

SPECIFICATION

Improved hydrodewaxing catalyst performance

This invention relates to a catalytic hydrodewaxing process utilizing a catalyst comprising acidic crystalline zeolitic material of a group such as ZSM-5 which has had its properties enhanced by controlling its alpha activity to within a certain specified range prior to its use in the hydrodewaxing operation. 5

Hydrocarbon conversion processes utilizing crystalline aluminosilicate zeolites have been the subject of extensive investigation as is obvious in both the patent and scientific literature. Catalytic hydrodewaxing operations utilizing ZSM-5 type zeolites are also known in the art and it is also generally known that the performance of these zeolites will be enhanced by treatment of the same with steam. In this connection, United States Patent 3,700,585 discloses and claims a hydrodewaxing operation utilizing ZSM-5 type zeolites and at column 8, lines 6 and following, points out that catalysts of improved selectivity and having other beneficial properties in some hydrocarbon conversion processes, such as catalytic cracking are obtained by subjecting the zeolite to treatment with steam at elevated temperatures ranging from about 427 to 816°C and preferably 538 to 760°C. That patent does not contain any specific examples of steaming a ZSM-5 type zeolite and the subsequent use thereof in hydrodewaxing operations. 10 15

United States Patent 4,053,532 is directed towards a hydrodewaxing operation involving a Fischer-Tropsch synthesis product utilizing ZSM-5 type zeolites. However, at column 11, lines 20 and following, it is disclosed that a further improvement can be realized in the Fischer-Tropsch operation or in hydrodewaxing a heavy gas oil stream with a ZSM-5 class of crystalline zeolites with respect to catalyst aging rate if the catalyst is preconditioned with a hydrogen/steam mixture. 20

United States Patent 3,755,145 is directed towards lube oil hydrocracking with ZSM-5 type zeolites utilizing a mixture of ZSM-5 containing a hydrogenation component and another zeolite. That patent discloses at column 5, that steaming of the catalyst mixture is beneficial. 25

United States Patent 3,956,102 is concerned with a process involving the hydrodewaxing of petroleum distillates utilizing a ZSM-5 type zeolite catalyst. That patent does not contain any specific disclosure of steaming of ZSM-5 type zeolites but it does refer to previously mentioned United States Patent 3,700,585 at column 1, lines 66 and following. 30

The present invention is based on the observation that the catalytic performance of certain acidic zeolite-containing catalysts can be improved by controlling the alpha activity of the catalyst to within the range of 55—150. The invention is directed towards an improvement in connection with the known technique of using catalysts comprising acidic zeolites such as those of the ZSM-5 type in hydrodewaxing operations and it resides in modifying such zeolites in order to obtain catalysts having a critical range of alpha values. 35

Although it had been previously known that steaming might be beneficial in enhancing the catalytic performance of certain zeolites in hydrodewaxing operations, nevertheless, this invention represents an improvement over the previously known state of the art in that it has now been discovered that there is a critical range of alpha values wherein catalytic performance can be optimized for hydrodewaxing operations. 40

In accordance with the present invention, there is provided a process for hydrodewaxing a petroleum or synthetic hydrocarbon charge which comprises contacting the charge in the presence of hydrogen, at elevated temperature and pressure, with a catalyst comprising an acidic crystalline aluminosilicate zeolite, the zeolite having a pore diameter greater than 5 Ångströms, a silica-to-alumina ratio of at least 12 and a constraint index within the range of 1 to 12, the catalyst having an alpha value of 55 to 150 and having been prepared from a crystalline aluminosilicate zeolite having an alpha value, or a potential alpha value, in excess of 150. 45

Methods of enhancing the catalytic properties of catalysts comprising such zeolites by controlling alpha activity include reducing the alpha activity of the zeolite by such techniques as partial coking, partial base exchange with basic cations such as sodium, dilution with a matrix or preferably by treatment with steam. Another technique for controlling alpha activity is by selection of the silica to alumina ratio of the zeolites within certain ranges. The desired silica to alumina ratio can be obtained either by synthesizing the zeolite so that it initially has the proper silica to alumina ratio or by treating a zeolite having too high an alumina content, i.e. a low silica to alumina ratio, with well known alumina removing materials such as strong mineral acids to achieve the proper ratio. It is also within the scope of this invention to use more than one of the above techniques to control the alpha activity. 50 55

