

PHOSPHORUS MODIFIED ZEOLITE CATALYSTS

FIELD OF THE INVENTION

[0001] This disclosure relates to phosphorus modified zeolite catalysts and their use in organic conversion reactions, such as the conversion of methanol to gasoline and diesel boiling range hydrocarbons.

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. The zeolite is modified with phosphorus oxide by impregnating the zeolite with a source of phosphate ions, such as an aqueous solution of an ammonium phosphate, followed by calcination. The phosphorus oxide modification is said to render the zeolite more active and/or benzene selective in the aromatization reaction.

[0003] In addition, U.S. Patent Application Publication No. 2010/0168489 discloses a bound phosphorus-modified zeolite catalyst, in which the binder material is treated with a mineral acid prior to being bound with the phosphorus-modified zeolite. Suitable binder materials are said to include inorganic oxides, such as alumina, clay, aluminum phosphate and silica-alumina. In the Examples, the binder material is a pseudoboehmite-type alumina available from Alcoa as HiQ™-40 grade (with a surface area of 250 m²/g). 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 0.01-0.15 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.

[0004] In the conversion of methanol to gasoline (MTG), the reaction is believed to be catalyzed by acid sites generated by framework aluminum inside the micropores of the zeolite catalyst. The role of the phosphorus can be to stabilize the zeolite framework aluminum against dealumination by the high temperature steam generated

as a by-product of the process. The role of the binder material can be to assist in maintaining the integrity of the catalyst particles in the catalyst bed. Surprisingly, however, it has now been found that the activity of a bound phosphorus-modified zeolite catalyst for the MTG reaction can be enhanced by employing a binder with a relatively low surface area (less than $200 \text{ m}^2/\text{g}$) and a particular mesopore distribution. This result is surprising, because binder particles can typically be larger than the opening of the microchannels of the zeolite, and hence penetration of binder into the zeolite micropores in such situations was not anticipated. Moreover, blockage of zeolite micropores by binder located at the pore mouth of the microchannels was not expected to occlude zeolite micropore volume in a zeolite with the three-dimensional pore structure favored for MTG reactions, such as in MFI zeolites.

SUMMARY OF THE INVENTION

[0005] In one aspect, the invention resides in a bound phosphorus-modified catalyst composition comprising a zeolite having a silica to alumina molar ratio of at least 40, *e.g.*, from about 40 to about 200, and a binder having a surface area less than $200 \text{ m}^2/\text{g}$, *e.g.*, less than $150 \text{ m}^2/\text{g}$ or less than or equal to $100 \text{ m}^2/\text{g}$, wherein the bound catalyst composition exhibits a mesopore size distribution with less than 20% of mesopores having a size below 10 nm before steaming in approximately 100% steam for about 96 hours at about 1000°F (about 538°C) and with more than 60% of mesopores having a size at least 21 nm after steaming in approximately 100% steam for about 96 hours at about 1000°F (about 538°C).

[0006] In some embodiments, the zeolite can have a constraint index of about 1 to about 12 and/or can comprise ZSM-5.

[0007] Additionally or alternately, the catalyst composition has an alpha value after steaming in $\sim 100\%$ steam for ~ 96 hours at $\sim 1000^\circ\text{F}$ ($\sim 538^\circ\text{C}$) of at least 20, *e.g.*, at least 40.

[0008] Additionally or alternately, the catalyst composition can have a microporous surface area of at least $375 \text{ m}^2/\text{g}$ and/or can contain phosphorus in an amount between about 0.1 wt% and about 3 wt%, *e.g.*, between about 0.5 wt% and about 2 wt%, of the total catalyst composition.

[0009] Additionally or alternately, the binder can comprise alumina and/or can be present in an amount between about 1 wt% and about 50 wt%, *e.g.*, between about 5 wt% and about 40 wt%, of the total catalyst composition.

