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3,331,768

PROCESS FOR UPGRADING NAPHTHA

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This invention relates to the upgrading of naphtha by selective hydro conversion processes, particularly hydrocracking. More particularly, it relates to the upgrading of naphthas by selective hydrocracking which is accomplished in the presence of a catalyst comprising a specific form of a crystalline metallo alumino-silicate having uniform pore openings of about 5 A.

It is customary to upgrade naphtha fractions for inclusion in the high quality motor gasoline necessary for modern automobiles. Normally, the upgrading will consist of either improving the octane rating or improving the "cleanliness" or gum forming properties of the naphtha. Upgrading of the octane rating is usually accomplished by means of such processes as thermal or catalytic reforming. The desired product is usually of about the same boiling range as the feed, with the molecules having been rearranged or reformed into higher octane-producing compounds. However, the extent of reforming of naphtha and naphtha-containing oils is usually limited

upon aromatics formation for octane improvement, is ineffective with feeds having low cycloparaffin concentration.

It will be realized, therefore, that a conversion process which is capable of selectively converting the low-octane-producing components of the naphtha feed to lower boiling components which are readily removed, with a minimum conversion of the high octane-producing components, is to be highly desired. Removal of the low octane components would thus result in enhancement of the naphtha octane number without appreciably altering its boiling range.

It has now been found that naphthas may be successfully upgraded by contacting them at suitable conditions of temperature and pressure in the presence of hydrogen with a zinc-containing crystalline metallo alumino-silicate zeolite having uniform effective pore openings of about 5 A. By "upgrading" is meant any hydro technique resulting in the formation of an improved or preferred product. This would include improved octane rating and cleanliness, lower sulfur content, etc. The hydro techniques contemplated include such processes as hydrofining, hydrocracking, hydrodealkylation, hydrogen transfer, etc., with the preferred process being hydrocracking. These processes will usually be conducted at elevated temperature and pressure in the presence of hydrogen. The following table sets forth suitable operating conditions for typical hydro techniques contemplated by the present invention.

Operation	Olefin Saturation	Hydrofining	Hydrocracking	Hydrodealkylation
Temperature, ° F.....	300-700	500-750	600-850	800-950
Pressure, p.s.i.g.....	100-3,000	100-1,500	500-2,500	200-1,000
Hydrogen Rate, c.f./b.....	100-5,000	100-3,000	1,000-10,000	1,000-5,000
Feed Rate, v./v./hr.....	0.5-3	0.5-3	0.25-5	0.25-10

owing to the formation of excessive coke as reaction temperature increases. For this reason, such processes as catalytic and thermal reforming and the like are usually designed to avoid excessive coke and dry gas make with, however, a corresponding limitation on the degree of naphtha improvement attainable. Upgrading of "cleanliness" or gum forming properties is also quite important with certain olefinic naphthas, especially naphthas produced in thermal cracking or coking operations. In this case, upgrading is usually accomplished by either passing the naphtha over a catalytic cracking catalyst or by hydrofining. Again the first of these alternates, i.e., catalytic cracking, results in an undesirable high gas and coke make; whereas the second, i.e., hydrofining, results in a loss of octane number.

Attempting at solving the above problems have generally involved one or more hydro techniques such as hydrocracking, hydroforming, hydrodealkylation, etc., which processes tend to form lesser amounts of coke and dry gas while at the same time resulting in improved octane product. However, indiscriminate use of hydrocracking, for example, to upgrade naphthas is often self-defeating since products boiling below the range of the feed are formed, thereby lowering the naphtha yield. Hydroforming or catalytic reforming are also not practical with certain naphtha feeds, e.g., coker naphthas, which contain appreciable sulfur, nitrogen and diolefins, again because of excessive coke make and rapid catalyst deactivation. Also, catalytic hydroforming, which depends

As will be demonstrated in the following examples, the catalyst used in the present invention has been found to be highly effective for the upgrading of naphtha feeds. Markedly improved octane number is achieved with a very low loss in naphtha yield, and a substantially lower coke make than that experienced in catalytic cracking. It should be emphasized that the zinc 5 A. alumino-silicate zeolite need not be combined with a metallic catalytic hydrogenation component, and yet effective selective hydrocracking can be achieved.