Alpha value or alpha activity is a measure of normal hexane cracking conversion relative to a silica-alumina cracking catalyst and the alpha test is described in a Letter to the Editor entitled "Superactive Crystalline Aluminosilicate Hydrocarbon cracking Catalyst" by P. B. Weisz and J. N. Miale, Journal of Catalysts, Vol. 4, No. 4, August 1965, pages 527—529. 60

The catalyst used in the process of the invention comprises a crystalline aluminosilicate zeolite having a silica-to-alumina mole ratio of at least 12, a constraint index of 1 to 12 and a pore diameter greater than 5 Å. Such crystalline aluminosilicate zeolites are members of a class of zeolites exhibiting some unusual properties. These zeolites induce profound transformation of aliphatic hydrocarbons to

aromatic hydrocarbons in commercially desirable yields and are generally highly effective in conversion reactions involving aromatic hydrocarbons. Although they have unusually low alumina contents, i.e. high silica to alumina ratios, they are very active even when the silica to alumina ratio exceeds 30. The activity is surprising since catalytic activity is generally attributed to framework aluminum atoms and cations associated with these aluminum atoms. These zeolites retain their crystallinity for long periods in spite of the presence of steam at high temperature which induces irreversible collapse of the framework of other zeolites, e.g., of the X and A type.

An important characteristic of the crystal structure of this class of zeolites is that it provides constrained access to, and egress from the intracrystalline free space by virtue of having a pore dimension greater than about 5 Angstroms and pore windows of about a size such as would be provided by 10-membered rings of oxygen atoms. It is to be understood, of course, that these rings are those formed by the regular disposition of the tetrahedra making up the anionic framework of the crystalline aluminosilicate, the oxygen atoms themselves being bonded to the silicon or aluminum atoms at the centers of the tetrahedra.

The silica to alumina ratio of the zeolite may be determined by conventional analysis. This ratio is meant to represent, as closely as possible, the ratio in the rigid anionic framework of the zeolite crystal and to exclude aluminum in any binder material which the zeolite may be composited or in cationic or other form within the channels. Although zeolites with a silica to alumina ratio of at least 12 are useful, it is preferred to use zeolites having higher ratios of at least about 30. Such zeolites, after activation, acquire an intracrystalline sorption capacity for normal hexane which is greater than that for water, i.e. they exhibit "hydrophobic" properties. It is believed that this hydrophobic character is advantageous in the present invention.

The type zeolites useful in this invention freely sorb normal hexane and have a pore dimension greater than 5 Angstroms. In addition, the structure must provide constrained access to larger molecules. It is sometimes possible to judge from a known crystal structure whether such constrained access exists. For example, if the only pore windows in a crystal are formed by 8-membered rings of oxygen atoms, then access by molecules of larger cross-section than normal hexane is excluded and the zeolite is not of the desired type. Windows of 10-membered rings are preferred, although, in some instances, excessive puckering or pore blockage may render these zeolites ineffective. Twelve-membered rings do not generally appear to offer sufficient constrained to produce the advantageous conversions, although puckered structures exist such as TMA offretite which is a known effective zeolite. Also, structures can be conceived, due to pore blockage or other cause, that may be operative.

Rather than attempt to judge from crystal structure whether or not a zeolite possesses the necessary constrained access, a simple determination of the "constraint index" may be made by passing, continuously a mixture of an equal weight of normal hexane and 3-methylpentane over a sample of zeolite at atmospheric pressure according to the following procedure. A sample of the zeolite, in the form of pellets or extrudate, is crushed to a particle size about that of coarse sand and mounted in a glass tube. Prior to testing, the zeolite is treated with a stream of air at 538°C for at least 15 minutes. The zeolite is then flushed with helium and the temperature adjusted between 288°C and 510°C to give an overall conversion between 10% and 80%. The mixture of hydrocarbons is passed at a 1 liquid hourly space velocity (i.e., 1 volume of liquid hydrocarbon per volume of zeolite per hour) over the zeolite with a helium dilution to give a helium to total hydrocarbon mole ratio of 4:1. After 20 minutes on stream, a sample of the effluent is taken and analyzed, most conveniently by gas chromatography, to determine the fraction remaining unchanged for each of the two hydrocarbons.

