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(54) **Titre : PROCEDES DE CONVERSION DE COMPOSES OXYGENES EN HYDROCARBURES**
(54) **Title: METHODS FOR CONVERTING OXYGENATES INTO HYDROCARBONS**

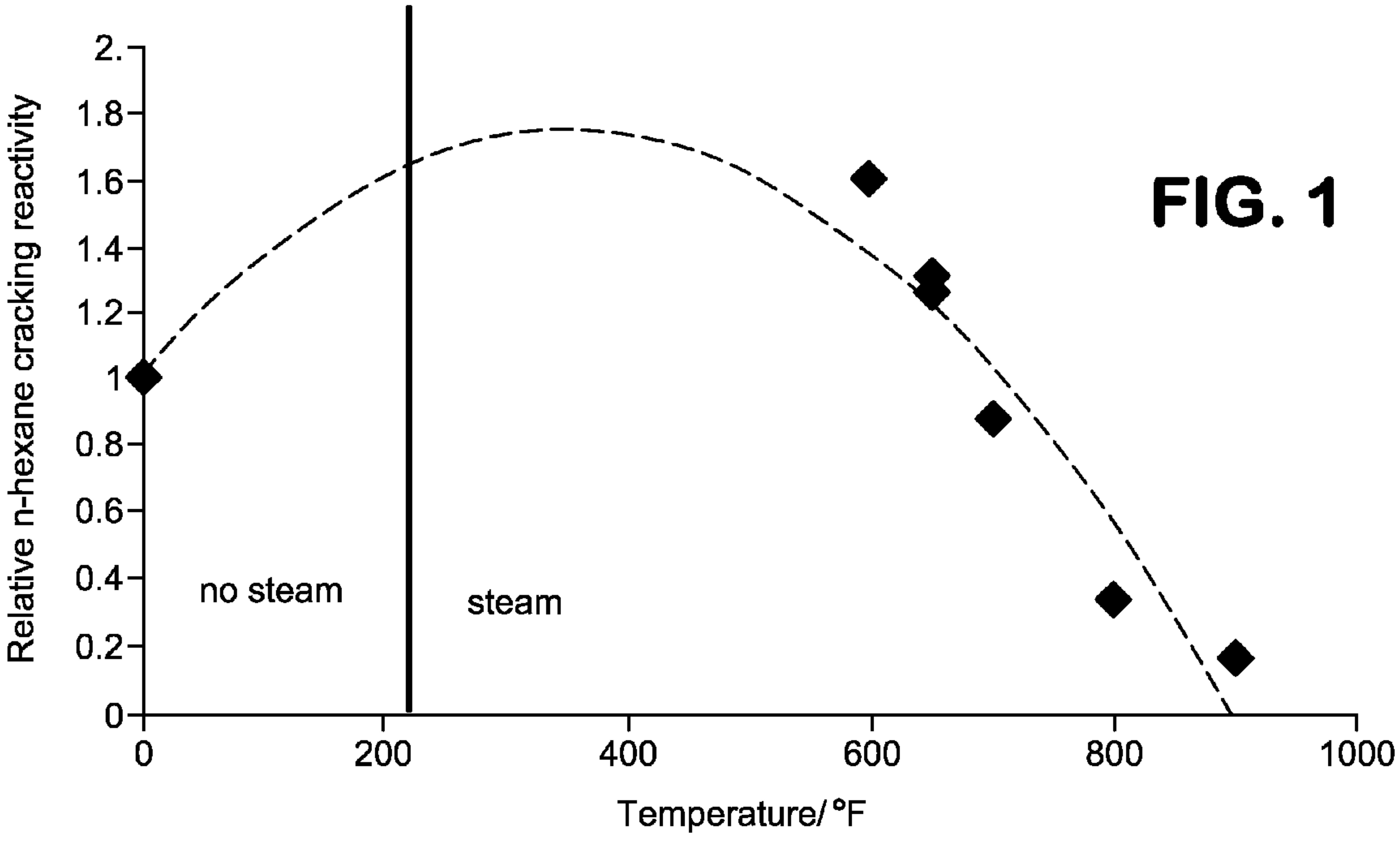
FIG. 1

(57) **Abrégé/Abstract:**
Methods are provided for performing a conversion reaction using a catalyst steamed under mild steaming conditions. Steaming a conversion catalyst under mild steaming conditions can provide an increased conversion activity and/or an increased run length for the catalyst during conversion of an oxygenate feed to aromatic hydrocarbons, such as benzene or xylene. Suitable conversion catalysts can include alumina bound catalysts including a medium pore molecular sieve.

