HYDROPROCESSING WITH BLENDED ZSM-48 CATALYSTS

FIELD OF THE INVENTION

[0001] This invention relates to processes involving blends of ZSM-48 catalysts.

BACKGROUND OF THE INVENTION

[0002] The demand for high quality basestocks for formulation into engine oils and other lubricating needs is increasing due to heightened environmental concerns. Basestocks quality is being impacted by demands for basestocks that meet Group II or Group III requirements. Thus there is pressure for producing basestocks that meet the requirements of viscosity index (VI), viscosity, pour point and/or volatility imposed by governmental regulations and original equipment manufacturers. The ability of solvent refining alone to economically meet these increased demands for higher basestock quality is limited. Even with the use of additives, formulated oils require higher basestock quality to meet the demands of modern engines. Also, the supply of crudes that are rich in paraffins, is limited.

[0003] Catalytic dewaxing has developed as an alternative to solvent based methods for producing high quality basestocks. Dewaxing catalysts function by two different mechanisms: those catalysts which function primarily by isomerization and those catalysts which function primarily by hydrocracking. There are few, if any, dewaxing catalysts with the ability to function solely by one mechanism to the exclusion of the other. Dewaxing by hydrocracking can be done with relatively low quality feedstocks. However, these feeds typically require more severe reaction conditions to achieve target basestock quality and this leads to lower basestock yields and further processing steps to mitigate undesirable species formed by hydrocracking.

[0004] Dewaxing catalysts which function primarily by isomerization convert waxy molecules into branched chain molecules. Branched chain

molecules can have desirable properties with regard to VI and pour point. ZSM-48 is an example of such a dewaxing catalyst. As noted in United States Patent Number 5,075,269, ZSM-48 is prepared using diquaternary ammonium compounds as directing agents. Both the directing agent and the silica-alumina ratio can influence crystal morphology, although the choice of directing agent is the greater factor. When using a diamine or tetraamine directing agent, rod- or needle-like crystals are produced. At high silica:alumina ratios using a diquaternary ammonium directing agent, the ZSM-48 produced has a platelet morphology. As the silica:alumina ratio is lowered using the preparative techniques described in United States Patent Number 5,075,269 or United States Patent Number 6,923,949, crystal purity becomes an increasing problem as competing crystalline forms other than ZSM-48 are produced, or the ZSM-48 contains heterostructural zeolite seeds.

[0005] It is known that crystal morphology can affect catalyst behavior, especially with regard to catalyst activity and stability. Also, it is generally desirable to have a small crystallite size as smaller crystals likewise favor higher activity and stability due to greater surface area for given amount of catalyst.

[0006] It would be highly advantageous to have ZSM-48 crystals that could be made with high purity and that would have high activity when used as a catalyst while exhibiting a favorable morphology.

SUMMARY OF THE INVENTION

[0007] In an embodiment, a method for dewaxing a hydrocarbon feedstock is provided. The method includes contacting the feedstock with a blend of ZSM-48 catalysts under catalytic dewaxing conditions to produce a dewaxed feedstock, the blend of ZSM-48 catalysts comprising

a) a first type of ZSM-48 crystals having a silica:alumina molar ratio of from 70 to 110 and being free of non-ZSM-48 seed crystals; and

b) a second type of ZSM-48 crystals, the first type of ZSM-48 crystals and second type of ZSM-48 crystals being different.

DESCRIPTION OF THE DRAWINGS

[0008] Figure 1 is a photomicrograph of the ZSM-crystals prepared at a template:silica ratio of 0.023 and showing the presence of some needle like crystals.

[0009] Figure 2 is a photomicrograph showing the absence of needle-like crystals for ZSM-48 crystals prepared from a reaction mixture having a template:silica ratio of 0.018.

[0010] Figure 3 is a photomicrograph showing the presence of needle-like crystals for ZSM-48 crystals prepared from a reaction mixture having a template:silica ratio of 0.029.

[0011] Figure 4 is a photomicrograph showing the absence of needle-like crystals for ZSM-48 crystals prepared from a reaction mixture having a template:silica ratio of 0.019.

[0012] Figure 5 is a graph showing iso-C10 yield as a function of n-C10 conversion.

[0013] Figure 6 is a graph showing reactor temperature vs. required temperature to meet the 370°C+ pour point.

DETAILED DESCRIPTION OF THE INVENTION

[0014] In various embodiments, the invention relates to hydroprocessing methods involving catalysts comprising blends of two or more types of ZSM-48 crystals. In particular, the invention relates to blends of ZSM-48 catalyst where at least a portion of the ZSM-48 is a novel high purity type of ZSM-48 having a SiO_2:Al_2O_3 ratio of less than 110 that does not contain a non-ZSM-48 seed crystal. This novel type of ZSM-48 crystals exhibits a higher activity than other types of ZSM-48 crystals.

[0015] Blends of two or more types of ZSM-48 crystals having different activities allow for tailoring of processes to provide a desired activity at a desired temperature. This tailoring of activity can be achieved without introducing undesired side reactions that might otherwise be enhanced by introducing another type of catalyst, such as another type of zeolite catalyst.

Synthesis of high purity ZSM-48 with SiO_2:Al_2O_3 ratio below 110

[0016] In various embodiments, the processes of this invention employ a blend of ZSM-48 crystal (or catalyst) types. In such embodiments, at least a portion of the blend includes catalyst composed of high purity ZSM-48 crystals having a SiO_2:Al_2O_3 ratio of 110 or less in a particular morphology, the high purity ZSM-48 crystals being free of non-ZSM-48 seed crystals. Preferably, the high purity ZSM-48 crystals are also free of ZSM-50. As described below, high purity ZSM-48 crystals having a SiO_2:Al_2O_3 ratio of 110 or less have a higher activity than other types of ZSM-48 crystals.

[0017] In the embodiments below, ZSM-48 crystals will be described variously in terms of "as-synthesized" crystals that still contain the organic template; calcined crystals, such as Na-form ZSM-48 crystals; or calcined and ion-exchanged crystals, such as H-form ZSM-48 crystals.

[0018] By "free of non-ZSM-48 seed crystals" is meant that the reaction mixture used for forming the ZSM-48 crystals does not contain non-ZSM-48 seed crystals. Instead, ZSM-48 crystals synthesized according to the invention are either synthesized without the use of seed crystals, or with ZSM-48 seed crystals for seeding. By "free of Kenyaite and ZSM-50" is meant that Kenyaite and ZSM-50, if any, are present in amounts that are not detectable by X-ray diffraction. Similarly, the high purity ZSM-48 according to the invention is also free of other non-ZSM-48 crystals to the degree that such other crystals are also not detectable by X-ray diffraction. This non-detectable determination was made on a Bruker D4 Endeavor instrument, manufactured by Bruker AXS, and

equipped with a Vantec-1 high-speed detector. The instrument was run using a silicon powder standard (Nist 640B) which is a material without stress. The full-width half-maximum (fwhm) for the standard peak at 28.44 degrees 2 theta is 0.132. The step size is 0.01794 degrees and the time/step is 2.0 seconds. The 2 theta scan used a Cu target at 35 kv and 45 ma. By "free of fibrous crystals" and "free of needle-like crystals" is meant that the fibrous and/or needle-like crystals, if any, are present in amounts that are not detectable by Scanning Electron Microscopy (SEM). Photomicrographs from SEM can be used to identify crystals with different morphologies. The resolution scale (1μm) is shown on the photomicrographs in the present figures.

