed stock re-
generators process about 5–60 tons of catalyst per min-
ute, 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 cata-
lyst 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 feed-
stock having appreciable amounts of vanadium and more
heavily contaminated with nickel than conventional hy-
drocarbon feeds. The invention also 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 and two p.p.m. vanadium is operable economically with a catalyst having an equilibrium nickel weight of catalyst
two or three or even more, times as high as normally
causes a severe penalty in cracking activity or selectivity.
The ability to operate at this higher level of metal on the
catalyst has a number of advantages. By allowing a
greater metal content on the catalyst this invention pro-
vides for a greater metal recovery than with the catalyst
catalysts when the catalyst fines are lost inadvertently or catalyst
particles are deliberately discarded, or when portions of the
reacted catalyst is subjected to demetallization procedures.
In conventional cracking systems the tolerance for poison-
ing metal oxide is seldom greater than about 200 p.p.m.
nickel and/or about 500 p.p.m. vanadium, measured as the oxides. According to this invention, the equilibrium nickel content level may be, and usually is higher than in ordinary cracking systems because of the particular composition of the catalyst, as set forth in this invention. The equilibrium nickel content may be allowed to reach as much as about 1000 p.p.m. NiO and may be maintained by the removal of catalyst from the system either purposely or inadvertently and the introduction of fresh catalyst. As mentioned, catalyst is usually unavoidably removed from the system in the form of fines which leave with effluent gases. In addition to that, when catalyst loss, it has been found expedient to discard purposely enough poisoned catalyst per unit time so that replacement with unpoisoned or less poisoned catalyst will usually keep the nickel content level at the desired equilibrium.

The amount of catalyst discard bears a definite relationship to the amount of nickel contaminant present in the feedstock and the equilibrium nickel content level tolerable in the processing unit. Thus, in the practice of this invention the discard requirement may be embodied in the following equation which defines the amount of catalyst which may be withdrawn to maintain the equilibrium nickel content level tolerable in a particular unit:

\[
Y = \frac{D}{Z} X - S
\]

In this equation Y equals the amount of discard (lbs. of catalyst/ft. of feedstock); X equals the amount of nickel in the feedstock (p.p.m.); Z equals the equilibrium nickel content level tolerable in the unit; D equals the feed density, lbs./ft. 3; and S equals stack loss, lbs. of catalyst/bbl. of feedstock.

Thus for a given desired equilibrium nickel content level and a given nickel content level and a given nickel content in the feedstock, variables which may be chosen or determined by the operator, the amount of discard or loss advantageous for the practice of this invention may be ascertained.

Catalyst discard based on the nickel content of the feed may not be sufficient to keep the vanadium level of the catalyst within tolerable limits because of the generally higher vanadium/nickel ratio in feedstocks and susceptibility of the catalyst to vanadium poisoning. Accordingly, the equilibrium vanadium content level may be maintained, in addition to that achieved concurrently with the discard procedures, by catalyst demetallization which may be accomplished by the intermittent or continuous withdrawal of contaminated catalyst from the cracking system, for example, from the regenerator standpipe. A suitable amount, generally a very small portion of the catalyst, may be removed from the cracking system preferably after the oxidation regeneration which serves to remove carbonaceous deposits. With a continuously circulating catalyst system, such as in the ordinary "fluid" system the portion of catalyst for treating may conven-
iently be an intermittently or continuously removed slipstream of catalyst from the regenerator standpipe.

In a continuous operation of the commercial type a satisfactory withdrawal and removal of vanadium from the poisoned catalyst. This treatment is preferably performed at a temperature at least about 500F. higher than the regeneration temperature, that is, the average temperature at which the major portion of carbon is removed from the catal-

The temperature of treatment with molecular oxygen-containing gas will generally be in the range of about 1000 to 1800F. but below a temperature where the catalyst undergoes any substantial deleterious change in its physical or chemical characteristics, preferably a temperature of about 1350 to 1350F. or even as high as 1600F. 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 latter 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% in the vanadium removal in subsequent stages of the process. This increase is over and above that which would have been obtained by other metals removal step(s) 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 this treatment. The gas may be oxygen, or a mixture of oxygen with inert gas, such as air or oxygen-enriched air, containing at least 1%, preferably at least about 10% O2. The partial pressure of oxygen in the treatment 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.

