

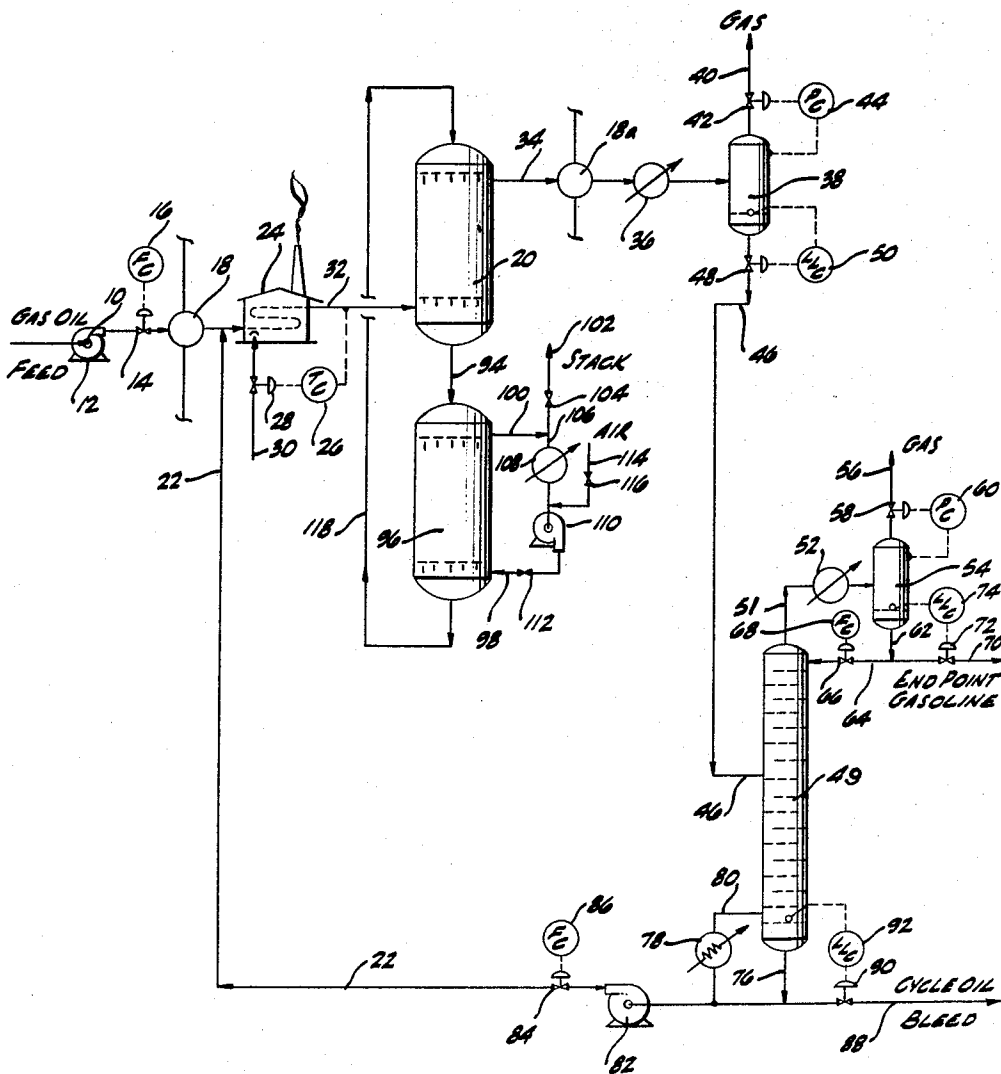
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HYDROCARBON CRACKING PROCESS AND CATALYST

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HYDROCARBON CRACKING PROCESS AND CATALYST

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This invention relates to the conversion of hydrocarbons and particularly to the catalytic cracking of hydrocarbon mixtures which are contaminated with certain organic nitrogen compounds.

A great proportion of automotive and aviation gasoline is produced by the catalytic cracking of higher boiling hydrocarbon fractions of petroleum origin. Specifically, gas oil fractions boiling above about 400° F. and having end points ranging from 600° F. to 800° F. and higher are heated to temperatures of the order of 750° F. to 950° F. and contacted with a cracking catalyst to produce substantial quantities of hydrocarbons boiling below 400° F. in the gasoline boiling range. Part of the feed stock is converted to gas, including hydrogen, and saturated and unsaturated hydrocarbons having from 1 to 4 carbon atoms per molecule. Some heavy hydrocarbonaceous material referred to generally as coke is deposited on the solid catalyst. The effluent from the cracking reaction is cooled and partly condensed, the gas phase is separated from the condensate, and the liquid product is usually stabilized and rerun and used as blending stock for the production of gasolines. This material has a relatively high antiknock rating due to the presence of branched chain paraffin hydrocarbons and olefin hydrocarbons.