[0010] Additionally or alternately, the catalyst can have a diffusivity for 2,2-dimethylbutane of greater than $1 \times 10^{-2} \text{ sec}^{-1}$ when measured at a temperature of $\sim 120^\circ\text{C}$ and a 2,2-dimethylbutane pressure of ~ 60 torr (~ 8 kPa).

[0011] In a further aspect, the invention can involve use of the unbound catalyst composition described herein in organic conversion reactions, such as the conversion of methanol to hydrocarbons boiling in the gasoline boiling range.

[0012] 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”, “Process for Producing 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.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] Figure 1 shows a graph comparing the normalized alpha values of the catalysts of Examples 1-2 after steaming in $\sim 100\%$ steam for ~ 96 hours at $\sim 1000^\circ\text{F}$ ($\sim 538^\circ\text{C}$).

[0014] Figure 2 shows a graph comparing the microporous surface area of the catalysts of Examples 1-2, normalized by zeolite content.

[0015] Figure 3 shows a graph comparing the diffusivity for 2,2-dimethylbutane of the catalysts of Examples 1-2 at a temperature of $\sim 120^\circ\text{C}$ and a 2,2-dimethylbutane pressure of ~ 60 torr (~ 8 kPa).

[0016] Figure 4 shows a graph comparing the mesopore size distribution of the catalysts of Examples 1-2.

[0017] Figure 5 shows a graph comparing the mesopore size distribution of the catalysts of Examples 1-2 after steaming in ~100% steam for ~96 hours at ~1000°F (~538°C).

DETAILED DESCRIPTION OF THE EMBODIMENTS

[0018] Described herein is a bound phosphorus-stabilized zeolite catalyst composition for use in any of a variety of organic conversion reactions, particularly, but not exclusively, in the conversion of methanol to hydrocarbons boiling in the gasoline boiling range.

[0019] The zeolite employed in the present catalyst composition can typically have a silica to alumina molar ratio of at least 40, *e.g.*, from about 40 to about 200. Generally, the zeolite can comprise at least one medium pore aluminosilicate zeolite having a Constraint Index of 1-12 (as defined in U.S. Patent No. 4,016,218). Suitable zeolites can include, but are not necessarily limited to, ZSM-5, ZSM-11, ZSM-12, ZSM-22, ZSM-23, ZSM-35, ZSM-48, and the like, as well as 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. In certain embodiments, the zeolite can comprise, consist essentially of, or be ZSM-5.

[0020] When used in the present catalyst composition, the zeolite can advantageously be present at least partly in the hydrogen form. Depending on the conditions used to synthesize the zeolite, this may implicate converting the zeolite from, for example, the alkali (*e.g.*, sodium) form. This can readily be achieved, *e.g.*, by ion exchange to convert the zeolite to the ammonium form, followed by calcination in air or an inert atmosphere at a temperature from about 400°C to about 700°C to convert the ammonium form to the active hydrogen form. If an organic structure directing agent is used in the synthesis of the zeolite, additional calcination may be desirable to remove the organic structure directing agent.

[0021] The zeolite can be combined with a binder, normally alumina, silica, or silica-alumina, which can be selected so as to have a surface area less than $200 \text{ m}^2/\text{g}$, for example less than $150 \text{ m}^2/\text{g}$ or less than or equal to $100 \text{ m}^2/\text{g}$. Suitable binders can comprise or be Pural™ 200 and/or Versal™ 300 alumina. Generally, the binder can be present in an amount between about 1 wt% and about 50 wt%, *e.g.*, between about 5 wt% and about 40 wt%, of the total catalyst composition.

