

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, together with a binder or matrix material resistant to the temperature and other conditions employed in the process. 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] U.S. Patent Nos. 6,423,879 and 6,504,072 disclose a process for the selective production of para-xylene which comprises reacting toluene with methanol in the presence of a catalyst comprising a porous crystalline material having a Diffusion Parameter for 2,2 dimethylbutane of about $0.1\text{--}15\text{ sec}^{-1}$ when measured at a temperature of 120°C and a 2,2 dimethylbutane pressure of 60 torr (8 kPa). The porous crystalline material is preferably a medium-pore zeolite, particularly ZSM-5, which has been severely steamed at a temperature of at least 950°C and which has been combined with about 0.05 to about 20 wt % of at least one oxide modifier, preferably an oxide of phosphorus, to control reduction of the micropore volume of the material during the steaming step. The porous crystalline material is normally combined with a binder or matrix material, preferably silica or a kaolin clay.

[0004] U.S. Patent No. 7,304,194 discloses a process for the hydrothermal treatment of a phosphorus-modified ZSM-5 catalyst. In the process, ZSM-5 having a silica/alumina

mole ratio of at least about 250 and a phosphorus content of from at least about 0.08 g P/g zeolite to about 0.15 g P/g zeolite is calcined at a temperature of at least 300°C and then contacted with steam at a temperature of from about 150°C about 250°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. The steamed, phosphorus modified zeolite may be used as a catalyst in unbound form or in combination with a binder material, such as alumina, clay, and silica.

[0005] In addition, 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.

[0006] In certain organic conversion processes, such as the conversion of methanol to gasoline and diesel boiling range hydrocarbons, the hydrothermal stability of the catalyst is of vital importance, since steam dealumination of a zeolite is irreversible and can drastically reduce catalyst life. However, although phosphorus modification is effective in enhancing zeolite hydrothermal stability, it has now been found that binders added to improve cohesive strength of the final catalyst, can negatively impact the utility of phosphorus modification. Thus, with certain binders, especially alumina-containing binders, the phosphorus can preferentially migrate to the binder alumina and can thus increase the coke selectivity of the catalyst. According to the invention, an unbound phosphorus modified zeolite catalyst composition has now been identified that can tend to exhibit higher steam stability and lower coke deactivation rates in methanol conversion reactions than other phosphorus modified compositions. The present catalyst composition can therefore be particularly attractive for use in the conversion of methanol to gasoline and diesel boiling range hydrocarbons and/or in other processes where high temperature steam is present.

SUMMARY

[0007] In one aspect, the invention resides in an unbound catalyst composition comprising a zeolite and phosphorus in an amount between about 0.1 and about 3 wt% of the total catalyst composition, the composition having an alpha value of at least 20 and at least one, and preferably at least two, of the following properties:

- (a) a mesoporosity of greater than 0.2 ml/g;
- (b) a microporous surface area of at least 375 m²/g;
- (c) a diffusivity for 2,2-dimethylbutane of greater than $1 \times 10^{-2} \text{ sec}^{-1}$ when measured at a temperature of ~120°C and a 2,2-dimethylbutane pressure of ~60 torr (~8 kPa); and
- (d) a coke deactivation rate constant less than or equal to 0.06 after steaming in ~100% steam for ~96 hours at ~1000°F (~538°C).

[0008] Conveniently, the catalyst composition can have an alpha value of at least 40, such as at least 75.

[0009] Conveniently, the catalyst composition can have a mesoporosity of greater than 0.3 ml/g and a microporous surface area of at least 380 m²/g.

[0010] In one embodiment, the catalyst composition can have a diffusivity for 2,2-dimethylbutane of greater than $1.25 \times 10^{-2} \text{ sec}^{-1}$, such as greater than $1.5 \times 10^{-2} \text{ sec}^{-1}$, when measured at a temperature of ~120°C and a 2,2-dimethylbutane pressure of ~60 torr (~8 kPa).

[0011] Typically, the catalyst composition can have a coke deactivation rate constant less than or equal to 0.05.

[0012] In one embodiment, the zeolite of the catalyst composition can have a constraint index of about 1 to about 12. Conveniently, the zeolite can have a silica to alumina molar ratio of zeolite from about 40 to about 200 and can generally comprise or be ZSM-5.

