IMPROVED CATALYST COMPOSITION

BACKGROUND OF THE INVENTION

[0001] The present invention relates to an improved catalyst composition. The catalyst may be used to effect various chemical conversions, and is particularly valuable for use in a process for producing alkylaromatics, particularly ethylbenzene and cumene, or for use in a process for oligomerization of olefins, particularly for production of dimers, trimers and tetramers of olefins, e.g. ethylene, propylene, butylene, or mixtures thereof.

[0002] Ethylbenzene and cumene are valuable commodity chemicals that are used industrially for the production of styrene monomer and coproduction of phenol and acetone respectively. Ethylbenzene may be produced by a number of different chemical processes but one process that has achieved a significant degree of commercial success is the vapor phase alkylation of benzene with ethylene in the presence of a solid, acidic ZSM-5 zeolite catalyst. Examples of such ethylbenzene production processes are described in U.S. Patent Nos. 3,751,504 (Keown), 4,547,605 (Kresge), and 4,016,218 (Haag).

[0003] More recently focus has been directed at liquid phase processes for producing ethylbenzene from benzene and ethylene since liquid phase processes operate at a lower temperature than their vapor phase counterparts and hence tend to result in lower yields of by-products. For example, U.S. Patent No. 4,891,458 (Innes) describes the liquid phase synthesis of ethylbenzene with zeolite Beta, whereas U.S. Patent No. 5,334,795 (Chu) describes the use of MCM-22 in the liquid phase synthesis of ethylbenzene.

[0004] Cumene has for many years been produced commercially by the liquid phase alkylation of benzene with propylene over a Friedel-Craft catalyst, particularly solid phosphoric acid or aluminum chloride. More recently, however, zeolite-based catalyst systems have been found to be more active and selective for propylation of benzene to cumene. For example, U.S. Patent No. 4,992,606 (Kushnerick) describes the use of MCM-22 in the liquid phase alkylation of benzene with propylene.

[0005] Alkylation processes for producing ethylbenzene and cumene in the presence of currently used catalysts inherently produce polyalkylated species as well as the desired monoalkylated product. The polyalkylated species are typically transalkylated with benzene to produce additional monoalkylated product, for example ethylbenzene or cumene, either by recycling the polyalkylated species to the alkylation reactor or, more frequently, by feeding the polyalkylated species to a separate transalkylation reactor having a transalkylation catalyst. Examples of catalysts which have been used in the alkylation of aromatic species, such as alkylation of benzene with ethylene or propylene, and in the transalkylation of polyalkylated species, such as polyethylbenzenes and polyisopropylbenzenes, are listed in U.S Patent No. 5,557,024 (Cheng) and include MCM-22, PSH-3, SSZ-25, zeolite X, zeolite Y, zeolite Beta, acid dealuminized mordenite and TEA-mordenite. Transalkylation over a small crystal (<0.5 micron) form of TEA-mordenite is also disclosed in U.S. Patent 6,984,764.

[0006] Where the alkylation step is performed in the liquid phase, it is also desirable to conduct the transalkylation step under liquid phase conditions. However, by operating at relatively low temperatures, liquid phase processes impose increased requirements on the catalyst, particularly in the transalkylation step where the bulky polyalkylated species must be converted to additional monoalkylated product without producing unwanted by-products. This has proved to be a significant problem in the case of cumene production where existing catalysts have either lacked the desired activity or have resulted in the production of significant quantities of by–products such as ethylbenzene and n-propylbenzene.

[0007] According to the present invention, it has now unexpectedly been found that a specific catalyst manufactured to exhibit a Proton Density Index ("PDI"), as herein defined, of greater than 1.0, for example, from greater than 1.0 to about 2.0, e.g. from about 1.01 to about 1.85, has a unique combination of activity and, importantly, selectivity, especially when used as a liquid phase alkylation catalyst for manufacture of monoalkylated product, particularly for the liquid phase alkylation of benzene to ethylbenzene, cumene or sec-butylbenzene. This obviates or reduces the demand in many instances for the difficult transalkylation reaction for conversion of unwanted bulky polyalkylated species.

SUMMARY OF THE INVENTION

[0008] According to one aspect of the invention, there is provided an improved catalyst. This catalyst may be used to effect conversion in chemical reactions, and is particularly useful in a process for selectively producing a desired monoalkylated aromatic compound comprising the step of contacting an alkylatable aromatic compound with an alkylating agent in the presence of the present catalyst under at least partial liquid phase conditions, said catalyst comprising an acidic, porous crystalline material and having a PDI of greater than 1.0, for example, from greater than 1.0 to about 2.0, e.g. from about 1.01 to about 1.85. Another aspect of the present invention is an improved alkylation catalyst for use in a process for the selective production of monoalkyl benzene comprising the step of reacting benzene with an alkylating agent under alkylation conditions in the presence of said alkylation catalyst which comprises an acidic, porous crystalline material and having a PDI of greater than 1.0, for example, from greater than 1.0 to about 2.0, e.g. from about 1.01 to about 1.85. The catalyst may comprise, for example, an acidic, crystalline molecular sieve having the structure of zeolite Beta, or one having an X-ray diffraction pattern including d-spacing maxima at 12.4±0.25, 6.9±0.15, 3.57±0.07 and 3.42±0.07 Angstroms, said catalyst having a PDI of greater than 1.0, for example, from greater than 1.0 to about 2.0, e.g. from about 1.01 to about 1.85. More particularly, the catalyst may comprise an acidic, crystalline molecular sieve having the structure of zeolite Beta, an MWW structure type material, e.g. MCM-22, or a mixture thereof.

[0009] For use of the present catalyst to effect alkylation of an alkylatable aromatic compound, the alkylating agent may include an alkylating aliphatic group having 1 to 5 carbon atoms. The alkylating agent may comprise, for example, ethylene, propylene, and/or the butenes, and the alkylatable aromatic compound in such an instance may comprise benzene.

[0010] A preferred catalyst of the present invention comprises an MWW structure type material, such as for example an acidic, crystalline silicate having the structure of MCM-22, PSH-3, SSZ-25, ERB-1, ITQ-1, ITQ-2, ITQ-30, MCM-36, MCM-49, MCM-56 and mixtures thereof.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] Fig. 1 shows the shallow bed CAVERN device used in experiments involving the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0012] The present invention relates to an improved catalyst for use in processes benefiting from high activity and/or selectivity. One such process involves production of monoalkylated aromatic compounds, particularly ethylbenzene, cumene, and sec-butylbenzene, by the liquid or partial liquid phase alkylation of alkylatable aromatic compound, particularly benzene. Another such process involves production of oligomers from olefins. More particularly, the present catalyst composition comprises an acidic, porous crystalline material and is manufactured to exhibit a PDI of greater than 1.0, for example, from greater than 1.0 to about 2.0, e.g. from about 1.01 to about 1.85.

[0013] As used herein, the term PDI when used in connection with a particular catalyst composition is defined as the proton density of the new, treated, catalyst composition measured at a given temperature, divided by the proton density of the original, untreated, catalyst composition measured at the same given temperature.

[0014] As used herein, the term "proton density" means the millimoles (mmol) of acidic protons and/or non-acidic protons per gram of catalyst composition. The proton density of the new, treated catalyst composition, and the proton density of the original, untreated catalyst composition are both measured at the same temperature, for example room temperature, e.g. from about 20°C to about 25°C.

