

PROCESS FOR PRODUCING PHOSPHORUS MODIFIED
ZEOLITE CATALYSTS

FIELD OF THE INVENTION

[0001] This disclosure relates to a process for producing phosphorus modified zeolite catalysts.

BACKGROUND OF THE INVENTION

[0002] Phosphorus modification is a known method of improving the performance of zeolite catalysts for a variety of chemical processes including, for example, the conversion of methanol to hydrocarbons and the methylation of toluene to produce xylenes. For example, U.S. Patent Nos. 4,590,321 and 4,665,251 disclose a process for producing aromatic hydrocarbons by contacting one or more non-aromatic compounds, such as propane, propylene, or methanol, with a catalyst containing a zeolite, such as ZSM-5, composited with an inorganic oxide binder. The catalyst is modified with phosphorus by impregnation with a source of phosphate ions, such as an aqueous solution of an ammonium phosphate, followed by calcination to produce phosphorus oxide in an amount of about 0.05% to 50%, preferably from about 0.7% to about 15%, by weight of the catalyst composite.

[0003] In addition, U.S. Patent No. 7,662,737 discloses a process for producing a bound phosphorus-modified zeolite catalyst, in which a zeolite, such as ZSM-5, which may be in the NH_4^+ or the H^+ form, is slurried with an aqueous solution of a phosphorus compound and then water is removed from the slurry to form a phosphorus-modified zeolite. The phosphorus-modified, pre-calcined zeolite is then mixed with an acid-treated inorganic oxide binder material selected from alumina, clay, aluminum phosphate and/or silica-alumina. After optional extrusion, the zeolite-binder mixture is heated at a temperature of about 400 °C or higher to form a bound zeolite catalyst, typically from 0.01 to about 0.15 gram of phosphorus per gram of zeolite. The catalyst is particularly intended for use in the alkylation of toluene with methanol to produce xylenes, but is also said to be useful in MTG processes. Similar processes of producing phosphorus-modified toluene methylation catalysts are disclosed in U.S.

Patent Nos. 7,368,410 and 7,507,685, and in U.S. Patent Application Publication Nos. 2007/0149384, 2008/0275280, and 2009/0036723.

[0004] U.S. Patent No. 7,285,511 discloses a process of modifying a zeolite catalyst to increase its para-xylene selectivity in toluene methylation reactions, wherein the method comprises forming a slurry consisting essentially of a binder-free ZSM-5-type zeolite having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio of from about 250 to about 1000 and an aqueous solution of a phosphorus-containing compound; and removing water from the slurry to provide a non-steamed, phosphorus treated ZSM-5 zeolite having a phosphorus content of from 0.04 g P/g zeolite or more and a pore volume of from 0.2 ml/g or less. The resultant phosphorus treated ZSM-5 can be used as a toluene methylation catalyst either in unbound form or may be composited with a binder, such as alumina, clay or silica. A similar process of producing a phosphorus-modified toluene methylation catalyst is disclosed in U.S. Patent Nos. 7,399,727.

[0005] U.S. Patent No 6,504,072 discloses selective production of para-xylene by the reaction of toluene with methanol over a severely steamed ZSM-5 catalyst combined with oxide modifier, preferably an oxide of phosphorus, to control the reduction of the micropore volume of the catalyst during the steaming step. Incorporation of phosphorus in the catalyst is conveniently accomplished by contacting the ZSM-5, either alone or in combination with a binder or matrix material, with a solution of an appropriate phosphorus compound, followed by drying and calcining to convert the phosphorus to an oxide form.

[0006] One desirable result of modifying a zeolite catalyst by the addition of phosphorus can be that the tendency for the zeolite to lose its catalytic activity when exposed to high temperature steam can be reduced. There is, however, significant interest in the development of phosphorus-modified zeolite catalysts in which the steam stabilization resulting from the phosphorus addition can be improved/maximized.

[0007] According to the present invention, it has now been found that a zeolite catalyst with improved steam stability can be produced by phosphorus treatment of a zeolite catalyst which is self-bound or is combined with a binder that is substantially free of aluminum.