The spent catalyst is either periodically or continuously regenerated, depending upon the type of cracking process, by burning in the presence of an oxygen-containing gas to produce a regenerated catalyst which has been freed of the coke deposit. The solid catalyst may be employed in the form of a static bed or in the form of a moving bed of granular solid material, or it may be fluidized in the hydrocarbon stream when the catalyst is in a powdered form. The mesh size range of the catalyst for static and moving bed processes is of the order of from about 2 to about 10 mesh and when a fluidized catalyst is to be used the material is a powder having a mesh size on the order of from 50 to over 200 mesh.

The quantity of gasoline obtained in the process varies with the nature of the feed oils, the temperature of cracking, the contact time with the catalyst, the type and activity of the catalyst, etc. In general gasoline yields on the order of above about 30% by volume of C₅ through 400° F. material based on the volume of gas oil feed can be obtained.

Many petroleum hydrocarbon cracking stocks are normally contaminated with organic nitrogen stocks which are not readily separable and which characteristically deactivate cracking catalysts and thereby reduce the yield of cracked gasoline. In general, the reduction in yield is directly proportional to the amount of organic nitrogen compounds present in the cracking stock. The organic nitrogen compounds which are normally incident in petroleum hydrocarbon fractions contain only nitrogen, hydrogen and carbon (i.e., they do not contain oxygen in the form of nitrates, etc.); accordingly, they are herein

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referred to as "hydrocarbon derivatives of nitrogen." For the most part, they are nitrogen bases or amines. Commonly they are the mono, di, tri, and tetra-alkylated pyridines and quinolines. There are probably other nitrogen compounds present which heretofore have been unidentified. The quantity of these materials in the feed varies with the source and type of the crude oil from which the feedstock is derived. The amount varies from 0.01% to values as high as 0.50%. East Texas gas oils are usually low in nitrogen compounds, and have nitrogen analyses of the order of about 0.01% to 0.02% by weight. There are also nonbasic hydrocarbon derivatives of nitrogen which appear to have a similar catalyst deactivating effect. Apparently these nitrogen-containing materials are readily adsorbed by and deactivate the active cracking centers of the catalyst and thus produce a pronounced deactivating effect.

Previous attempts to overcome these detrimental results have involved acid treating of the feed with dilute sulfuric acid whereby water soluble salts of the nitrogen bases are formed and they are thus readily removed from the feedstock. This however does not remove the nonbasic nitrogen compounds from the feed. Catalytic hydrogenation, such as occurs in desulfurization and denitrogenation in the presence of hydrogen and a catalyst such as cobalt molybdate, will effectively remove substantially all of the organic sulfur compounds but only part of the hydrocarbon derivatives of nitrogen. Frequently the nitrogen analysis of a gas oil feedstock so treated will be of the order of 0.15% by weight. In order to remove substantial quantities of this residual nitrogen, hydrogenation pressures in excess of 5,000 p.s.i. are required. Such a process is extremely expensive and it is at present unwarranted economically. Clay treating of such feedstocks is partially successful in reducing the nitrogen analysis, but sufficient nitrogen compounds remain that the catalyst is rapidly deactivated by these materials.

The present invention is directed to an improved cracking catalyst and cracking process which are substantially immune to the effect of such nitrogen compounds.

It is therefore a primary object of this invention to provide an improved catalytic cracking catalyst process for the cracking of higher boiling hydrocarbon fractions contaminated with hydrocarbon derivatives of nitrogen.

It is a more specific object of this invention to provide a process for catalytically cracking in the presence of a hydrocarbon cracking process and a natural or synthetic zeolitic metallo alumino silicate which is activated by partial dehydration.

It is another specific object of this invention to provide in such a cracking process a cracking catalyst which comprises a physical mixture of a cracking catalyst such as acid treated natural clay and a natural or synthetic zeolitic metallo alumino silicate having pores of at least 7 Å. in diameter.

It is a still further object of this invention to provide in a hydrocarbon cracking process an improved hydrocarbon cracking catalyst comprising a synthetic silica alumina gel prepared in the presence of such a natural or synthetic zeolitic metallo alumino silicate.

Other objects and advantages of the present invention will become apparent to those skilled in the art as the description and illustration thereof proceed.