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(54) **Title**: METHODS FOR CONVERTING OXYGENATES INTO HYDROCARBONS

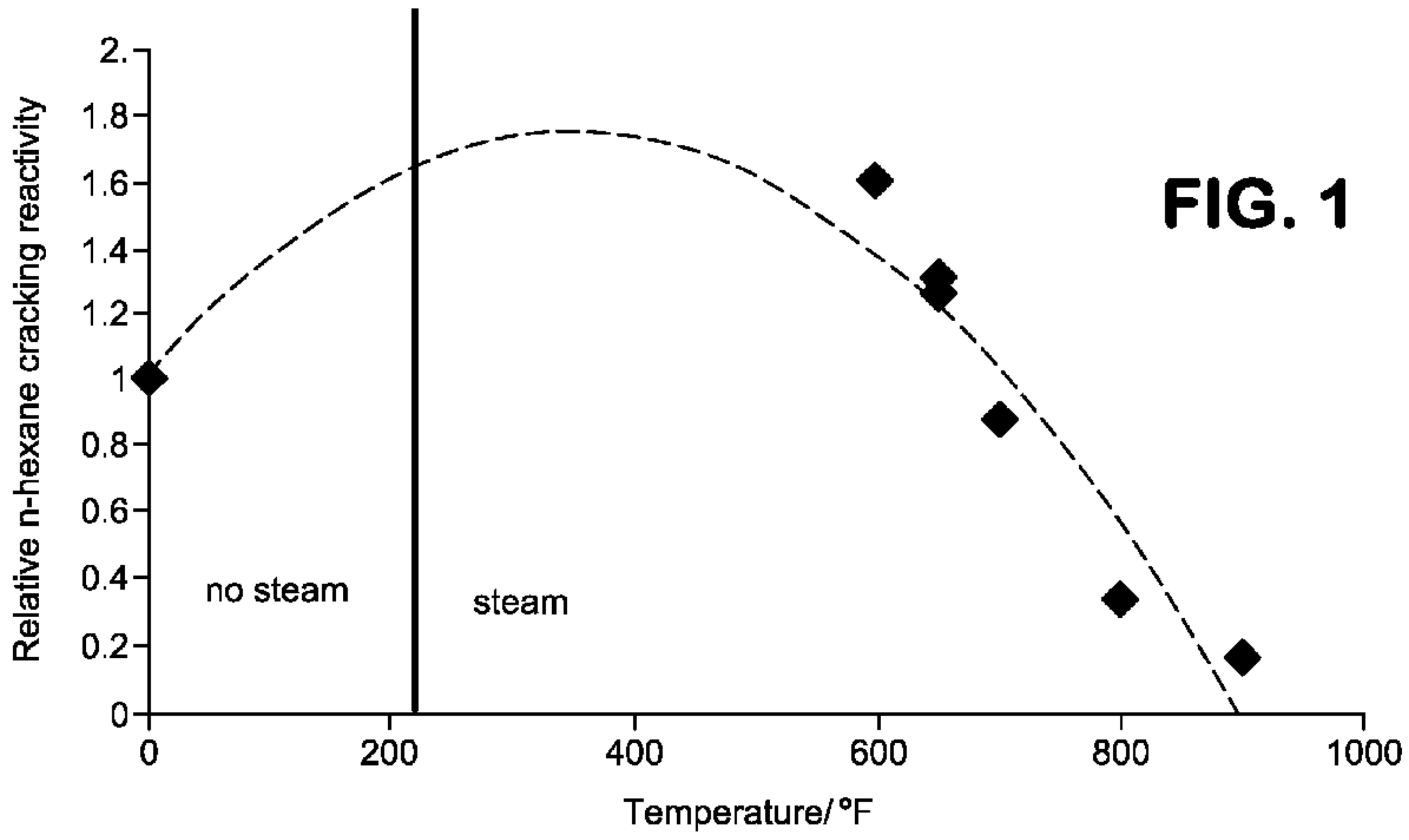


FIG. 1

(57) **Abstract**: Methods are provided for performing a conversion reaction using a catalyst steamed under mild steaming conditions. Steaming a conversion catalyst under mild steaming conditions can provide an increased conversion activity and/or an increased run length for the catalyst during conversion of an oxygenate feed to aromatic hydrocarbons, such as benzene or xylene. Suitable conversion catalysts can include alumina bound catalysts including a medium pore molecular sieve.