[0008] It should be noted that this application is related to U.S. Provisional Application Nos. 61/548,015, 61/548,038, 61/548,044, 61/548,052, 61/548,057, and

61/548,064, each filed on October 17, 2011, the entire contents of each of which are hereby incorporated by reference herein, to the extent necessary to describe any portion of the instant invention detailed therein. This application is also related to five other co-pending international (PCT) applications, each filed on even date herewith and claiming the benefit to the aforementioned U.S. provisional patent applications, and which are entitled “Process for Producing Phosphorus Modified Zeolite Catalysts”, “Phosphorus Modified Zeolite Catalysts”, “Phosphorus Modified Zeolite Catalysts”, “Phosphorus Modified Zeolite Catalysts”, and “Selective Dehydration of Alcohols to Dialkyl Ethers”, respectively, the entire contents of each of which are hereby further incorporated by reference herein, to the extent necessary to describe any portion of the instant invention detailed therein.

SUMMARY OF THE INVENTION

[0009] In one aspect, the invention resides in a process for producing a phosphorus-modified zeolite catalyst, said process comprising: (a) forming as-synthesized zeolite crystals into a shaped catalyst body either in the absence of a separate inorganic oxide binder or in the presence of a separate inorganic oxide binder which is substantially free of aluminum; (b) converting the zeolite crystals to the hydrogen form; (c) removing any organic directing agent employed in the synthesis of the zeolite crystals; (d) treating the shaped catalyst body with an aqueous solution of a phosphorus compound; and (e) heating the treated catalyst body to remove water and convert the phosphorus compound to an oxide form.

[0010] Conveniently, the zeolite crystals can be formed into a shaped catalyst body in the presence of a separate inorganic oxide binder containing less than 5 wt%, for example less than 3 wt%, of aluminum.

[0011] Conveniently, the forming (a) can be accomplished by extrusion.

[0012] In some embodiments, the zeolite crystals can be mixed with a silica binder prior to the forming (a).

[0013] Additionally or alternately in some embodiments, the converting (b) can be accomplished before the forming (a).

[0014] Additionally or alternately in some embodiments, the removing (c) can be accomplished before the forming (a).

[0015] Conveniently, the treating (d) can be accomplished by impregnation, such as with an aqueous solution of a phosphorus oxyacid.

[0016] Conveniently, the catalyst body can comprise from about 0.1 wt% to about 3 wt% of elemental phosphorus present as an oxide of phosphorus.

[0017] Conveniently, the heating in (e) can be conducted at a temperature from about 350°C to about 650°C for a time from about 0.2 hours to about 5.0 hours.

[0018] Conveniently, the zeolite can have a molar ratio of silica to alumina from about 20 to about 200, *e.g.*, from about 20 to about 150.

[0019] Conveniently, the zeolite can comprise, consist essentially of, or be ZSM-5.

[0020] In further aspects, the invention can reside in a phosphorus-modified zeolite catalyst produced by the process described herein, and/or in use of the catalyst in organic conversion reactions, especially in a process for conversion of methanol to hydrocarbons.

DETAILED DESCRIPTION OF THE EMBODIMENTS

[0021] Described herein is a process for producing a phosphorus-modified zeolite catalyst. In the present process, the phosphorus incorporation can be accomplished after the zeolite has been formed into a shaped catalyst body, either in the absence of a separate inorganic oxide binder (self-bound) or in the presence of a separate inorganic oxide binder which can advantageously be substantially free of aluminum. In particular, it has been found that, by omitting the binder or by employing a binder that is substantially aluminum-free, the thermal stability of the catalyst can be significantly improved, as compared with a conventional alumina-bound catalyst containing the same amount of phosphorus.

[0022] The present process can be employed to produce a phosphorus-modified zeolite catalyst containing any known zeolite or mixture of zeolites. In one embodiment, the catalyst described herein can comprise, consist essentially of, or be at least one medium pore zeolite having a Constraint Index of 2-12 (as defined in U.S. Patent No. 4,016,218). Suitable medium pore molecular sieves can include, but are not limited to, ZSM-5, ZSM-11, ZSM-12, ZSM-22, ZSM-23, ZSM-35, ZSM-48, and the like, and combinations thereof. ZSM-5 is described in detail in U.S. Patent Nos. 3,702,886 and RE 29,948. ZSM-11 is described in detail in U.S. Patent No. 3,709,979.