Briefly, the present invention comprises an improved process and catalyst for hydrocarbon cracking to produce gasoline boiling range materials, which process employs as a catalyst a granular solid hydrocarbon cracking catalyst containing a natural or synthetic zeolitic metallo alumino silicate adsorbent having pores of at least 7 Å.

in diameter. The feedstock is heated to cracking conditions of temperature and pressure and passed in contact with the hydrocarbon cracking catalyst usually in the vapor phase. The solid cracking catalyst may be utilized in the form of a static bed of catalyst granules having a mesh size of about 4 to 8 which is periodically regenerated, or it may be used in the form of a downwardly moving bed of similarly sized granules which are circulated through the hydrocarbon cracking zone and a catalyst regeneration zone. The feedstock vapor may also be treated according to this invention in the presence of a fluidized body of powdered cracking catalyst which is also circulated through a cracking zone.

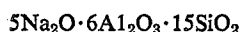
The hydrocarbon cracking step of the process is conducted at temperatures of the order of from 750° F. to 950° F. and at relatively low operating pressures such as between about atmospheric and about 50 p.s.i.g. The catalyst-to-oil ratio on a weight basis may be varied between relatively wide limits customarily employed in cracking processes, namely, between about 0.05 and about 50 pounds of catalyst per pound of oil. Ordinarily, catalyst to oil ratios of the order of about 5 to about 30 are employed with fluidized catalyst and from about 0.1 to about 5 with moving beds of catalyst.

The improved catalytic agent according to the present invention may comprise in part either an acid treated natural clay catalyst of the Filtrol type or the synthetic silica alumina bead catalyst also conventionally employed. The improvement according to this invention in one modification comprises the addition to form a physical mixture of between about 50% and about 99% by weight of either or both of the aforementioned cracking catalysts with between about 1% and about 50% by weight of a natural or synthetic metallo alumino silicate adsorbent having pores of at least 7 Å. in diameter and which exhibits particularly high adsorptive forces for hydrocarbon derivatives of nitrogen in preference to the hydrocarbons of the same or similar boiling ranges. As stated above, this catalytic mixture may be employed as a mixture of granules of about 4 to 8 mesh and contacted with the hydrocarbon feed stream as a static or a moving bed. The mixture may also comprise a physical mixture of powders having mesh ranges of the order of 50 to 200 mesh.

In another modification, the catalyst of this invention is prepared by manufacturing the synthetic silica alumina bead catalyst in the customary way from a hydrous gel which has been formed in the presence of from about 1% to about 50% by weight of the metallo alumino silicate zeolite. This material may be incorporated in the gel prior to the partial dehydration by means of which the zeolite is ordinarily activated. The gel beads thus formed comprise a composite of the silica alumina cracking catalyst and the zeolite. This composite is activated by partial dehydration effected on heating to temperatures of the order of 500° to 1200° F. The resulting catalyst is apparently not necessarily a physical mixture, but appears to behave for purposes of the present invention substantially the same as a physical mixture.

The acid treated natural clay cracking catalysts and the synthetic alumina bead cracking catalysts are well known articles of commerce presently available from catalyst manufacturers. The specific zeolitic metallo alumino silicate employed in the present invention is described in detail below.

The present invention may not be carried out with the commonly available solid granular adsorbents. It has been found that the particular adsorbents which are highly efficient in the preparation of the hydrocarbon cracking catalyst and in the process of the present invention are synthetic crystalline partially dehydrated metallo alumino silicates. The composition of one typical synthetic zeolite having a pore size of about 13 Å. is



It may be prepared by heating stoichiometric quantities of alumina and silica and excess caustic under pressure. The excess is washed out. Other desired metal ions may then be introduced by ion exchange. Part of the sodium in this material can be ion exchanged with concentrated salt solutions at superatmospheric pressure and temperatures of 150–300° C. to introduce other metal ions. For purposes of hydrocarbon cracking in the process of this invention, the pore size must be at least 7 Å., and smaller pores appear to be practically ineffective. The metallo alumino silicate exerts preferential adsorptive forces for hydrocarbon derivatives of nitrogen in great preference to the hydrocarbons of the same boiling range.

In the process of this invention the solid zeolitic material utilized in this hydrocarbon cracking process appears to be deactivated only very slowly. The material may be regenerated to remove the accumulation on the material of traces of very high molecular weight hydrocarbonaceous materials present simultaneously and at the same temperature as are spent cracking catalysts, that is, by passing a dilute oxygen-containing stream in contact therewith at temperatures on the order of 850° to 1100° F. Oxygen concentrations of from 0.1% to about 21% by volume may be used. At the higher catalyst-to-oil ratios where the coke laydown in weight percent of the catalyst is low, pure air may be used.