[0015] The amount of protons on a catalyst sample is measured by a solid-state nuclear magnetic resonance method for characterizing the amount of acidic protons and non-acidic protons on such catalyst sample as described herein. These acidic and non-acidic protons may be present as any hydrogen-containing moiety, or proton-containing moiety, including, but not limited to H, H^+, OH, OH^-, and other species. The nuclear magnetic resonance method includes, but is not limited to, magic angle spinning (MAS) NMR. Sample preparation is the key in NMR measurement of the amount of such protons on the catalyst samples. A trace amount of water will strongly distort the ^1H NMR intensity due in part to the fast ^1H chemical exchange involving Bronsted acid sites and a water molecule.

[0016] The method for producing the present catalyst composition comprises the steps of:

(a) providing a first, untreated catalyst, i.e. one not having been treated according to steps (b) and (c) of this invention, comprising an acidic, porous crystalline material, said first catalyst having a first hydration state measured in millimoles (mmol) of protons per gram of catalyst;

(b) contacting the first catalyst of step (a) with water in liquid or gaseous form, at a contact temperature of up to about 500°C, such as from about 1°C to about 500°C, preferably from about 1°C to about 99°C, for a contact time of at least about 1 second, preferably from about 1 minute to about 60 minutes, to generate a second catalyst having a second hydration state measured in mmol of protons per gram of catalyst, said second hydration state being greater than said first hydration state, i.e. the product of step (b) has a higher proton density than the step (a) catalyst; and

(c) drying the second catalyst resulting from step (b) at a drying temperature of up to about 550°C, preferably from about 20°C to about 550°C, more preferably from about 100°C to about 200°C, for a drying time of at least about 0.01 hour, preferably from about 0.1 to about 24 hours, more preferably from about 1 to about 6 hours, to generate the catalyst composition having a third hydration state measured in mmol of protons per gram of catalyst between said first and second hydration states. The step (c) product will have a Proton Density Index of greater than 1.0, for example, from greater than 1.0 to about 2.0, e.g. from about 1.01 to about 1.85.

[0017] During drying step (c), acidic protons and/or non-acidic protons are removed from the catalyst contacted with water in liquid or gaseous form in accordance with step (b). However, care must be taken during drying step (c) to avoid removal of essentially all acidic and/or non-acidic protons of the catalyst resulting from step (b). The hydration state of the step (c) product will be higher than that of the starting step (a) catalyst and lower than that of the step (b)

product. It is recognized that increases in proton density are not simply the conversion of Lewis acid sites to Bronsted acid sites. Not wishing to be bound by any theory of operation, it is believed that contacting a catalyst comprising an acidic, porous crystalline material and having a first hydration state with water in liquid or gaseous form under certain contact time and temperature conditions creates a catalyst having a second hydration state higher than the first hydration state. This, followed by drying under certain controlled drying time and temperature conditions may change the nature, type, and/or the amount of acidic and/or non-acidic protons on such catalyst which are associated with the chemical reaction, to generate a catalyst composition having a third hydration state between that of the first and second hydration states, whereby the catalyst composition will have a Proton Density Index of greater than about 1.0. That is, such catalyst comprising an acidic, porous crystalline material and treated by the method of this invention has a greater proton density, and/or a greater number of acidic and/or non-acidic protons as compared to the same catalyst which is not treated by such method. In other words, PDI is defined as the proton density of the third hydration state catalyst composition divided by the proton density of that catalyst in the first hydration state, both prepared and measured in the same manner.

[0018] The term "aromatic" in reference to the alkylatable aromatic compounds which may be useful as feedstock in a process beneficially utilizing the present catalyst is to be understood in accordance with its art-recognized scope. This includes alkyl substituted and unsubstituted mono- and polynuclear compounds. Compounds of an aromatic character that possess a heteroatom may also be useful.

[0019] Substituted aromatic compounds that can be alkylated herein must possess at least one hydrogen atom directly bonded to the aromatic nucleus. The aromatic rings can be substituted with one or more alkyl, aryl, alkaryl, alkoxy, aryloxy, cycloalkyl, halide, and/or other groups that do not interfere with the alkylation reaction.

[0020] Suitable aromatic compounds include benzene, naphthalene, anthracene, naphthacene, perylene, coronene, and phenanthrene, with benzene being preferred.

[0021] Generally the alkyl groups that can be present as substituents on the aromatic compound contain from 1 to about 22 carbon atoms and usually from about 1 to 8 carbon atoms, and most usually from about 1 to 4 carbon atoms.

[0022] Suitable alkyl substituted aromatic compounds include toluene, xylene, isopropylbenzene, n-propylbenzene, alpha-methylnaphthalene, ethylbenzene, mesitylene, durene, cymenes, butylbenzene, pseudocumene, o-diethylbenzene, m-diethylbenzene, p-diethylbenzene, isoamylbenzene, isohexylbenzene, pentaethylbenzene, pentamethylbenzene, 1,2,3,4- tetraethylbenzene, 1,2,3,5-tetramethylbenzene, 1,2,4-triethylbenzene, 1,2,3-trimethylbenzene, m-butyltoluene, p-butyltoluene, 3,5-diethyltoluene, o-ethyltoluene, p-ethyltoluene, m-propyltoluene, 4-ethyl-m-xylene, dimethylnaphthalenes, ethylnaphthalene, 2,3-dimethylanthracene, 9-ethylanthracene, 2-methylanthracene, o-methylanthracene, 9,10-dimethylphenanthrene, and 3-methyl-phenanthrene. Higher molecular weight alkylaromatic compounds can also be used as starting materials and include aromatic hydrocarbons such as are produced by the alkylation of aromatic hydrocarbons with olefin oligomers. Such products are frequently referred to in the art as alkylate and include hexylbenzene, nonylbenzene, dodecylbenzene, pentadecylbenzene, hexyltoluene, nonyltoluene, dodecyltoluene, pentadecytoluene, etc. Very often alkylate is obtained as a high boiling fraction in which the alkyl group attached to the aromatic nucleus varies in size from about C_6 to about C_{12}. When cumene or ethylbenzene is the desired product, the present process produces acceptably little by-products such as xylenes. The xylenes made in such instances may be less than about 500 ppm.

[0023] Reformate containing a mixture of benzene, toluene and/or xylene constitutes a particularly useful feed for an alkylation process beneficially utilizing the present catalyst.

[0024] The alkylating agents which are useful as feedstock in a process beneficially utilizing the catalyst of this invention generally include any aliphatic or aromatic organic compound having one or more available alkylating aliphatic groups capable of reaction with the alkylatable aromatic compound, preferably with the alkylating group possessing from 1 to 5 carbon atoms. Examples of suitable alkylating agents are olefins such as ethylene, propylene, the butenes

(including 1-butene, 2-butenes, and mixtures thereof), and the pentenes; alcohols (inclusive of monoalcohols, dialcohols, trialcohols, etc.) such as methanol, ethanol, the propanols, the butanols, and the pentanols; aldehydes such as formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, and n-valeraldehyde; and alkyl halides such as methyl chloride, ethyl chloride, the propyl chlorides, the butyl chlorides, and the pentyl chlorides, and so forth.