ZSM-12 is described in U.S. Patent No. 3,832,449. ZSM-22 is described in U.S. Patent No. 4,556,477. ZSM-23 is described in U.S. Patent No. 4,076,842. ZSM-35 is described in U.S. Patent No. 4,016,245. ZSM-48 is more particularly described in U.S. Patent No. 4,234,231.

[0023] Additionally or alternately, the catalyst described herein can comprise one or more large pore zeolites having a Constraint Index less than 2. Suitable large pore molecular sieves can include, but are not limited to, zeolite beta, zeolite Y, Ultrastable Y (USY), Dealuminized Y (Deal Y), mordenite, ZSM-3, ZSM-4, ZSM-18, ZSM-20, and the like, and combinations thereof. ZSM-14 is described in U.S. Patent No. 3,923,636. ZSM-20 is described in U.S. Patent No. 3,972,983. Zeolite beta is described in U.S. Patent Nos. 3,308,069, and RE 28,341. Low sodium Ultrastable Y molecular sieve (USY) is described in U.S. Patent Nos. 3,293,192 and 3,449,070. Dealuminized Y zeolite (Deal Y) may be prepared by the method found in U.S. Patent No. 3,442,795. Zeolite UHP-Y is described in U.S. Patent No. 4,401,556. Mordenite is a naturally occurring material but is also available in synthetic forms, such as TEA-mordenite (*i.e.*, synthetically 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.

[0024] Further additionally or alternately, the catalyst described herein can comprise at least one molecular sieve of the MCM-22 family. As used herein, the term “molecular sieve of the MCM-22 family” (or “material of the MCM-22 family” or “MCM-22 family material” or “MCM-22 family zeolite”) includes one or more of:

- molecular sieves made from a common first degree crystalline building block unit cell, which unit cell has the MWW framework topology. (A unit cell is a spatial arrangement of atoms which if tiled in three-dimensional space describes the crystal structure. Such crystal structures are discussed in the “Atlas of Zeolite Framework Types”, Fifth Edition, 2001, the entire contents of which are incorporated by reference herein);
- molecular sieves made from a common second degree building block, being a 2-dimensional tiling of such MWW framework topology unit cells, forming a monolayer of one unit cell thickness, preferably one c-unit cell thickness;
- molecular sieves made from common second degree building blocks, being layers of one or more than one unit cell thickness, wherein the layer of more

than one unit cell thickness can be made from stacking, packing, or binding at least two monolayers of one unit cell thickness. The stacking of such second degree building blocks can be in a regular fashion, an irregular fashion, a random fashion, or any combination thereof; and

- molecular sieves made by any regular or random 2-dimensional or 3-dimensional combination of unit cells having the MWW framework topology.

[0025] Molecular sieves of the MCM-22 family can include those molecular sieves 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. The X-ray diffraction data used to characterize the material can be obtained by standard techniques using the K-alpha doublet of copper as incident radiation and a diffractometer equipped with a scintillation counter and associated computer as the collection system.

[0026] Materials of the MCM-22 family can additionally or alternately include, but are not limited to, 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 International Patent Publication No. WO97/17290), MCM-36 (described in U.S. Patent No. 5,250,277), MCM-49 (described in U.S. Patent No. 5,236,575), MCM-56 (described in U.S. Patent No. 5,362,697), UZM-8 (described in U.S. Patent No. 6,756,030), and mixtures thereof.

[0027] In certain preferred embodiments, the catalyst described herein can comprise or be ZSM-5. Additionally or alternately, the catalyst described herein can comprise or be a zeolite having a silica to alumina molar ratio from about 20 to about 200, for example from about 20 to about 150.