By using the catalytic material containing the cracking ingredient and the zeolitic ingredient, gas oil contaminated with hydrocarbon derivatives of nitrogen may be cracked at cracking conditions of temperature and pressure to produce gasoline in yields which are substantially the same and in some cases higher than the gasoline yields obtained from the same feedstock from which all of the nitrogen compounds have been removed chemically.

The following table of data indicates the marked poisoning effect upon gasoline yield from gas oil of relatively minute amounts of hydrocarbon derivatives of nitrogen. The feedstock was introduced into a static bed of acid treated natural clay (Filtrol) cracking catalyst at a pressure of about 25 p.s.i.g., and average cracking temperature of 875° F. and at a liquid hourly space velocity measured in volumes of liquid feed per volume bulk catalyst per hour of 0.50. The C₅ to 410° F. gasoline yield is expressed in volume percent of the gas oil feed.

TABLE I
Effect of nitrogen content on gasoline yield

Nitrogen Contamination, Percent by Weight	Gasoline Yield, Volume Percent of Feed
0.016	32.7
0.054	29.7
0.060	24.5
0.182	21.3
0.204	22.7
0.403	18.0
0.431	12.0

It is readily apparent that as little as about 0.3% by weight of nitrogen in the feedstock effectively reduces the gasoline yield by as much as 35%.

According to the principles of the present invention, a Los Angeles Basin gas oil boiling between 400° F. and 760° F. and analyzing 0.34% by weight nitrogen (Kjeldahl) was catalytically cracked at a temperature of 875° F., 25 p.s.i.g. pressure, and 0.50 liquid hourly space velocity. The catalyst employed was a physical mixture of 90% by weight of acid treated natural clay and 10% by weight of a 13 Å. metallo alumino silicate zeolite. The C₅ through 410° F. gasoline yield under these conditions was 31.4% by volume of feed.

This material, spent by a coke deposit after a continued use under the above conditions, was regenerated in the customary manner for hydrocarbon cracking catalysts by contacting it with a mixture of flue gas containing

about 2.5% air and at temperatures ranging from 975° F. to 1050° F. A repeat run under the same conditions produced a gasoline yield of 31.5% indicating that substantially no permanent deactivation of the zeolite is effected under either the cracking or regeneration conditions.

Another catalyst mixture containing 77% by weight of the same acid treated natural clay and 23% by weight of the 13 A. zeolite was employed to crack catalytically the same gas oil feed under the same conditions. The C₅ through 410° F. gasoline yield was 33.4% by volume.

Substantially identical results were obtained using a synthetic metallo aluminosilicate having 10 A. pores.

The addition of metallo aluminosilicates having 4 A. and 5 A. pore diameters gave gasoline yields substantially equal to those listed above in Table I.

The same gas oil feed was cracked catalytically under the same cracking conditions as in the previous examples using 100% by weight of the acid treated natural clay and without the addition of the zeolite. The C₅ through 410° F. gasoline yield was 19.8% by volume of the feed.

It is apparent that the presence of the zeolite in the cracking catalyst mixture effectively neutralizes the catalyst against the adverse effects of the nitrogen compounds present in the feed. It is believed that this effect is due to the fact that the zeolite exhibits a highly preferential adsorption for these same nitrogen compounds in preference to the hydrocarbon compounds of the same boiling range even at cracking temperatures. This has however not been established fully as yet.

In an additional experimental hydrocarbon cracking operation, a physical mixture of 85% by weight of synthetic silica alumina bead cracking catalyst containing several thousandths percent chromium as a regeneration reaction catalyst was mixed with 15% by weight of the 13 A. zeolite. Under the same cracking conditions as in the previous examples the C₅ through 410° F. gasoline yield was 33.2% by volume of the feed.

Catalytically cracking this feedstock in the presence of the synthetic alumina bead catalyst alone under the same conditions produced a gasoline of only 21.2% by volume.

A synthetic silica alumina bead cracking catalyst was prepared by adding 17% by weight of the finished catalyst of the undehydrated and unactivated 13 A. zeolite to the mixed silica alumina gel. This mixture was formed into beads in the conventional manner and partially dehydrated and activated by heating to temperatures in the range of about 950° F. A dry, hard, substantially spherical bead is thus formed containing about 17% of the 13 A. zeolite.