[0025] Mixtures of light olefins are useful as alkylating agents in the alkylation process utilizing the catalyst of this invention. Also, such mixtures of light olefins are useful as reactants in the oligomerization processes of this invention. Accordingly, mixtures of ethylene, propylene, butenes, and/or pentenes which are major constituents of a variety of refinery streams, e.g., fuel gas, gas plant off-gas containing ethylene, propylene, etc., naphtha cracker off-gas containing light olefins, refinery FCC propane/propylene streams, etc., are useful alkylating agents and oligomerization reactants. For example, a typical FCC light olefin stream possesses the following composition:

	Wt.%	Mole %
Ethane	3.3	5.1
Ethylene	0.7	1.2
Propane	4.5	15.3
Propylene	42.5	46.8
Isobutane	12.9	10.3
n-Butane	3.3	2.6
Butenes	22.1	18.32
Pentanes	0.7	0.4

[0026] For these uses of the present catalyst, products may include ethylbenzene from the reaction of benzene with ethylene, cumene from the reaction of benzene with propylene, ethyltoluene from the reaction of toluene with ethylene, cymenes from the reaction of toluene with propylene, and sec-butylbenzene from the reaction of benzene and n-butenes, a mixture of heavier olefins from the oligomerization of light olefins. Particularly preferred uses of the

present catalyst relate to the production of cumene by the alkylation of benzene with propylene, production of ethylbenzene by the alkylation of benzene with ethylene, production of sec-butylbenzene by the alkylation of benzene with butenes, and oligomerization of ethylene, propylene, butylene, or mixtures thereof.

[0027] The organic conversion processes contemplated for use of the catalyst of this invention include, but are not limited to, alkylation of aromatic compounds and oligomerization of olefins and may be conducted such that the reactants are brought into contact with the required catalyst in a suitable reaction zone such as, for example, in a flow reactor containing a fixed bed of the catalyst composition, under effective conversion conditions. Such conditions include a temperature of from about 0°C to about 1000°C, preferably from about 0°C to about 800°C, a pressure of from about 0.1 to about 1000 atmospheres, preferably from about 0.125 to about 500 atmospheres, and a feed weight hourly space velocity (WHSV) of from about 0.01 to 500 hr^{-1}, preferably from about 0.1 to about 100 hr^{-1}. If a batch reactor is used, the reaction time will be from about 1 minute to about 100 hours, preferably from about 1 hour to about 10 hours.

[0028] An alkylation process utilizing the catalyst of this invention may be conducted such that the organic reactants, i.e., the alkylatable aromatic compound and the alkylating agent, are brought into contact with the present catalyst in a suitable reaction zone such as, for example, in a flow reactor containing a fixed bed of the catalyst composition, under effective alkylation conditions. Such conditions include a temperature of from about 0°C to about 500°C, preferably from about 10°C to about 260°C, a pressure of from about 0.2 to about 250 atmospheres, preferably from about 1 to about 55 atmospheres, a molar ratio of alkylatable aromatic compound to alkylating agent of from about 0.1:1 to about 50:1, preferably from about 0.5:1 to about 10:1, and a feed weight hourly space velocity (WHSV) based on the alkylating agent of from about 0.1 to 500 hr^{-1}, preferably from about 0.5 to about 100 hr^{-1}.

[0029] The reactants can be in either the vapor phase or partially or completely in the liquid phase and can be neat, i.e. free from intentional admixture or dilution with other material, or they can be brought into contact with the alkylation catalyst composition with the aid of carrier gases or diluents such as,

for example, hydrogen or nitrogen.

[0030] When benzene is alkylated with ethylene to produce ethylbenzene, the alkylation reaction is preferably carried out in the liquid phase under conditions including a temperature of from about 150°C to about 300°C, more preferably from about 170°C to about 260°C; a pressure up to about 200 atmospheres, more preferably from about 20 atmospheres to about 55 atmospheres; a weight hourly space velocity (WHSV) based on the ethylene alkylating agent of from about 0.1 to about 20 hr^{-1}, more preferably from about 0.5 to about 6 hr^{-1}; and a ratio of benzene to ethylene in the alkylation reactor of from about 0.5:1 to about 30:1 molar, more preferably from about 1:1 to about 10:1 molar.

[0031] When benzene is alkylated with propylene to produce cumene, the reaction may also take place under liquid phase conditions including a temperature of up to about 250°C, preferably up to about 150°C, e.g., from about 10°C to about 125°C; a pressure of about 250 atmospheres or less, e.g., from about 1 to about 30 atmospheres; a weight hourly space velocity (WHSV) based on propylene alkylating agent of from about 0.1 hr^{-1} to about 250 hr^{-1}, preferably from about 1 hr^{-1} to about 50 hr^{-1}; and a ratio of benzene to propylene in the alkylation reactor of from about 0.5:1 to about 30:1 molar, more preferably from about 1:1 to about 10:1 molar.

[0032] When benzene is alkylated with an alkylating agent selected from the group consisting of 1-butene, 2-butene and mixtures thereof, to produce sec-butylbenzene, the reaction may also take place under liquid phase conditions including a temperature of from about 50 to about 250°C, preferably from about 100 to about 200°C; a pressure of about 3.5 to about 35 atmospheres, preferably from about 7 to about 27 atmospheres; a WHSV based on the butene alkylating agent of from about 0.1 to about 20 hr^{-1}, preferably from about 1 to about 10 hr^{-1}; and a ratio of benzene to the butene alkylating agent from about 1:1 to about 10:1, preferably from about 1:1 to about 4:1 molar.

[0033] The catalyst of the present invention may comprise one or more acidic, porous crystalline materials or molecular sieve having the following structures: of zeolite Beta (described in U.S. Patent No. 3,308,069); or an MWW structure type

such as, for example, those having an X-ray diffraction pattern including d-spacing maxima at 12.4±0.25, 6.9±0.15, 3.57±0.07 and 3.42±0.07 Angstroms.

[0034] As used herein, an "acidic, porous crystalline material" means a porous crystalline material or molecular sieve containing acidic protons sufficient to catalyze hydrocarbon conversion reactions.

[0035] Examples of MWW structure type materials include MCM-22 (described in U.S. Patent No. 4,954,325), PSH-3 (described in U.S. Patent No. 4,439,409), SSZ-25 (described in U.S. Patent No. 4,826,667), ERB-1 (described in European Patent No. 0293032), ITQ-1 (described in U.S. Patent No 6,077,498), ITQ-2 (described in U.S. Patent No. 6,231,751), ITQ-30 (described in WO 2005-118476), MCM-36 (described in U.S. Patent No. 5,250,277), MCM-49 (described in U.S. Patent No. 5,236,575) and MCM-56 (described in U.S. Patent No. 5,362,697). The catalyst can include the molecular sieve in unbound or self-bound form or, alternatively, the molecular sieve can be combined in a conventional manner with an oxide binder as hereinafter detailed. For certain applications of the catalyst, the average particle size of the catalyst or the acidic, porous crystalline materials or molecular sieve component may be from about 0.05 to about 200 microns, for example, from 20 to 200 microns.

[0036] When used as catalyst for alkylation, the alkylation reactor effluent contains the excess aromatic feed, monoalkylated product, polyalkylated products, and various impurities. The aromatic feed is recovered by distillation and recycled to the alkylation reactor. Usually a small bleed is taken from the recycle stream to eliminate unreactive impurities from the loop. The bottoms from the distillation may be further distilled to separate monoalkylated product from polyalkylated products and other heavies.

[0037] The polyalkylated products separated from the alkylation reactor effluent may be reacted with additional aromatic feed in a transalkylation reactor, separate from the alkylation reactor, over a suitable transalkylation catalyst. The transalkylation catalyst may comprise one or a mixture of acidic, porous, crystalline materials or molecular sieves having the structure of zeolite Beta, zeolite Y, mordenite or an MWW structure type material having an X-ray diffraction pattern including d-spacing maxima at 12.4±0.25, 6.9±0.15, 3.57±0.07 and 3.42±0.07

Angstroms.