The "constraint index" is calculated as follows:

$$\text{Constraint Index} = \frac{\log_{10} (\text{fraction of n-hexane remaining})}{\log_{10} (\text{fraction of 3-methylpentane remaining})}$$

The constraint index approximates the ratio of the cracking rate constants for the two hydrocarbons. Zeolites suitable for the present invention are those having a constraint index in the approximate range of 1 to 12. Constraint Index (CI) values for some typical crystalline aluminosilicates (CAS) are:

CAS	CI
ZSM-5	8.3
ZSM-11	8.7
ZSM-12	2
ZSM-38	2
ZSM-35	4.5
Clinoptilolite	3.4
TMA Offretite	3.7
Beta	0.6
ZSM-4	0.5

	CAS	C.I.	
	H-Zeolon	0.4	
	REY	0.4	
5	Amorphous Silica-Alumina	0.6	
	Erionite	38	5

It is to be realized that the above constraint index values typically characterize the specified zeolites but that such are the cumulative result of several variables used in determination and calculation thereof. Thus, for a given zeolite depending on the temperature employed within the
 10 aforesaid range of 288 to 510°C, with accompanying conversion between 10% and 60%, the
 10 constraint index may vary within the indicated approximate range of 1 to 12. Likewise, other variables
 10 such as the crystal size of the zeolite, the presence of possible occluded contaminants and binders
 10 intimately combined with the zeolite may affect the constraint index. It will accordingly be understood
 10 by those skilled in the art that the constraint index, as utilized herein, while affording a highly useful
 10 means for characterizing the zeolites of interest is approximate, taking into consideration the manner of
 15 its determination; with probability, in some instances, of compounding variable extremes. 15

While the above experimental procedure will enable one to achieve the desired overall conversion
 of 10 to 60% for most catalyst samples and represents preferred conditions, it may occasionally be
 necessary to use somewhat more severe conditions for samples of very low activity, such as those
 having a very high silica to alumina ratio. In those instances, a temperature of up to about 538°C. and
 20 a liquid hourly space velocity of less than one, such as 0.1 or less, can be employed in order to achieve 20
 a minimum total conversion of about 10%.

The class of zeolites defined herein is exemplified by ZSM-5, ZSM-11, ZSM-12, ZSM-35 and
 ZSM-38 and other similar materials. ZSM-5 is described in U. S. Patent 3,702,886.

ZSM-11 is described in U.S. Patent 3,709,979.

25 ZSM-12 is described in U. S. Patent 3,832,449. 25

ZSM-35 is described in U. S. Patent 4,016,245.

ZSM-38 is described in U. S. Patent 4,046,859.

The specific zeolites described, when prepared in the presence of organic cations, are catalytically
 inactive, possibly because the intracrystalline free space is occupied by organic cations from the
 30 forming solution. They may be activated by heating in an inert atmosphere at 538°C for one hour, for 30
 30 example, followed by base exchange with ammonium salts followed by calcination at 538°C in air. The
 30 presence of organic cation in the forming solution may not be absolutely essential to the formation of
 30 this type zeolite; however, the presence of these cations does appear to favor the formation of this type
 of zeolite by base exchange with ammonium salts followed by calcination in air at about 1000°F for
 35 from about 15 minutes to about 24 hours. 35

Natural zeolites may sometimes be converted to this type zeolite by various activation procedures
 and other treatments such as base exchange, steaming, alumina extraction and calcination, in
 combinations. Natural minerals which may be so treated include ferrierite, brewsterite, stilbite,
 dachiardite, epistilbite, heulandite, and clinoptilolite. The preferred crystalline aluminosilicates are
 40 ZSM-5, ZSM-11, ZSM-12, ZSM-38 and ZSM-35, with ZSM-5 particularly preferred. 40

In a preferred aspect of this invention, the zeolites are those having a crystal framework density,
 in the dry hydrogen form, of not substantially below 1.6 grams per cubic centimeter. It has been found
 that zeolites which satisfy all of these criteria are most desired. Therefore, the preferred zeolites used
 according to this invention are those having a constraint index, as defined above of 1 to 12, a
 45 silica to alumina ratio of at least 12, a pore diameter greater than 5 Å and a dried crystal density of not 45
 45 less than 1.6 grams per cubic centimeter. The dry density for known structures may be calculated
 45 from the number of silicon plus aluminum atoms per 100 cubic Angstroms, as given, e.g., on Page 19
 of the article on Zeolite Structure by W. M. Meier. This paper is included in "Proceedings of the
 Conference on Molecular Sieves, London, April 1967", published by the Society of Chemical Industry,
 50 London, 1968. When the crystal structure is unknown, the crystal framework density may be 50
 50 determined by classical pycnometer techniques. For example, it may be determined by immersing the
 50 dry hydrogen form of the zeolite in an organic solvent which is not sorbed by the crystal. It is possible
 that unusual sustained activity and stability of this class of zeolites is associated with its high crystal
 anionic framework density of not less than 1.6 grams per cubic centimeter. This high density, of course,
 55 must be associated with a relative small amount of free space within the crystal, which might be 55
 55 expected to result in more stable structures. This free space, however, is important as the locus of
 catalytic activity.