[0019] The X-ray diffraction pattern (XRD) of the ZSM-48 crystals according to the invention is that exhibited by ZSM-48, i.e., the D-spacings and relative intensities correspond to those of pure ZSM-48. While XRD can be used to establish the identity of a given zeolite, it cannot be used to distinguish a particular morphology. For example, the needle-like and platelet forms for a given zeolite will exhibit the same diffraction patterns. In order to distinguish between different morphologies, it is necessary to use an analytical tool with greater resolution. An example of such a tool is scanning electron microscopy (SEM). Photomicrographs from SEM can be used to identify crystals with different morphologies.

[0020] The ZSM-48 crystals after removal of the structural directing agent have a particular morphology and a molar composition according to the general formula:

$$(n)SiO_2:Al_2O_3$$

where n is from 70 to 110, preferably 80 to 100, more preferably 85 to 95. In another embodiment, n is at least 70, or at least 80, or at least 85. In yet another embodiment, n is 110 or less, or 100 or less, or 95 or less. In still other

embodiments, Si may be replaced by Ge and Al may be replaced by Ga, B, Fe, Ti, V, and Zr.

[0021] The as-synthesized form of ZSM-48 crystals is prepared from a mixture having silica, alumina, base and hexamethonium salt directing agent. In an embodiment, the molar ratio of structural directing agent:silica in the mixture is less than 0.05, or less than 0.025, or less than 0.022. In another embodiment, the molar ratio of structural directing agent:silica in the mixture is at least 0.01, or at least 0.015, or at least 0.016. In still another embodiment, the molar ratio of structural directing agent:silica in the mixture is from 0.015 to 0.025, preferably 0.016 to 0.022. In an embodiment, the as-synthesized form of ZSM-48 crystals has a silica:alumina molar ratio of 70 to 110. In still another embodiment, the as-synthesized form of ZSM-48 crystals has a silica:alumina molar ratio of at least 70, or at least 80, or at least 85. In yet another embodiment, the as-synthesized form of ZSM-48 crystals has a silica:alumina molar ratio of 110 or less, or 100 or less, or 95 or less. For any given preparation of the as-synthesized form of ZSM-48 crystals, the molar composition will contain silica, alumina and directing agent. It should be noted that the as-synthesized form of ZSM-48 crystals may have molar ratios slightly different from the molar ratios of reactants of the reaction mixture used to prepare the as-synthesized form. This result may occur due to incomplete incorporation of 100% of the reactants of the reaction mixture into the crystals formed (from the reaction mixture).

[0022] The ZSM-48 zeolite in either a calcined or as-synthesized form typically forms agglomerates of small crystals that may have crystal sizes in the range of about 0.01 to about 1 μm. These small crystals are desirable for they generally lead to greater activity. Smaller crystals mean greater surface area which leads to a greater number of active catalytic sites per given amount of catalyst. Preferably, the ZSM-48 crystals in either a calcined or as-synthesized form have a morphology containing no fibrous crystals. By fibrous is meant crystals that have a L/D ratio of > 10/1, where L and D represent the length and

diameter of the crystal. In another embodiment, the ZSM-48 crystals in either a calcined or as-synthesized form have a low quantity or are free of needle-like crystals. By needle-like is meant crystals that have a L/D ratio of < 10/1, preferably less than 5/1, more preferably between 3/1 and 5/1. The SEM shows that crystals prepared according to the methods herein have no detectable crystals having a fibrous or needle-like morphology. This morphology alone or coupled with the low silica:alumina ratios leads to catalysts having high activity as well as desirable environmental features.

[0023] The ZSM-48 composition is prepared from an aqueous reaction mixture comprising silica or silicate salt, alumina or soluble aluminate salt, base and directing agent. To achieve the desired crystal morphology, the reactants in reaction mixture have the following molar ratios:

SiO_2:Al_2O_3 = 70 to 110
H_2O: SiO_2 = 1 to 500
OH^-: SiO_2 = 0.1 to 0.3
OH^-: SiO_2 (preferred) = 0.14 to 0.18
template : SiO_2 = 0.01 – 0.05
template: SiO_2 (preferred) = 0.015 to 0.025

[0024] In the above ratios, two ranges are provided for both the base:silica ratio and the structure directing agent:silica ratio. The broader ranges for these ratios include mixtures that result in the formation of ZSM-48 crystals with some quantity of Kenyaite and/or needle-like morphology. For situations where Kenyaite and/or needle-like morphology is not desired, the preferred ranges should be used, as is further illustrated below in the Examples.

[0025] The silica source is preferably precipitated silica and is commercially available from Degussa. Other silica sources include powdered silica including precipitated silica such as Zeosil® and silica gels, silicic acid colloidal silica such as Ludox® or dissolved silica. In the presence of a base, these other silica

sources may form silicates. The alumina may be in the form of a soluble salt, preferably the sodium salt and is commercially available from US Aluminate. Other suitable aluminum sources include other aluminum salts such as the chloride, aluminum alcoholates or hydrated alumina such as gamma alumina, pseudobohemite and colloidal alumina. The base used to dissolve the metal oxide can be any alkali metal hydroxide, preferably sodium or potassium hydroxide, ammonium hydroxide, diquaternary hydroxide and the like. The directing agent is a hexamethonium salt such as hexamethonium dichloride or hexamethonium hydroxide. The anion (other than chloride) could be other anions such as hydroxide, nitrate, sulfate, other halide and the like. Hexamethonium dichloride is N,N,N,N',N',N'-hexamethyl-1,6-hexanediammonium dichloride.

[0026] In the synthesis of the ZSM-48 crystals, the reactants including silicate salt, aluminate salt, base and directing agent are mixed together with water in the ratios set forth above and heated with stirring at 100 to 250 °C. The crystals may be formed from reactants or in the alternative, ZSM-48 seed crystals may be added to the reaction mixture. The ZSM-48 seed crystals may be added to enhance the rate of crystal formation but do not otherwise affect crystal morphology. The preparation is free of other non-ZSM-48 types of seed crystals such as zeolite Beta. The ZSM-48 crystals are purified, usually by filtration, and washed with deionized water.

[0027] In an embodiment, the crystals obtained from the synthesis according to the invention have a composition that is free of non ZSM-48 seed crystals and free of ZSM-50. Preferably, the ZSM-48 crystals will have a low quantity of Kenyaite. In an embodiment, the amount of Kenyaite can be 5% or less, or 2% or less, or 1% or less. In an alternative embodiment, the ZSM-48 crystals can be free of Kenyaite.