[0013] In one embodiment, the catalyst composition can comprise phosphorus in an amount between about 0.01 and about 2 wt% of the total catalyst composition.

[0014] In a further aspect, the invention can reside in 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.

[0015] 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

[0016] Figure 1 is a graph comparing the alpha values of the calcined catalyst extrudates of Examples 1-6.

[0017] Figure 2 is a graph comparing the alpha values of the calcined catalyst extrudates of Examples 1-6 after steaming at ~1000°F (~538°C) in ~100% steam for ~96 hours.

[0018] Figure 3 is a graph comparing the alpha, alpha zero and coke deactivation rate constant values of the calcined catalyst extrudates of Examples 4-6.

[0019] Figure 4 is a graph comparing the alpha, alpha zero and coke deactivation rate constant values of the calcined catalyst extrudates of Examples 4-6 after steaming at ~1000°F (~538°C) in ~100% steam for ~96 hours.

DETAILED DESCRIPTION OF THE EMBODIMENTS

[0020] Described herein is an unbound phosphorus-stabilized zeolite catalyst composition and its 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. In some cases, the present catalyst composition can alternatively be referred to as being self-bound. The terms “unbound” and “self-bound” are intended to be synonymous

and mean that the present catalyst composition can be advantageously free of any of the inorganic oxide binders, such as alumina and/or silica, frequently combined with zeolite catalysts to enhance their physical properties.

[0021] The zeolite employed in the present catalyst composition can generally 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 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 a preferred embodiment, the zeolite can comprise or be ZSM-5.

[0022] The chemical composition of the zeolite is not necessarily critical, although the zeolite can advantageously contain sufficient aluminum to provide the phosphorus-stabilized zeolite catalyst with an initial alpha value, before any steaming, of at least 10, for example of at least 20 or at least 50. Alpha value can 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 include a constant temperature of ~538°C and a variable flow rate as described in detail in the Journal of Catalysis, v. 61, p. 395. The higher alpha values correspond with a more active cracking catalyst. In certain embodiments, a zeolite having the desired activity can have a silica to alumina molar ratio from about 40 to about 200.

[0023] 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 require converting the zeolite from, for example, the alkali (sodium) form. This can readily be achieved by ion exchange to convert the zeolite to the ammonium form, followed by calcination in air or an inert atmosphere, *e.g.*, at a temperature from about 400°C to about 700°C, to convert the ammonium form to the active hydrogen form.

[0024] 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%, for example between about 0.05 wt% and about 2 wt%, elemental phosphorus, by weight 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 into the catalyst composition. Generally, phosphorus addition can be achieved by spraying and/or impregnating the catalyst composition (and/or a precursor thereto) with a solution of a phosphorus compound. Suitable phosphorus compounds can include, but are not limited to, phosphonic, phosphinous, phosphorus, and phosphoric acids, salts and esters of such acids, phosphorous halides, and the like, as well as 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.

[0025] The catalyst composition can employ the phosphorus treated zeolite in its original crystalline form and/or after formulation into catalyst particles, such as by extrusion. A process for producing zeolite extrudates in the absence of a binder, *e.g.*, is disclosed in U.S. Patent No. 4,582,815, the entire contents of which are incorporated herein by reference.

[0026] In addition to the alpha value, the 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 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 mesoporosity of greater than 0.2 ml/g, for example greater than 0.3 ml/g; (b) a microporous surface area of at least 375 m²/g, for example at least 380 m²/g; and (c) a coke deactivation rate constant less than or equal to 0.06, for example less than or equal to 0.05, less than 0.05, less than or equal to 0.04, or less than 0.04, after steaming in ~100% steam for about 96 hours at about 1000°F (about 538°C). It should be understood by one of ordinary skill in the art that properties (a) and

(b) above, unlike property (c), are measured before any steaming of the catalyst composition.

[0027] Of these properties, mesoporosity and diffusivity for 2,2-dimethylbutane can be determined by a number of factors, including, for a given zeolite, crystal size. Microporous surface area can be determined by the pore size of the zeolite and the availability of the zeolite pores at the surfaces of the catalyst particles. Producing a zeolite catalyst with the desired minimum mesoporosity, microporous surface area, and 2,2-dimethylbutane diffusivity should be well within the expertise of anyone of ordinary skill in zeolite chemistry.

