

PHOSPHORUS MODIFIED ZEOLITE CATALYST

FIELD OF THE INVENTION

[0001] This disclosure relates to a phosphorus modified zeolite catalyst and its 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 No. 7,304,194 discloses a process for the hydrothermal treatment of a phosphorus-modified ZSM-5 catalyst. The ZSM-5 has a silica/alumina mole ratio of at least about 200, a crystal particle size of at least 0.5 micron and may be used in unbound form or combined with a binder selected from alumina, clay, or silica. The phosphorus-modified zeolite contains from about 0.01 g P/g zeolite to about 0.15 g P/g zeolite and is calcined at a temperature of at least 300°C to produce a catalyst having a BET surface area of 150-200 m²/g determined by N₂ adsorption techniques. The calcined catalyst is then treated with steam at a temperature of from about 150°C to about 350°C. The steamed, phosphorus modified zeolite is said to exhibit improved para-selectivity and methanol selectivity when used as a catalyst in toluene methylation reactions.

[0004] 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. 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.

[0005] Current catalysts for the conversion of methanol to gasoline (MTG) also generally employ a bound phosphorus-modified zeolite catalyst. The MTG reaction is catalyzed by acid sites generated by framework aluminum inside the micropores of the zeolite catalyst, whereas 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 but, with certain binders, especially alumina-containing binders, the phosphorus can preferentially migrate to the binder alumina and/or can increase the coke selectivity of the catalyst. There is therefore a need for an improved catalyst for use in the conversion of methanol to gasoline.

SUMMARY OF THE INVENTION

[0006] 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, phosphorus in an amount between about 0.1 wt% and about 3 wt% of the total catalyst composition, and a binder that is essentially free of aluminum, wherein the catalyst composition exhibits at least one, and preferably at least two, of the following properties: (a) a microporous surface area of at least 340 m²/g; (b) a diffusivity for 2,2-dimethylbutane of greater than 1.2 x 10⁻² sec⁻¹, *e.g.*, greater than 1.5 x 10⁻² sec⁻¹, when measured at a temperature of ~120°C and a 2,2-dimethylbutane pressure of ~60 torr (~8 kPa); (c) an alpha value after steaming in ~100% steam for ~96 hours at ~1000°F (~538°C) of at least 20, *e.g.*, of at least 40; and (d) a coke deactivation rate constant less than or equal to 0.06 after steaming in ~100% steam for ~96 hours at ~900°F (~482°C).

[0007] Conveniently, the silica to alumina molar ratio of the zeolite can be from about 40 to about 200.

[0008] Conveniently, the zeolite can have a constraint index of about 1 to about 12 and in one embodiment comprises ZSM-5.

[0009] Conveniently, the catalyst composition can contain phosphorus in an amount between about 0.5 wt% and about 2 wt%, of the total catalyst composition.

[0010] Conveniently, 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. In one embodiment, the binder can comprise or be silica.

[0011] In a further aspect, the invention can reside in use of bound phosphorus-modified 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 1-4 after steaming in ~100% steam for about 96 hours at ~1000°F (~538°C).

[0014] Figure 2 shows a graph comparing the microporous surface area of the catalysts of Examples 1-3, normalized by zeolite content.

[0015] Figure 3 shows a graph comparing the diffusivity for 2,2-dimethylbutane of the catalysts of Examples 1-3 at a temperature of about 120°C and a 2,2-dimethylbutane pressure of ~60 torr (~8 kPa).

[0016] Figure 4 shows a graph comparing the normalized alpha values and the coke deactivation rate constants of the catalysts of Example 6 after steaming in ~100% steam for about 96 hours at ~900°F (~482°C).

DETAILED DESCRIPTION OF THE EMBODIMENTS

[0017] Described herein are bound phosphorus-stabilized zeolite catalyst compositions and their use in a variety of organic conversion reactions, particularly, but not exclusively, in the conversion of methanol to hydrocarbons boiling in the gasoline boiling range.

[0018] The zeolite employed in the present catalyst composition can typically have a silica to alumina molar ratio of at least 40, for example from about 40 to about 200. Generally, the zeolite can comprise at least one medium pore aluminosilicate zeolite, *e.g.*, 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, 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. In certain preferred embodiments, the zeolite can comprise or be ZSM-5.