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 NH4 + ions or organic-substituted NH4 + ions such as methyl ammonium and quaternary hydrocarbon radical ammoniums. This aqueous wash solution can be prepared by addition of a dry reagent or a concentrated solution of the reagent to water. Ammonia or methylamine gas may be dissolved directly in water.

The amount of ammonium ion in the solution is suf-

ficient 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 215F. 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 obtained. 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 re slurried 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 a repetition of the basic aqueous am-
monium wash after a repeated high temperature oxygen treatment usually does serve to diminish further the vanadium content of the catalyst.

In practicing this invention at the refinery, that portion of the poisoned catalyst, usually containing about 0.5 percent of vanadium, which is necessary for nickel control, is removed as discard. This amount of discard (pounds of catalyst per barrel of feedstock) is, as stated above, may conveniently be determined from the relationship existing between it and the feedstock nickel content and the nickel equilibrium concentration. Where necessary, for vanadium control, a portion of regenerated catalyst is also removed and treated with an oxygen-containing gas at a temperature and for a length of time found to be sufficient to increase vanadium removal without unduly damaging the catalyst. Then the treated catalyst is washed with the aqueous ammonia solution and returned to the cracking unit, for example, to the regenerator. The amount of metal removed in practicing the combination of steps, i.e., the discard and demetallization procedures, will control catalyst metal contaminants at or below a tolerable level. In situations where the feedstock nickel content or total metal content becomes excessively high, a nickel demetallization treatment may prove advantageous. Accordingly certain demetallization procedures may be employed such as the sulfiding, chlorination, washing, etc. techniques described below. The chlorination procedures are also helpful for vanadium removal in addition to or substituted for, the vanadium removal techniques described above.

Sulfiding, for instance, may be accomplished by contacting the metal-poisoned catalyst with a sulfur-containing vapor such as elemental sulfur vapors or more conveniently a volatile sulfide such as H₂S, CS₂ or a mercaptan, at a pressure from atmospheric to about 1000 p.s.i.g. and at 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 may include a sulfur-containing vapor partial pressure of about 0.1 to 30 p.s.i.g. or more, preferably about 0.5 to 15 p.s.i.g. Hydrogen sulfide is the preferred sulfiding agent. The sulfiding gas may contain about 10 to 100 mole percent H₂S, preferably at least about 80 mole percent H₂S. 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 nickel to be removed. The sulfiding may be 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.

Subsequent to sulfidation, the metal poisoning catalyst may conveniently be chlorinated at a moderate elevated temperature, up to about 700° or even 1000 °F, wherein the catalyst composition and activity is not materially harmed by the treatment and a substantial amount of the poisoning metal 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 some other halogen, preferably HCI, in combination with a promoter, preferably a carbon or sulfide 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 vaporous mixture of chlorine gas with low molecular weight hydrocarbons such as methane, n-pentane, etc.

The stoichiometric amount of chlorine required to convert the above quantity of catalyst 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 not available for a prolonged contact time with the 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 acid conditions preferably are maintained as regards the catalyst as well as the chlorinating 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 only if 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 a continuous treatment for the same degree of effectiveness and results. 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 30 parts chlorine per part of promoter, preferably about 1–10 parts chlorine per part of promoter. A chlorinating gas comprising about 1–30 weight percent chlorine, based on the catalyst, together with one per cent or more S₂Cl₂ gives good results. Preferably, such a gas provides 1–10 percent Cl₂ and about 1.5 percent S₂Cl₂ based on the catalyst. A "saturated" mixture of CCl₄ and Cl₂ or HCl can be made by bubbling chlorine or hydrogen chloride gas at room temperature through a vessel containing CCl₄; such a mixture generally contains about 1 part CCl₄:5–10 parts Cl₂ 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 the chlorination. The chlorination may take about 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.

After 24 hours or the catalyst may be washed in a liquid aqueous medium to remove, for instance, nickel chloride, preferably after the catalyst is cooled to avoid the use of excessive pressures to maintain the liquid phase. The catalyst structure may be quite sensitive to HCl formed in the treatment, so that several precautions should be observed in the aqueous liquid washing. A greatly excess of water can be used, for instance, sufficient to give a slurry containing only minor amounts of solids. Also, the catalyst should not be allowed to remain in this slurry for too long a time, ordinarily not more than about 5 minutes; a residue time of 2 to 3 minutes in the original wash is general practice.