METHODS FOR CONVERTING OXYGENATES INTO HYDROCARBONS

FIELD OF THE INVENTION

[0001] Catalysts and methods are provided for manufacture of olefins and aromatics from oxygenate feeds.

BACKGROUND OF THE INVENTION

[0002] Conversion of methanol to olefins and other unsaturated compounds is commonly used reaction scheme for chemical manufacture. Conventional methods can involve exposing a methanol-containing feed to a molecular sieve, such as ZSM-5. In addition to forming olefins, some desirable aromatic compounds can also be formed, such as para-xylene.

[0003] U.S. Patent Nos. 4,049,573 and 4,088,706 disclose conversion of methanol to a hydrocarbon mixture rich in C_2-C_3 olefins and mononuclear aromatics, particularly p-xylene, by contacting the methanol at a temperature of 250-700°C and a pressure of 0.2 to 30 atmospheres with a crystalline aluminosilicate zeolite catalyst which has a Constraint Index of 1-12 and which has been modified by the addition of an oxide of boron or magnesium either alone or in combination or in further combination with oxide of phosphorus. The above-identified disclosures are incorporated herein by reference.

[0004] Methanol can be converted to gasoline employing the MTG (methanol to gasoline) process. The MTG process is disclosed in the patent art, including, for example, U.S. Patent Nos. 3,894,103; 3,894,104; 3,894,107; 4,035,430 and 4,058,576. U.S. Patent No. 3,894,102 discloses the conversion of synthesis gas to gasoline. MTG processes provide a simple means of converting syngas to high-quality gasoline. The ZSM-5 catalyst used is highly selective to gasoline under methanol conversion conditions, and is not known to produce distillate range fuels, because the C_{10}+ olefin precursors of the desired distillate are rapidly converted via hydrogen transfer to heavy polymethylaromatics and C_4 to C_8 isoparaffins under methanol conversion conditions.

[0005] Olefinic feedstocks can also be used for producing C_5+ gasoline, diesel fuel, etc. In addition to the basic work derived from ZSM-5 type zeolite catalysts, a number of discoveries contributed to the development of the industrial process known as Mobil Olefins to Gasoline/Distillate ("MOGD"). This process has significance as a safe, environmentally acceptable technique for utilizing feedstocks that contain lower olefins, especially C_2 to C_5 alkenes. U.S. Patent Nos. 3,960,978 and 4,021,502 disclose conversion of C_2 to C_5 olefins alone or in admixture with paraffinic components, into higher hydrocarbons over crystalline zeolites having controlled acidity. U.S. Patent Nos. 4,150,062, 4,211,640 and 4,227,992 have also contributed improved processing techniques to the MOGD system. The above-identified disclosures are incorporated herein by reference.

[0006] Conversion of lower olefins, especially propene and butenes, over ZSM-5 is effective at moderately elevated temperatures and pressures. The conversion products are sought as liquid fuels, especially the C_5+ aliphatic and aromatic hydrocarbons. Olefinic gasoline is produced in good yield by the MOGD process and may be recovered as a product or recycled to the reactor system for further conversion to distillate-range products. Operating details for typical MOGD units are disclosed in U.S. Patent Nos. 4,445,031, 4,456,779, and 4,433,185, each of which is incorporated herein by reference.

[0007] In addition to their use as shape selective oligomerization catalysts, the medium pore ZSM-5 type catalysts are useful for converting methanol and other lower aliphatic alcohols or corresponding ethers to olefins. Particular interest has been directed to a catalytic process (MTO) for converting low cost methanol to valuable hydrocarbons rich in ethene and C_3+ alkenes. Various processes are described in U.S. Patent Nos. 3,894,107, 3,928,483, 4,025,571, 4,423,274, and 4,433,189, each of which are incorporated herein by reference. It is generally known that the MTO process can be optimized to produce a major fraction of C_2 to C_4 olefins. Prior process proposals have included a separation section to recover ethene and other gases from by-product water and C_5+ hydrocarbon liquids. The oligomerization process conditions which favor the production of C_{10} to C_{20} and higher aliphatics tend to convert only a small portion of ethene as compared to C_3+ olefins.