[0019] 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, getting to the hydrogen form may involve converting the zeolite from, for example, the alkali (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, such as 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, calcination may be additionally desirable to remove the organic structure directing agent.

[0020] The zeolite can be combined with a binder, generally an inorganic oxide, that is essentially free of aluminum. In the present specification, a binder that is “essentially free of aluminum” should be understood to mean a binder containing less than 10 wt% aluminum, for example less than 7 wt%, less than 5 wt%, less than 3 wt%, less than 1 wt%, less than 0.5 wt%, less than 0.1 wt%, or no detectable aluminum, as measured by XRF/ICP. A suitable binder is silica. Generally, the binder can be present in an amount between about 1 wt% and about 50 wt%, for example between about 5 wt% and about 40 wt%, of the total catalyst composition. Combining the zeolite and the binder can generally be achieved by mulling an aqueous mixture of the zeolite and binder and then extruding the mixture into catalyst pellets. A process for producing zeolite extrudates using a silica binder is disclosed in, for example, U.S. Patent No. 4,582,815, the entire contents of which are incorporated herein by reference.

[0021] 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, for example 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 or formulation of the zeolite and binder into the bound 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.

[0022] The bound phosphorus-stabilized zeolite catalyst composition employed herein can advantageously exhibit both (i) a diffusivity for 2,2-dimethylbutane of greater than $1.5 \times 10^{-2} \text{ sec}^{-1}$, for example at least $1.7 \times 10^{-2} \text{ sec}^{-1}$ or at least $2 \times 10^{-2} \text{ sec}^{-1}$, when measured at a temperature of about 120°C and a 2,2-dimethylbutane pressure of

about 60 torr (about 8 kPa) and (ii) a coke deactivation rate constant, as calcined, of less than 0.2, *e.g.*, less than about 0.15 or less than about 0.12. The bound phosphorus-stabilized zeolite catalyst composition employed herein can additionally or alternately be characterized by at least one, and preferably at least two or in some embodiments all, of the following properties: (a) a microporous surface area of at least 340 m²/g, for example of at least 375 m²/g; (b) an alpha value after steaming in ~100% steam for ~96 hours at ~1000°F (~538°C) of at least 20, for example of at least 40 or of at least 60; and (d) a coke deactivation rate constant less than or equal to 0.06, for example less than 0.05 or less than 0.04, after steaming in ~100% steam for ~96 hours at ~1000°F (~538°C). It should be appreciated by one of ordinary skill in the art that property (a) above, unlike properties (b) and (c), are measured before any steaming of the catalyst composition.

[0023] Of these properties, micoporosity and diffusivity for 2,2-dimethylbutane can be determined by a number of factors including, but not limited to, the pore size and crystal size of the zeolite and the accessibility of the zeolite pores at the surfaces of the catalyst particles. Producing a zeolite catalyst with the desired microporous surface area and 2,2-dimethylbutane diffusivity should be well within the expertise of anyone of ordinary skill in zeolite chemistry.

[0024] Alpha value is 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. Pat. 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 include a constant temperature of about 538°C and a variable flow rate as described in detail in the Journal of Catalysis, v. 61, p. 395. The higher alpha values can tend to correspond to a more active cracking catalyst. Since the present catalyst composition is 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 bound catalyst composition to retain a significant alpha value, namely at least 20, after steaming in ~100% steam for ~96 hours at ~1000°F (~538°C).

[0025] The coke deactivation rate constant can be a measure of the rate at which the catalyst deactivates and is explained in more detail in the Examples.

[0026] The phosphorus-modified bound zeolite catalyst composition 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.*, C₆ 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, phosphorus in an amount between about 0.1 wt% and about 3 wt% of the total catalyst composition, and a binder that is essentially free of aluminum, wherein the bound catalyst, as calcined at a temperature of at least about 1000°F (about 538°C) for at least about 3 hours, exhibits (i) a diffusivity for 2,2-dimethylbutane of greater than $1.5 \times 10^{-2} \text{ sec}^{-1}$, *e.g.*, at least $1.7 \times 10^{-2} \text{ sec}^{-1}$ or at least $2 \times 10^{-2} \text{ sec}^{-1}$, when measured at a temperature of about 120°C and a 2,2-dimethylbutane pressure of about 60 torr (about 8 kPa), and (ii) a coke deactivation rate constant less than about 0.15, and wherein the bound catalyst composition further exhibits at least one of the following properties: (a) a microporous surface area of at least 340 m²/g, *e.g.*, at least 375 m²/g; (b) 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; and (c) a coke deactivation rate constant less than or equal to 0.06, *e.g.*, less than 0.05 or less than 0.04 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 the silica to alumina molar ratio of the zeolite is from about 40 to about 200.