Crystal framework densities of some typical zeolites are:

	Zeolite	Void volume	Framework density	
	Ferrierite	0.28 cc/cc	1.76 g/cc	
5	Mordenite	.28	1.7	
	ZSM-5, -11	.29	1.79	5
	Dachiardite	.32	1.72	
	L	.32	1.61	
	Clinoptilolite	.34	1.71	
10	Laumontite	.34	1.77	
	ZSM-4 (Omega)	.38	1.65	10
	Heulandite	.39	1.69	
	P	.41	1.57	
	Offretite	.40	1.55	
15	Levynite	.40	1.54	
	Erionite	.35	1.51	15
	Gmelinite	.44	1.46	
	Chabazite	.47	1.45	
	A	.5	1.3	
	Y	.48	1.27	
20	The crystal size of the synthesized zeolite is generally within the approximate range of .01 to 40 microns.			20
25	The zeolites used in the invention can have the original cations associated therewith replaced by a wide variety of other cations according to techniques well known in the art. Typical replacing cations include hydrogen, ammonium and metal cations including mixtures of the same. Of the replacing metallic cations, particular preference is given to cations of metals such as rare earth metals, manganese and calcium.			25
30	Typical ion exchange techniques would be to contact the particular zeolite with a salt of the desired replacing cation or cations. Although a wide variety of salts can be employed, particular preference is given to chlorides, nitrates and sulfates.			
	Representative ion exchange techniques are disclosed in a wide variety of patents, including United States Patents 3,140,249; 3,140,251; and 3,140,253.			30
35	Following contact with the salt solution of the desired replacing cation, the zeolites are then preferably washed with water and dried at a temperature ranging from 66°C to about 316°C and thereafter calcined in air or an inert gas at temperatures ranging from about 260 to 816°C for periods of time ranging from 1 to 48 hours or more.			35
40	Although not required for successful operation, the zeolites can also be used in intimate combination with a hydrogenating component such as tungsten, vanadium, molybdenum, rhenium, nickel, cobalt, chromium, manganese, or a noble metal such as platinum or palladium. Such component can be exchanged into the catalyst composition, impregnated therein or physically intimately admixed therewith, or can be impregnated in or onto the zeolite, for example, by treating the zeolite with a platinum metal-containing ion. Suitable platinum compounds include chloroplatinic acid, platinum chloride and various compounds containing the platinum amine complex.			40
45	The compounds of the useful platinum or other metals can be divided into compounds in which the metal is present in the cation of the compound and compounds in which it is present in the anion of the compound. Both types of compounds which contain the metal in the ionic state can be used. A solution in which platinum metal is in the form of a cation or cationic complex, e.g., $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$ is particularly useful. It is to be understood that the presence of a hydrogenating component is not required and is optional.			45
50	Prior to use, the zeolites should be dehydrated at least partially. This can be done by heating to a temperature in the range of 200 to 600°C in an atmosphere, such as air or nitrogen, and at atmospheric or subatmospheric pressures for between 1 and 48 hours. Dehydration can also be performed at lower temperatures merely by using a vacuum, but a longer time is required to obtain a sufficient amount of dehydration.			50
55	As pointed out above, the process of this invention is concerned with hydrodewaxing of hydrocarbon feedstocks including petroleum as well as synthetic hydrocarbon feedstocks such as those resulting from the conversion of synthesis gas. The term "hydrodewaxing" is used in the specification and claims in its broadest sense and is intended to mean the removal of those hydrocarbons which readily solidify (waxes) from hydrocarbon stocks. Hydrocarbon feeds which can be treated include lubricating oil stocks as well as those which have a freeze point or pour point problem, i.e. stocks boiling above about 177°C such as whole crude, distillates and bright stock.			55
60	Hydrodewaxing conditions include temperatures between 260°C and 538°C and pressures between 100 and 3000 psig (790 and 20770 kPa) but preferably between 200—700 psig (1480 and 4930 kPa). The liquid hourly space velocity is generally between 0.1 and 10, preferably between 0.5			60

and 4 and the hydrogen to hydrocarbon mole ratio is generally between 1 and 20, preferably between 2 and 10.