[0008] The methanol to olefin process (MTO) operates at high temperature and near 30 psig in order to obtain efficient conversion of the methanol to olefins. These process conditions, however, produce an undesirable amount of aromatics and C_2 olefins and require a large investment in plant equipment.

[0009] The olefins to gasoline and distillate process (MOGD) operates at moderate temperatures and elevated pressures to produce olefinic gasoline and distillate products.

When the conventional MTO process effluent is used as a feed to the MOGD process, the aromatic hydrocarbons produced in the MTO unit are desirably separated and a relatively large volume of MTO product effluent has to be cooled and treated to separate a C_2- light gas stream, which is unreactive, except for ethene which is reactive to only a small degree, in the MOGD reactor, and the remaining hydrocarbon stream has to be pressurized to the substantially higher pressure used in the MOGD reactor.

[0010] U.S. Patent No. 4,579,993 describes a method for treating silica-bound catalysts for use in conversion of methanol to hydrocarbon (or hydrocarbonaceous) products. The catalysts correspond to molecular sieves bound in a silica matrix. The treatment method includes a combination of steaming the catalyst and performing an acid-extraction on the catalyst prior to use for methanol conversion. The examples describe both alumina-bound and silica-bound catalysts that, after steaming, have alpha values of about 25 or less.

[0011] U.S. Patent No. 6,372,949 describes methods for using catalysts containing 10 member ring zeolites for conversion of methanol to gasoline. The zeolite catalysts can be steamed prior to use in the conversion reaction. The examples describe steaming of the zeolite catalysts to produce steamed catalysts with alpha values of about 100 or less.

[0012] U.S. Patent No. 4,326,994 describes methods for enhancing zeolite catalytic activity based on steaming a zeolite catalyst under specific combinations of water partial pressure and steaming temperature. The combinations of water partial pressure and steaming temperature are defined by the formula $0.01*F_T < (P*t) < 10*F_T$, where P is the partial pressure of water (in atmospheres) during steaming, t is the time (in hours) of steaming, and F_T is defined as $2.6x10^{-9}e^{16000/T}$ (T in Kelvin). The examples provided include steaming at temperatures of 750°F or higher.

SUMMARY OF THE INVENTION

[0013] In an aspect, a method of converting a feed to form olefins and aromatics is provided, including steaming a catalyst in the presence of at least 0.01 atm (1 kPa) of water at a temperature of about 450°F (221°C) to about 700°F (371°C) for at least about 0.25 hours to form a steamed catalyst, the catalyst comprising a molecular sieve having at least one 10-member ring channel and having no ring channels larger than a 10-member ring channel; and exposing a feed comprising at least about 30 wt% of methanol, dimethyl ether, or a combination thereof to the steamed catalyst under effective conversion conditions to form a conversion effluent comprising ethylene, propylene, and at least one aromatic (preferably para-xylene), the effective conversion conditions including a temperature of about 200°C to about 700°C, or about 350°C to about 600°C, or about 450°C to about 550°C.

[0014] In some aspects, the catalyst can be an alumina-bound catalyst that includes about 10 wt% to about 80 wt% of an alumina binder. Optionally, the catalyst can have an alpha value of at least about 200 prior to steaming and an alpha value that is at least about 25 higher after steaming, such as an alpha value of at least about 300. Optionally, the steaming conditions can include one or more of, or two or more of, a) a partial pressure of steam of at least about 0.5 atm (51 kPa), or at least about 0.9 atm (91 kPa); b) a steaming temperature of about 650°F (343°C) or less, or about 625°F (329°C) or less, or about 600°F (316°C) or less; and c) a length of steaming of about 16 hours or less, or about 12 hours or less, or about 8.5 hours or less, or about 4.5 hours or less.

[0015] In still another aspect, a method of converting an oxygenate feed to form hydrocarbons is provided, the method including: steaming a catalyst in the presence of at least 0.9 atm (91 kPa) of water at a temperature of about 450°F (221°C) to about 650°F (343°C) for at about 0.25 hours to about 16 hours to form a steamed catalyst, the catalyst comprising a molecular sieve having at least one 8-member ring channel, 10-member ring channel, or 12-member ring channel and having no ring channels larger than a 12-member ring channel; and exposing a feed comprising at least about 50 wt% of methanol, dimethyl ether, or a combination thereof to the steamed catalyst under effective conversion conditions to form a conversion effluent comprising one or more hydrocarbons, the effective conversion conditions including a temperature of about 200°C to about 700°C.