[0028] In addition to the zeolite, the catalyst employed in the present process may contain a separate inorganic oxide binder that is substantially free of aluminum. By “substantially free” is meant the separate inorganic oxide binder should contain less than 5 wt% of aluminum, for example less than 3 wt%, less than 1 wt%, less than 0.5 wt%, less than 0.3 wt%, less than 0.1 wt%, less than 0.05 wt%, or completely free of measurable aluminum. Examples of suitable inorganic oxide binders can include, but are not necessarily limited to, silica, titania, zirconia, and the like, and mixtures thereof with each other and other metal oxides (again typically not including alumina). The

inorganic oxide binder can be present in an amount from about 5 wt% to about 65 wt%, for example from about 10 wt% to about 35 wt%, of the total catalyst. Alternatively, the present zeolite catalyst may be formed into a shaped catalyst body without the aid of a separate binder, *i.e.*, the catalyst may be self-bound. For more information on the production of silica-rich catalysts, reference is directed to U.S. Patent No. 4,582,815, the entire contents of which are incorporated herein by reference.

[0029] To produce the desired phosphorus-modified catalyst, as-synthesized crystals of the target zeolite can be formed into a slurry with a solvent, generally water, and, where applicable, a substantially aluminum-free inorganic oxide binder. The resultant slurry can then be formed into a shaped catalyst body, generally by extrusion, and the catalyst body can then be treated with an aqueous solution of a phosphorus compound, such as a phosphorus oxyacid. Phosphorus treatment can conveniently be accomplished by impregnation. After phosphorus treatment, the treated catalyst body can be heated to remove the water and to convert the phosphorus compound to an oxide form. Heating can be conducted, advantageously in an oxidizing environment such as in air, at a temperature from about 350°C to about 650°C for an appropriate time, *e.g.*, from about 0.2 hours to about 5.0 hours. Typically, the final catalyst can comprise from about 0.1 wt% to about 3 wt% of elemental phosphorus, present as an oxide of phosphorus.

[0030] Generally, but not always, the as-synthesized zeolite crystals used to produce the desired catalyst can contain an organic directing agent used in the synthesis of the zeolite. Such directing agents can frequently block the pores of the zeolite and so should generally be removed before the zeolite is used catalytically. In this case, although the directing agent can be removed prior to formation of the shaped catalyst body, in some preferred embodiments, the directing agent can be removed by heating the shaped catalyst body in an oxidizing or non-oxidizing environment (*e.g.*, in air) at a temperature from about 400°C to about 820°C for an appropriate time, *e.g.*, from about 0.3 hours to about 3 hours. Typically, heating to remove the organic directing agent can be conducted before phosphorus treatment of the shaped catalyst body.

[0031] In addition, many zeolite synthesis processes can be conducted under alkaline conditions in the presence of alkali metal ions, especially sodium ions. In this case, the as-synthesized zeolite crystals can often be in the sodium form and so should

be converted to the catalytically active hydrogen form before use. Such conversion can typically be achieved by ion exchange with ammonium cations and heating to drive off the ammonia, thus leaving the H^+ form of the zeolite. Again, although these steps can be conducted on the as-synthesized zeolite crystals before catalyst formation, in some preferred embodiments, ammonium exchange and subsequent conversion to the hydrogen form can be conducted on the shaped catalyst body. Typically, conversion of the zeolite to the hydrogen form can be conducted before phosphorus treatment of the shaped catalyst body, but after removal of the organic directing agent employed in the synthesis of the zeolite.

[0032] The phosphorus-modified ZSM-5 catalyst produced by the present process can be particularly useful in any organic conversion process where the hydrothermal stability of the catalyst is important. Examples of such processes can include, but are not necessarily limited to, fluid catalytic cracking of heavy hydrocarbons to gasoline and diesel boiling range hydrocarbons, methylation and disproportionation of toluene to produce xylenes, n-paraffin (*e.g.*, C_6 and higher) cyclization, conversion of methanol to gasoline and diesel boiling range hydrocarbons, and the like, and combinations and/or integrations thereof.

[0033] The invention can additionally or alternately include one or more of the following embodiments.

[0034] Embodiment 1. A process for producing a phosphorus-modified zeolite catalyst, said process comprising: (a) forming zeolite crystals into a shaped catalyst body either in the absence of a separate inorganic oxide binder or in the presence of a separate inorganic oxide binder which is substantially free of aluminum; (b) converting the zeolite crystals to the hydrogen form; (c) removing any organic directing agent employed in the synthesis of the zeolite crystals; (d) treating the shaped catalyst body with an aqueous solution of a phosphorus compound; and (e) heating the treated catalyst body to remove the water and convert the phosphorus compound to an oxide form.