The zeolites utilized in this invention are preferably incorporated or otherwise admixed with a matrix. Matrix materials are well known in the art and include inorganic oxides such as clay, silica, alumina and silica-alumina. The matrix which is used is preferably non-catalytic, with alumina being particularly preferred.

As stated above, the catalysts used in the hydrodewaxing process of the present invention comprise an acidic crystalline aluminosilicate zeolite of pore diameter greater than 5Å, a silica-to-alumina ratio of at least 12 and a constraint index of from 1 to 12, and have alpha values of 55 to 150, having been prepared from crystalline aluminosilicate zeolites having alpha values, or potential alpha values, in excess of 150. The high alpha activity, or potentially high alpha activity, of the zeolites can be reduced to the alpha values of 55 to 150 required for the catalysts used in the hydrodewaxing process of the invention by a variety of techniques, used alone or in combination.

For example, it is known in the art that the alpha activity of a zeolite can be reduced by using basic cations such as sodium to replace a portion of the cationic species of the zeolites. Techniques of this type are described in United States Patent 3,899,544. Thus, by way of specific illustration, if an acidic ZSM-5 zeolite has an initial alpha value in excess of 150, for example 177, a portion of its hydrogen ions can be replaced by sodium ions until its alpha activity is within the desired range.

Still another method of reducing the alpha activity is by partial coking. As is known in the art, when acidic zeolite-containing catalysts are utilized for various hydrocarbon conversion processes a material which is commonly referred to as coke deposits on the catalyst. This material has a tendency to deactivate the zeolite and, as such, partial coking is an effective way of reducing the initially high alpha activity of the zeolite down to the desired levels.

Another technique which can be employed for the reduction of the initially high alpha activity is to use the zeolites in combination with an inert matrix either by using a catalyst particle which contains both matrix and zeolite or by using separate particles of both the zeolite and the matrix.

However, the preferred method for reducing the initially high activity of the zeolites is steaming.

As pointed out above still another method of regulating the alpha activity is by suitable selection of the silica-to-alumina ratio of the zeolites within a certain range. In this respect, it is generally known in the art that the lower the aluminum content of the crystal structure of the zeolite, the less sites there are at which a cation can attach so that the alpha activity of the zeolite is diminished. In this connection, the following correlation has been found between composites of 35 weight % alumina and 65 weight % acid ZSM-5 having particular silica to alumina ratios, and alpha values.

35	<i>Silica/alumina ratio of ZSM-5</i>	<i>Alpha value of composite of 35 wt.% Al₂O₃ and 65 wt.% acid ZSM-5</i>	35
	70	177	
	140	125	
	220	100	
40	500	37	40

From the above, it can be seen that an unsteamed composite of 35 weight % alumina and 65 weight % ZSM-5 zeolite having a silica to alumina ratio of 140 or 220 would satisfy the alpha value requirement, while a composite of 35 weight % alumina and 65 weight % HZSM-5 would still have an alpha value in excess of 150, making it unsuitable for use in the process of the invention without treatment to reduce its alpha value to the required 55 to 150 range. It is also to be understood that a combination of all the above techniques can be used. In this connection, it is specifically noted that a composite of 35 weight % alumina and 65 weight % ZSM-5 zeolite having a silica to alumina ratio of about 220 has a corresponding alpha value of 100. As will be shown in Example 13 below, this zeolite does, indeed, provide an effective control of a hydrodewaxing operation in the unsteamed state.

However, still further improvement can be obtained if the material is steamed.

In certain cases, the catalyst used in the process of the invention may be prepared from a zeolite that does not have an alpha value in excess of 150, even though that zeolite is capable of attaining an alpha value in excess of 150. For example, if an as synthesized ZSM-5 of silica-to-alumina ratio 140 is composited with alumina in a weight ratio of 65:35, the sodium and organic nitrogen-containing cations within the crystalline structure of the zeolite will depress the alpha value of the catalyst to a low level. If, however, that catalyst is subsequently treated to convert the zeolite into its acid form, the alpha value of the catalyst will increase to about 125 by virtue of the fact that the zeolite itself, in its acid form, has an alpha value in excess of 150. Such a catalyst is considered as having been prepared from a zeolite having a potential alpha value in excess of 150.