As an additional preferred embodiment of the present invention, it has been found that the activity and effectiveness of the catalysts used herein may be substantially improved by contact with sulfur prior to their use in the selective hydrocracking processes. The catalyst is preferably sulfactivated to enhance its activity by contact either with a sulfur-containing feed or, if the feed has a low sulfur content, with hydrogen sulfide or an added sulfur compound which is readily convertible to hydrogen sulfide at the hydro conditions employed, e.g., carbon disulfide, etc. The extent of this sulfactivation treatment should be sufficient to incorporate 0.5 to 15 wt. percent sulfur into the catalyst. The beneficial effect of sulfactivation will be demonstrated in the examples to follow.

It is fully recognized that the prior art has taught the cracking of various petroleum and hydrocarbon materials with crystalline alumino-silicate zeolites commonly referred to as molecular sieves. For example, U.S. Patents Nos. 2,971,903 and 2,971,904 disclose various hydro-

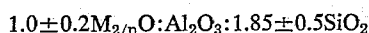
carbon conversion processes employing crystalline aluminosilicates having uniform pore openings between about 6 and 15 Å. As mentioned above, the present invention employs crystalline aluminosilicates having uniform pore openings of about 5 Å., which pore size has been found to be necessary and critical to the successful upgrading of the naphtha feeds contemplated. The prior art has also recognized the possibility of selectively converting normal paraffins by means of 5 Å. molecular sieves for such purposes as dewaxing, etc. These uses derive from the ability of these crystalline zeolite materials to selectively admit certain sized molecules into their pores while rejecting others. Since these materials are now well known adsorbents and catalysts, they provide highly efficient and valuable tools for selectively converting specified constituents of a hydrocarbon feed. For example, U.S. Patent 3,039,953 discloses the selective conversion of normal paraffins with a 5 Å. molecular sieve zeolite. Also, U.S. Patent 3,140,322 relates generally to selective catalytic conversion utilizing crystalline zeolites, and mentions dehydration, catalytic cracking, hydrogenation, etc.

The present invention is to be distinguished from these and similar teachings. Firstly, the 5 Å. crystalline aluminosilicate employed herein in the zinc cation exchanged form can be free of any metallic hydrogenation catalyzing component and yet will surprisingly and uniquely exhibit selective hydrocracking activity. Reference to the aforementioned U.S. 3,140,322, for example, indicates that the selective hydrogenation process therein disclosed was accomplished with a crystalline aluminosilicate zeolite catalyst having the usual metallic hydrogenation component such as platinum or palladium combined therewith. Again, the catalyst used in the present invention need not include such metallic hydrogenation component and yet, surprisingly, is a highly effective hydroconversion catalyst.

Secondly, the present invention is to be further distinguished from the above prior art teachings by the surprising discovery that a particular 5 Å. crystalline aluminosilicate zeolite; namely, the zinc-containing form, is so superior to other cation exchanged forms, including the nickel form, as to clearly be the material of choice. The use of the surprisingly more active zinc form in the process of the invention is therefore to be regarded as essential.

The process of the invention should also be distinguished from the conventional adsorption-desorption processes which are well known in the art. The present process involves selective treatment of certain less desired components to lower boiling components and does not involve merely a mechanical separation as does the conventional adsorption-desorption phenomenon. For example, the increase in octane number of the naphtha product is due to conversion of normally liquid, straight chain hydrocarbons, both paraffinic or olefinic, to butane and lighter components. The converted products are not retained within the pores of the zeolite which remain relatively free of hydrocarbons, and a desorption step is unnecessary thereby making the process economically attractive.

The crystalline metallo aluminosilicate zeolites having uniform pore openings of about 5 Å. contemplated for use in this invention are well known and available in synthetic or natural form. For example, a suitable starting material, referred to as "Zeolite A" in U.S. Patent 2,882,243, has a molar formula (dehydrated form) of



where M is a metal usually sodium and n is its valence. It may be prepared by heating a mixture containing Na_2O , Al_2O_3 , SiO_2 , and H_2O (supplied by suitable source materials) at a temperature of about 100° C. for 15 minutes to 90 hours or longer. Suitable ratios of these reactants are fully described in the aforementioned patent.