[0030] Embodiment 3. The catalyst composition of any one of the previous embodiments, wherein said zeolite has a constraint index of about 1 to about 12.

[0031] Embodiment 4. The catalyst composition of any one of the previous embodiments, wherein said zeolite comprises or is ZSM-5.

[0032] Embodiment 5. The catalyst composition of any one of the previous embodiments, wherein the bound catalyst composition contains phosphorus in an amount between about 0.5 wt% and about 2 wt% of the total catalyst composition.

[0033] Embodiment 6. 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.

[0034] Embodiment 7. The catalyst composition of any one of the previous embodiments, wherein the binder comprises silica.

[0035] Embodiment 8. The catalyst composition of any one of the previous embodiments, wherein the alpha value after steaming in approximately 100% steam for about 96 hours at about 1000°F (about 538°C) is at least 60.

[0036] Embodiment 9. The catalyst composition of any one of the previous embodiments, wherein the bound catalyst composition exhibits at least two of the properties (a) to (c).

[0037] Embodiment 10. The catalyst composition of any one of the previous embodiments, wherein the bound catalyst composition exhibits all of the properties (a) to (c).

[0038] Embodiment 11. 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.

[0039] Embodiment 12. The process of embodiment 12, wherein said organic compound conversion comprises the conversion of methanol to hydrocarbons boiling in the gasoline boiling range.

[0040] The invention will now be more particularly described with reference to the Examples and the accompanying drawings.

EXAMPLES

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

[0041] A mixture of ~80 wt% of as-synthesized NaZSM-5 zeolite (having a silica to alumina molar ratio of about 50 and containing the organic directing agent used in its synthesis) was blended in a muller with ~20 wt% of Versal™-300 alumina binder. 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 P-modified unbound ZSM-5 catalyst

[0042] A sample of as-synthesized NaZSM-5 zeolite was extruded without the use of binder. The sample was calcined in nitrogen for ~3 hours at ~1000°F (~538°C), exchanged with an ammonium nitrate solution, and calcined in air for ~3 hours at ~1000°F (~538°C). The extrudate was impregnated with phosphoric acid to a target level of ~1.2 wt% phosphorus via aqueous incipient wetness impregnation. The sample was dried and then calcined for ~3 hours at ~1000°F (~538°C). The resultant product was labeled Catalyst B and had the properties summarized in Table 1 below.

Example 3. Preparation of P-modified unbound small crystal ZSM-5 catalyst

[0043] A sample of as-synthesized small crystal NaZSM-5 zeolite was extruded without the use of binder. The sample was calcined in nitrogen for ~3 hours at ~1000°F (~538°C), exchanged with an ammonium nitrate solution, and calcined in air for ~3 hours at ~1000°F (~538°C). The extrudate was impregnated with phosphoric acid to a target level of ~1.2 wt% phosphorus via aqueous incipient wetness impregnation. The sample was dried and then calcined for ~3 hours at ~1000°F (~538°C). The resultant product was labeled Catalyst C and had the properties summarized in Table 1 below.

Example 4. Preparation of P-modified silica-bound ZSM-5 catalyst

[0044] A mixture of ~80 wt% as-synthesized small crystal NaZSM-5 zeolite was extruded with ~20 wt% Ultrasil™ silica. The sample was calcined in nitrogen for ~3 hours at ~1000°F (~538°C), exchanged with an ammonium nitrate solution, and calcined in air for ~3 hours at ~1000°F (~538°C). The extrudate was 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 for ~3 hours at ~1000°F (~538°C). The resultant product was labeled Catalyst D and had the properties summarized in Table 1 below.

Table 1

Cat	Si/Al ₂	Binder type	Binder content, wt%	P (wt% based on zeolite)
A	~50	Al ₂ O ₃	~20	~1.0
B	~50	N/A	0	~1.2
C	~50	N/A	0	~1.2
D	~50	SiO ₂	~20	~1.0

Example 5. Alpha Testing

[0045] Samples of the Catalysts A-D were tested for their n-hexane cracking activity (alpha test) after steaming in ~100% H₂O atmosphere for ~96 hours at ~1000°F (~538°C). The n-hexane cracking activity, expressed as alpha value, can be a measure of 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]

[0046] The flow rate was adjusted to maintain a conversion between about 5% and about 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.