BRIEF DESCRIPTION OF THE FIGURES

[0016] FIG. 1 shows cracking activity for catalysts steamed under various steaming conditions.

DETAILED DESCRIPTION OF THE EMBODIMENTS

Overview

[0017] In various aspects, catalysts described herein can be used to convert an oxygenate feed (such as methanol and/or dimethyl ether) into aromatics and/or olefins with improved catalyst lifetime and/or improved catalyst activity. One of the difficulties in converting oxygenate feeds to products such as gasoline or other aromatics can be that the conversion catalyst can have a strong tendency to deactivate over time. For example, coke typically forms as a side product during the conversion of an oxygenate feed to gasoline or other aromatics. The coke can accumulate on the conversion catalyst and can result in blocking of acidic sites on the conversion catalyst. This can cause a corresponding loss of catalyst activity. Such a loss in catalyst activity can become apparent in a matter of a few days. This can pose challenges to performing a methanol conversion process in a fixed bed reaction system. Additionally, although methanol conversion catalysts can be regenerated, the activity of the catalyst can be degraded with each regeneration cycle, so that an increased frequency of regeneration can lead to a more rapid need to entirely replace a catalyst.

[0018] Catalysts for conversion of methanol (and other oxygenates) to gasoline and/or aromatics can be based on zeolites or other molecular sieves. At least a portion of the activity of a zeolite-based catalyst for conversion of methanol can be based on the number of acidic sites on the catalyst. Increasing the number of acidic sites, such as by reducing the ratio of silicon to aluminum in the zeolite framework, can increase the activity of a zeolite catalyst for methanol conversion. However, reducing the silicon to aluminum ratio also has the potential to increase the amount of coke formed during methanol conversion, at least for sufficiently low silicon to aluminum ratios.

[0019] One option for reducing or minimizing coke formation can be to reduce the number of acidic sites on the catalyst. For example, a catalyst can be steamed under sufficiently severe conditions for a period of time to decrease the number of acidic sites. However, reducing the number of acidic sites can lead to a corresponding reduction in catalyst activity for methanol conversion. The reduced activity of a catalyst having a reduced number of acidic sites can require operating a methanol conversion process at higher temperatures and/or more severe operating conditions in order to achieve full conversion of the methanol feed. Such higher severity conditions can tend to reduce the yield of gasoline and/or aromatics from a conversion process.

[0020] In various aspects, instead of steaming a catalyst under conditions with sufficient severity to reduce the number of acidic sites on a catalyst, the catalyst can be steamed under relatively mild conditions. Without being bound by any particular theory, it is believed that steaming under relatively mild conditions can make more acidic sites available on a catalyst. However, this does not necessarily correspond to an increase in the number of acidic sites, as the mild steaming conditions may additionally or alternatively make existing acidic sites more readily available for reaction. Conventionally, increasing the number of acidic sites (or number of "apparent" acidic sites) by any method would be believed to cause increased coking with a corresponding decrease in run length for a catalyst. It has been unexpectedly determined, however, that using mild steaming conditions can provide improved run length and/or improved catalyst activity. This can allow for increased run lengths (and therefore reduced regeneration frequency) for a conversion process. In some aspects, a catalyst steamed under effective mild steaming conditions can be used for a methanol conversion process that has an improved run (cycle) length while allowing the conversion process to be performed at lower conversion temperatures.