[0038] The X-ray diffraction data used to characterize said above catalyst structures are obtained by standard techniques using the K-alpha doublet of copper as the incident radiation and a diffractometer equipped with a scintillation counter and associated computer as the collection system. Materials having the above X-ray diffraction lines include, for example, MCM-22 (described in U.S. Patent No.4,954,325), PSH-3 (described in U.S. Patent No. 4,439,409), SSZ-25 (described in U.S. Patent No. 4,826,667), ERB-1 (described in European Patent No. 0293032), ITQ-1 (described in U.S. Patent No 6,077,498), ITQ-2 (described in U.S. Patent No. 6,231,751), ITQ-30 (described in WO 2005-118476), MCM-36 (described in U.S. Patent No. 5,250,277), MCM-49 (described in U.S. Patent No. 5,236,575) and MCM-56 (described in U.S. Patent No. 5,362,697), with MCM-22 being particularly preferred.

[0039] Zeolite Beta is disclosed in U.S. Patent No. 3,308,069. Zeolite Y and mordenite occur naturally but may also be used in one of their synthetic forms, such as Ultrastable Y (USY), which is disclosed in U.S. Patent No. 3,449,070, Rare earth exchanged Y (REY), which is disclosed in U.S. Patent No. 4,415,438, and TEA-mordenite (i.e., synthetic mordenite prepared from a reaction mixture comprising a tetraethylammonium directing agent), which is disclosed in U.S. Patent Nos. 3,766,093 and 3,894,104. However, in the case of TEA-mordenite for use in the transalkylation catalyst, the particular synthesis regimes described in the patents noted lead to the production of a mordenite product composed of predominantly large crystals with a size greater than 1 micron and typically around 5 to 10 micron. It has been found that controlling the synthesis so that the resultant TEA-mordenite has an average crystal size of less than 0.5 micron results in a transalkylation catalyst with materially enhanced activity for liquid phase aromatics transalkylation.

[0040] The required small crystal TEA-mordenite for transalkylation can be produced by crystallization from a synthesis mixture having a molar composition

[0041] within the following ranges:

		Useful	Preferred
$R/R+Na^+$	=	>0.4	0.45 – 0.7
OH^-/SiO_2	=	<0.22	0.05 – 0.2
Si/Al_2	=	>30 – 90	35 - 50
H_2O/OH	=	50 – 70	50 -60

[0042] The crystallization is conducted at a temperature of 90 to 200°C, for a time of 6 to 180 hours.

[0043] The catalyst of the present invention may include an inorganic oxide material matrix or binder. Such matrix materials include synthetic or naturally occurring substances as well as inorganic materials such as clay, alumina, silica and/or metal oxides. The latter may be either naturally occurring or in the form of gelatinous precipitates or gels including mixtures of silica and metal oxides. Naturally occurring clays which can be composited with the inorganic oxide material include those of the montmorillonite and kaolin families, which families include the subbentonites and the kaolins commonly known as Dixie, McNamee, Georgia and Florida clays or others in which the main mineral constituent is halloysite, kaolinite, dickite, nacrite or anauxite. Such clays can be used in the raw state as originally mined or initially subjected to calcination, acid treatment or chemical modification.

[0044] Specific useful catalyst matrix or binder materials employed herein include silica, alumina, zirconia, titania, silica-alumina, silica-magnesia, silica-zirconia, silica-thoria, silica-beryllia, silica-titania as well as ternary compositions such as silica-alumina-thoria, silica-alumina-zirconia, silica-alumina-magnesia and silica-magnesia-zirconia. The matrix can be in the form of a cogel. A mixture of these components could also be used.

[0045] The relative proportions of the acidic, porous, crystalline material or molecular sieve and binder or matrix, if present, may vary widely with the crystalline material or molecular sieve content ranging from about 1 to about 99 percent by weight, and more usually in the range of about 30 to about 80 percent

by weight of the total catalyst. Of course, the catalyst may comprise a self-bound material or molecular sieve or an unbound material or molecular sieve, thereby being about 100% acidic, porous crystalline material or molecular sieve.

[0046] The catalyst of the present invention, or its acidic, porous crystalline material or molecular sieve component, may or may not contain added functionalization, such as, for example, a metal of Group VI (e.g. Cr and Mo), Group VII (e.g. Mn and Re) or Group VIII (e.g. Co, Ni, Pd and Pt), or phosphorus.

Experimental Methods

[0047] The following equipment and feed pretreatment methods were used in the experiments described in the non-limiting examples of the invention.

Equipment

[0048] A 300ml Parr batch reaction vessel equipped with a stir rod and static catalyst basket was used for the activity and selectivity measurements. The reaction vessel was fitted with two removable vessels for the introduction of benzene and propylene respectively.

Feed Pretreatment

[0049] Commercial grade benzene was pretreated with molecular sieve 13X, molecular sieve 4A, Engelhard F-24 Clay, and Selexsorb CD. Polymer grade propylene obtained from a commercial specialty gases source was pretreated with molecular sieve 5A and Selexsorb CD. Ultra high purity grade nitrogen obtained from a commercial specialty gases source was pretreated with molecular sieve 5A and Selexsorb CD. All feed pretreatment materials were dried in a 260°C oven for 12 hours before using. All references to benzene, propylene and nitrogen, refer to the commercial grade benzene, the polymer grade propylene, and the ultra high purity grade nitrogen, that have been pretreated as described herein.

[0050] The following NMR procedure for determining proton density was used in the experiments described in the non-limiting examples of the invention.

NMR Procedure for Determining Proton Density

[0051] In the present invention, the NMR procedure for determining the proton density of a catalyst sample is as follows. The proton density of a catalyst sample may be determined using a shallow bed CAVERN device, shown in Fig. 1. In

Fig. 1, a CAVERN device is shown which is comprised of an upper housing 5 and lower housing 6 connected by joint 12, having a mechanism 11 for lifting a glass trapdoor 16 over a catalyst bed 14, means for a vacuum line 20, and means for heating via thermocouple 13. A 5 mm o.d. glass tube 17 slides over a 3 mm stainless steel rod 15, and rests between the endcap 18 and the glass trapdoor 16. The stainless steel rod 15 is retracted by turning the mechanism 11, whereby the glass tube 17 raises the glass trapdoor 16 above the catalyst bed 14. By gently turning or shaking the CAVERN device, the catalyst sample (not shown) falls into the MAS rotor 19. This process works for zeolites and metal oxide powders. Further details regarding the operation of the CAVERN device are disclosed in Xu, T.; Haw, J. F. *Top. Catal.* 1997, 4, 109-118, incorporated herein by reference.

[0052] In order to determine the proton density of a catalyst sample, a thin layer of the catalyst sample was spread out in the catalyst bed 14 of the CAVERN device, and the temperature of the catalyst sample via thermocouple 13 was raised to the desired temperature for evaluating the catalyst sample ("Specified NMR Pretreatment Temperature") under sufficient vacuum by vacuum line 20 to remove any moisture absorbed on the catalyst sample. The catalyst sample was typically held at the desired temperature for 2 hours under such vacuum prior to NMR measurement.