[0047] Figure 1 shows the alpha values, normalized by the nominal amounts of zeolite that went into the extrudate formulation. The alumina-containing reference Catalyst A exhibited a relatively low alpha value, while the alumina-free catalysts B, C, and D exhibited a significantly higher alpha value. In particular, Catalysts, B, C, and D exhibited an alpha value greater than 40 in the n-hexane cracking test after treatment in ~100% H₂O atmosphere for ~96 hours at ~1000°F (~538°C). It was surprising that the elimination of the alumina binder in catalyst formulations B and C, and the replacement of the alumina binder with a silica binder in catalyst formulation D, resulted in a dramatic increase in alpha value after steaming.

Example 6. Microporous surface area

[0048] The MTG reaction generally takes 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 of Catalysts A-D were calcined for ~6 hours at ~1000°F (~538°C) in air prior to measurement of the micropore surface area by N₂-BET. The micropore surface areas were normalized by the zeolite content present in the extrudates, and the results are shown in Figure 2. The formulation without added binder presented a higher microporosity, compared with the reference formulation A containing the 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 formulations B and C in an MTG application, relative to the alumina-containing formulation A. The results were surprising, because binder particles are typically larger than the opening of the microchannels of the zeolite and hence penetration of binder into the zeolite micropores was therefore 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. The preferred catalyst extrudate had a micropore surface area of at least 375 m²/g zeolite.

Example 7. Diffusivity for 2,2-dimethylbutane

[0049] The porosity of a zeolite can play a role in product selectivity and coke formation in reactions involving the zeolite. Fast diffusion of reactants into and of products out of zeolite micropores can be advantageous, or even necessary, to obtain the desired product composition and/or to prevent coke formation. Samples of Catalysts A-C were calcined in air for ~6 hours at ~1000°F (~538°C) prior to measurement of the diffusivity of 2,2-dimethyl-butane (2,2-DMB). The diffusivity was calculated from the rate of 2,2-DMB uptake and the amount of hexane uptake using the following equation:

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

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

[0050] Hexane and 2,2-DMB uptakes were measured in two separate experiments using a microbalance. Prior to hydrocarbon adsorption, about 50 mg 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 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 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 Figure 3, from which it can be seen that Catalysts B and C exhibited a higher 2,2-DMB diffusivity than Catalyst A. Preferred catalysts can advantageously exhibit a hydrocarbon diffusivity greater than $1.2 \times 10^{-2} \text{ sec}^{-1}$, for example greater than $1.5 \times 10^{-2} \text{ sec}^{-1}$ or greater than $2 \times 10^{-2} \text{ sec}^{-1}$, using 2,2-dimethyl butane (2,2-DMB) as hydrocarbon.

Example 8. Coke Resistance

[0051] Coke resistance can be an important property of a catalyst intended for the application in the MTG reaction. The acid sites in the catalyst are generally believed not only to catalyze the MTG reaction but also to catalyze the formation of coke, which

can eventually deactivate the catalyst. In order to ensure a continuous process, the catalyst should typically be regenerated periodically from coke. The ability to maintain n-hexane cracking activity in the alpha test was used as a measure for the coking stability of the catalyst.

[0052] The catalysts used in the test were produced in the same way as Examples 1 and 2, but with higher nominal P loadings of ~1.8 wt% and ~1.6 wt%, respectively, on the extrudate. The resultant catalysts were designated Catalysts A1 and B1 and had the properties shown in Table 2 below.

Table 2.

Catalyst	P content in extrudate, wt%	Binder type	Binder content, wt%
A1	1.8	Al ₂ O ₃	20
B1	1.6	none	0.

[0053] The samples A1 and B1 listed in Table 2 were analyzed for their coke resistance. Samples in Table 2 were steamed for ~96 hours at ~900°F (~482°C) and subsequently evaluated for their coke resistance in the alpha test described above. For the evaluation of the coke resistance of the catalyst in the n-hexane cracking reaction, the alpha values measured at ~4, ~11, ~18, and ~25 minutes were plotted as a function of time, and fitted by an exponential function given in the following equation:

$$\alpha = \alpha_0 * e^{-ct^{1/3}}$$

where α_0 is the alpha value at time 0, and c is the coke deactivation rate constant.