As mentioned above, a preferred method for reducing an initially high alpha activity is steaming. Steaming is preferably carried out at elevated temperatures ranging from 149 to 815°C at either atmospheric or elevated pressures. The steaming can be carried out in atmospheres of 100% steam or an atmosphere of steam and an inert gas.

If the catalyst is to be steamed *in situ*, it is expedient to use mixtures of steam and hydrogen at pressures from 50—200 psig (445 to 1480 kPa) and temperatures from 371 to 482°C for periods of time ranging from 1—48 hours. The exact reduction in alpha activity is a function of steam partial pressure, temperature and time. None of these variables is critical *per se* and the only requirement is that the steaming be carried out in order to obtain the critical range of alpha values.

For a nickel exchanged acid ZSM-5 (NiH/ZSM-5) steaming with a 50/50 mixture by volume of steam and hydrogen at 790 kPa and 427°C for 12—24 hours is satisfactory.

Following the treatment with steam, the nickel exchange acidic ZSM-5 type zeolite is preferably sulfided by treatment with a sulfiding compound such as hydrogen sulfide at elevated temperatures of about 232 to 343°C.

The following examples illustrate the invention. All parts are by weight.

Example 1

Catalyst preparation

The catalyst used in the steaming studies was prepared by mixing a dried, as synthesized, ZSM-5 zeolite having a silica/alumina ratio of about 70 with alumina and water and extruding into 1/16" (1.6 mm) diameter pellets. The extruded material contained 65 parts ZSM-5 per 35 parts alumina.

The dried extrudate was calcined for three hours at 538°C in flowing nitrogen. After cooling, the extrudate was contacted with an ammonium nitrate exchange solution (about 0.08 parts NH_4NO_3 /part extrudate) for one hour at ambient temperature. This exchange was then repeated until the sodium level was less than 0.05 wt.%. The extrudate was then contacted with a nickel nitrate exchange solution (about 0.1 part $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ /part extrudate) for two hours at about 80—90°C. After this exchange, the extrudate was washed, dried and calcined in a flowing gas mixture (approximately 10% air—90% nitrogen) at 538°C for six hours. The resulting catalyst was then determined to have an alpha value of 177.

Example 2

The catalyst of Example 1 was treated with 100% steam for 16 hours at 538°C and 0 psig. (100 kPa). It was then determined to have an alpha value of 22.

Example 3

The catalyst of Example 1 was treated with 100% steam for 2 hours at 538°C. and 0 psig. (100 kPa). It was then determined to have an alpha value of 55.

Example 4

The catalyst of Example 1 was treated with 100% steam for 3 hours at 482°C and 0 psig. (100 kPa). It was then determined to have an alpha value of 90.

Example 5

The catalyst of Example 1 was treated with 100% steam for 6 hours at 454°C and 0 psig. (100 kPa). It was then determined to have an alpha value of 111.

Example 6

The catalyst of Example 1 was treated with 100% steam for 4 hours at 454°C and 0 psig. (100 kPa). It was then determined to have an alpha value of 135.

Example 7

The catalyst of Example 1 was treated with a 30/70 mixture by volume of steam and hydrogen for 6 hours at 427°C and 100 psig (790 kPa). It was then determined to have an alpha value of 145.

Example 8

The catalyst of Example 1 was treated with a 40/60 mixture by volume of steam and hydrogen for 24 hours at 427°C and 100 psig (790 kPa). It was then calculated to have an alpha value of 58.

Example 9

The catalysts of Examples 1—6 were evaluated for hydrodewaxing Nigerian gas oil after having been sulfided by treatment with hydrogen sulfide over a temperature range of 232—343°C.

The hydrodewaxing was carried out at 400 psig (2860 kPa), 1 LHSV, and 2500 SCFH/B (445 NiH_2I gas oil charge) and the results are shown in Figure 1 wherein the temperature required for —17.8°C (0°F) pour point is plotted against time on stream. The approximate aging rate for the unsteamed catalyst of Example 1 (alpha 177) is also indicated by the solid line.