[0035] Embodiment 2. The process of embodiment 1, wherein the zeolite crystals are formed into a shaped catalyst body in the presence of a separate inorganic oxide binder which contains less than 5 wt% of aluminum.

[0036] Embodiment 3. The process of any one of the previous embodiments,

wherein the zeolite crystals are mixed with a silica binder prior to the forming (a).

[0037] Embodiment 4. The process of any one of the previous embodiments, wherein the forming (a) is accomplished by extrusion.

[0038] Embodiment 5. The process of any one of the previous embodiments, wherein the converting (b) is accomplished before the forming (a).

[0039] Embodiment 6. The process of embodiment 5, wherein the removing (c) is accomplished before the forming (a).

[0040] Embodiment 7. The process of any one of the previous embodiments, wherein the treating (d) is accomplished by impregnation, *e.g.*, with an aqueous solution of a phosphorus oxyacid.

[0041] Embodiment 8. The process of any one of the previous embodiments, wherein the heating in (e) is conducted at a temperature from about 350°C to about 650°C for a time of about 0.2 hours to about 5.0 hours.

[0042] Embodiment 9. The process of any one of the previous embodiments, wherein the zeolite has a molar ratio of silica to alumina from about 20 to about 200, *e.g.*, from about 20 to about 150.

[0043] Embodiment 10. The process of any one of the previous embodiments, wherein the zeolite comprises ZSM-5.

[0044] Embodiment 11. A phosphorus-modified zeolite catalyst produced by the process of any one of the previous embodiments.

[0045] Embodiment 12. A process for organic compound conversion employing contacting a feedstock with the phosphorus-modified zeolite catalyst of embodiment 11 under organic compound conversion conditions.

[0046] Embodiment 13. The process of embodiment 12, wherein said organic compound conversion comprises the conversion of methanol to hydrocarbons boiling in the gasoline boiling range.

[0047] The invention will now be more particularly described with reference to the following non-limiting Examples and the accompanying drawings.

EXAMPLES

[0048] In the Examples, the ZSM-5 crystal employed was an as-synthesized sodium form ZSM-5 having a silica to alumina molar ratio of about 50, produced using tetrapropylammonium bromide as a structure directing agent.

[0049] In the Examples, alpha values are used to provide an indication of the catalytic cracking activity of a catalyst, compared to a standard catalyst, and to help assess the relative rate constant (rate of normal hexane conversion per volume of catalyst per unit time). The alpha value is based on the activity of a silica-alumina cracking catalyst taken as an alpha of 1 (Rate Constant $\approx 0.016 \text{ sec}^{-1}$). The Alpha Test is described in U.S. Patent No. 3,354,078; in the Journal of Catalysis, 4, 527 (1965); 6, 278 (1966); and 61, 395 (1980), each incorporated herein by reference as to that description. The experimental conditions of the test used herein include ~ 100 torr (~ 13 kPa) hexane vapor pressure in He carrier gas flowing through a reactor held at $\sim 1000^\circ\text{F}$ ($\sim 538^\circ\text{C}$).

Example 1. Phosphorus addition to zeolite during extrusion with alumina

[0050] Alumina (~ 200 grams on solids basis) was first added to a mixer and dry mulled. Deionized water (~ 100 grams) was then added to moisten the alumina, followed by addition of an amount of phosphoric acid (~ 0 , ~ 61 , ~ 122 , or ~ 183.2 grams, respectively, on solids basis) to achieve targeted phosphorus levels. Na-ZSM-5 crystals (~ 800 grams on solids basis) and additional deionized water were then added, and the mixtures were mulled for ~ 10 - 30 minutes to achieve the desired consistency for extrusion. Mixtures with four different phosphorus levels (~ 0 , ~ 1.7 , ~ 3.4 , and ~ 4.2 wt%, respectively) were thereby prepared. Each mixture was then extruded into $\sim 1/16''$ cylinders. The extrudates were dried overnight (~ 8 - 16 hours) at $\sim 250^\circ\text{F}$ ($\sim 121^\circ\text{C}$) and then precalcined in nitrogen for ~ 3 hours at $\sim 1000^\circ\text{F}$ ($\sim 538^\circ\text{C}$). Each extrudate was then exchanged twice with a 1N aqueous solution of ammonium nitrate. The resultant exchanged catalyst was dried overnight at $\sim 250^\circ\text{F}$ ($\sim 121^\circ\text{C}$) and then calcined in air for ~ 3 hours at $\sim 1000^\circ\text{F}$ ($\sim 538^\circ\text{C}$).