[0022] To enhance the steam stability of the zeolite without excessive loss of its initial acid activity, the present catalyst composition can contain phosphorus in an amount between about 0.01 wt% and about 3 wt% elemental phosphorus, *e.g.*, between about 0.05 wt% and about 2 wt%, of the total catalyst composition. The phosphorus can be added to the catalyst composition at any stage during synthesis of the zeolite and/or formulation of the zeolite and binder into the catalyst composition. Generally, phosphorus addition can be achieved by spraying and/or impregnating the final catalyst composition (and/or a precursor thereto) with a solution of a phosphorus compound. Suitable phosphorus compounds can include, but are not limited to, phosphinic [$\text{H}_2\text{PO}(\text{OH})$], phosphonic [$\text{HPO}(\text{OH})_2$], and phosphoric [$\text{PO}(\text{OH})_3$] acids, salts and esters of such acids, phosphorous halides, and the like, and combinations thereof. After phosphorus treatment, the catalyst can generally be calcined, *e.g.*, in air at a temperature from about 400°C to about 700°C to convert the phosphorus to an oxide form.

[0023] The bound phosphorus-stabilized zeolite catalyst composition employed herein can be characterized by at least one, and preferably at least two, of the following properties: (a) a microporous surface area of at least $375 \text{ m}^2/\text{g}$; (b) a diffusivity for 2,2-dimethylbutane of greater than $1.2 \times 10^{-2} \text{ sec}^{-1}$, when measured at a temperature of $\sim 120^\circ\text{C}$ and a 2,2-dimethylbutane pressure of $\sim 60 \text{ torr}$ ($\sim 8 \text{ kPa}$); (c) an alpha value after steaming in $\sim 100\%$ steam for ~ 96 hours at $\sim 1000^\circ\text{F}$ ($\sim 538^\circ\text{C}$) of at least 20, *e.g.*, at least 40; (d) a mesopore size distribution with less than 20% of mesopores having a size below 10 nm; and (e) a mesopore size distribution with more than 60% of mesopores having a size at least 21 nm after steaming in approximately 100% steam for about 96 hours at about 1000°F (about 538°C). It should be appreciated by one of ordinary skill in the art that properties (a), (b), and (d) above, unlike properties (c) and (e), are measured before any steaming of the catalyst composition.

[0024] Of these properties, microporosity and diffusivity for 2,2-dimethylbutane can be determined by a number of factors, including but not necessarily limited to the pore size and crystal size of the zeolite and the availability of the zeolite pores at the surfaces of the catalyst particles. Mesopore size distribution can be determined mainly by the surface area of the binder. Given the disclosure herein regarding the use of a relatively low surface area binder, producing a zeolite catalyst with the desired mesopore size distribution, microporous surface area, and 2,2-dimethylbutane diffusivity should be well within the expertise of anyone of ordinary skill in zeolite chemistry.

[0025] Alpha value can advantageously be a measure of the acid activity of a zeolite catalyst, as compared with a standard silica-alumina catalyst. The alpha test is described in U.S. Patent No. 3,354,078; in the Journal of Catalysis, v. 4, p. 527 (1965); v. 6, p. 278 (1966); and v. 61, p. 395 (1980), each incorporated herein by reference as to that description. The experimental conditions of the test used herein can include a constant temperature of $\sim 538^{\circ}\text{C}$ and a variable flow rate, as described in detail in the Journal of Catalysis, v. 61, p. 395. The higher alpha values can generally correspond to a more active cracking catalyst. Since the present catalyst composition can be intended for use in reactions such as MTG, where the zeolite can be subject to hydrothermal dealumination of the zeolite, it can be important for the catalyst composition to retain a significant alpha value, namely at least 20, after steaming in $\sim 100\%$ steam for ~ 96 hours at $\sim 1000^{\circ}\text{F}$ ($\sim 538^{\circ}\text{C}$).

[0026] The phosphorus-modified zeolite catalyst described herein 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.

[0027] The invention can additionally or alternately include one or more of the following embodiments.