[0028] The coke deactivation rate constant can be a measure of the rate at which the catalyst deactivates when subjected to a routine alpha test and is defined in the Examples.

[0029] 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., C₆ and higher) cyclization, conversion of methanol to gasoline and diesel boiling range hydrocarbons, and the like, and combinations and/or integrations thereof.

[0030] The invention can additionally or alternately include one or more of the following embodiments.

[0031] Embodiment 1. An unbound catalyst composition comprising a zeolite and phosphorus in an amount between about 0.01 wt% and about 3 wt% of the total catalyst composition, wherein the unbound 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), (ii) a coke deactivation rate constant less than about 0.15, and (iii) an alpha value of at least 10, and wherein the unbound catalyst composition further exhibits at least one of the following properties: (a) a mesoporosity of greater than 0.2 ml/g; (b) a microporous surface area of at least 375 m²/g; 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).

[0032] Embodiment 2. The catalyst composition of embodiment 1, wherein the as calcined alpha value is at least 20, *e.g.*, at least 50.

[0033] Embodiment 3. The catalyst composition of any one of the previous embodiments, wherein the mesoporosity is greater than 0.3 ml/g.

[0034] Embodiment 4. The catalyst composition of any one of the previous embodiments, wherein the microporous surface area is at least 380 m²/g.

[0035] Embodiment 5. The catalyst composition of any one of the previous embodiments, wherein the 2,2-dimethylbutane diffusivity is at least $1.7 \times 10^{-2} \text{ sec}^{-1}$, *e.g.*, 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).

[0036] Embodiment 6. The catalyst composition of any one of the previous embodiments, wherein the coke deactivation rate constant is less than or equal to 0.04, *e.g.*, less than 0.04, after steaming in approximately 100% steam for about 96 hours at about 1000°F (about 538°C).

[0037] Embodiment 7. The catalyst composition of any one of the previous embodiments, wherein the composition has at least two of said properties (a) to (c), *e.g.*, all three of said properties (a) to (c).

[0038] Embodiment 8. The catalyst composition of any one of the previous embodiments, The catalyst composition of claim 1, wherein said zeolite has a constraint index from about 1 to about 12.

[0039] Embodiment 9. The catalyst composition of any one of the previous embodiments, wherein said zeolite comprises or is ZSM-5.

[0040] Embodiment 10. The catalyst composition of any one of the previous embodiments, wherein a silica to alumina molar ratio of zeolite is from about 40 to about 200.

[0041] Embodiment 11. The catalyst composition of any one of the previous embodiments, wherein the phosphorus is present in an amount between about 0.05 wt% and about 2 wt% of the total catalyst composition.

[0042] Embodiment 12. A process for organic compound conversion employing contacting a feedstock with the catalyst composition of any one of the previous embodiments under organic compound conversion conditions.

[0043] 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.

[0044] The invention will now be more particularly described with reference to the following non-limiting Examples and the accompanying drawings.

EXAMPLES

Examples 1-3. Production of self-bound ZSM-5 catalysts

[0045] ZSM-5 crystal (~1.4 kg on a solids basis) was added to a mixer and dry milled. Then, approximately 190 grams of deionized water was added during mulling. After about 10 minutes, ~28 grams of ~50 wt% caustic solution mixed with about 450 grams of deionized water were added to the mixture and milled for an additional ~5 minutes. The mixture was then extruded into ~1/10" quadralobes. The extrudates were dried overnight (~8-16 hours) at ~250°F (~121°C) and then calcined in nitrogen for ~3 hours at ~1000°F (~538°C). The extrudates were then exchanged twice with a 1N solution of ammonium nitrate. The exchanged crystal was dried overnight at ~250°F (~121°C) and then calcined in air for ~3 hours at ~1000°F (~538°C). Three different ZSM-5 crystals were self-bound using the described procedure. These catalysts were analyzed using nitrogen porosimetry and inductively coupled plasma (ICP) elemental analysis, and the results are summarized in Table 1 below.