One suitable process for preparing such materials synthetically involves, for example, the mixing of sodium silicate, preferably sodium metasilicate, with sodium aluminate under carefully controlled conditions. The sodium silicate employed should have a ratio of soda to silica between about 0.8 to 1 and about 2 to 1, and the sodium aluminate may have a ratio of soda to alumina in the range of from about 1 to 1 to about 3 to 1. The amounts of the sodium silicate and sodium aluminate solutions employed should be such that the ratio of silica to alumina in the final mixture ranges from about 0.8 to 1 to about 3 to 1 and preferably from about 1 to 1 to about 2 to 1. Preferably, the aluminate is added to the silicate at ambient temperature with sufficient agitation to produce a homogeneous mixture. The mixture is then heated to a temperature of from about 180° to about 215° F. and held at that temperature for a period of from about 0.5 to about 3 hours or longer. The crystals may be formed at lower temperatures but longer reaction periods will be required. At temperatures above about 250° F. a crystalline composition having the requisite uniform size pore openings is not obtained. During the crystallization step, the pH of the solution should be maintained on the alkaline side, at about 12 or higher. At lower pH levels, crystals having the desired properties are not as readily formed.

The products produced by the above procedure will have uniform pore openings of about 4 Å. as produced in the sodium form. They may then be converted to products having uniform pore openings of about 5 Å. by replacement of the sodium via conventional ion-exchange techniques with various cations such as calcium, magnesium, cobalt, nickel, iron, manganese, zinc, etc., all of which are not suitable for purposes of this invention.

Natural zeolites having effective pore diameters of about 5 Å. are also herein contemplated and will include such materials as erionite, chabazite, analcite, mordenite, lebrynite, natrolite, etc. Thus, both the natural and synthetic varieties of 5 Å. zeolites are contemplated with the only limitation being one of pore size. As indicated, the pore size must be sufficient to substantially admit the straight chain hydrocarbons but insufficient to admit the valuable high octane producing components, such as the aromatics, so as to avoid their hydrocracking. This capacity should, therefore, be demonstrated at the particular hydrocracking conditions contemplated, since the effective pore diameter of these zeolite materials often varies with temperature and pressure.

In accordance with the invention, it has been found that indiscriminate use of the above-mentioned cations is not suitable for the selective hydrocracking process of the invention. More particularly, it has been found that the cation utilized must specifically be a polyvalent, difficultly reducible cation. By "difficultly reducible" is meant a cation which is not reducible to a lower valence state or to the free metal by hydrogen at the hydrocracking conditions utilized. Of the above-mentioned cations, only manganese and zinc have been found suitable for purposes of the present invention, with zinc being so substantially better than manganese that it is the cation of choice. Thus, the catalyst used in the present invention is prepared from a crystalline aluminosilicate which, after zinc cation exchange, has uniform effective pore openings of about 5 Å. in diameter. The most preferred cation solution will be an aqueous solution of a zinc salt such as zinc chloride, zinc acetate, etc. The extent of ion exchange should be sufficient to reduce the alkali metal, e.g. sodium content, of the zeolite to less than about 5 wt. percent, preferably less than about 1 wt. percent. It will be understood that although the most preferred catalysts will be prepared by using zinc cation as the sole exchanging cation, the presence of zinc together with other exchanging cations will also be highly useful. Thus, the zinc may be introduced alone or with other polyvalent

cations by either ion-exchanging the zeolite with mixed salt solution or by sequential ion-exchange treatments. Preferably the zeolite will have a major portion of its cation content supplied by zinc with perhaps minor portions of residual sodium as well as minor portions of other ions which may also have been introduced via ion exchange for various purposes.