[0028] Embodiment 1. A bound phosphorus-modified catalyst composition comprising a zeolite having a silica to alumina molar ratio of at least 40, *e.g.*, from about 40 to about 200, and a binder having a surface area less than $200 \text{ m}^2/\text{g}$, *e.g.*, less than $150 \text{ m}^2/\text{g}$ or less than or equal to $100 \text{ m}^2/\text{g}$, wherein the bound catalyst composition exhibits a mesopore size distribution with less than 20% of mesopores having a size below 10 nm before steaming in approximately 100% steam for about 96 hours at about 1000°F (about 538°C) and with more than 60% of mesopores having a size at least 21 nm after steaming in approximately 100% steam for about 96 hours at about 1000°F (about 538°C).

[0029] Embodiment 2. The catalyst composition of embodiment 1, wherein said zeolite has a constraint index from about 1 to about 12.

[0030] Embodiment 3. The catalyst composition of any one of the previous embodiments, wherein said zeolite comprises ZSM-5.

[0031] Embodiment 4. The catalyst composition of any one of the previous embodiments, wherein the bound catalyst composition exhibits an alpha value after steaming in approximately 100% steam for about 96 hours at about 1000°F (about 538°C) of at least 20, *e.g.*, of at least 40.

[0032] Embodiment 5. The catalyst composition of any one of the previous embodiments, wherein the bound catalyst composition exhibits a microporous surface area of at least $375 \text{ m}^2/\text{g}$.

[0033] Embodiment 6. The catalyst composition of any one of the previous embodiments, further comprising phosphorus in an amount between about 0.1 wt% and about 3 wt%, *e.g.*, between about 0.5 wt% and about 2 wt%, of the total catalyst composition.

[0034] Embodiment 7. The catalyst composition of any one of the previous embodiments, wherein the binder is present in an amount between about 1 wt% and about 50 wt%, *e.g.*, between about 5 wt% and about 40 wt%, of the total catalyst composition.

[0035] Embodiment 8. The catalyst composition of any one of the previous embodiments, wherein the binder comprises alumina.

[0036] Embodiment 9. The catalyst composition of any one of the previous embodiments, wherein the zeolite has a diffusivity for 2,2-dimethylbutane of greater

than $1.2 \times 10^{-2} \text{ sec}^{-1}$, when measured at a temperature of about 120°C and a 2,2-dimethylbutane pressure of about 60 torr (about 8 kPa).

[0037] Embodiment 10. A process for organic compound conversion employing contacting a feedstock with the bound catalyst composition of any one of the previous embodiments under organic compound conversion conditions.

[0038] Embodiment 11. The process of embodiment 10, wherein said organic compound conversion comprises the conversion of methanol to hydrocarbons boiling in the gasoline boiling range.

[0039] The invention will now be more particularly described with reference to the Examples and the accompanying drawings.

EXAMPLES

Example 1. Preparation of ZSM-5/Versal™-300 alumina catalyst

[0040] A mixture of ~80 wt% of as-synthesized NaZSM-5 zeolite (containing the organic directing agent used in its synthesis and having the properties summarized in Table 1 below) was blended in a muller with ~20 wt% of Versal™-300 alumina binder. Versal™-300 alumina used herein exhibited a surface area of about 250-300 m²/g.

[0041] The blend was extruded, and the resultant extrudate sample was calcined in nitrogen for ~3 hours at ~1000°F (~538°C) to decompose the organic template into a carbonaceous deposit. The calcined extrudate was then exchanged with an ammonium nitrate solution to convert the zeolite from the sodium to the ammonium form, whereafter the extrudate was calcined in air for ~3 hours at ~1000°F (~538°C) to convert the zeolite from the ammonium to the hydrogen form. At the same time carbonaceous deposits were removed by oxidation. The thus obtained H-ZSM-5-Al₂O₃ extrudate was then impregnated with phosphoric acid to a target level of ~0.96 wt% phosphorus via aqueous incipient wetness impregnation. The sample was dried and then calcined in air for ~3 hours at ~1000°F (~538°C). The resultant product was labeled Catalyst A and had the properties summarized in Table 1 below.