Catalyst Steaming Conditions

[0021] Prior to using a catalyst for conversion of oxygenates (such as methanol) to gasoline, aromatics and/or olefins, the catalyst can be steamed under effective steaming conditions. In various aspects, the catalyst for conversion can be steamed under mild steaming conditions, such as steaming conditions that can lead to an increase in the number of apparent available acidic sites in the catalyst. This can lead to an increase in catalyst activity and/or lifetime for conversion of methanol and/or dimethyl ether to gasoline or other aromatics and olefins. General examples of effective steaming conditions including exposing a catalyst to an atmosphere comprising steam at a temperature of about 450°F (about 232°C) to about 700°F (about 371°C), for example about 500°F (260°C) to about 700°F (about 371°C), about 550°F (about 288°C) to about 700°F (about 371°C), about 600°F (about 316°C) to about 700°F (about 371°C), about 450°F (about 232°C) to about 650°F (about 343°C), about 500°F (about 260°C) to about 650°F (about 343°C), or about 550°F (about 288°C) to about 650°F (about 343°C). The atmosphere can include as little as 1 vol% water and up to 100 vol% water. In various aspects, the partial pressure of steam in the effective steaming conditions can be about 0.005 atm (about 0.5 kPag) to about 5 atm (about 510 kPag), for example about 0.005 atm (about 0.5 kPag) to about 1 atm (about 100 kPag), about 0.005 atm (about 0.5 kPag) to about 2 atm (about 200 kPag), about 0.01 atm (about 1 kPag) to about 2 atm (about 200 kPag), about 0.01 atm (about 1 kPag) to about 1 atm (about 100 kPag), about 0.1 atm (about 10 kPag) to about 2 atm (about 200 kPag), about 0.1 atm (about 10 kPag) to about 1 atm (about 100 kPag), about 0.25 atm (about 25 kPag) to about 2 atm (about 200 kPag), about 0.25 atm (about 25 kPag) to about 1 atm (about 100 kPag), about 0.50 atm (about 50 kPag) to about 2 atm (about 200 kPag), about 0.50 atm (about 50 kPag) to about 1 atm (about 100 kPag), about 0.75 atm (about 76 kPag) to about 2 atm (about 200 kPag), about 0.75 atm (about 76 kPag) to about 1 atm (about 100 kPag), about 0.90 atm (about 90 kPag) to about 2 atm (about 200 kPag), or about 0.90 atm (about 90 kPag) to about 1 atm (about 100 kPag). The catalyst can be exposed to the steam for any convenient period of time, such as about 10 minutes (about 0.15 hours) to about 48 hours. In some aspects, the time for exposure of the catalyst to steam is at least about 0.25 hours, such as about 0.25 hours to about 48 hours, about 0.25 hours to about 24 hours, about 0.25 hours to about 16 hours, about 0.25 hours to about 15 hours, about 0.25 hours to about 12 hours, about 0.25 hours to about 8 hours, about 0.25 hours to about 4 hours, about 0.25 hours to about 2 hours, about 0.5 hours to about 24 hours, about 0.5 hours to about 16 hours, about 0.5 hours to about 15 hours, about 0.5 hours to about 12 hours, about 0.5 hours to about 8 hours, about 0.5 hours to about 4 hours, about 0.5 hours to about 2 hours, about 0.75 hours to about 24 hours, about 0.75 hours to about 16 hours, about 0.75 hours to about 15 hours, about 0.75 hours to about 12 hours, about 0.75 hours to about 8 hours, about 0.75 hours to about 4 hours, about 0.75 hours to about 2 hours, about 1 hour to about 24 hours, about 1 hour to about 16 hours, about 1 hour to about 15 hours, about 1 hour to about 12 hours, about 1 hour to about 8 hours, about 1 hour to about 4 hours, or about 1 hour to about 2 hours.

[0022] In some aspects, the effective steaming conditions can be characterized based on a combination of the partial pressure of water during steaming and a length of time for steaming. In such aspects, a suitable combination of conditions can be determined by multiplying the pressure, expressed in units of atmospheres, by the length of steaming, expressed in units of hours. For example, for effective steaming conditions based on a steaming temperature of about 700°F (about 644°K) or less, the product of the pressure (in atmospheres) multiplied by the steaming time (in hours) can be about 12.5 or less, for example about 4.5 or less or about 1.5 or less, and optionally can be at least about 0.25. As another example, for effective steaming conditions based on a steaming temperature of about 650°F (about 617°K), the product of the pressure (in atmospheres) multiplied by the steaming time (in hours) can be about 16.0 or less, for example about 12.5 or less, about 8.5 or less, or about 4.5 or less, and optionally can be at least about 0.25. As still another example, for effective steaming conditions based on a steaming temperature of about 625°F (about 603°K), the product of the pressure (in atmospheres) multiplied by the steaming time (in hours) can be about 16.0 or less, for example about 12.5 or less, about 8.5 or less, or about 4.5 or less, and optionally can be at least about 0.25. As yet another example, for effective steaming conditions based on a steaming temperature of about 600°F (about 589°K), the product of the pressure (in atmospheres) multiplied by the steaming time (in hours) can be about 16.0 or less, for example about 12.5 or less, about 8.5 or less, or about 4.5 or less, and optionally can be at least about 0.25.