The feedstocks contemplated for use in the present process will generally be naphtha or high naphtha-containing feeds and may consist of either low boiling or high boiling naphthas. A typical low boiling feed has a boiling range of about 50 to 350° F., preferably 80 to 200° F., whereas the heavy naphtha has a boiling range of 275 to 550° F., preferably 300 to 450° F. These naphthas, both low boiling and high boiling, are exemplified by virgin naphtha fractions such as C₅-C₆ naphtha, heavy virgin naphtha, heavy coker naphtha, heavy steam cracked naphtha, heavy catalytic naphtha, etc.

The invention will be further understood by reference to the following examples which are given for illustrative purposes.

Example 1

This example illustrates the preparation and use of a zinc-containing crystalline alumino-silicate having uniform pore openings of about 5 Å. in the selective hydrocracking of a heavy coker naphtha feed and a C₅-C₆ naphtha feed. The zinc crystalline alumino-silicate was prepared as follows:

A charge of 500 grams of commercial sodium "Zeolite A" having pore openings of about 4 Å. in diameter and a silica to alumina mole ratio of about 2:1 was suspended in 2000 grams of water and a solution containing one

TABLE I.—SELECTIVE HYDROCRACKING] OF NAPHTHAS

	Feed			
	Heavy Coker Naphtha		Light C ₅ -C ₆ Naphtha	
	Feed	Product	Feed	Product
Product Distribution, wt. percent:				
C ₁ -----		1.3		1.2
C ₂ -----		1.2		1.3
C ₃ -----		7.6		18.0
C ₄ -----		6.8		7.8
C ₅ +-----	100	83.1	100	71.7
Inspections C ₅ -430° F., Octane Number Data:				
Research, Clear-----		64.0	57.2	72.9
Research plus 3 cc. TEL-----	49.8	80.8	83.0	91.2
Motor, Clear-----		61.1	57.3	72.0
Motor plus 3 cc. TEL-----	67.3			92.0

The excellent catalyst performance with the light C₅-C₆ naphtha is attributed to previous sulfactivation by the sulfur in the coker naphtha feed which initially contacted the catalyst. The octane number improvement in the coker naphtha feed, which ordinarily does not respond well to conventional treatment such as hydroforming, is considered to be outstanding.

The superior upgrading ability of the selective hydrocracking process of the invention is compared to conventional hydrofining or catalytic cracking in the following table.

TABLE II.—SELECTIVE HYDROCRACKING vs. HYDROFINING OR CATALYTIC CRACKING HEAVY COKER NAPHTHA FEED

Operation	Feed	Selective Hydrocracking	Hydrofining	Catalytic Cracking
		Catalyst		
		Zn 5° A. Zeolite A	Cobalt Molybdate on Alumina	Silica-Alumina
Temperature, ° F.-----		850	550	900
Pressure, p.s.i.g.-----		500	1,000	Atm.
Inspections, C ₅ -430° F.:				
Yield, Vol. percent-----	100	179.4	199	73.3
Research Octane No. plus 3 cc. TEL-----	49.8	80.8	60	50.6
Motor Octane No. plus 3 cc. TEL-----	67.3		71.3	77.1
Nitrogen, wt. percent-----	0.03	0.01	0.01	
Sulfur, wt. percent-----	0.22	0.11	0.02	0.16
Feed Lost as Coke, wt. percent-----		0.16	<1.0	2.3

¹ C₅+ yield.

pound of zinc chloride in 500 cc. of water was added slowly with good agitation at ambient temperature. Agitation was continued at ambient temperature for at least 4 hours. The suspension was allowed to settle, the mother liquor was removed by filtration. This procedure was performed on the wet solids two more times so that the total number of exchanges was three. After the third exchange the product was water washed by reslurrying in about 2000 cc. of water for about one hour followed by removal of the wash liquid by filtration. The wash was repeated two times and the product dried. The sodium content of the product was found to be 0.83%. The dried product was pelleted and charged to small pilot plant reactors, heated in a hydrogen stream at atmospheric pressure and 850° F., and used to successively selectively hydrocrack the above feeds at 0.5 v./v./hr., 500 p.s.i.g., and a hydrogen rate of 2000 to 3000 s.c./bbl. of feed. The results are shown in the following table.