[0053] The thus prepared catalyst sample was loaded into a 5 mm NMR rotor, such as MAS rotor 19, and the rotor was sealed with a Kel-F end cap by manipulating the CAVERN device. All the operations were performed while the catalyst sample was still under vacuum, ensuring the sample integrity for NMR study. After the desired NMR spectra were acquired, the weight of MAS rotor 19, the catalyst sample and the endcap 18 was determined followed by weight determination of the rotor and the endcap 18 upon unpacking the catalyst sample. The difference in the two weights was the amount of the catalyst sample in the MAS rotor 19.

[0054] ^{1}H NMR experiments were performed on a 400 MHz solid state NMR spectrometer operating at 399.8 MHz for ^{1}H. Quantitative ^{1}H spectra were obtained by the use of rotor-synchronized spin-echo sequence ($\pi/2 - t_{D1} - \pi - t_{D2} -$ Echo) using 8 to 12 kHz spinning speeds. Typically, 3.5-μs $\pi/2$ pulses, t_{D1} of 125-μs and

t_{D2} of 113.1 μs were used for a spinning speed of 9 kHz. Spectra acquired using the solid echo sequence showed some background signal, presumably from the spinning module and the endcap 18 of the MAS rotor 19. A solid echo sequence with DEPTH removes the background signal from the spectra. The DEPTH sequence consisted of a 90° pulse (3.5-μs) followed by two 180° pulses. A description of the DEPTH sequence appears in Corey, D.G.; Ritchey, W.M. *J. Magn. Reson.* 1988, 80, 128, incorporated herein by reference. A pulse delay of 10 seconds was sufficient for quantifying proton density of the catalyst samples tested. Acetone was used as secondary standard for ^1H shift (2.1 ppm). All the reported chemical shifts were referenced to tetramethylsilane (TMS) at 0 ppm.

[0055] The proton densities for various "as synthesized" acidic, porous crystalline materials not yet treated in accordance with the present invention, and therefore in the first hydration state, are as follows:

Acidic Porous Crystalline Material	Proton Density
Zeolite Beta	3.10 mmol protons/gram zeolite Beta
MCM-22	2.24 mmol protons/gram MCM-22
MCM-36	2.14 - 2.24 mmol protons/gram MCM-36
MCM-49	2.14 mmol protons/gram MCM-49
MCM-56	2.14 - 2.24 mmol protons/gram MCM-56

[0056] Of course, these acidic, porous crystalline materials in the third hydration state of having undergone treatment according to the method of the present invention would have proton densities greater than those listed above for the same material in the first hydration state.

[0057] The following method for determination of the Proton Density Index (PDI) was used in the experiments described in the non-limiting examples of this invention.

Determination of Proton Density Index

[0058] The PDI of a particular catalyst composition is determined from the ratio of the proton density of the new, treated catalyst composition to the proton density of the original, untreated catalyst composition. Such new, treated catalyst

composition may be treated in accordance with the proton adjustment techniques described herein or other techniques that alter proton density. Also, such original, untreated catalyst composition may or may not be treated in accordance with the proton adjustment techniques described herein or other techniques that alter proton density. As noted above, the term "proton density" as used herein means the millimoles (mmol) of acidic protons and/or non-acidic protons per gram of catalyst composition. The proton density of the new, treated catalyst composition, and the proton density of the original, untreated catalyst composition are both measured at the same temperature, for example room temperature, e.g. from about 20°C to about 25°C. Therefore, the PDI of particular catalyst composition is defined as the proton density of the new, treated, catalyst composition measured at a given temperature, divided by the proton density of the original, untreated, catalyst composition measured at the same given temperature.

[0059] The NMR spectrometer used to determine proton density was a Varian Infinity Plus 400MHz solid state NMR with an Oxford AS400 magnet.

[0060] The following catalyst reactivity testing procedure was used in the non-limiting examples of the invention.

Catalyst Reactivity Testing Procedure

[0061] To prepare a catalyst composition for reactivity testing, a specified amount of a catalyst sample was dried in the presence of air in an oven at a specified ex-situ drying temperature ("Specified Ex-situ Drying Temperature") for 2 hours. The catalyst sample was removed from the oven and weighed. Quartz chips were used to line the bottom of a basket followed by loading of the catalyst sample into the basket on top of the first layer of quartz. Quartz chips were then placed on top of the catalyst sample. The basket containing the catalyst sample and quartz chips were placed in an oven at the Specified Ex-situ Drying Temperature in the presence of air for about 16 hours.

[0062] The reactor and all lines were cleaned with a suitable solvent (such as toluene) before each experiment. The reactor and all lines were dried in air after cleaning to remove all traces of cleaning solvent. The basket containing the catalyst sample and quartz chips were removed from the oven, immediately placed in the reactor, and the reactor was immediately assembled. The reactor

temperature was set to an in-situ drying temperature ("Specified In-situ Drying Temperature") and purged with 100 SCCM of nitrogen for 2 hours.

[0063] The reactor temperature was then reduced to 130°C, the nitrogen purge was discontinued and the reactor vent closed. A 156.1 gram quantity of benzene was loaded into a 300 cc transfer vessel, performed in a closed system. The benzene vessel was pressurized to 100 psig with a nitrogen source and the benzene was transferred into the reactor. The agitator speed was set to 500 rpm and the reactor was allowed to equilibrate for 1 hour.

[0064] A 75 cc Hoke transfer vessel was then filled with 28.1 grams of liquid propylene and connected to the reactor vessel, and then connected with a 300 psig nitrogen source. After the one-hour benzene stir time had elapsed, the propylene was transferred from the Hoke vessel to the reactor. The 300 psig nitrogen source was maintained connected to the propylene vessel and open to the reactor during the duration of the test to maintain constant reaction pressure of 300 psig. Liquid product samples were taken at 30, 60, 120, 150, 180 and 240 minutes after addition of the propylene. These samples were then analyzed by Gas Chromatography with a Flame Ionization Detector and procedures known to those skilled in the art.

[0065] In these examples, the selectivity of the catalyst sample ("Catalyst Selectivity") to the desired isopropylbenzene (cumene) product was calculated as the ratio of isopropylbenzene to diisopropylbenzene (IPB/DIPB) after propylene conversion reached 100%. A higher IPB/DIPB ratio means a greater selectivity of the catalyst sample to isopropylbenzene (cumene). Also, in these examples the catalytic activity of the catalyst samples was determined by calculating the 2nd order kinetic rate constant using mathematical techniques well known to those skilled in the art ("Catalyst Activity").

[0066] The following proton content adjustment techniques were used in the experiments described in the non-limiting examples of the invention.

Proton Content Adjustment Techniques

A. Proton Content Adjustment Technique #1

[0067] In one embodiment of the invention, a sample of catalyst comprising an acidic, porous crystalline material and having a first hydration state measured

in mmol of protons per gram of catalyst, was placed into a suitable container. Water in liquid form, specifically deionized water, was transferred into the container slowly so as to displace air from the catalyst sample by filling from the bottom up. Water was added until the catalyst sample was completely covered with water and the level of the water was approximately 1/4" above the catalyst sample. The catalyst sample and water were allowed to remain undisturbed under these conditions for a specified contact time ("Contact Time") of at least about 1 second preferably from about 1 minute to about 60 minutes or greater, to generate a catalyst sample having a second hydration state (measured in mmol of protons per gram of catalyst sample), in which the said second hydration state being greater that said first hydration state. After the Contact Time, the water was decanted and the catalyst sample was allowed to dry in air at ambient conditions for at least 8 hours, to generate a catalyst sample having a third hydration state (measured in mmol of protons per gram of catalyst sample).