[0054] Since the coke deactivation rate constant, c, can be sensitive to flow rates, it can be important to keep the flow constant during the four points of measurement. The results are shown in Figure 4.

[0055] The alpha values for the catalysts, A1 and B1, were 51 and 99, respectively. Evaluation of the coke deactivation rate constant revealed that the initial alpha values, α_0 , were 64 and 106, respectively. The corresponding coke deactivation rate constants were 0.08 and 0.03, respectively. It was surprising that the sample B1, exhibiting a higher alpha and initial alpha value, was characterized by a lower coke deactivation

constant than A1. The preferred catalyst, B1 had a higher coke resistance and was characterized by a coke deactivation rate constant smaller than 0.05, or smaller than 0.04, in the alpha test.

Example 9. Preparation of P-modified ZSM-5/Versal-300 alumina catalyst

[0056] A mixture of ~80 wt% of as-synthesized NaZSM-5 zeolite (having a silica to alumina molar ratio of about 50 and containing the organic directing agent used in its synthesis) was blended in a muller with ~20 wt% of Versal™-300 alumina binder. 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. 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 another ~3 hours at ~1000°F (~538°C) to convert the zeolite from the ammonium to the hydrogen form. At the same time, any carbonaceous deposits (*e.g.*, from the decomposition of the organic template and/or from the ammonium nitrate exchange) 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 another ~3 hours at ~1000°F (~538°C). The resultant product was labeled Catalyst A'' and had the properties summarized in Table 3 below.

Example 10. Preparation of P-modified unbound ZSM-5 catalyst

[0057] A sample of as-synthesized NaZSM-5 zeolite was extruded without the use of binder. The sample was calcined in nitrogen for ~3 hours at ~1000°F (~538°C), exchanged with an ammonium nitrate solution, and calcined in air for another ~3 hours at ~1000°F (~538°C). The extrudate was impregnated with phosphoric acid to a target level of ~1.2 wt% phosphorus via aqueous incipient wetness impregnation. The sample was dried and then calcined for another ~3 hours at ~1000°F (~538°C). The resultant product was labeled Catalyst B'' and had the properties summarized in Table 3 below.

Example 11. Preparation of P-modified unbound small crystal ZSM-5 catalyst

[0058] A sample of as-synthesized small crystal NaZSM-5 zeolite was extruded without the use of binder. The sample was calcined in nitrogen for ~3 hours at ~1000°F (~538°C), exchanged with an ammonium nitrate solution, and calcined in air for another ~3 hours at ~1000°F (~538°C). The extrudate was impregnated with phosphoric acid to a target level of ~1.2 wt% phosphorus via aqueous incipient wetness impregnation. The sample was dried and then calcined for another ~3 hours at ~1000°F (~538°C). The resultant product was labeled Catalyst C'' and had the properties summarized in Table 3 below.

Example 12. Preparation of P-modified silica-bound ZSM-5 catalyst

[0059] A mixture of ~80 wt% as-synthesized small crystal NaZSM-5 zeolite was extruded with ~20 wt% Ultrasil™ silica. The sample was calcined in nitrogen for ~3 hours at ~1000°F (~538°C), exchanged with an ammonium nitrate solution, and calcined in air for another ~3 hours at ~1000°F (~538°C). The extrudate was 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 for another ~3 hours at ~1000°F (~538°C). The resultant product was labeled Catalyst D'' and had the properties summarized in Table 3 below.

Comparative Example 13. Preparation of P-modified silica-bound ZSM-5 catalyst

[0060] A mixture of ~80 wt% of as-synthesized NaZSM-5 zeolite (having a silica to alumina molar ratio of about 28 and containing the organic directing agent used in its synthesis) was blended in a muller with ~20 wt% of Ultrasil™ silica binder. The blend was extruded and the resultant extrudate sample was calcined in nitrogen for ~3 hours at ~1000°F (~538°C). The calcined extrudate was then exchanged with an ammonium nitrate solution, and then calcined in air for another ~3 hours at ~1000°F (~538°C). The 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 another ~3 hours at ~1000°F (~538°C). The resultant product was labeled Catalyst E and had the properties summarized in Table 3 below.