As can be seen, the required equilibration temperature was lowest for the catalyst of alpha 111 followed by the catalyst of alpha 90, followed by the catalyst of alpha 135, followed by alpha 55. The catalyst having an alpha value of 22 required the highest temperature.

The results of Figure 1 are replotted in Figure 3 to show the effect of alpha activity on equilibration temperature. As can be seen, optimum results are obtained within the range of 55—150

alpha. Better results are achieved at 80—135 alpha and even better results are achieved at 90—120 alpha. In addition, Figure 3 also includes information in connection with steaming catalysts comprising Zeolites having silica to alumina ratios of 220:1 and 40:1. As can be seen, improved results are obtained. In this connection, the triangle in Figure 3 represents a catalyst comprising ZSM-5 zeolite having a silica to alumina ratio of 220:1. The broken line shows the decline in equilibration temperature as this material was steamed.

Example 10

The catalysts of Examples 7—8 were evaluated for hydrodewaxing an Arabian Light 343 to 413°C gas oil after having been sulfided by treatment with hydrogen sulfide over a temperature range of 232 to 343°C.

The hydrodewaxing was carried out at 400 psig (2860 kPa), at an LHSV of 3.0, and 2500 SCF H₂/B (445 NIH₂/l gas oil charge) and the results are shown in Figure 2 where the temperature required for -17.8°C (0°F) pour point is plotted against days on stream.

Example 11

The catalyst described in Example 7 and evaluated as described in Example 10, was subsequently regenerated in an air/nitrogen mixture to remove carbonaceous deposits. It was then further treated with a 40/60 mixture by volume of steam and hydrogen for 6 hours at 427°C and 100 psig (790 kPa). After this treatment, it was determined to have an alpha value of 84.

Example 12

The catalyst of Example 11 was evaluated for hydrodewaxing by the procedure described in Example 10. The results are shown in Figure 2 where temperature required for -17.8°C (0°F) pour point is plotted against days on stream.

As can be seen, the catalyst having an alpha value of 84 (Example 11) required the lowest temperature followed by the catalyst having an alpha value of 58 (Example 8). The catalyst of alpha 145 (Example 7) required the highest temperature.

The properties of the Nigerian and Arabian Light gas oils used in Examples 9 and 10 are shown in the following table.

Table 1

	Nigerian gas oil	Arabian light gas oil
Gravity, °API	25.6	26.3
Pour Point, (°F) °C	(+95) +35	(+65) +18.3
Cloud Point, (°F) °C	(+94) +34.4	(+68) +20
Hydrogen, % wt.	12.67	12.40
Sulfur, % wt.	0.23	2.33
Nitrogen, % wt.	0.08	0.035
CCR, % wt.	0.04	>0.01
K.V. at 40°C, CS	31.90	16.16
Paraffins, % wt.	30.9	—
Naphthenes, % wt.	33.2	—
Aromatics, % wt.	35.9	—
<i>Distillation, °F (°C)</i>		
<i>D1160</i>		
IBP	(548) 287	(604) 318
5% Vol	(671) 355	(685) 363
10% Vol	(693) 367	(692) 367
30% Vol	(721) 383	(706) 374
50% Vol	(745) 396	(721) 383
70% Vol	(771) 411	(738) 392
90% Vol	(810) 432	(762) 406
95% Vol	(824) 440	(770) 410

Example 13

This example illustrates that effective control of alpha activity can be achieved by control of the silica to alumina ratio of the zeolite.

The catalyst used was prepared by mixing a dried, as synthesized, ZSM-5 zeolite having a silica to alumina ratio of about 220 with alumina and water and extruding into 1/16" (1.6 mm) diameter pellets. The extruded material contained 65 parts ZSM-5 per 35 parts of alumina.

The dried extrudate was calcined for three hours at 538°C in flowing nitrogen. After cooling, the extrudate was contacted with a 1 normal ammonium nitrate solution (about 5 cc per gram of

extrudate) for one hour at ambient temperature. This exchange was repeated until the sodium level was less than about 0.05 weight per cent. The extrudate was then dried at about 121°C and then contacted with a 1 N nickel nitrate solution (5 cc/gm of extrudate) for four hours at 88°C. After this exchange, the extrudate was washed, dried and calcined in flowing air at 538°C for three hours. The resulting catalyst was determined to have an alpha value of 100.