[0028] In an embodiment, the crystals obtained from the synthesis according to the invention have a morphology that is free of fibrous morphology. Fibrous

morphology is not desired, as this crystal morphology inhibits the catalytic dewaxing acitivty of ZSM-48. In another embodiment, the crystals obtained from the synthesis according to the invention have a morphology that contains a low percentage of needle-like morphology. The amount of needle-like morphology present in the ZSM-48 crystals can be 10% or less, or 5% or less, or 1% or less. In an alternative embodiment, the ZSM-48 crystals can be free of needle-like morphology. Low amounts of needle-like crystals are preferred for some applications as needle-like crystals are believed to reduce the activity of ZSM-48 for some types of reactions. To obtain a desired morphology in high purity, the ratios of silica:alumina, base:silica and directing agent:silica in the reaction mixture according to embodiments of the invention should be employed. Additionally, if a composition free of Kenyaite and/or free of needle-like morphology is desired, the preferred ranges should be used.

[0029] According to United States Patent Number 6,923,949, heterostructural, non-ZSM-48 seeding is used to prepare ZSM-48 crystals having a silica:alumina ratio less than 150:1. According to US 6,923,949, the preparation of pure ZSM-48 with silica:alumina ratios down to 50:1 or less is dependent on the use of heterostructural seeds such as zeolite Beta seeds.

[0030] If heterogeneous seed crystals are not used, as one synthesizes ZSM-48 with increasingly lower silica:alumina ratios, the formation of the impurity ZSM-50 becomes more of a factor. Ratios of directing agent:silica greater than about 0.025 typically produce mixed phase aggregates containing needle-like crystals. Preferably, the ratio of directing agent:silica is about 0.022 or less. Ratios of directing agent: silica below about 0.015 begin to produce a product containing Kenyaite. Kenyaite is an amorphous layered silicate and is a form of natural clay. It does not exhibit zeolite type activity. Instead, it is relatively inert in the presence of reaction conditions typically present when a feedstock is exposed to ZSM-48. Thus, while the presence of Kenyaite in a ZSM-48 sample is tolerable in some applications, the presence of Kenyaite tends to reduce the

overall activity of the ZSM-48. Ratios of hydroxide:silica (or other base:silica) and silica:alumina ratios are also important to the morphology of the crystals formed as well as to purity of crystals formed. Ratios of silica:alumina are also important to catalyst activity. The base:silica ratio is a factor affecting the formation of Kenyaite. The use of a hexamethonium directing agent is a factor for the production of a product not containing a fibrous material. The formation of needle-like morphology is a function of the silica:alumina ratio and structure directing agent:silica ratio.

[0031] The as-synthesized ZSM-48 crystals should be at least partially dried prior to use or further treatment. Drying may be accomplished by heating at temperatures of from 100 to 400°C, preferably from 100 to 250°C. Pressures may be atmospheric or subatmospheric. If drying is performed under partial vacuum conditions, the temperatures may be lower than those at atmospheric pressures

[0032] Catalysts are typically bound with a binder or matrix material prior to use. Binders are resistant to temperatures of the use desired and are attrition resistant. Binders may be catalytically active or inactive and include other zeolites, other inorganic materials such as clays and metal oxides such as alumina, silica and silica-alumina. Clays may be kaolin, bentonite and montmorillonite and are commercially available. They may be blended with other materials such as silicates. Other porous matrix materials in addition to silica-aluminas include other binary materials such as silica-magnesia, silica-thoria, silica-zirconia, silica-beryllia and silica-titania as well as ternary materials such as silica-alumina-magnesia, silica-alumina-thoria and silica-alumina-zirconia. The matrix can be in the form of a co-gel. The bound ZSM-48 may range from 10 to 100 wt.% ZSM-48, based on bound ZSM-48 with the balance being binder.

[0033] ZSM-48 crystals as part of a catalyst may also be used with a metal hydrogenation component. Metal hydrogenation components may be from

Groups 6 -12 of the Periodic Table based on the IUPAC system having Groups 1 - 18, preferably Groups 6 and 8-10. Examples of such metals include Ni, Mo, Co, W, Mn, Cu, Zn, Ru, Pt or Pd, preferably Pt or Pd. Mixtures of hydrogenation metals may also be used such as Co/Mo, Ni/Mo, Ni/W and Pt/Pd, preferably Pt/Pd. The amount of hydrogenation metal or metals may range from 0.1 to 5 wt.%, based on catalyst. Methods of loading metal onto ZSM-48 catalyst are well known and include, for example, impregnation of ZSM-48 catalyst with a metal salt of the hydrogenation component and heating. The ZSM-48 catalyst containing hydrogenation metal may also be sulfided prior to use. The catalyst may also be steamed prior to use.

[0034] High purity ZSM-48 crystals made according to the above embodiments have a relatively low silica:alumina ratio. This lower silica:alumina ratio mean that the present catalysts are more acidic. In spite of this increased acidity, they have superior activity and selectivity as well as excellent yields. They also have environmental benefits from the standpoint of health effects from crystal form and the small crystal size is also beneficial to catalyst activity.

[0035] In addition to the embodiments described above, in still another embodiment, the invention relates to high purity ZSM-48 composition having a silica:alumina molar ratio of from 70 to 110, the ZSM-48 being free of non-ZSM-48 seed crystals and fibrous crystals. Preferably, the ZSM-48 crystals also have a low content or are free of needle-like crystals. Another embodiment relates to a ZSM-48 crystals which in an as-synthesized form comprise ZSM-48 having a silica:alumina molar ratio of from 70 to 110 and are formed from a reaction mixture containing a hexamethonium directing agent in a hexamethonium:silica molar ratio from 0.01 to 0.05, preferably from 0.015 to 0.025. In this embodiment, the as-synthesized ZSM-48 crystals are free of non-ZSM-48 seed crystals and fibrous crystals. Preferably, the ZSM-48 crystals also have a low content of needle-like crystals or are free of needle-like crystals.

[0036] In still a further embodiment, the as-synthesized ZSM-48 crystals are calcined thereby removing the hexamethonium structure directing agent to form high purity Na-form ZSM-48. This Na-form ZSM-48 can also be ion exchanged to form H-form ZSM-48. In still another embodiment, the as-synthesized form of ZSM-48 crystals or the calcined ZSM-48 (Na-form or H-form) is combined with at least one of a binder and hydrogenation metal.

[0037] In yet another embodiment, the invention relates to a method for making ZSM-48 crystals which comprises: preparing an aqueous mixture of silica or silicate salt, alumina or aluminate salt, hexamethonium salt and alkali base wherein the mixture has the following molar ratios: silica:alumina from 70 to 110, base:silica from 0.1 to 0.3, preferably from 0.14 to 0.18 and hexamethonium salt:silica from 0.01 to 0.05, preferably from 0.015 to 0.025; heating the mixture with stirring for a time and temperature sufficient for crystal formation. Optionally, seed crystals of ZSM-48 can be added to the reaction mixture. The above procedure results in as-synthesized ZSM-48 crystals that contain the hexamethonium structure directing agent.