B. Proton Content Adjustment Technique #2

[0068] In another embodiment of the invention, a sample of catalyst is exposed to water in the vapor form (with or without a suitable carrier, such as nitrogen) at a specified contact temperature ("Contact Temperature") and at a specified contact pressure ("Contact Pressure").

[0069] In still another embodiment of the invention, the catalyst sample that has first been treated in accordance with Proton Content Adjustment Technique #1 is then treated in accordance with Proton Content Adjustment Technique #2.

[0070] In still yet another embodiment of the invention, the catalyst sample that has first been treated in accordance with Proton Content Adjustment Technique #2 is then treated in accordance with Proton Content Adjustment Technique #1.

[0071] Non-limiting examples of the catalyst samples made in accordance with the methods of this invention, and the use of such catalyst samples in alkylation experiments, are described with reference to the following experiments.

Example 1

[0072] The catalyst sample of this Example 1 comprised 80wt% MCM-49 and 20wt% alumina (Al_2O_3) and its proton density was determined in accordance with

the NMR Procedure for Determining Proton Density, described above, at the Specified NMR Pretreatment Temperature of 250°C. The proton density was 1.71 mmol per gram of catalyst (first hydration state).

[0073] A 0.5 gram portion of the catalyst sample of this Example 1 was tested in accordance with the Catalyst Reactivity Testing Procedure at the Specified Ex-situ Drying Temperature of 250°C and the Specified In-situ Drying Temperature of 170°C. The Catalyst Selectivity of this catalyst sample was 5.92, determined as the weight ratio of isopropylbenzene to diisopropylbenzene (IPB/DIPB). The Catalyst Activity of this catalyst sample was 363.

Example 2

[0074] Another portion of the catalyst sample of Example 1 was treated in accordance with Proton Content Adjustment Technique #1 at a Contact Time of approximately 1 hour, to produce the treated catalyst sample of this Example 2 having a third hydration state. The proton density of the third hydration state of the treated catalyst sample was 1.85 mmol per gram of catalyst (third hydration state), determined in accordance with the NMR Procedure for Determining Proton Density, described above, at the Specified NMR Pretreatment Temperature of 250°C.

[0075] A 0.5 gram portion of the treated catalyst sample of this Example 2 was tested in accordance with the Catalyst Reactivity Testing Procedure at the Specified Ex-situ Drying Temperature of 250°C and the Specified In-situ Drying Temperature of 170°C. The Catalyst Selectivity of this catalyst sample was 6.94, determined as the weight ratio of IPB/DIPB. The Catalyst Activity of this catalyst sample was 383.

[0076] The PDI of the catalyst sample of this Example 2 was determined to be 1.08, and represents an 8% increase in the proton content (determined as mmol of protons per gram of catalyst) as compared to the catalyst sample of Example 1. The Catalyst Selectivity (IPB/DIPB) of the catalyst sample of this Example 2 displayed an increase of 17%, and the Catalyst Activity displayed an increase of 5.5%, as compared to the catalyst sample of Example 1.

Example 3

[0077] The catalyst sample of this Example 3 comprised 80wt% zeolite Beta and 20wt% alumina and its proton density was determined in accordance with the NMR Procedure for Determining Proton Density, described above, at the Specified NMR Pretreatment Temperature of 250°C. The proton density was 2.48 mmol per gram of catalyst (first hydration state).

[0078] A 1.0 gram portion of the catalyst sample of this Example 3 was tested in accordance with the Catalyst Reactivity Testing Procedure at the Specified Ex-situ Drying Temperature of 250°C and the Specified In-situ Drying Temperature of 170°C. The Catalyst Selectivity of this catalyst sample was 5.62, determined as the weight ratio of IPB/DIPB. The Catalyst Activity of this catalyst sample was 23.

Example 4

[0079] Another portion of the catalyst sample of Example 3 was treated in accordance with Proton Content Adjustment Technique #1 at a Contact Time of approximately 1 hour, to produce a treated catalyst of this Example 4 having a third hydration state. The proton density of the treated catalyst was 2.77 mmol per gram of catalyst (third hydration state), determined in accordance with the NMR Procedure for Determining Proton Density, described above, at the Specified NMR Pretreatment Temperature of 250°C.

[0080] A 1.0 gram portion of the treated catalyst of this Example 4 was tested in accordance with the Catalyst Reactivity Testing Procedure at the Specified Ex-situ Drying Temperature of 250°C and the Specified In-situ Drying Temperature of 170°C. The Catalyst Selectivity of this catalyst sample was 9.35, determined as the weight ratio of IPB/DIPB. The Catalyst Activity of this catalyst sample was 4.

[0081] The PDI of the catalyst sample of this Example 4 was determined to be 1.12, and represents a 12% increase in proton content (determined as mmol of protons per gram of catalyst) as compared to the catalyst sample of Example 3. The Catalyst Selectivity (IPB/DIPB) of the catalyst sample of this Example 4 displayed an increase of 66%, and the Catalyst Activity was still 17.4% of that of Example 3.

Example 5

[0082] The catalyst sample of Example 1 was treated in nitrogen that was saturated with water vapor in accordance with Proton Content Adjustment Technique #2 at a Contact Temperature of 220°C and a Contact Pressure of 50 psig. The resulting catalyst was then treated in accordance with Proton Content Adjustment Technique #1, to produce the treated catalyst sample of this Example 5 having a third hydration state. The proton density of the treated catalyst was 1.76 mmol per gram of catalyst (third hydration state), determined in accordance with the NMR Procedure for Determining Proton Density, described above, at the Specified NMR Pretreatment Temperature of 250°C.

[0083] A 0.5 gram portion of the treated catalyst of this Example 5 was tested in accordance with the Catalyst Reactivity Testing Procedure at the Specified Ex-situ Drying Temperature of 250°C and the Specified In-situ Drying Temperature of 170°C. The Catalyst Selectivity of the catalyst sample was 6.80, determined as the weight ratio of IPB/DIPB. The Catalyst Activity of this catalyst sample was 377.

[0084] The PDI of the catalyst sample of this Example 5 was determined to be 1.03, and represents a 3% increase in proton content (determined as mmol of protons per gram of catalyst), as compared to the catalyst sample of Example 1. The Catalyst Selectivity (IPB/DIPB) of the catalyst sample of this Example 5 displayed an increase of 15%, and the Catalyst Activity displayed an increase of 4%, as compared to the catalyst sample of Example 1.

Example 6

[0085] The catalyst sample of this Example 6 comprised 80wt% MCM-49 and 20wt% alumina and its proton density was determined in accordance with the NMR Procedure for Determining Proton Density, described above, at the Specified NMR Pretreatment Temperature of 150°C. The proton density was found to be 2.59 mmol per gram of catalyst (first hydration state).

[0086] A 0.5 gram portion of the catalyst sample of this Example 6 was tested in accordance with the Catalyst Reactivity Testing Procedure at the Specified Ex-situ Drying Temperature of 150°C and the Specified In-situ Drying Temperature of 150°C. The Catalyst Selectivity of this catalyst sample was 5.92, determined as

the weight ratio of isopropylbenzene to diisopropylbenzene (IPB/DIPB). The Catalyst Activity of this catalyst sample was 275.

Example 7

[0087] Another portion of the catalyst sample of Example 6 was treated in accordance with Proton Content Adjustment Technique #1 at a Contact Time of approximately 1 hour, to produce the treated catalyst sample of this Example 7 having a third hydration state. The proton density of the treated catalyst was 3.16 mmol per gram of catalyst determined in accordance with the NMR Procedure for Determining Proton Density, described above, at the Specified NMR Pretreatment Temperature of 150°C.