The above catalyst was then evaluated for the hydrodewaxing of Nigerian gas oil previously described and after about 10 days it equilibrated at a temperature of 413°C.

Thus, the above example shows that the improved hydrodewaxing operations can be carried out merely by controlling the silica to alumina ratio. It is to be understood, however, that it is possible to obtain even better results in some cases if a combination of techniques are used for the reduction of alpha values. In this connection, the data of Example 13 does appear at Figure 3, previously described, and as can be seen this same catalyst material when steamed so as to reduce its alpha value to approximately 75 equilibrated at still a lower temperature.

Claims

1. A process for hydrodewaxing a petroleum or synthetic hydrocarbon charge which comprises contacting the charge in the presence of hydrogen, at elevated temperature and pressure, with a catalyst comprising an acidic crystalline aluminosilicate zeolite, the zeolite having a pore diameter greater than 5 Ångstroms, a silica-to-alumina ratio of at least 12 and a constraint index within the range of 1 to 12, the catalyst having an alpha value of 55 to 150 and having been prepared from a crystalline aluminosilicate zeolite having an alpha value, or a potential alpha value, in excess of 150.

2. A process according to claim 1, wherein the acidic zeolite has a hydrogenation/dehydrogenation component associated therewith.

3. A process according to claim 2, wherein the hydrogenation/dehydrogenation component is nickel.

4. A process according to any preceding claim, wherein the alpha activity of the catalyst is 65 to 135.

5. A process according to any preceding claim, wherein the alpha activity of the catalyst is 90 to 120.

6. A process according to any preceding claim, wherein the zeolite is ZSM-5 or ZSM-11.

7. A process according to any preceding claim, wherein the reduction of alpha activity is accomplished by steaming.

8. A process according to any preceding claim, wherein the reduction of alpha activity is accomplished by control of the silica-to-alumina ratio of the zeolite.

9. A process according to any preceding claim, wherein the reduction of alpha activity is accomplished by base exchange of the zeolite with alkali metal cations.



extrudate) for one hour at ambient temperature. This exchange was repeated until the sodium level was less than about 0.05 weight per cent. The extrudate was then dried at about 121°C and then contacted with a 1 N nickel nitrate solution (5 cc/gm of extrudate) for four hours at 88°C. After this exchange, the extrudate was washed, dried and calcined in flowing air at 538°C for three hours. The resulting catalyst was determined to have an alpha value of 100.

The above catalyst was then evaluated for the hydrodewaxing of Nigerian gas oil previously described and after about 10 days it equilibrated at a temperature of 413°C.

Thus, the above example shows that the improved hydrodewaxing operations can be carried out merely by controlling the silica to alumina ratio. It is to be understood, however, that it is possible to obtain even better results in some cases if a combination of techniques are used for the reduction of alpha values. In this connection, the data of Example 13 does appear at Figure 3, previously described, and as can be seen this same catalyst material when steamed so as to reduce its alpha value to approximately 75 equilibrated at still a lower temperature.

Claims

1. A process for hydrodewaxing a petroleum or synthetic hydrocarbon charge which comprises contacting the charge in the presence of hydrogen, at elevated temperature and pressure, with a catalyst comprising an acidic crystalline aluminosilicate zeolite, the zeolite having a pore diameter greater than 5 Ångstroms, a silica-to-alumina ratio of at least 12 and a constraint index within the range of 1 to 12, the catalyst having an alpha value of 55 to 150 and having been prepared from a

crystalline aluminosilicate zeolite having an alpha value, or a potential alpha value, in excess of 150.

2. A process according to claim 1, wherein the acidic zeolite has a hydrogenation/dehydrogenation component associated therewith.

3. A process according to claim 2, wherein the hydrogenation/dehydrogenation component is nickel.

4. A process according to any preceding claim, wherein the alpha activity of the catalyst is 65 to 135.

5. A process according to any preceding claim, wherein the alpha activity of the catalyst is 90 to 120.

6. A process according to any preceding claim, wherein the zeolite is ZSM-5 or ZSM-11.

7. A process according to any preceding claim, wherein the reduction of alpha activity is accomplished by steaming.

8. A process according to any preceding claim, wherein the reduction of alpha activity is accomplished by control of the silica-to-alumina ratio of the zeolite.

9. A process according to any preceding claim, wherein the reduction of alpha activity is accomplished by base exchange of the zeolite with alkali metal cations.