Hydroprocessing with ZSM-48 catalysts

[0038] ZSM-48 catalysts are useful as dewaxing catalysts for hydrocarbon feedstocks. A preferred feedstock is a lube oil basestock. Such feedstocks are wax-containing feeds that boil in the lubricating oil range, typically having a 10% distillation point greater than 650°F (343°C), measured by ASTM D 86 or ASTM D2887, and are derived from mineral or synthetic sources. The feeds may be derived from a number of sources such as oils derived from solvent refining processes such as raffinates, partially solvent dewaxed oils, deasphalted oils, distillates, vacuum gas oils, coker gas oils, slack waxes, foots oils and the like, and Fischer-Tropsch waxes. Preferred feeds are slack waxes and Fischer-Tropsch waxes. Slack waxes are typically derived from hydrocarbon feeds by solvent or propane dewaxing. Slack waxes contain some residual oil and are typically

deoiled. Foots oils are derived from deoiled slack waxes. Fischer-Tropsch waxes are prepared by the Fischer-Tropsch synthetic process.

[0039] Feedstocks may have high contents of nitrogen- and sulfur-contaminants. Feeds containing up to 0.2 wt. % of nitrogen, based on feed and up to 3.0 wt. % of sulfur can be processed in the present process. Sulfur and nitrogen contents may be measured by standard ASTM methods D5453 and D4629, respectively.

[0040] The feedstocks may be hydrotreated prior to dewaxing. For hydrotreating, the catalysts are those effective for hydrotreating such as catalysts containing Group 6 metals (based on the IUPAC Periodic Table format having Groups from 1 to 18), Groups 8-10 metals, and mixtures thereof. Preferred metals include nickel, tungsten, molybdenum, cobalt and mixtures thereof. These metals or mixtures of metals are typically present as oxides or sulfides on refractory metal oxide supports. The mixture of metals may also be present as bulk metal catalysts wherein the amount of metal is 30 wt. % or greater, based on catalyst. Suitable metal oxide supports include oxides such as silica, alumina, silica-aluminas or titania, preferably alumina. Preferred aluminas are porous aluminas such as gamma or eta. The amount of metals, either individually or in mixtures, ranges from about 0.5 to 35 wt. %, based on the catalyst. In the case of preferred mixtures of groups 9-10 metals with group 6 metals, the groups 9-10 metals are present in amounts of from 0.5 to 5 wt. %, based on catalyst and the group 6 metals are present in amounts of from 5 to 30 wt. %. The amounts of metals may be measured by methods specified by ASTM for individual metals including atomic absorption spectroscopy or inductively coupled plasma-atomic emission spectrometry.

[0041] Hydrotreating conditions include temperatures of up to 426 °C, preferably from 150 to 400 °C, more preferably 200 to 350 °C, a hydrogen partial pressure of from 1480 to 20786 kPa (200 to 3000 psig), preferably 2859 to 13891 kPa (400 to 2000 psig), a space velocity of from 0.1 to 10 $hr.^{-1}$, preferably 0.1 to

5 $hr.^{-1}$, and a hydrogen to feed ratio of from 89 to 1780 m^3/m^3 (500 to 10000 scf/B), preferably 178 to 890 m^3/m^3 .

[0042] Dewaxing conditions include temperatures of up to 426 °C, preferably from 250-400 °C, more preferably 275 to 350°C, pressures of from 791 to 20786 kPa (100 to 3000 psig), preferably 1480 to 17339 kPa (200 to 2500 psig), liquid hourly space velocities of from 0.1 to 10 $hr.^{-1}$, preferably 0.1 to 5 $hr.^{-1}$ and hydrogen treat gas rates from 45 to 1780 m^3/m^3 (250 to 10000 scf/B), preferably 89 to 890 m^3/m^3 (500 to 5000 scf/B).

[0043] The dewaxed basestock may be hydrofinished. It is desired to hydrofinish the product resulting from dewaxing in order to adjust product qualities to desired specifications. Hydrofinishing is a form of mild hydrotreating directed to saturating any lube range olefins and residual aromatics as well as to removing any remaining heteroatoms and color bodies. The post dewaxing hydrofinishing is usually carried out in cascade with the dewaxing step. Generally the hydrofinishing will be carried out at temperatures from about 150 °C to 350 °C., preferably 180 °C. to 250 °C. Total pressures are typically from 2859 to 20786 kPa (about 400 to 3000 psig). Liquid hourly space velocity is typically from 0.1 to 5 $hr.^{-1}$, preferably 0.5 to 3 $hr.^{-1}$ and hydrogen treat gas rates of from 44.5 to 1780 m^3/m^3 (250 to 10,000 scf/B).

[0044] Hydrofinishing catalysts are those containing Group 6 metals (based on the IUPAC Periodic Table format having Groups from 1 to 18), Groups 8-10 metals, and mixtures thereof. Preferred metals include at least one noble metal having a strong hydrogenation function, especially platinum, palladium and mixtures thereof. The mixture of metals may also be present as bulk metal catalysts wherein the amount of metal is 30 wt. % or greater based on catalyst. Suitable metal oxide supports include low acidic oxides such as silica, alumina, silica-aluminas or titania, preferably alumina. The preferred hydrofinishing catalysts for aromatics saturation will comprise at least one metal having relatively strong hydrogenation function on a porous support. Typical support

materials include amorphous or crystalline oxide materials such as alumina, silica, and silica-alumina. The metal content of the catalyst is often as high as about 20 weight percent for non-noble metals. Noble metals are usually present in amounts no greater than about 1 wt. %. A preferred hydrofinishing catalyst is a mesoporous material belonging to the M41S class or family of catalysts. The M41S family of catalysts are mesoporous materials having high silica contents whose preparation is further described in J. Amer. Chem. Soc., 1992, 114, 10834. Examples included MCM-41, MCM-48 and MCM-50. Mesoporous refers to catalysts having pore sizes from 15 to 100 Angstroms. A preferred member of this class is MCM-41 whose preparation is described in United States Patent Number 5,098,684. MCM-41 is an inorganic, porous, non-layered phase having a hexagonal arrangement of uniformly-sized pores. The physical structure of MCM-41 is like a bundle of straws wherein the opening of the straws (the cell diameter of the pores) ranges from 15 to 100 Angstroms. MCM-48 has a cubic symmetry and is described for example is United States Patent Number 5,198,203 whereas MCM-50 has a lamellar structure. MCM-41 can be made with different size pore openings in the mesoporous range. The mesoporous materials may bear a metal hydrogenation component, which is at least one of Group 8, Group 9 or Group 10 metals. Preferred are noble metals, especially Group 10 noble metals, most preferably Pt, Pd or mixtures thereof.

Hydroprocessing with ZSM-48 catalyst blends

[0045] Figure 6 depicts the activity of two different types of ZSM-48 catalyst for achieving a desired pour point for a feedstock. The upper curve shows the reaction temperature required for a catalyst containing ZSM-48 crystals with a SiO_2:Al_2O_3 ratio of about 200 to achieve a desired pour point for the 370°C+ fraction of the processed feed. The lower curve shows the same relationship for a catalyst containing high purity ZSM-48 crystals with a SiO_2:Al_2O_3 ratio of less than 110. As shown in Figure 6, the ZSM-48 catalyst containing the crystals with the lower SiO_2:Al_2O_3 ratio can achieve the same pour

point at a temperature that is roughly 10°C lower than the ZSM-48 catalyst containing the crystals with the higher SiO_2:Al_2O_3 ratio.