[0088] A 0.5 gram portion of the treated catalyst of this Example 7 was tested in accordance with Catalyst Reactivity Testing Procedure at the Specified Ex-situ Drying Temperature of 150°C and the Specified In-situ Drying Temperature of 150°C. The Catalyst Selectivity of this catalyst sample was 7.81, determined as the weight ratio of IPB/DIPB. The Catalyst Activity of this catalyst sample was 251.

[0089] The PDI of the catalyst sample of this Example 7 was determined to be 1.22, and represents a 22% increase in proton content (determined as mmol of protons per gram of catalyst), as compared to the catalyst sample of Example 6. The Catalyst Selectivity (IPB/DIPB) of the catalyst sample of Example 7 displayed an increase of 32%, and the Catalyst Activity decreased only slightly to 91% of that of the catalyst in Example 6.

Example 8

[0090] The catalyst sample of this example comprised 65wt% MCM-22 and 35wt% alumina and its proton density was determined in accordance with the NMR Procedure for Determining Proton Density, described above, at the Specified NMR Pretreatment Temperature of 250°C. The proton density was 1.46 mmol per gram of catalyst (first hydration state).

[0091] A 1.0 gram portion of the catalyst sample of this Example 8 was tested in accordance with Catalyst Reactivity Testing Procedure at the Specified Ex-situ Drying Temperature of 250°C and the Specified In-situ Drying Temperature of 170°C. The Catalyst Selectivity of the catalyst sample was 5.46, determined as

the weight ratio of isopropylbenzene to diisopropylbenzene (IPB/DIPB). The Catalyst Activity of this catalyst sample was 272.

Example 9

[0092] A portion of the catalyst sample of Example 8 that had become at least partially deactivated was regenerated according to the following two-step procedure. First, the catalyst sample was heated to a temperature of 385°C in an atmosphere having less than 2.0 vol. % hydrogen and hydrocarbons. The oxygen concentration was initially increased to 0.4 vol. %, and then increased again to 0.7 vol. % while the maximum catalyst temperature was maintained at 467°C. Second, the catalyst was heated to 450°C in an atmosphere having an oxygen concentration of 0.7 vol. %, which was increased to 7.0 vol. % while the maximum catalyst temperature was maintained at 510°C.

[0093] This catalyst sample was then treated according to Proton Content Adjustment Technique #1 at a Contact Time of approximately 1 hour, to produce the treated catalyst of this Example 9 having a third hydration state. The proton density of the treated catalyst was 1.97 mmol per gram of catalyst (third hydration state), determined in accordance with the NMR Procedure for Determining Proton Density, described above, at the Specified NMR Pretreatment Temperature of 250°C.

[0094] A 1.0 gram portion of the treated catalyst sample of this Example 9 was tested in accordance with Catalyst Reactivity Testing Procedure at the Specified Ex-situ Drying Temperature of 250°C and the Specified In-situ Drying Temperature of 170°C. The Catalyst Selectivity of this catalyst sample was 6.29, determined as the weight ratio IPB/DIPB. The Catalyst Activity of this catalyst sample was 174.

[0095] The PDI of the catalyst sample of Example 9 was determined to be 1.35, and represents a 35% increase in the proton content (determined as mmol of protons per gram of catalyst), as compared to the catalyst sample of Example 8. The Catalyst Selectivity (IPB/DIPB) of the catalyst sample of this Example 9 displayed a 15% increase, and the Catalyst Activity was still 64% of that of the catalyst of Example 8.

Example 10

[0096] The catalyst sample described in Example 6 was treated in accordance with Proton Content Adjustment Technique #2 at a Contact Temperature of 220°C and a Contact Pressure of 50 psig in nitrogen that was saturated with water vapor. The resulting catalyst sample was then treated in accordance with to Proton Content Adjustment Technique #1, to produce the treated catalyst of this Example 10 having a third hydration state. The proton density of this treated catalyst sample was determined in accordance with the NMR Procedure for Determining Proton Density, described above, at the Specified NMR Pretreatment Temperature of 150°C. The proton density was 2.67 mmol per gram of catalyst (third hydration state).

[0097] A 0.5 gram portion of the treated catalyst sample of this Example 10 was tested in accordance with Catalyst Reactivity Testing Procedure at the Specified Ex-situ Drying Temperature of 150°C and the Specified In-situ Drying Temperature of 150°C. The Catalyst Selectivity of this catalyst sample was 7.09, determined as the weight ratio IPB/DIPB. The Catalyst Activity of this catalyst sample was 244.

[0098] The PDI of the catalyst sample of this Example 10 was determined to be 1.03, and represents a 3% increase in the proton content (determined as mmol of protons per gram of catalyst) as compared to the catalyst sample of Example 6. The Catalyst Selectivity (IPB/DIPB) of the catalyst sample of Example 10 displayed an increase of 20%, and the catalyst activity decreased only slightly to 89% of that of the catalyst of Example 6.

Example 11 (Comparative)

[0099] The catalyst sample of this Example 11 comprised porous non-crystalline tungsten-zirconia ($WZrO_2$) and its proton density was determined in accordance with the NMR Procedure for Determining Proton Density, described above, at the Specified NMR Pretreatment Temperature of 250°C. The proton density was 0.37 mmol per gram of catalyst (first hydration state).

[0100] A 0.5 gram portion of the catalyst sample of this Example 11 was tested in accordance with Catalyst Reactivity Testing Procedure at the Specified Ex-situ Drying Temperature of 250°C and the Specified In-situ Drying

Temperature of 170°C. The Catalyst Selectivity was 13.70, determined as the weight ratio of isopropylbenzene to diisopropylbenzene (IPB/DIPB). The Catalyst Activity of this catalyst sample was 1.

Example 12 (Comparative)

[0101] The catalyst sample of Example 11 was treated in accordance with the Proton Content Adjustment Technique #1 at a Contact Time of approximately 1 hour, to produce a treated catalyst sample of this Example 12 having a third hydration state. The proton density of the treated catalyst sample was 0.41 mmol per gram of catalyst (third hydration state), determined in accordance with the NMR Procedure for Determining Proton Density, described above, at the Specified NMR Pretreatment Temperature of 250°C.

[0102] A 0.5 gram portion of the treated catalyst of this Example 12 was tested in accordance with Catalyst Reactivity Testing Procedure at the Specified Ex-situ Drying Temperature of 250°C and the Specified In-situ Drying Temperature of 170°C. The Catalyst Selectivity of this catalyst sample was 9.62, determined as the weight ratio IPB/DIPB. The Catalyst Activity of this catalyst sample was 1.

[0103] The PDI of the catalyst sample of Example 12 was determined to be 1.11, and represents an 11% increase in the proton content (determined as mmol of protons per gram of catalyst), as compared to the catalyst of Example 11. However, the Catalyst Selectivity (IPB/DIPB) of the catalyst sample of this Example 12 displayed a 29.8% decrease, as compared to the catalyst sample of Example 11. The Catalyst Activity remained the same as the catalyst sample of Example 11.

[0104] All patents, patent applications, test procedures, priority documents, articles, publications, manuals, and other documents cited herein are fully incorporated by reference for all jurisdictions in which such incorporation is permitted.

[0105] When numerical lower limits and numerical upper limits are listed herein, ranges from any lower limit to any upper limit are contemplated.