The superior performance of selective hydrocracking with the zinc 5 Å. zeolite is thus illustrated. A substantial amount of hydrofining and hydrodenitrogenation was also realized.

Example 2

This example demonstrates the superiority of the zinc modification of the catalyst of the invention over other cationic forms. The catalyst of Example 1 was used. An Arabian C₅-C₆ light naphtha having a boiling range of 110° to 156° F. (95% overhead) and a sulfur content of 1% was employed as the feedstock. The catalyst was sulfactivated by contact with the feed containing 1% added carbon disulfide. Catalyst performance was measured by the disappearance of normal C₅ and C₆ paraffins and their conversion to C₄- gas produced by selective hydrocracking of these components. The results are shown below in Table III.

TABLE III.—SELECTIVE HYDROCRACKING OF ARABIAN C₅-C₆ NAPHTHA (1% CS₂)
[850° F., 500 p.s.i.g., 0.5 v./v./hr., about 2000 c.f./b. exit hydrogen rate]

	Feed	Cation Modification of Zeolite				
		Zn	Ca	Mg	Mn	Ni
C ₄ - Product, wt. percent.....	1.8	45.7	7.6	11.4	17.3	5.6
Disappearance of n-C ₅ +n-C ₆ , wt. percent.....		37.3	9.1	8.6	12.4	4.8
n-C ₅ in Total Product, wt. percent.....	24.2	7.6	17.7	18.0	17.1	19.8
n-C ₆ in Total Product, wt. percent.....	22.9	2.2	20.3	20.5	17.6	22.5

It is observed that the zinc modification of the catalyst produced the greatest reduction in normal C₅ and normal C₆ content, and that the nickel modification, which contained a recognized hydrogenation component, gave the poorest performance. The manganese modification, although not comparable to the zinc form, was somewhat more active than either the calcium or magnesium forms.

the other ion modifications were relatively unresponsive to sulfactivation. Of these other modifications the manganese form appeared to be most responsive to sulfur activation, although much less than the zinc form. Selective hydrocracking in all of these operations is demonstrated by the high ratio of paraffins to olefins in the C₄- gas.

Example 4

To demonstrate the advantage of the selective hydrocracking process of the invention, the zinc catalyst of the previous examples was used for the selective catalytic cracking of the Arabian C₅-C₆ naphtha feed at the same temperature and feed rate but in the absence of hydrogen pressure and hydrogen flow. (To avoid effects of extraneous gases the system was purged with nitrogen and then with hydrogen, and hydrogen was present at one atmosphere pressure at the start of the operation.) The results, as compared to those obtained by selective hydrocracking, are shown below.

TABLE V.—SELECTIVE HYDROCRACKING VS. SELECTIVE CATALYTIC CRACKING ARABIAN C₅-C₆ NAPHTHA FEED; ZINC 5 A. ZEOLITE CATALYST
[850° F.; 0.5 v./v./hr.]

Operation	Feed	Hydrocracking		Catalytic Cracking	
Pressure, p.s.i.g.....		500	500	0 (Atm.)	0 (Atm.)
Exit Hydrogen Rate, c.f./b.....		2,000	2,000	0	0
Extraneous Sulfur in Feed as CS ₂ , wt. percent.....		0	1	0	1
C ₄ - Product, wt. percent.....	1.8	10.1	45.7	1.6	6.8
Disappearance of n-C ₅ +n-C ₆ , wt. percent.....		9.8	37.3	4.1	6.9
n-C ₅ in Total Product, wt. percent.....	24.2	17.9	7.6	19.8	19.0
n-C ₆ in Total Product, wt. percent.....	22.9	19.4	2.2	23.3	21.2
Ratio, Paraffin/Olefin in C ₄ - Gas.....		36	88		3.3

Example 3

As previously indicated, sulfactivation of the catalyst of the invention is to be preferred. To demonstrate this, the catalysts of Example 2 were tested prior to contact with added sulfur and all showed reduced activity. Test conditions were the same as in Example 2, except that the feed was free of sulfur compounds. The results of these tests are summarized below in comparison with the excellent results obtained with sulfur-promoted zinc catalyst.