Example 2. Preparation of ZSM-5/Pural™ 200 alumina catalyst

[0042] The process of Example 1 was repeated, except that Pural™ 200 alumina was substituted as the alumina binder. Pural™ 200 alumina used herein exhibited a

surface area of about 90 m²/g. The resultant product was labeled Catalyst B and had the properties summarized in Table 1 below.

Table 1.

Cat	Si/Al ₂	microporous surface area (m ² /g)	Alpha	Alpha after steaming*	2,2-DMB Diffusiv. (10 ⁻⁶ sec ⁻¹)	P (wt% based on zeolite)
A		370		18	11,000	1.2
B		395		47	14,000	1.2

* Alpha value per gram of zeolite after steaming in ~100% steam for ~96 hours at ~1000°F (~538°C)

Example 3. Alpha testing

[0043] MTG reactions are typically catalyzed over acid sites. The acidity of the catalyst can tend to decrease with time on stream in the MTG reactor, perhaps due to the effect of hydrothermal dealumination of the zeolite. In order to assess the ability of the catalyst to withstand the hydrothermal stress in the MTG reactor, the steaming conditions in the MTG reactor were simulated by a hydrothermal treatment in a laboratory reactor. The acidity of the catalysts was then measured by its n-hexane cracking activity (alpha test).

[0044] The n-hexane cracking activity, expressed as alpha value, can be a measure for the acidity of the catalyst. Alpha value is defined as the ratio of the first order rate constant for n-hexane cracking, relative to a silica-alumina standard, and can be determined using the following formula:

$$\alpha = A * \ln(1-X) / \tau$$

where:

A: includes the reference rate constant & unit conversion ≈ -1.043

X: fractional conversion

τ : residence time = wt / ($\rho * F$)

ρ : packing density [g/cm³]

F: gas flow rate [cm³/min]

wt: catalyst weight [g]

[0045] The flow rate was adjusted to maintain a conversion between 5% and 25%. Four data points were measured at ~4, ~11, ~18, and ~25 minutes. The alpha value was the relative first order rate constant at ~18 minutes.

[0046] Prior to the alpha test, samples were steamed in ~100% H₂O atmosphere for ~96 hours at ~1000°F (~538°C). The alpha activity (value) was normalized by the nominal amount of zeolite used in the preparation of the extrudate. The results are shown in Table 1 above and Figure 1 and demonstrate that the reference catalyst containing alumina A exhibited a relatively low alpha value (18), while the catalyst extrudate containing alumina B exhibited a significantly higher alpha value (47). It was surprising that the replacement of the standard alumina binder with a different type of alumina binder resulted in a dramatic increase in alpha activity (value) after steaming.

Example 4. Microporous surface area

[0047] The MTG reaction can tend to take place inside the zeolite micropores. It can, therefore, be beneficial to improve/maximize the zeolitic micropore volume in order to achieve maximum MTG activity. Samples selected of Catalysts A and B were heated under vacuum (*e.g.*, at most 10^{-4} atm, corresponding to at most 10 Pa, or alternately at most 10^{-5} atm, corresponding to at most 1 Pa) for ~4 hours at ~350°C prior to measurement of the micropore surface area by N₂-BET. The micropore surface areas were normalized by the zeolite content present in Catalysts A and B, and the results are shown in Table 1 above and Figure 2. It can be seen that Catalyst B exhibited a higher microporosity, compared with the reference Catalyst A containing a standard alumina binder. Since the acid sites responsible for MTG activity are believed to be located inside the zeolite micropores, this result indicated an advantage of Catalyst B in an MTG application, relative to the standard alumina binder in Catalyst A. The result was surprising, because binder particles can typically be larger than the opening of the microchannels of the zeolite, and penetration of binder into the zeolite micropores was hence not anticipated. Moreover, blockage of zeolite micropores by binder located at the pore mouth of the microchannels was not expected to occlude zeolite micropore volume in a zeolite with three-dimensional pore structure, as in MFI. It was thus not obvious that changing the type of alumina binder would result in an increase in micropore surface area.