The water used may be distilled or deionized prior to contact with the chlorinated catalyst. However, the aqueous medium can contain extraneous ingredients in trace amounts, so long as the medium is essentially water and the ingredients do not interfere with demetallization or adversely affect the properties of the catalyst. Temperatures above 212° F. and elevated pressures may be used but the results do not seem to justify the added equipment. The aqueous liquid is preferably acid and a weakly acidic condition may be obtained by the chlorides generally present in a chlorinated catalyst which has not been purged too severely.

After the wash the slurry can be filtered to give a filter...
cake which may be reslurried with more 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. After this or after the final treatment which is to be used in the deactivation procedure, the catalyst is conducted to its conversion system, for instance to the hydrocarbon conversion reactor or catalyst regenerator, although it may be desirable first to dry the catalyst filter cake or filter cake slurry at say about 250 to 450 °F., and also, prior to reusing the cata-
lyst in the conversion operation it can be calcined in air as described above.

Alternative to the removal of nickel contaminants by procedures involving contact of the catalyst with aqueous media after chlorination nickel poison may be removed from the catalyst as the volatile nickel carboxyl by treatment with carbon monoxide, as described in copending applic-
ation Serial No. 47,598, filed April 8, 1960, incor-
porated herein by reference. In such a procedure the catalyst is treated with hydrogen at an elevated tempera-
ture during which nickel contaminant is reduced to the elemental state, then treated, preferably under elevated pressure and at a lower temperature with carbon monoxide, during which nickel carboxyl is formed and flushed off the catalyst surface.

Hydrogenation takes place at a temperature of about 800 to 1600 °F, at a pressure from atmospheric or less up to about 1000 p.s.i.g. with a vapor containing 10 to 100% hydrogen. Preferred conditions are a pressure up to about 15 p.s.i.g. and a temperature of about 1100° to 1300 °F. and a hydrogen content greater than about 80 mole percent. The hydrogenation is continued until sur-
face accumulations of poisoning metals, particularly nickel, are substantially reduced to the elemental state.

Carbotylation takes place at a temperature substantially lower than the hydrogenation, from about ambient time to 300 °F. maximum and at a pressure up to about 2000 p.s.i.g., with a gas containing about 50 to 100 mole percent CO. Preferred conditions include greater than about 90 mole percent CO, a pressure of up to about 800 p.s.i.g. and a temperature of about 100° to 800 °F. The CO treatment generally serves both to convert the ele-
mental metals, especially nickel and iron, to volatile carboxyls and to remove the carboxyls.

The following examples of the method of this invention are to be considered illustrative only and not limiting.

Example I

A crude oil containing nickel and vanadium contami-
nants is fractionated to produce a 650 °F. + boiling resi-
dual fraction. The residual fraction (atmospheric re-
duced crude) is solvent deasphalted to produce a gas oil containing about 1.2 p.p.m. NiO and 2.5 p.p.m. V₂O₅.

This feedstock is sent to a catalytic cracker at a tem-
perature of about 900 to 925 °F. and a pressure of about 5 to 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 after calcination contains about 51 weight percent Al₂O₃, and has 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 recovered. The residue, including gas-oil fractions, is recycled to the cracker for further processing. A portion of the silica-alumina catalyst, about 0.2 pound per barrel of feed, is lost from the system with the effluent gases. Another portion of the silica-alumina catalyst, about 0.2 pound per barrel of feed is continuously removed from the catalyst as discard in order to maintain the equilibrium NiO content at about 1000 p.p.m. This amount was determined according to the equation establishing the relationship between the desired equilibrium nickel content level and the nickel content in equilibrium nickel content level and the nickel content in the feedstock. Consequently about 0.4 pound of virgin catalyst is added to the cracking reactor for each barrel of fresh feed processed to make up for these catalyst losses

The remainder of the catalyst is continuously removed from the demetallization reactor and brought to a regenerator and back to the crack. Average residence time in the re-
generator is about 10 minutes at a temperature of about 1100 °F. to produce a catalyst having a carbon level of about 0.4%. About 20 tons of the cracking catalyst inven-
tory is sent each day as a side stream from the regenerator to demetallization. In the demetallization process the cata-
lyst is held in air for about 3 hours at about 1300 °F. and then cooled to about 300 °F. The catalyst is then slurried with water containing about 10 to 15 pounds of ammonia per ton of catalyst for about 15 minutes and continuously filtered and washed to remove vanadia. The demetalliza-
tion procedure removes about 25% of the vanadium from the catalyst and serves, along with the discard and loss of poisoned catalyst, to control the equilibrium vanadium content level at about 1200 p.p.m. V₂O₅. The demetalled catalyst is returned to the regenerator.