The disappearance of normal paraffins, the amount of C₄- gas from the selective hydrocracking of the normal paraffins, and the high ratio of paraffins to olefins in the C₄- gas, all demonstrate the superiority of the hydro operation as compared to the non-hydro operation.

Example 5

Foregoing examples have illustrated selective hydrocracking of normal paraffins with sulfactivated zinc 5 A.

TABLE IV.—SELECTIVE HYDROCRACKING OF ARABIAN C₅-C₆ NAPHTHA
[850° F., 500 p.s.i.g., 0.5 v./v./hr., about 2000 c.f./b. exit hydrogen rate]

	Feed	Cation Modification of Zeolite					
		Zn	Zn	Ca	Mg	Mn	Ni
CS ₂ in Feed, wt. percent.....		1	0	0	0	0	0
C ₄ - Product, wt. percent.....	1.8	45.7	10.1	10.1	11.1	15.5	9.9
Disappearance of n-C ₅ +n-C ₆ , wt. percent.....		37.3	9.8	10.0	11.2	12.9	8.9
n-C ₅ in Total Product, wt. percent.....	24.2	7.6	17.9	18.1	16.6	16.7	17.7
n-C ₆ in Total Product, wt. percent.....	22.9	2.2	19.4	19.0	19.3	17.5	20.5
Ratio, Paraffin/Olefin in C ₄ - Gas.....		88	36	10	12	19	11

As shown above, in the absence of sulfur, hydrocracking activity was substantially reduced. Under sulfur-free conditions the manganese modification may be considered to be slightly more active than the zinc. When the above data are compared to those of Example 2, remarkable enhancement in hydrocracking activity of the zinc modification in the presence of sulfur is observed, whereas

zeolite catalyst leaving the aromatics, naphthenes and branched paraffins essentially unreacted. The selective properties of the zinc zeolite 5 A. catalyst is demonstrated further by comparison with a zinc faujasite catalyst having pore openings of about 10-13 Å. The latter has greater hydrocracking activity, but is relatively non-selective, as indicated by conversion of aromatics and

other desired high octane components. The comparison is shown below.

TABLE VI—SELECTIVE HYDROCRACKING OF ZINC FAUJASITE VS. ZINC 5 A. ZEOLITE ARABIAN C₅-C₈ NAPHTHA FEED

[500 p.s.i.g., 0.5 v./v./hr., about 2,000 c.f./b. exit H₂ rate]

	Feed	Catalyst		
		Zinc 5 A. Zeolite	Zinc Faujasite	
Catalyst Activation		Hydro Feed+1% CS ₂		
Activation Temperature, ° F.		850	700	700
Operating Temperature, ° F.		850	700	600
CS ₂ in Feed During Operation, wt. percent.		1	1	0.25
Product Yields:				
n-C ₅ , wt. percent.	24.2	7.6	8.3	18.3
n-C ₆ , wt. percent.	22.9	2.2	2.9	18.7
C ₅ /K Fraction, wt. percent.	98.2	54.3	34.8	88.5
Mass Spectrograph Analysis of C ₅ +200° F. Portion:				
Aromatics, wt. percent.	1.5	4.2	0.3	0.5
Naphthenes, wt. percent.	8.7	16.2	4.0	3.2
Paraffins, wt. percent.	89.8	79.6	95.7	96.3

As indicated, the zinc faujasite produced more extensive overall hydrocracking, but of a relatively non-selective nature, as indicated by the loss of aromatics and naphthenes.

What is claimed is:

1. A process for improving the octane rating of naphtha fractions which comprises contacting said fractions at elevated temperature and pressure in the presence of hydrogen with a sulfactuated catalyst comprising a zinc-containing crystalline aluminosilicate zeolite having uniform pore openings of about 5 Å.