[0046] More generally, high purity ZSM-48 crystals with a SiO_2:Al_2O_3 ratio of less than 110 have increased activity relative to other types of ZSM-48 crystals at a given reaction temperature. Alternatively, the processing temperature required for processing a feedstock to achieve a desired product characteristic is lower for catalysts containing high purity ZSM-48 crystals having a SiO_2:Al_2O_3 ratio of 110 or less as compared to catalysts containing other types of ZSM-48 crystals. In various embodiments, the temperature difference for achieving a desired product characteristic (such as pour point) between a catalyst containing high purity ZSM-48 having a SiO_2:Al_2O_3 ratio of 110 or less versus another type of ZSM-48 catalyst can be at least 5°C, or at least 10°C, or at least 20°C, or at least 30°C.

[0047] In an embodiment, the two or more types of ZSM-48 crystals used in ZSM-48 blends according to the invention can have different activities based on one or more characteristics of the ZSM-48 types. One characteristic that leads to differences in activity is the presence of non-ZSM-48 seed crystals in the ZSM-48. Another characteristic that can lead to differences in activity is the morphology of the crystals. For example, crystals having a fibrous morphology are believed to have a lower reactivity than other types of crystals. In some embodiments, the presence of needle-like morphology can also indicate a difference in activity. Still another characteristic is the presence of impurities, such as Kenyaite. Yet another characteristic is the SiO_2:Al_2O_3 ratio of the crystal types. Crystals with a SiO_2:Al_2O_3 ratio below about 110 have a higher activity than crystals with a SiO_2:Al_2O_3 ratio above about 110.

[0048] The activity difference between different types of ZSM-48 crystals can be exploited in a variety of ways. For example, lowering the necessary reaction temperature to achieve a desired result prolongs the life of hydroprocessing catalysts. This can directly lead to cost savings, as exposing

ZSM-48 catalyst to a lower processing temperature will increase the lifetime of the catalyst (or otherwise increase the amount of time between catalyst replacements).

[0049] Another potential benefit is the ability to tune the activity of a blend of ZSM-48 catalysts to match a desired location on a temperature versus yield curve. Although lower processing temperatures can prolong catalyst lifetime, some existing processing configurations require a minimum temperature in a reactor where a hydroprocessing catalyst such as ZSM-48 is employed. For example, some lube processing facilities lack interstage heating between the dewaxing reactor and the hydrofinishing reactor. If the temperature in the dewaxing reactor is too low, and/or if the heat loss between the dewaxing reactor and the hydrofinishing reactor is too large, the dewaxed product entering the hydrofinishing reactor will not be at a sufficient temperature for effective hydrofinishing. Blends of ZSM-48 catalyst can be used to produce a blended catalyst composition that corresponds to the minimum temperature needed for the reactor. This allows the process to be optimized using standardized catalyst formulations, as opposed to having to synthesize a specific catalyst to match the reactor requirements.

[0050] In another example, blends of ZSM-48 catalyst can be used to match a desired activity to a desired temperature for processes involving cascaded reactions within a single reactor. One typical hydrotreating process is to subject a feedstock to a hydrodesulfurization step, followed by a dewaxing step, followed by a hydrofinishing step. It can be desirable to integrate these reactions, such as in a single reactor. In situations where multiple hydroprocessing steps are cascaded together, large variations in temperature between the cascaded steps can be difficult to maintain. ZSM-48 catalysts are suitable catalysts for use as a dewaxing catalyst in such integrated hydroprocessing schemes. By using blends of ZSM-48 catalysts, a desired combination of yield and temperature of operation can be selected, in order to reduce or minimize temperature differences between

the steps preceeding or following the hydroprocessing step involving the blended ZSM-48 catalysts.

[0051] Using blends of ZSM-48 to tailor the activity of a catalyst system provides advantages over using a blend of ZSM-48 with another type of catalyst, such as another type of zeolite. ZSM-48 is a selective dewaxing catalyst that functions primarily by isomerizing long chain molecules to introduce branches into the chain. This is in contrast to many other types of zeolite catalysts, such as ZSM-5, ZSM-11, USY zeolite, and mordenite, that operate primarily by cracking of long chain molecules to produce shorter chains. Because ZSM-48 does not favor cracking reactions, ZSM-48 can be used in hydroprocessing of a feedstock (such as dewaxing) while reducing or minimizing the amount of feedstock lost due to conversion to smaller, lighter components. By using blends of ZSM-48 to adjust the catalyst properties to match a desired yield curve, use of catalysts that would increase the amount of undesirable side reactions (such as cracking) can be avoided.

[0052] In an embodiment, ZSM-48 crystals having a SiO_2:Al_2O_3 ratio of less than 110 described above can be combined with various other types of ZSM-48 crystals. For example, ZSM-48 crystals as described above that have a SiO_2:Al_2O_3 ratio of less than 110 can be blended with ZSM-48 crystals having a SiO_2:Al_2O_3 ratio of greater than 110, such ZSM-48 crystals with a SiO_2:Al_2O_3 ratio of greater than 150, or greater than 200. Alternatively, ZSM-48 crystals with a SiO_2:Al_2O_3 ratio of 110 or less as described above can be blended with ZSM-48 crystals that contains non-ZSM-48 seed crystals. In still another embodiment, ZSM-48 crystals with a SiO_2:Al_2O_3 ratio of 110 or less can be blended with ZSM-48 crystals that are partially in the form of a less desirable morphology. The ZSM-48 crystals that are partially in the less desirable morphology can include ZSM-48 crystals that are at least partially in a fibrous morphology. Alternatively, the ZSM-48 crystals in the less desirable morphology can include ZSM-48 crystals having a greater percentage of needle-

like morphology than the high purity ZSM-48 crystals, such as at least 1%, or at least 2%, or at least 5%, or at least 10% crystals in a needle-like morphology. In yet another embodiment, the high purity ZSM-48 crystals with a SiO_2:Al_2O_3 ratio of less than about 110 can be blended with ZSM-48 containing a larger percentage of Kenyaite than the high purity ZSM-48 crystals, such as at least 1%, or at least 2%, or at least 5%, or at least 10%.

[0053] In an embodiment, the high purity ZSM-48 crystals having a SiO_2:Al_2O_3 ratio of 110 or less can preferably have a SiO_2:Al_2O_3 ratio of 100 or less, or 90 or less, or 80 or less. Alternatively, the SiO_2:Al_2O_3 ratio of the high purity ZSM-48 crystals can be 70 or more, or 80 or more.

[0054] In various embodiments, the different types of ZSM-48 crystals can be blended together in any convenient manner. For example, the ZSM-48 crystals having a SiO_2:Al_2O_3 ratio of 110 or less as described above can be blended together with another type of ZSM-48 crystals prior to formulation of the crystals into a catalyst. Alternatively, two or more types of ZSM-48 crystals can be formulated separately into catalysts, and the formulated catalysts can be blended together.