This material was employed under the same conditions as given previously in the catalytically cracking of the same Los Angeles Basin gas oil. The C₅ through 410° F. gasoline yield so obtained was 33.1% by volume.

The catalyst of the present invention successfully overcomes the poisoning effects heretofore noted in the catalytic cracking of gas oils contaminated with substantial quantities of hydrocarbon derivatives of nitrogen. This adverse effect is apparently overcome whether a physical mixture of cracking catalyst and the zeolite is employed or whether the catalyst is simultaneously prepared from a homogeneous material produced by the simultaneous dehydration of a mixture of silica alumina gel and the hydrous precursor of the metallo aluminosilicate adsorbent. The 35% of gasoline yield previously lost due to catalyst poisoning is thus re-obtained through the use of the specific solid contact material of the present invention.

Although the procedures involved in the several types of catalytic cracking processes in general are well known, the use of the catalyst of this invention in a recirculating solids bed cracking process is illustrated in the accompanying drawing which comprises a schematic flow diagram of such a cracking process which employs the improved

catalyst of this invention. It should be understood however that the catalyst of this invention performs as well in static beds, and the following moving bed modification should not be considered as a limitation.

Referring now more particularly to the drawing, the gas oil feed contaminated with hydrocarbon derivatives of nitrogen is introduced through line 10 by means of pump 12 at a rate controlled by valve 14 and flow controller 16. The material is partially heated in exchanger 18 through indirect heat exchange with the effluent from cracking zone 20. This exchange occurs in exchanger 18a. The partially preheated feed may be mixed if desired with a certain quantity of cycle oil flowing through line 22 and the material is introduced into feed heater and vaporizer 24. Herein the feed is vaporized and brought to a temperature of about 860° F. controlled by means of temperature controller 26 in conjunction with valve 28 in fuel line 30. The gas oil vapor at the above indicated temperature is passed through transfer line 32 upwardly through cracking zone 20 countercurrently to a downwardly moving bed of granular solid hydrocarbon cracking catalyst of this invention.

The cracked effluent is removed from cracking zone 20 through line 34 and passed through exchanger 18a in which it is partially cooled in preheating the feedstock. The partially cooled effluent is cooled and condensed in condenser 36 and the mixed stream of vapor and liquid flows into vapor liquid separator 38. From this separator is removed an uncondensed gas fraction by means of line 40 controlled by valve 42 and pressure controller 44. The condensate comprises a mixture of gasoline product and uncracked gas oil. This material is removed through line 46 at a rate controlled by valve 48 in conjunction with liquid level controller 50.

The condensate mixture is introduced into distillation column 49 in which the lighter hydrocarbon fractions pass overhead in the vapor phase through line 51. This material is substantially completely condensed in condenser 52 and introduced into reflux drum 54. A relatively small amount of gas is produced from drum 54 through line 56 controlled by valve 58 and pressure controller 60. The gasoline condensate flows from drum 54 through line 62 and is partly passed through line 64 as reflux to column 49 at a rate controlled by valve 66 and flow controller 68. The remainder is sent to storage or further processing facilities not shown through line 70 at a rate controlled by valve 72 and liquid level controller 74.

Uncracked hydrocarbon materials boiling higher than the desired end point of the gasoline accumulate in the bottom of distillation column 49 and are removed therefrom through line 76. Part of this material is reboiled in reboiler 78 and is returned to the bottom of the column through line 80 supplying heat for the distillation. Another part of this uncracked material may be recycled for re cracking with fresh feed through line 22 by means of pump 82 and at a rate controlled by valve 84 and flow controller 86. Repeated cracking of this cycle oil causes it to become more refractory due to its increased aromatic hydrocarbon content. Accordingly a cycle oil bleed stream is removed through line 88 at a rate controlled by valve 90 and liquid level controller 92 to avoid the buildup of the refractory hydrocarbons.