Example 5. Diffusivity for 2,2-dimethylbutane

[0048] The porosity of a zeolite can play a role in product selectivity and/or coke formation in reactions involving the zeolite. Fast diffusion of reactants into and of products out of zeolite micropores can be desirable to obtain the desired product composition and/or to prevent coke formation. Samples of Catalysts A and B were calcined in air for ~6 hours at ~1000°F (~538°C) prior to measurement of the diffusivity of 2,2-dimethylbutane (2,2-DMB). The diffusivity was calculated from the rate of 2,2-DMB uptake and the amount of hexane uptake using the following formula:

$$D/r^2 = k * (2,2\text{-DMB uptake rate} / \text{hexane uptake})$$

where

D/r^2 : diffusivity [10^{-6} sec^{-1}]

2,2-DMB uptake rate: [$\text{mg/g/min}^{0.5}$]

Hexane uptake: [mg/g]

k: proportionality constant

[0049] Hexane and 2,2-DMB uptakes were measured in two separate experiments using a microbalance. Prior to hydrocarbon adsorption, about 50 mg of the particular catalyst sample was heated in air for ~30 minutes to ~500°C in order to remove moisture and hydrocarbon/coke impurities. For hexane adsorption, the particular sample was cooled to ~90°C and subsequently exposed to a flow of ~100 mbar hexane in nitrogen at ~90°C for ~40 minutes. For 2,2-DMB adsorption, the particular sample was cooled to ~120°C after the air calcination step and exposed to a 2,2-dimethylbutane pressure of ~60 torr (~8 kPa) for ~30 minutes. The results are shown in Table 1 above and Figure 2. It can be seen that Catalyst B exhibited higher 2,2-DMB uptake than Catalyst A. The formulation of a zeolite into an extrudate with a binder can result in the blockage or narrowing of the pore mouth. The higher diffusivity of the preferred catalyst B suggested a larger degree of unobstructed zeolite channels and pore openings. The preferred alumina binder B appeared to have less negative interactions with the active zeolite component. It was inventive to design an extrudate that would display these favorable properties with an alumina binder.

Example 6. Mesoporosity

[0050] Mesoporosity is a property that can be beneficial to the diffusion of reactants to the zeolite surface and to the release of products away from the zeolite surface. Mesoporosity is defined herein as pores having diameters between about 2 nm and about 50 nm, and can be measured from the hysteresis of the N₂-BET. Larger pores can allow faster transport of reactants and products to and from the zeolite surface. Figure 4 shows the pore size distribution for the two Catalysts A and B after calcination for ~6 hours in air at ~1000°F (~538°C). Both samples, as calcined, displayed a maximum in the pore size distribution curve at around 20-25 nm. However, Catalyst A exhibited a pronounced shoulder extending from the maximum towards narrower pores down to about 6 nm. Catalyst B displayed much less porosity in the regime between 6 nm and the maximum of the pore size distribution curve. From the N₂-pore size distribution curve, it was believed that Catalyst B might have slightly enhanced diffusion properties relative to sample A.

[0051] Table 2 compares the mesopore volume in the pore size range from 3-10 nm pore diameter with the total mesopore volume for the two catalysts A and B after calcination for ~6 hours in air at ~1000°F (~538°C). Mesopore volumes were determined from the integrals of the PSD curve shown in Figure 4 within the ranges indicated.

Table 2. Mesopore volumes for Catalysts A and B after calcination

Fraction of small mesopore volume (<10 nm), calcined				
Cat	Small pore volume (range in nm) ml/g	Pore volume (range in nm)	Total pore volume (range in nm) ml/g	Fraction of mesopores <10 nm
A	0.164 (3-10)	0.265 (10-49)	0.429 (3-49)	0.38
B	0.036 (3-10)	0.230 (10-43)	0.266 (3-43)	0.14

[0052] From Table 2, it can be seen that the fraction of small mesopores ranging from 3-10 nm relative to the total measured mesopore volume was ~14% for Catalyst B and ~38% for Catalyst A.