[0055] Blends of ZSM-48 catalysts can include two or more types of ZSM-48 crystals. The amount of each type of ZSM-48 crystal in the blend can be any suitable or convenient amount. In an embodiment, the amount of high purity ZSM-48 crystals having a SiO_2:Al_2O_3 ratio of 110 or less can be at least 10%, or at least 25%, or at least 50%, or at least 75%, or at least 90%, or at least 95% of the ZSM-48 crystals in the blend. Alternatively, the amount of high purity ZSM-48 crystals having a SiO_2:Al_2O_3 ratio of 110 or less can be 99% or less, or 95% or less, or 90% or less, or 75% or less, or 50% or less of the ZSM-48 crystals in the blend.

[0056] In still other embodiments, stacked beds of ZSM-48 of different types can be used to dewax a feedstock. In many embodiments, stacked beds of ZSM-48 can deliver similar performance to blends of ZSM-48.

[0057] In an embodiment, stacked beds of ZSM-48 can be used for multi-stage dewaxing of a feedstock with elevated levels of sulfur and/or nitrogen. Due to the higher activity, the high purity ZSM-48 having a SiO_2:Al_2O_3 ratio of 110 or less can be used in a first catalyst bed to contact the feedstock. Contact with the first bed of ZSM-48 will convert some sulfur and nitrogen species to H_2S and NH_3, which will improve the activity of following catalyst beds. Another type of ZSM-48 could then be placed in a second catalyst bed. Due to the activity difference between the types of ZSM-48, both beds could be operated at the same temperature.

[0058] This invention is further illustrated by the following examples.

EXAMPLE 1

[0059] A mixture was prepared from 1200 g of water, 40 g of hexamethonium chloride (56% solution), 228 g of Ultrasil PM (a precipitated silica powder from Degussa), 12 g of sodium aluminate solution (45%), and 40 g of 50% sodium hydroxide solution. The mixture had the following molar composition:

SiO_2/Al_2O_3	=	106
H_2O/ SiO_2	=	20.15
OH^-/ SiO_2	=	0.17
Na^+/ SiO_2	=	0.17
Template/SiO_2	=	0.023

[0060] The mixture was reacted at 320°F (160°C) in a 2-liter autoclave with stirring at 250 RPM for 48 hours. Those of skill in the art will recognize that factors such as the size of the autoclave and the type of stirring mechanism can make other stirring speeds and times desirable. The product was filtered, washed with deionized (DI) water and dried at 250°F (120°C). The XRD pattern of the as-synthesized material showed the typical pure phase of ZSM-48 topology. The SEM of the as-synthesized material shows that the material was composed of

agglomerates of crystals with mixed morphologies (needle-like and irregularly shaped crystals). The resulting ZSM-48 crystals had a SiO_2/Al_2O_3 molar ratio of ~ 100/1. Figure 1 is a photomicrograph of the ZSM-48 crystals. This comparative example at template:silica ratio of 0.023 shows the presence of some needle-like crystals.

EXAMPLE 2

[0061] A mixture was prepared from water, hexamethonium chloride (56% solution), Ultrasil PM, sodium aluminate solution (45%), and 50% sodium hydroxide solution. The prepared mixture had the following molar composition:

SiO_2/Al_2O_3	=	106
H_2O/ SiO_2	=	20.15
OH^-/ SiO_2	=	0.17
Na^+/ SiO_2	=	0.17
Template/SiO_2	=	0.018

[0062] The mixture was reacted at 320°F (160°C) in an autoclave with stirring at 250 RPM for 48 hours. The product was filtered, washed with deionized (DI) water and dried at 250°F (120°C). The XRD pattern of the as-synthesized material showed the typical pure phase of ZSM-48 topology. The SEM of the as-synthesized material shows that the material was composed of agglomerates of small irregularly shaped crystals (with an average crystal size of about 0.05 microns). The resulting ZSM-48 crystals had a SiO_2/Al_2O_3 molar ratio of ~ 94/1. Figure 2 is a photomicrograph of the resulting ZSM-crystals. Figure 2 shows the absence of needle-like crystals for ZSM-48 according to the invention.

EXAMPLE 3

[0063] A mixture was prepared from water, hexamethonium chloride (56% solution), Ultrasil Modified, sodium aluminate solution (45%), 50% sodium

hydroxide solution, and 5 wt% (relative to the silica charge) of ZSM-48 seed crystals. The mixture had the following molar composition:

SiO_2/Al_2O_3	=	103
H_2O/ SiO_2	=	14.8
OH^-/ SiO_2	=	0.17
Na^+/ SiO_2	=	0.17
$Template/SiO_2$	=	0.029

[0064] The mixture was reacted at 320°F (160°C) in an autoclave with stirring at 250 RPM for 48 hours. The product was filtered, washed with deionized (DI) water and dried at 250°F (120°C). The XRD pattern of the as-synthesized material showed the typical pure phase of ZSM-48 topology. The SEM of the as-synthesized material shows that the material was composed of agglomerates of elongated (needle-like) crystals (with an average crystal size of < 1 microns). The resulting ZSM-48 crystals had a SiO_2/Al_2O_3 molar ratio of ~ 95/1. Figure 3 is a photomicrograph of the resulting ZSM-crystals. This comparative example shows the presence of needle-like crystals for ZSM-48 synthesized from a reaction mixture having a template:silica ratio of 0.029.

EXAMPLE 4

[0065] A mixture was prepared from water, hexamethonium chloride (56% solution), Ultrasil Modified, sodium aluminate solution (45%), 50% sodium hydroxide solution, and 5 wt% (relative to the silica charge) of ZSM-48 seed crystals. The mixture had the following molar composition:

SiO_2/Al_2O_3	=	103
H_2O/ SiO_2	=	14.7
OH^-/ SiO_2	=	0.17
Na^+/ SiO_2	=	0.17
$Template/SiO_2$	=	0.019

[0066] The mixture was reacted at 320°F (160°C) in an autoclave with stirring at 250 RPM for 24 hours. The product was filtered, washed with deionized (DI) water and dried at 250°F (120°C). The XRD pattern of the as-synthesized material showed the typical pure phase of ZSM-48 topology. The SEM of the as-synthesized material shows that the material was composed of agglomerates of small irregularly shaped crystals (with an average crystal size of about 0.05 microns). The resulting ZSM-48 crystals had a SiO_2/Al_2O_3 molar ratio of 89. Figure 4 is a photomicrograph of the resulting ZSM-crystals. This example of ZSM-48 crystals according to the invention shows the absence of needle-like crystals.

EXAMPLE 5

[0067] A mixture was prepared from water, hexamethonium chloride (56% solution), Ultrasil Modified, sodium aluminate solution (45%), 50% sodium hydroxide solution, and 3.5 wt% (relative to the silica charge) of ZSM-48 seed crystals. The mixture had the following molar composition:

SiO_2/Al_2O_3	=	103
H_2O/ SiO_2	=	14.6
OH^-/ SiO_2	=	0.17
Na^+/ SiO_2	=	0.17
$Template/SiO_2$	=	0.015

[0068] The mixture was reacted at 320°F (160°C) in an autoclave with stirring at 250 RPM for 48 hours. The product was filtered, washed with deionized (DI) water and dried at 250°F (120°C). The XRD pattern of the as-synthesized material showed the mixture of ZSM-48 and trace of Kenyaite impurity.