Table 3

Cat	Si/Al ₂	Binder type	Binder content, wt%	P (wt% based on zeolite)
A''	~50	Al ₂ O ₃	~20	~1.0
B''	~50	N/A	0	~1.2
C''	~50	N/A	0	~1.2
D''	~50	SiO ₂	~20	~1.0
E	~28	SiO ₂	~20	~1.0

Example 14. Characterizations of Samples from Examples 9-13

[0061] For the samples made according to Examples 9-13 and detailed in Table 3 above (A'', B'', C'', D'', and E, respectively), the following tests were conducted. Alpha testing was done according to Example 5, on samples that were treated by steaming in ~100% H₂O atmosphere for ~96 hours at ~1000°F (~538°C). Microporous surface area testing was done according to Example 6, on as calcined samples. Diffusivity testing for 2,2-dimethylbutane was done according to Example 7, on samples that were calcined in air for ~6 hours at ~1000°F (~538°C) prior to measurement. Coke resistance testing, however, in order to measure coke deactivation rate constants, was done similarly to, but slightly different than, Example 8 – coke resistance testing for these samples was done after the samples were steamed for ~96 hours at ~1000°F (~538°C), not at ~900°F (~482°C). Coke resistance testing was additionally done for these samples on as calcined samples. The results of these characterizations are shown in Table 4 below.

Table 4

Catalyst	Alpha value (as steamed)	Surface area (m ² /g)	2,2-DMB Diffus. (*10 ⁻² sec ⁻¹)	Coke Deact. Rate Const. (steamed)	Coke Deact. Rate Const. (as calcined)
A''	33	385	1.42	0.43	0.30
B''	103	429	2.14	0.01	0.10
C''	81	385	2.51	0.02	0.02
D''	100	409	1.76	0.01	0.03
E	128	386	0.03	0.05	0.22

[0062] 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, phosphorus in an amount between about 0.1 wt% and about 3 wt% of the total catalyst composition, and a binder that is essentially free of aluminum, wherein the bound catalyst, as calcined at a temperature of at least about 1000°F (about 538°C) for at least about 3 hours, exhibits

(i) a diffusivity for 2,2-dimethylbutane of greater than $1.5 \times 10^{-2} \text{ sec}^{-1}$ when measured at a temperature of about 120°C and a 2,2-dimethylbutane pressure of about 60 torr (about 8 kPa), and

(ii) a coke deactivation rate constant less than about 0.15, and wherein the bound catalyst composition further exhibits at least one of the following properties:

- (a) a microporous surface area of at least $375 \text{ m}^2/\text{g}$;
- (b) an alpha value after steaming in approximately 100% steam for about 96 hours at about 1000°F (about 538°C) of at least 40; and
- (c) a coke deactivation rate constant less than 0.05 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 the silica to alumina molar ratio of the zeolite is from about 40 to about 200.

3. The catalyst composition of claim 1, wherein said zeolite has a constraint index of about 1 to about 12.

4. The catalyst composition of claim 1, wherein said zeolite comprises ZSM-5.

5. The catalyst composition of claim 1, wherein the bound catalyst composition contains phosphorus in an amount between about 0.5 wt% and about 2 wt% of the total catalyst composition.

6. The catalyst composition of claim 1, wherein the binder is present in an amount

between about 1 wt% and about 50 wt% of the total catalyst composition.

7. The catalyst composition of claim 1, wherein the binder is present in an amount between about 5 wt% and about 40 wt% of the total catalyst composition.

8. The catalyst composition of claim 1, wherein the binder comprises silica.

9. The catalyst composition of claim 1, wherein the alpha value after steaming in approximately 100% steam for about 96 hours at about 1000°F (about 538°C) is at least 60.

10. The catalyst composition of claim 1, wherein coke deactivation rate constant after steaming in approximately 100% steam for about 96 hours at about 1000°F (about 538°C) is less than 0.04.

11. The catalyst composition of claim 1, wherein the bound catalyst composition exhibits at least two of the properties (a) to (c).

12. The catalyst composition of claim 1, wherein the bound catalyst composition exhibits all of the properties (a) to (c).

13. A process for organic compound conversion employing contacting a feedstock with the bound catalyst composition of claim 1 under organic compound conversion conditions.

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