Example 2. Phosphorus addition to alumina-bound zeolite

[0051] ZSM-5 (~800 grams on solids basis) and Versal™ 300 alumina (~200 grams on solids basis) were added to a mixer and dry milled. While mulling, ~492 grams of deionized water were added to achieve the desired consistency for extrusion. The mixture was then extruded into ~1/16" cylinders. The extrudates were dried overnight (~8-16 hours) at ~250°F (~121°C) and then precalcined in nitrogen for ~3 hours at ~1000°F (~538°C). The extrudate was then exchanged twice with a 1N aqueous solution of ammonium nitrate. The exchanged catalyst was dried overnight at ~250°F (~121°C) and then calcined in air for ~3 hours at ~1000°F (~538°C). The extrudate was then impregnated via incipient wetness with targeted levels of ~2, ~4, or ~6 wt% phosphorus (actual levels as indicated in Table 1 below) using an aqueous solution of phosphoric acid. The impregnated crystal was then dried at ~250°F (~121°C) overnight and then calcined in air for ~3 hours at ~1000°F (~538°C).

Example 3. Phosphorous addition to silica-bound zeolite

[0052] ZSM-5 (~800 grams on solids basis) and Ultrasil™ VN3SP silica (~100 grams on solids basis) were added to a mixer and dry milled. Ludox™-40 silica (~100 grams) was then added to the mixture followed by the addition of ~60 grams of ~50 wt% caustic (NaOH) solution. While mulling, ~85 grams of deionized water were added to achieve the desired consistency for extrusion. The mixture was then extruded into ~1/16" cylinders. The extrudates were dried overnight (~8-16 hours) at ~250°F (~121°C) and then precalcined in nitrogen for ~3 hours at ~1000°F (~538°C). The extrudate was then exchanged twice with a 1N aqueous solution of ammonium nitrate. The exchanged catalyst was dried overnight at ~250°F (~121°C) and then calcined in air for ~3 hours at ~1000°F (~538°C). The extrudate was then impregnated via incipient wetness with targeted levels of ~2, ~4, or ~6 wt% phosphorus (actual levels as indicated in Table 1 below) using an aqueous solution of phosphoric acid. The impregnated crystal was then dried at ~250°F (~121°C) overnight and then calcined in air for ~3 hours at ~1000°F (~538°C).

Example 4. Phosphorous addition to self-bound zeolite

[0053] ZSM-5 crystal (~1.4 kg on solids basis) was added to a mixer and dry mulled. Approximately 190 grams of deionized water was then added during mulling. After about 10 minutes, ~28 grams of ~50 wt% caustic (NaOH) solution mixed with approximately 450 grams of water were added to the mixture and mulled for an additional ~5 minutes. The mixture was then extruded into ~1/10" quadrilobes. The extrudates were dried overnight (~8-16 hours) at ~250°F (~121°C) and then precalcined in nitrogen for ~3 hours at ~1000°F (~538°C). The extrudate was then exchanged twice with a 1N aqueous solution of ammonium nitrate. The exchanged catalyst was dried overnight at ~250°F (~121°C) and then calcined in air for ~3 hours at ~1000°F (~538°C). The extrudate was then impregnated via incipient wetness with targeted levels of ~2, ~4, or ~6 wt% phosphorus (actual levels as indicated in Table 1 below) using an aqueous solution of phosphoric acid. The impregnated crystal was then dried at ~250°F (~121°C) overnight and then calcined in air for ~3 hours at ~1000°F (~538°C).