EXAMPLE 6

[0069] A mixture was prepared from water, hexamethonium chloride (56% solution), Ultrasil Modified, sodium aluminate solution (45%), 50% sodium

hydroxide solution, and 3.5 wt% (relative to the silica charge) of ZSM-48 seed crystals. The mixture had the following molar composition:

SiO_2/Al_2O_3	=	102.4
H_2O/ SiO_2	=	14.8
OH^-/ SiO_2	=	0.20
Na^+/ SiO_2	=	0.20
$Template/SiO_2$	=	0.019

[0070] The mixture was reacted at 320°F (160°C) in an autoclave with stirring at 250 RPM for 48 hours. The product was filtered, washed with deionized (DI) water and dried at 250°F (120°C). The XRD pattern of the as-synthesized material synthesized from a reaction mixture having a base:silica ratio of 0.20 showed the mixture of ZSM-48 and Kenyaite impurity.

EXAMPLE 7

[0071] A mixture was prepared from water, hexamethonium chloride (56% solution), Ultrasil PM, sodium aluminate solution (45%), 50% sodium hydroxide solution, and 3.5 wt% (relative to the silica charge) of ZSM-48 seed crystals. The mixture had the following molar composition:

SiO_2/Al_2O_3	=	102.4
H_2O/ SiO_2	=	14.8
OH^-/ SiO_2	=	0.15
Na^+/ SiO_2	=	0.15
$Template/SiO_2$	=	0.019

[0072] The mixture was reacted at 320°F (160°C) in an autoclave with stirring at 250 RPM for 48 hours. The product was filtered, washed with deionized (DI) water and dried at 250°F (120°C). The XRD pattern of the as-synthesized material showed the typical pure phase of ZSM-48 topology.

EXAMPLE 8

[0073] A mixture was prepared from water, hexamethonium chloride (56% solution), Ultrasil PM, sodium aluminate solution (45%), and 50% sodium hydroxide solution. The mixture had the following molar composition:

SiO_2/Al_2O_3	=	90
H_2O/ SiO_2	=	20.1
OH^-/ SiO_2	=	0.17
Na^+/ SiO_2	=	0.17
$Template/SiO_2$	=	0.025

[0074] The mixture was reacted at 320°F (160°C) in an autoclave with stirring at 250 RPM for 48 hours. The product was filtered, washed with deionized (DI) water and dried at 250°F (120°C). The XRD pattern of the as-synthesized material showed the typical ZSM-48 topology and a trace of ZSM-50 impurity was identified. The product showed the presence of some needle-like morphology.

EXAMPLE 9

[0075] 65 parts (basis: calcined 538 °C) of high activity ZSM-48 crystal (Example #4) were mixed with 35 parts of pseudoboehmite alumina (basis: calcined 538 °C) in a Simpson muller. Sufficient water was added to produce an extrudable paste on a 2" Bonnot extruder. The mix of ZSM-48, pseudoboehmite alumina, and water containing paste was extruded and dried in a hotpack oven at 121 °C overnight. The dried extrudate was calcined in nitrogen @ 538 °C to decompose and remove the organic template. The N_2 calcined extrudate was humidified with saturated air and exchanged with 1 N ammonium nitrate to remove sodium (spec: < 500 ppm Na). After ammonium nitrate exchange, the extrudate was washed with deionized water to remove residual nitrate ions prior to drying. The ammonium exchanged extrudate was dried at 121 °C overnight and calcined in air at 538 °C. After air calcination, the extrudate was steamed for

3 hrs @ 900 °F. The steamed extrudate was impregnated with tetrammine platinum nitrate (0.6 wt% Pt) using incipient wetness. After impregnation, the extrudate was dried overnight at 250 °F and calcined in air at 360 °C to convert the tetrammine nitrate salt to platinum oxide.

EXAMPLE 10

[0076] The dewaxing catalyst of Example 9 was tested in a n-C_{10} hydroisomerization test. Catalyst temperatures were varied from 162 to 257 °C under flowing H_2 (100 sccm) at 1 atm pressure to adjust n-C_{10} conversions from 0 to 95%+. The high activity ZSM-48 containing catalyst showed excellent iso-C_{10} yields with minimal cracking as a function of n-C_{10} conversion and reaction temperature. Figure 5 is a graph showing iso-C_{10} yield as a function of n-C_{10} conversion for a catalyst according to an embodiment of the invention and a catalyst with a silica:alumina ratio of about 200.

EXAMPLE 11

[0077] This example relates to the preparation of HA-ZSM-48 with seeding with regular ZSM-48 crystals. A mixture was prepared using water, hexamethonium chloride (56% solution), Ultrasil PM, sodium aluminate solution (45%), and 50% sodium hydroxide solution. About 5 wt% (relative to the silica charge) of ZSM-48 seed was then added the mixture. The mixture had the following molar composition:

SiO_2/Al_2O_3	=	103
H_2O/SiO_2	=	14.7
OH^-/SiO_2	=	0.17
Na^+/SiO_2	=	0.17
Template/SiO_2	=	0.019

[0078] The mixture was reacted at 320°F (160°C) in an autoclave with stirring at 250 RPM for 24 hours. The product was filtered, washed with deionized (DI) water and dried at 250°F (120°C). The XRD pattern of the as-synthesized material shows pure phase of ZSM-48 topology. The assynthesized crystals were converted into the hydrogen form by two ion exchanges with ammonium nitrate solution at room temperature, followed by drying at 250°F (120°C) and calcination at 1000°F (540°C) for 6 hours. The resulting ZSM-48 crystals had a SiO_2/Al_2O_3 molar ratio of ~ 88.5/1.

EXAMPLE 12

[0079] This example shows the preparation of ZSM-48 with seeding using 5 wt.% (relative to the silica charge) of Beta crystals. Heterostructural seeding using Beta crystals is described in United States Patent Number 6,923,949. A mixture was prepared from 1000 g of water, 25 g of hexamethonium chloride (56% solution), 190 g of Ultrasil PM (a precipitated silica powder produced from Degussa), 10 g of sodium aluminate solution (45%), and 33.3 g of 50% sodium hydroxide solution. The 10 g of Beta seed (SiO_2/Al_2O_3 ~ 35/1) was then added the mixture. The mixture had the following molar composition:

SiO_2/Al_2O_3 = 106

H_2O/SiO_2 = 20

OH^-/SiO_2 = 0.17

$Na+/SiO_2$ = 0.17

Template/SiO_2 = 0.018

[0080] The mixture was reacted at 320°F (160°C) in a 2 liter autoclave with stirring at 250 RPM for 48 hours. The product was filtered, washed with deionized (DI) water and dried at 250°F (120°C). The XRD pattern of the as-synthesized material shows pure phase of ZSM-48 topology. Clearly, no Beta phase was observed on XRD pattern of the synthesized product. The as-synthesized crystals were converted into the hydrogen form by two ion

exchanges with ammonium nitrate solution at room temperature, followed by drying at 250°F (120°C) and calcination at 1000°F (540°C) for 6 hours. The resulting ZSM-48 crystals had a SiO_2/Al_2O_3 molar ratio of ~ 87.2.