Examples 4-6. Phosphorus addition to self-bound ZSM-5 catalysts

[0046] Each of the self-bound catalysts of Examples 1-3 was impregnated via incipient wetness with ~1.2 wt% phosphorus using a solution of phosphoric acid. The impregnated crystals were then dried overnight (~8-16 hours) at ~250°F (~121°C) and then calcined in air for ~3 hours at ~1000°F (~538°C). The resultant P-containing catalysts were again analyzed using nitrogen porosimetry and ICP elemental analysis, and the results are also summarized in Table 1 below.

Examples 7-12. Steam deactivation of self-bound ZSM-5 catalysts

[0047] The catalysts of Examples 1-6 were steamed in ~100% steam for about 96 hours at ~1000°F (~538°C). The resultant steamed catalysts were again analyzed using

nitrogen porosimetry and ICP elemental analysis, and the results are further summarized in Table 1 below.

Example 13. 2,2-Dimethylbutane sorption

[0048] The hydrocarbon diffusivity, expressed as the inverse of the characteristic diffusion time, D/τ^2 , was determined by the rate of 2,2-dimethylbutane (2,2-DMB) uptake for each of the catalysts of Examples 1-12. Prior to hydrocarbon adsorption, about 50 mg of the sample was heated in air to $\sim 500^\circ\text{C}$, *e.g.*, to remove moisture and any hydrocarbon or coke impurities. For 2,2-DMB adsorption, the sample was cooled to $\sim 120^\circ\text{C}$ after the air calcination step and then exposed to a flow of ~ 60 torr (~ 8 kPa) of 2,2-DMB in nitrogen. Again, the results are summarized in Table 1.

Example 14. Alpha testing

[0049] The catalysts of Examples 1-12 were screened for acid activity with hexane cracking in a routine alpha test at standard conditions (~ 100 torr, or ~ 13 kPa, hexane vapor pressure in He carrier gas flowing through a reactor held at $\sim 1000^\circ\text{F}$, or $\sim 538^\circ\text{C}$). During the test, the flow rate was adjusted to achieve a conversion of between about 5% and about 15%. Four data points were taken at ~ 4 , ~ 11 , ~ 18 , and ~ 25 minutes at relatively constant flow. The Alpha value represented the ratio of the first order rate constant, at ~ 18 minutes, for n-hexane cracking, relative to a silica-alumina standard.

[0050] The alpha value was determined as follows:

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

where A – Reference rate constant
 X – Fractional Conversion
 τ – Residence Time

[0051] The four Alpha values were then plotted as a function of time and fitted by an exponential function to determine the rate of coke deactivation:

$$\alpha = \alpha_0 * \exp(-ct^{1/3})$$

where α_0 – Alpha zero measured at time = 0
c – Coke deactivation rate constant
t – time, min

[0052] The results of the alpha testing are also summarized in Table 1 and Figures 1-4. From these results, it can be seen that the initial alpha values of both the phosphorus-free and the phosphorus-containing catalysts were roughly proportional to the amount of free aluminum in the catalyst. Free aluminum is defined herein as the total aluminum minus the phosphorus content.

[0053] It can also be seen that the non-phosphorus stabilized catalysts of Examples 1-3 exhibited high initial alpha values (~1100, ~540, and ~410, respectively) but their steamed counterparts of Examples 7-9 showed a marked decrease in alpha values (to ~7, ~14, and ~4, respectively).

[0054] For the phosphorus stabilized catalysts of Examples 4-6, although the initial alpha values were slightly lower (~700, ~200, and ~160, respectively) than their phosphorus-free counterparts, the steamed versions of Examples 10-12 exhibited better retention of alpha value (~58, ~95, and ~100, respectively) than their steamed phosphorus-free counterparts.

[0055] From Figures 3 and 4, it can be seen that, for the steamed catalysts of Examples 7-12, the phosphorus-stabilized self-bound ZSM-5 catalysts with Si/Al₂ ratios of at least 20, a calcined 2,2-DMB diffusivity of at least 10,000 10⁻⁶ sec⁻¹, and a mesoporsity of at least 0.2 ml/g exhibited the best combination of alpha value retention on steaming and low coke deactivation rate. As shown in Figure 4, the catalyst of Example 11 exhibited essentially no coke deactivation.