Example 5: Measurement of hexane cracking activity of P-stabilized catalysts

[0054] The ZSM-5 containing extrudates of Examples 1-4 were analyzed for phosphorus content and steamed for ~96 hours at ~1000°F (~538°C) and ~14.7 psia steam partial pressure. The as-prepared and steamed catalysts were then screened for acidic activity with hexane cracking measurements in a routine Alpha test. The Alpha values and phosphorus levels of the extrudates from Examples 1-4 are shown in Table 1 below. The results show that the alumina-containing catalysts from Examples 1 and 2 have much lower alpha activity than the silica and self-bound catalysts from Examples 3 and 4 after steaming. Both silica and self-bound catalysts with approximately 0.8 wt% P retain ~110 alpha value after steaming as compared to the same catalysts with no P that retain ~14 and ~11 alpha value after steaming.

Table 1.

Catalyst	Phosphorus wt %	Alpha value (as prepared)	Alpha value (as steamed)
Example 1a	0.0	~300	~13
Example 1b	~1.7	~270	~5.3
Example 1c	~3.4	~250	~12
Example 1d	~4.2	~240	~19
Example 2a	0.0	~320	~13
Example 2b	~2.7	~340	~22
Example 2c	~4.2	~210	~38
Example 2d	~5.3	~160	~79
Example 3a	0.0	~580	~14
Example 3b	~0.8	~240	~110
Example 3c	~1.6	~170	~96
Example 3d	~2.4	~99	~26
Example 4a	0.0	~540	~11
Example 4b	~0.84	~290	~110
Example 4c	~1.67	~160, ~210	~85
Example 4d	~2.47	~70	~47, ~29

[0055] While the present invention has been described and illustrated by reference to particular embodiments, those of ordinary skill in the art will appreciate that the invention lends itself to variations not necessarily illustrated herein. For this reason, then, reference should be made solely to the appended claims for purposes of determining the true scope of the present invention.

CLAIMS

What is claimed is:

1. A process for producing a phosphorus-modified zeolite catalyst, said process comprising:
 - (a) forming zeolite crystals into a shaped catalyst body either in the absence of a separate inorganic oxide binder or in the presence of a separate inorganic oxide binder which is substantially free of aluminum;
 - (b) converting the zeolite crystals to the hydrogen form;
 - (c) removing any organic directing agent employed in the synthesis of the zeolite crystals;
 - (d) treating the shaped catalyst body with an aqueous solution of a phosphorus compound; and
 - (e) heating the treated catalyst body to remove the water and convert the phosphorus compound to an oxide form.
2. The process of claim 1, wherein the zeolite crystals are formed into a shaped catalyst body in the presence of a separate inorganic oxide binder which contains less than 5 wt% of aluminum.
3. The process of claim 1 or claim 2, wherein the zeolite crystals are mixed with a silica binder prior to the forming (a).
4. The process of any one of the previous claims, wherein the forming (a) is accomplished by extrusion.
5. The process of any one of the previous claims, wherein the converting (b) is accomplished before the forming (a).
6. The process of claim 5, wherein the removing (c) is accomplished before the forming (a).
7. The process of any one of the previous claims, wherein the treating (d) is

accomplished by impregnation, *e.g.*, by impregnation with an aqueous solution of a phosphorus oxyacid.

8. The process of any one of the previous claims, wherein the heating in (e) is conducted at a temperature from about 350°C to about 650°C for a time of about 0.2 hours to about 5.0 hours.

9. The process of any one of the previous claims, wherein the zeolite has a molar ratio of silica to alumina from about 20 to about 200, *e.g.*, from about 20 to about 150.

10. The process of any one of the previous claims, wherein the zeolite comprises ZSM-5.

11. A phosphorus-modified zeolite catalyst produced by the process of any one of the previous claims.

12. A process for organic compound conversion employing contacting a feedstock with the phosphorus-modified zeolite catalyst of claim 11 under organic compound conversion conditions.

13. The process of claim 12, wherein said organic compound conversion comprises the conversion of methanol to hydrocarbons boiling in the gasoline boiling range.