2. The process of claim 1 wherein the sodium content of said zeolite is less than about 5 wt. percent.

3. The process of claim 1 wherein the sodium content of said zeolite is less than about 1 wt. percent.

4. The process of claim 1 wherein a major proportion of the cation content of said zeolite is supplied by zinc cation.

5. The process of claim 1 wherein said catalyst is sulfactuated by contact with a sulfur-containing compound.

6. The process of claim 1 wherein said catalyst is sulfactuated by contact with a sulfur-containing feed.

7. The process of claim 1 wherein said naphtha fractions are essentially sulfur-free and wherein a sulfur compound capable of being converted to hydrogen sulfide at said conditions is added to said naphtha fractions, whereby said catalyst becomes sulfactuated by contact therewith.

8. The process of claim 1 wherein said catalyst is sulfactuated by contact with hydrogen sulfide.

9. A process for improving the octane rating of naphtha fractions by selectively hydrocracking straight chain hydrocarbons contained therein which comprises contacting said naphtha fractions at hydrocracking conditions in the presence of hydrogen with a sulfactuated catalyst comprising a crystalline aluminosilicate zeolite having uniform pore openings of about 5 Å., said zeolite having a major proportion of its cation content supplied by zinc cation, and recovering a naphtha product of improved octane rating.

10. The process of claim 9 wherein said catalyst is otherwise free of added metallic hydrogenation component.

11. The process of claim 9 wherein said catalyst is sulfactuated by contact with a sulfur-containing compound.

12. The process of claim 9 wherein said naphtha frac-

tions are substantially sulfur free and wherein a sulfur compound capable of being converted to hydrogen sulfide at said hydrocracking conditions is added to said feedstock, whereby said catalyst becomes sulfactuated by contact with said feedstock.

13. A catalyst composition comprising a sulfactuated zinc-containing crystalline aluminosilicate zeolite having uniform pore openings of about 5 Å.

14. The composition of claim 13 wherein a major proportion of the cation content of said zeolite is supplied by zinc cation.

15. The process of claim 5 wherein said contacting with sulfur-containing compound is sufficient to incorporate 0.5 to 15 wt. percent sulfur into said catalyst.

16. The process of claim 11 wherein said contacting with sulfur-containing compound is sufficient to incorporate 0.5 to 15 wt. percent sulfur into said catalyst.

17. The process of claim 1 wherein said temperature is within the range of 600° to 850° F. and wherein said pressure is within the range of 500 to 2500 p.s.i.g.

18. The composition of claim 13 which contains about 0.5 to 15 wt. percent sulfur.

19. The process of claim 9 wherein said hydrocracking conditions include a temperature of 600° to 850° F., a pressure of 500 to 2500 p.s.i.g., a hydrogen rate of 1000 to 10,000 cubic feet per barrel and a feed rate of 0.25 to 5 v./v./hr.

20. A process for selectively hydrocracking naphtha fractions containing straight-chain hydrocarbons and non-straight chain hydrocarbons to thereby improve the octane rating which comprises contacting said fractions in a catalyst zone maintained at elevated temperature and pressure, flowing a substantial amount of hydrogen gas into said pressurized catalyst zone, and recovering naphtha product having a substantially reduced straight-chain hydrocarbon content and a substantially improved motor octane rating, wherein the catalyst in said zone comprises a sulfactuated, crystalline aluminosilicate zeolite having uniform pore openings of about 5 angstrom units and containing zinc.

21. The process of claim 20, wherein said zinc is in the cationic form and wherein said catalyst contains about 0.5 to 15 wt. percent sulfur.

22. The process of claim 21, wherein said temperature is within the range of 600° to 850° F. and wherein said pressure is within the range of 500 to 2500 p.s.i.g.

23. The process of claim 20, wherein said zeolite has a major proportion of its cation content supplied by zinc cation.

24. A catalyst composition comprising a sulfactuated crystalline aluminosilicate zeolite having uniform pore openings of about 5 angstrom units, said zeolite containing zinc but being otherwise free of added metallic hydrogenation component.

25. The process of claim 1, wherein said zinc-containing catalyst is otherwise free of added metallic hydrogenation component.

26. The process of claim 20, wherein said zinc-containing catalyst is otherwise free of added metallic hydrogenation component.

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