[0053] Figure 5 shows the pore size distribution for Catalysts A and B after steaming for ~6 hours at ~1000°F (~538°C) in ~100% H₂O atmosphere. Catalyst A

showed a maximum around 21 nm in the pore size distribution curve, while Catalyst B had its maximum shifted to larger pore diameters at around 34 nm.

[0054] Table 3 compares the mesopore volumes in the pore size range below and above 21 nm for Catalysts A and B after steaming for ~6 hours at ~1000°F (~538°C) in ~100% H₂O atmosphere. Mesopore volumes were determined from the integrals of the PSD curve shown in Figure 5 within the ranges indicated.

Table 3. Mesopore volumes for Catalysts A and B after steaming

Fraction of large mesopore volume (>21 nm), steamed 96h 1000F				
Cat	Pore volume (range in nm) ml/g	Pore volume (range in nm) ml/g	Total pore volume (range in nm) ml/g	Fraction of mesopores > 21nm
A	0.274 (3-21)	0.142 (21-44)	0.416 (3-44)	0.34
B	0.091 (3-21)	0.345 (21-97)	0.436 (3-97)	0.79

[0055] From Table 3, it can be seen that Catalyst B displayed a larger pore volume in the range above 21 nm than Catalyst A. The fraction of relatively large mesopores (pore diameter above 21 nm) was ~79% for Catalyst B, compared to ~34% for Catalyst A.

[0056] 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 bound phosphorus-modified catalyst composition comprising a zeolite having a silica to alumina molar ratio of at least 40, *e.g.*, from about 40 to about 200, and a binder having a surface area less than 200 m²/g, *e.g.*, less than 150 m²/g or less than or equal to 100 m²/g, wherein the bound catalyst composition exhibits a mesopore size distribution with less than 20% of mesopores having a size below 10 nm before steaming in approximately 100% steam for about 96 hours at about 1000°F (about 538°C) and with more than 60% of mesopores having a size at least 21 nm after steaming in approximately 100% steam for about 96 hours at about 1000°F (about 538°C).
2. The catalyst composition of claim 1, wherein said zeolite has a constraint index from about 1 to about 12.
3. The catalyst composition of claim 1 or claim 2, wherein said zeolite comprises ZSM-5.
4. The catalyst composition of any one of the previous claims, wherein the bound catalyst composition exhibits an alpha value after steaming in approximately 100% steam for about 96 hours at about 1000°F (about 538°C) of at least 20, *e.g.*, at least 40.
5. The catalyst composition of any one of the previous claims, wherein the bound catalyst composition exhibits a microporous surface area of at least 375 m²/g.
6. The catalyst composition of any one of the previous claims, further comprising phosphorus in an amount between about 0.1 wt% and about 3 wt%, *e.g.*, between about 0.5 wt% and about 2 wt%, of the total catalyst composition.
7. The catalyst composition of any one of the previous claims, wherein the binder is present in an amount between about 1 wt% and about 50 wt%, *e.g.*, between about 5 wt% and about 40 wt%, of the total catalyst composition.

8. The catalyst composition of any one of the previous claims, wherein the binder comprises or is alumina.
9. The catalyst composition of any one of the previous claims, wherein the zeolite has a diffusivity for 2,2-dimethylbutane of greater than $1.2 \times 10^{-2} \text{ sec}^{-1}$, when measured at a temperature of about 120°C and a 2,2-dimethylbutane pressure of about 60 torr (about 8 kPa).
10. A process for organic compound conversion employing contacting a feedstock with the bound catalyst composition of any one of the previous claims under organic compound conversion conditions.
11. The process of claim 10, wherein said organic compound conversion comprises the conversion of methanol to hydrocarbons boiling in the gasoline boiling range.