The spent catalyst, containing its deactivating deposit of coke and apparently the adsorbed hydrocarbon derivatives of nitrogen, is discharged through line 94 from the bottom of cracking zone 20 and flows into catalyst regeneration zone 96. Through regeneration zone 96 is recirculated a regeneration gas comprising a mixture of flue gas and air or other oxygen-containing gas. The regeneration gas is introduced through line 98, and within regeneration zone 96 oxidizes deactivating components and effects their removal with the liberation of heat. The spent flue gas flows through line 100 and part of this gas is discharged through line 102 at a rate controlled by

valve 104 to the stack. The remainder of the flue gas is recirculated through line 106 and regeneration gas cooler 108 by means of recycle blower 110. The flue gas recirculation rate is controlled by valve 112 and a controlled quantity of air or other oxygen-containing gas is introduced through line 114 at a rate controlled by valve 116. The regenerated catalyst is discharged from the bottom of regenerator 96 and is returned by solids conveyor 118 to the top of cracking zone 20 and re-use therein. The conveyor 118 may be any type appropriate to the form of the cracking catalyst. For example, a bucket elevator may be employed to carry granular catalyst from the regenerator to the reactivator. Such catalyst may also be conveyed in the well known pneumatic or gas lift system in which the catalyst granules are suspended in the lift gas stream such as flue gas. If a powdered catalyst is employed it is most conveniently conveyed pneumatically in suspension in such a lift gas.

A particular embodiment of the present invention has been hereinabove described in considerable detail by way of illustration. It should be understood that various other modifications and adaptations thereof may be made by those skilled in this particular art without departing from the spirit and scope of the invention as set forth in the appended claims.

We claim:

1. In a catalytic cracking process wherein a petroleum hydrocarbon feedstock is contacted with a compact bed of a solid active cracking catalyst under hydrocarbon cracking conditions to produce hydrocarbons of the gasoline boiling range, said catalyst being one whose cracking activity is normally adversely affected by the presence of hydrocarbon derivatives of nitrogen in the feedstock, and said feedstock containing hydrocarbon derivatives of nitrogen in amounts sufficient to have an adverse effect on the cracking activity of said catalyst, the improvement which consists in intimately admixing a molecular sieve adsorbent with said catalyst prior to effecting said contacting, said molecular sieve adsorbent being a synthetic solid partially dehydrated zeolitic metallo alumino silicate having substantially uniform pores of between about 7 A. and about 13 A. in diameter; and thereafter contacting said feed stock with the resulting mixture of said adsorbent and cracking catalyst under hydrocarbon cracking conditions.

2. A process according to claim 1 wherein said molecular sieve adsorbent comprises between about 1% and about 50% by weight of the said mixture.

3. A process according to claim 1 wherein said molecular sieve adsorbent has a composition corresponding substantially to $5\text{Na}_2\text{O} \cdot 6\text{Al}_2\text{O}_3 \cdot 15\text{SiO}_2$ and has pores of about 13 A. in diameter.

4. The process for cracking a petroleum hydrocarbon mixture in the presence of an active hydrocarbon cracking catalyst, said hydrocarbon mixture containing hydrocar-

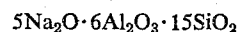
bon derivatives of nitrogen in normally incident amounts sufficient to have an adverse effect on the cracking activity of said catalyst, which process comprises vaporizing said mixture and introducing it into a hydrocarbon conversion zone maintained under hydrocarbon cracking conditions of temperature and pressure, and therein contacting the vaporized mixture with a compact bed of an intimate mixture of said cracking catalyst and a synthetic partially dehydrated zeolitic metallo alumino silicate having substantially uniform pores of between about 7 A. and about 13 A. in diameter, said hydrocarbon cracking catalyst being one which in the absence of said metallo alumino silicate is adversely affected by said hydrocarbon derivatives of nitrogen under said hydrocarbon cracking conditions.

5. A process according to claim 4 wherein said molecular sieve adsorbent has a composition corresponding substantially to $5\text{Na}_2\text{O} \cdot 6\text{Al}_2\text{O}_3 \cdot 15\text{SiO}_2$ and has pores approximately 13 A. in diameter.

6. A process as defined by claim 4 wherein said intimate mixture contains between about 50 and about 99 percent by weight of said hydrocarbon cracking catalyst and between about 1 and about 50 percent by weight of said metallo alumino silicate.

7. A process as defined by claim 4 wherein said intimate mixture is prepared by admixing a hydrous silica-alumina gel with the hydrated precursor of said metallo alumino silicate, and thereafter partially dehydrating the mixture by heating the same to a temperature between about 500° F. and about 1200° F.

8. A process as defined by claim 7 wherein said intimate mixture contains between about 50 and about 99 percent by weight of said silica-alumina gel and between about 1 and about 50 percent by weight of a partially dehydrated zeolitic metallo alumino silicate having substantially uniform pores of about 13 A. in diameter and a composition corresponding substantially to



and said hydrocarbon cracking conditions include a temperature between about 750° F. and about 950° F. and a pressure between about atmospheric and about 50 p.s.i.g.

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