[0106] While the illustrative embodiments of the invention have been described with particularity, it will be understood that various other modifications will be apparent to and may be readily made by those skilled in the art without

departing from the spirit and scope of the invention. Accordingly, it is not intended that the scope of the claims appended hereto be limited to the examples and descriptions set forth herein but rather that the claims be construed as encompassing all the features of patentable novelty which reside in the present invention, including all features which would be treated as equivalents thereof by those skilled in the art to which the invention pertains.

CLAIMS:

We Claim:

1. A method for producing a catalyst composition, said method comprising the steps of:

(a) providing a first catalyst comprising an acidic, porous crystalline material, said first catalyst having a first hydration state;

(b) contacting said first catalyst of step (a) with water in liquid or gaseous form at a contact temperature up to about 500°C, to generate a second catalyst having a second hydration state greater than said first hydration state; and

(c) drying said second catalyst of step (b) at a drying temperature of up to about 550°C, to generate said catalyst composition having a third hydration state between said first and second hydration states, whereby said catalyst composition has a Proton Density Index of greater than about 1.0.

2. The method of claim 1, wherein the acidic, porous crystalline material is an aluminosilicate zeolite.

3. The method of claim 1, wherein the acidic, porous crystalline material is selected from the group consisting of MWW structure type material, zeolite Beta and mixtures thereof.

4. The method of claim 1, wherein the acidic, porous crystalline material comprises an MWW structure type.

5. The method of claim 4, wherein said acidic, porous crystalline material is selected from the group consisting of MCM-22, PSH-3, SSZ-25, ERB-1, ITQ-1, ITQ-2, ITQ-30, MCM-36, MCM-49, MCM-56 and mixtures thereof.

6. The method of claim 1, wherein the first catalyst further comprises a binder.

7. The method of claim 6, wherein said binder comprises an inorganic material selected from the group consisting of clay, silica, alumina, metal oxide and mixtures thereof.

8. The method of claim 1, wherein step (b) is conducted at a contact temperature of from about 1°C to about 99°C for from about 1 minute to about 60 minutes, and step (c) is conducted at a drying temperature of from about 100°C to about 200°C for from about 0.01 to about 24 hours.

9. The method of claim 2, wherein said acidic, porous crystalline material has an average particle size of from about 0.05 to about 200 microns.

10. The method of claim 1, wherein said catalyst composition resulting from step (c) has a Proton Density Index of from greater than 1.0 to about 2.0.

11. The method of claim 1, wherein said catalyst composition resulting from step (c) has a Proton Density Index of from about 1.01 to about 1.85.

12. A catalyst composition made by the method comprising the steps of:

(a) providing a first catalyst comprising an acidic, porous crystalline material, said first catalyst having a first hydration state;

(b) contacting said first catalyst of step (a) with water in liquid or gaseous form at a contact temperature up to about 500°C to generate a second catalyst having a second hydration state greater than said first hydration state; and

(c) drying said second catalyst of step (b) at a drying temperature of up to about 550°C to generate said catalyst composition having a third hydration state between said first and second hydration states, whereby

said catalyst composition has a Proton Density Index of greater than about 1.0.

13. The catalyst composition of claim 12, wherein the acidic, porous crystalline material is an aluminosilicate zeolite.

14. The catalyst composition of claim 12, wherein the acidic, porous crystalline material is selected from the group consisting of an MWW structure type material, zeolite Beta and mixtures thereof.

15. The catalyst composition of claim 12, wherein the acidic, porous crystalline material comprises an MWW structure type.

16. The catalyst composition of claim 15, wherein said acidic, porous crystalline material is selected from the group consisting of MCM-22, PSH-3, SSZ-25, ERB-1, ITQ-1, ITQ-2, ITQ-30, MCM-36, MCM-49, MCM-56 and mixtures thereof.

17. The catalyst composition of claim 12, wherein said first catalyst comprises a binder.

18. The catalyst composition of claim 17, wherein said binder comprises an inorganic material selected from the group consisting of clay, silica, alumina, metal oxide and mixtures thereof.

19. The catalyst composition of claim 12, wherein step (b) is conducted at a temperature of from about 1°C to about 99°C for from about 1 minute to about 60 minutes, and step (c) is conducted at a temperature of from about 100°C to about 200°C for from about 0.1 to about 24 hours.

20. The catalyst composition of claim 12, wherein said acidic, porous crystalline material has an average particle size of from about 0.05 to about 200 microns.

21. The catalyst composition of claim 12 having a Proton Density Index of from greater than 1.0 to about 2.0.

22. The catalyst composition of claim 12 having a Proton Density Index of from about 1.01 to about 1.85.

23. The catalyst composition of claim 12, wherein the acidic, porous crystalline material has an X-ray diffraction pattern including d-spacing maxima at 12.4±0.25, 6.9±0.15, 3.57±0.07 and 3.42±0.07 Angstroms.

24. The catalyst composition of claim 23, wherein said acidic, porous crystalline material is selected from the group consisting of MCM-22, PSH-3, SSZ-25, ERB-1, ITQ-1, ITQ-2, ITQ-30, MCM-36, MCM-49, MCM-56 and mixtures thereof.

25. The catalyst composition of claim 23, wherein said acidic, porous crystalline material has the structure of MCM-22, MCM-36, MCM-49 or MCM-56.

26. The catalyst composition of claim 23, wherein said first catalyst further comprises an inorganic binder material selected from the group consisting of clay, silica, alumina, metal oxide and mixtures thereof.

27. The catalyst composition of claim 23 having a Proton Density Index of from greater than 1.0 to about 2.0.

28. The catalyst composition of claim 23 having a Proton Density Index of from about 1.01 to about 1.85.

29. The catalyst composition of claim 12, wherein the acidic, porous crystalline molecular sieve has the structure of zeolite Beta.

30. The catalyst composition of claim 29, wherein said first catalyst further comprises an inorganic binder material selected from the group consisting of clay, silica, alumina, metal oxide and mixtures thereof.

31. The catalyst composition of claim 29 having a Proton Density Index of from greater than 1.0 to about 2.0.

32. The catalyst composition of claim 29 having a Proton Density Index of from about 1.01 to about 1.85.

33. A catalyst composition comprising an acidic, porous crystalline material having the structure of MCM-22, said acidic, porous crystalline material having a proton density of greater than 2.24 mmol protons per gram.

34. The catalyst composition of claim 33 having a Proton Density Index of from greater than 1.0 to about 2.0.

35. A catalyst composition comprising an acidic, porous crystalline material having the structure of MCM-36, said acidic, porous crystalline material having a proton density of greater than 2.24 mmol protons per gram.

36. The catalyst composition of claim 35 having a Proton Density Index of from greater than 1.0 to about 2.0.

37. A catalyst composition comprising an acidic, porous crystalline material having the structure of MCM-49, said acidic, porous crystalline material having a proton density of greater than 2.14 mmol protons per gram.

38. The catalyst composition of claim 37 having a Proton Density Index of from greater than 1.0 to about 2.0.

39. A catalyst composition comprising an acidic, porous crystalline material having the structure of MCM-56, said acidic, porous crystalline material having a proton density of greater than 2.24 mmol protons per gram.

40. The catalyst composition of claim 39 having a Proton Density Index of from greater than 1.0 to about 2.0.

41. A catalyst composition comprising an acidic, porous crystalline material having the structure of zeolite Beta, said acidic, porous crystalline material having a proton density of greater than 3.10 mmol protons per gram.

42. The catalyst composition of claim 41 having a Proton Density Index of from greater than 1.0 to about 2.0.