Example II

A 115,000 B/D crude refining operation was modified
so that the operation of its vacuum stills and solvent deasphalting unit produced an increase in fluid cracking feed-
stock from 35,670 B/D to 38,065 B/D with concomitant feedstock metals content increases of from about 0.35 to .60 p.p.m. NiO and about 0.55 to 0.95 p.p.m. V₂O₅.

This increased burden of metals in fluid feed is eco-
nomically handled by the use of a nickel resistant catalyst similar to that described and used in Example I and a sim-
ple demetallization process to remove vanadia. The usual stack loss of 0.2 pound of catalyst per barrel of fresh feed maintained the equilibrium nickel content at or below about 1000 p.p.m. NiO with this feedstock as determined by the relationship defined hereinbefore. The vanadia content was controlled by demetallizing about a 7 tons per day slip-stream of regenerated catalyst by continuously air treating at about 1300 °F. for about 2 hours. The cata-
lyst is cooled to about 600 °F. and slurried with water containing about 10 to 15 pounds of ammonia per ton of catalyst for about 15 minutes and continuously filtered and washed to remove vanadia. The demetalliza-
tion removes about 15% of the vanadia content from the catalyst and serves to control the equilibrium vanadium content level at about 1200 p.p.m. V₂O₅. The demetalled catalyst is returned to the regenerator. It is claimed:

1. A method for producing gasoline in a hydrocarbon
   cracking system having a catalytic cracking zone and a
   catalyst regeneration zone which comprises cracking at
   elevated temperature in said cracking zone a hydrocarbon
   feedstock heavier than gasoline and containing at least
   about 0.3 p.p.m. nickel and at least about 0.5 p.p.m.
   vanadium containing, measured as the oxides, said
   cracking being conducted in the presence of a fluidized
   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 and during which cracking
   the catalyst becomes contaminated with nickel and
   vanadium of said hydrocarbon feedstock, cycling the
   catalyst between the cracking zone and the catalyst re-
   generation zone in which last closed carbon is oxidized at
   an elevated temperature and thereby removed from the cata-
   lyst, discarding from the system that portion of con-
   taminated catalyst which satisfies the equation

\[ Y = \frac{D}{2b} - S \]

where Y equals the catalyst discard, Z equals the desired
equilibrium nickel content level of the catalyst, X equals
the nickel content of the feedstock, D equals the feedstock
density and S equals the stack loss, thereby maintaining
an equilibrium amount of nickel on the catalyst no greater than about 1000 p.p.m., measured as NiO, bleeding a portion of the vanadium-contaminated catalyst from the cracking system, removing vanadium from the catalyst and returning resulting devanadized catalyst to a hydrocarbon cracking system.

2. The method of claim 1 in which the nickel level on the catalyst is maintained between about 200 and 1000 p.p.m., and in which the bled, substantially carbon-free catalyst is contacted for at least about 15 minutes with a gas containing molecular oxygen at a temperature of about 1150 to 1800° F., to increase subsequent vanadium removal from the said catalyst, said subsequent removal being accomplished by converting the vanadium to a compound selected from the group consisting of volatile vanadium salts and vanadium salts dispersible in an aqueous medium, by contact at elevated temperature with a gas reactive with the vanadium.

3. The method of claim 1 in which the liquid hydrocarbon feedstock contains more than about 0.6 p.p.m. nickel and 0.95 p.p.m. vanadium impurities measured as the oxides.

4. The method of claim 1 in which the normally liquid hydrocarbon feedstock contains more than about 1.0 p.p.m. nickel impurities.

5. The method of claim 1 in which the nickel level on the catalyst is maintained between about 200 and 1000 p.p.m.

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