EXAMPLE 13

[0081] This example shows the preparation of ZSM-48 using seeding with 10 wt.% (relative to the silica charge) of Beta seeds. The same reactants, formulation, and procedure as Example 2 were used, except that double amount of Beta crystals was added as seeding agent. The XRD pattern of the as-synthesized material shows pure phase of ZSM-48 topology. Clearly, no Beta phase was observed on XRD pattern of the synthesized product. The as-synthesized crystals were converted into the hydrogen form by two ion exchanges with ammonium nitrate solution at room temperature, followed by drying at 250°F (120°C) and calcination at 1000°F (540°C) for 6 hours. The resulting ZSM-48 crystals had a SiO_2/Al_2O_3 molar ratio of ~ 80/1.

EXAMPLE 14

[0082] The products from Examples 11-13 were tested using a hexane adsorption test. The hexane adsorption test is a measure of the pore volume of any given catalyst. The calcined catalysts prepared as above were heated in a thermogravimetric analyzer (TGA) under nitrogen at 500 °C for 30 min. The dried catalyst was then cooled to 90 °C and exposed to n-hexane at a partial pressure of 75 torr. The weight changes as n-hexane uptake were measured by micro balance in the TGA instrument. An Alpha value was also determined for each crystal. The Alpha value for a catalyst is a standardized measure of the catalyst activity relative to the activity of a reference catalyst. The results are summarized in Table 1.

TABLE 1

Sample	n-Hexane, (mg/g)	Estimated % Beta in product	Alpha Value

Example11, HA-ZSM-48 reaction seeded with ZSM-48 crystals	37.7	0	70
Example12: HA-ZSM-48 reaction seeded with ~5% (to silica charged) of Beta seed	42.4	~ 5.3	~ 125
Example13: HA-ZSM-48 reaction seeded with ~ 10 % (to silica charged) of Beta seed	48.3	~ 12	180
Beta seed crystals used in Examples 12 & 13	126	100	690

[0083] Based on the data shown in Table 1, the added Beta seed crystals were not dissolved in the crystallization and remained in the synthesized product. The conclusion was supported by the increasing adsorption data of n-hexane on Examples 12 & 13. The conclusion is also supported by the increasing alpha value of the catalysts as the weight percentage of beta in the crystals increases. The n-hexane adsorption and alpha value increases demonstrate that the ZSM-48 crystals with a heterogeneous seed have a different reactivity than the ZSM-48 crystals with a homogeneous seed.

[0084] Note that the Alpha Value is an approximate indication of the catalytic cracking activity of the catalyst compared to a standard catalyst and it gives the relative rate constant (rate of normal hexane conversion per volume of catalyst per unit time). It is based on the activity of the highly active silica-alumina cracking catalyst taken as an Alpha of 1 (Rate Constant=0.016 sec^{-1}). The Alpha Test is conventionally known, and is described, for example, in U.S. Pat. No. 3,354,078; in the Journal of Catalysis, vol. 4, p. 527 (1965); vol. 6, p. 278 (1966); and vol. 61, p. 395 (1980).

EXAMPLE 15

[0085] This example compares the activity credit for ZSM-48 according to the invention relative to a ZSM-48 with a higher silica:alumina ratio. A 600N slack wax was dewaxed at 1000 psig (6996 kPa), LHSV of 1.0 *l*/hr and treat gas

rate of 2500 scf/B (445 m^3/m^3). Figure 6 is a graph showing reactor temperature vs. required temperature to meet the 370°C+ pour point. In Figure 6, the difference between the upper line (representing ZSM-48 with a higher silica:alumina ratio) and the lower line (ZSM-48 according to the invention) represents the activity credit.

WHAT IS CLAIMED IS:

1. A method for dewaxing a hydrocarbon feedstock which comprises: contacting a feedstock with a blend of ZSM-48 catalysts under catalytic dewaxing conditions to produce a dewaxed feedstock, the blend of ZSM-48 catalysts comprising

a) a first type of ZSM-48 crystals having a silica:alumina molar ratio of from 70 to 110 and being free of non-ZSM-48 seed crystals; and

b) a second type of ZSM-48 crystals, the first type of ZSM-48 crystals and second type of ZSM-48 crystals being different.

2. The method of claim 1, wherein the second type of ZSM-48 crystals comprises ZSM-48 crystals containing non-ZSM-48 seed crystals.

3. The method of claim 1, wherein the second type of ZSM-48 crystals comprise ZSM-48 crystals with a SiO_2:Al_2O_3 ratio of greater than 110.

4. The method of claim 1, wherein the second type of ZSM-48 crystals include ZSM-48 crystals having a fibrous morphology.

5. The method of claim 1, wherein the second type of ZSM-48 crystals include a greater percentage of Kenyaite than the first type of ZSM-48 crystals.

6. The method of claim 1, wherein the ZSM-48 crystals are blended by formulating the first type of ZSM-48 crystals into first catalyst particles, formulation the second type of ZSM-48 crystals into second catalyst particles, and mixing the first and second catalyst particles.

7. The method of claim 1, wherein the ZSM-48 crystals are blended by formulating catalyst particles containing both the first type of ZSM-48 crystals and the second type of ZSM-48 crystals.

8. The method of claim 1, wherein the first type of ZSM-48 crystals are free of crystals having a fibrous morphology.

9. The method of claim 1, wherein the first type of ZSM-48 crystals are free of crystals having a needle-like morphology.

10. The method of claim 1, wherein the first type of ZSM-48 crystals are free of Kenyaite.

11. The method of claim 1, wherein the first type of ZSM-48 crystals are free of ZSM-50.

12. The method of claim 1, wherein the feedstock is hydrotreated under hydrotreating conditions prior to contacting the blended ZSM-48 catalyst.

13. The method of claim 1, wherein the dewaxed feedstock is hydrofinished under hydrofinishing conditions.

14. The method of claim 1, wherein the catalytic dewaxing conditions include temperatures of from 250-426°C, pressures of from 791 to 20786 kPa (100 to 3000 psig), liquid hourly space velocities of from 0.1 to 10 hr^{-1}, and hydrogen treat gas rates from 45 to 1780 m^3/m^3 (250 to 10000 scf/B).

15. The method of claim 12, wherein the hydrotreating conditions include temperatures of from 150 to 426 °C, a hydrogen partial pressure of from 1480 to 20786 kPa (200 to 3000 psig), a space velocity of from 0.1 to 10 hr^{-1}, and a hydrogen to feed ratio of from 89 to 1780 m^3/m^3 (500 to 10000 scf/B).

16. The method of claim 13 wherein the hydrofinishing conditions include at temperatures from about 150 to 350°C, total pressures of from 2859 to 20786 kPa (about 400 to 3000 psig), liquid hourly space velocity of from 0.1 to 5 hr^{-1}, and hydrogen treat gas rates of from 44.5 to 1780 m^3/m^3 (250 to 10,000 scf/B).