Table 1

Ex.	Si/Al	P/Al	Meso-PV, ml/g	Alpha	Alpha Deactivation Constant	2,2-DMB Rate (mg/g/min ^{0.5})	2,2-DMB Diffusivity (10 ⁻⁶ sec ⁻¹)	Microporous Surface Area, m ² /g
1	~14	0	~0.087	~1100		~13	~601	~424
2	~25	0	~0.340	~540		~61	~13500	~401
3	~36	0	~0.049	~410		~2	~19	~309
4	~14	~0.4	~0.074	~700	~0.138	~9	~376	~360
5	~25	~0.7	~0.341	~200	~0.103	~74	~21400	~396
6	~36	~1.0	~0.044	~160	~0.049	~1	~7	~253
7	~14	0	~0.089	~7		~14	~808	~320
8	~25	0	~0.422	~14		~114	~50500	~300
9	~36	0	~0.048	~4		~4	~70	~361
10	~14	~0.4	~0.076	~58	~0.173	~9	~396	~297
11	~25	~0.7	~0.373	~95	~0.001	~69	~18200	~283
12	~36	~1.0	~0.038	~100	~0.085	~3	~26	~322

Example 15. 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 2 below.

Example 16. 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 2 below.

Example 17. 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 2 below.

Example 18. 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 2 below.

Example 19. 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 2 below.

Table 2

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 20. Microporous surface area

[0061] 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'', B'', C'', D'', and E from Examples 15-19 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. Preferred catalyst extrudates exhibited a micropore surface area of at least 375 m²/g zeolite.

Example 21. Characterizations of Samples from Examples 15-19

[0062] For the samples made according to Examples 15-19 and detailed in Table 2 above (A'', B'', C'', D'', and E, respectively), the following tests were conducted. Alpha testing and coke resistance testing (in order to measure coke deactivation rate constants) was done according to Example 14, on samples that were treated by steaming in ~100% H₂O atmosphere for ~96 hours at ~1000°F (~538°C). Coke resistance testing was additionally done for these samples, however, on as calcined samples (not steamed). Microporous surface area testing was done according to Example 20, on as calcined samples. Diffusivity testing for 2,2-dimethylbutane was done according to Example 13, on samples that were calcined in air for ~6 hours at ~1000°F (~538°C) prior to measurement. The results of these characterizations are shown in Table 3 below.

Table 3

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

[0063] 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. An unbound catalyst composition comprising a zeolite and phosphorus in an amount between about 0.01 wt% and about 3 wt% of the total catalyst composition, wherein the unbound 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),

(ii) a coke deactivation rate constant less than about 0.15, and

(iii) an alpha value of at least 10,

and wherein the unbound catalyst composition further exhibits at least one of the following properties:

(a) a mesoporosity of greater than 0.2 ml/g;

(b) a microporous surface area of at least 375 m²/g; 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 alpha value is at least 20, *e.g.*, at least 50.

3. The catalyst composition of claim 1 or claim 2, wherein the mesoporosity is greater than 0.3 ml/g.

4. The catalyst composition of any one of the previous claims, wherein the microporous surface area is at least 380 m²/g.

5. The catalyst composition of any one of the previous claims, wherein the 2,2-dimethylbutane diffusivity is at least $1.7 \times 10^{-2} \text{ sec}^{-1}$, *e.g.*, 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).

6. The catalyst composition of any one of the previous claims, wherein the coke deactivation rate constant is less than or equal to 0.04, *e.g.*, less than 0.04, after steaming in approximately 100% steam for about 96 hours at about 1000°F (about 538°C).
7. The catalyst composition of any one of the previous claims, wherein the composition has at least two of said properties (a) to (c), *e.g.*, all three of said properties (a) to (c).
8. The catalyst composition of any one of the previous claims, wherein said zeolite has a constraint index from about 1 to about 12.
9. The catalyst composition of any one of the previous claims, wherein said zeolite comprises or is ZSM-5.
10. The catalyst composition of any one of the previous claims, wherein a silica to alumina molar ratio of zeolite is from about 40 to about 200.
11. The catalyst composition of any one of the previous claims, wherein the phosphorus is present in an amount between about 0.05 wt% and about 2 wt% of the total catalyst composition.
12. A process for organic compound conversion employing contacting a feedstock with the catalyst composition of any one of the previous claims 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.