[0023] In aspects involving steaming at a temperature of about 450°F (about 232°C) to about 700°F (about 371°C) as described above, the alpha value of an acidic molecular sieve (e.g., zeolite) catalyst can be increased. Alpha value is a measure of the acid activity of a zeolite catalyst as compared with a standard silica-alumina catalyst. The alpha test gives the relative rate constant (rate of normal hexane conversion per volume of catalyst per unit time) of the test catalyst relative to the standard catalyst which is taken as an alpha of 1 (Rate Constant≈0.016 sec^{-1}) The alpha test is described in U.S. Patent No. 3,354,078 and in the Journal of Catalysis, Vol. 4, p. 527 (1965); Vol. 6, p. 278 (1966); and Vol. 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, Vol. 61, p. 395. The higher alpha values have been correlated to correspond with a more active cracking catalyst.

[0024] For example, prior to steaming at a temperature of about 450°F (about 232°C) to about 700°F (about 371°C) under effective steaming conditions as described above, a suitable catalyst for conversion of methanol and/or dimethyl ether can have an alpha value of at least about 20, for example at least about 50, at least about 100, at least about 150, at least about 200, at least about 250, or at least about 300, such as potentially up to about 1000 or more. After steaming, the alpha value of the catalyst can increase by at least about 10, for example at least about 25 or at least about 50. This can result in a steamed catalyst with an alpha value of at least about 300, for example at least about 350, at least about 375, or at least about 400, and potentially up to an alpha value of about 2000 or less, for example about 1500 or less or about 1000 or less.

[0025] In other aspects, the steamed catalyst can have an increased lifetime or cycle length for use in a reaction for conversion of methanol to hydrocarbons, such as conversion of methanol to olefins and aromatics or conversion of methanol to gasoline. In such aspects, a cycle length for a catalyst can be measured based on any convenient conditions that are effective for conversion of methanol that also initially result in conversion of 99% of the methanol in a feed. Under conditions that initially convert at least 99% of the methanol in a feed, a cycle length can be defined based on the amount of time a catalyst can be used for the methanol conversion until the conversion drops below 99% of the methanol in the feed. For example, the steamed catalyst can have a cycle length that is at least about 15% greater than the cycle length of the catalyst prior to steaming, for example at least about 30% greater, for example at least about 50% greater, at least about 75% greater, at least about 90% greater, or at least about 100% greater, such as up to about 300% greater. Additionally or alternately, the steamed catalyst can have an n-hexane cracking activity that is at least 10% greater than the cracking activity of the catalyst prior to steaming, for example at least about 20%, at least about 30%, at least about 40%, at least about 50%, at least about 60%, at least about 70%, at least about 80%, or at least about 90%.

[0026] In some alternative aspects, a catalyst can be steamed under conditions suitable for preparing a catalyst for conversion of methanol and/or dimethyl ether to aromatics (such as benzene, toluene, and xylene) and olefins (such as ethylene and/or propylene). This is in contrast to conversion of methanol to gasoline. In this type of alternative aspect, instead of increasing the number of acidic sites for reaction, the steaming can reduce the overall number of acidic sites. As a result, the steaming in this alternative aspect can reduce the alpha value of a steamed catalyst relative to the unsteamed catalyst. This can produce a catalyst with a reduced or minimized number of acidic reaction sites that is suitable for conversion of methanol to olefins while reducing or minimizing the amount of coke produced. In such alternative aspects for production of olefins, examples of effective steaming conditions including exposing a catalyst to an atmosphere comprising steam at a temperature of at least about 375°C, such as about 400°C to about 850°C, about 400°C to about 750°C, about 400°C to about 650°C, about 500°C to about 850°C, about 500°C to about 750°C, or about 500°C to about 650°C. The atmosphere can include as little as 1 vol% water and up to 100 vol% water. The catalyst can be exposed to the steam for any convenient period of time, such as about 1 hour to about 48 hours. In some aspects, the time for exposure of the catalyst to steam can be at least about 1 hour, such as about 1.25 hours to about 8 hours, about 1.25 hours to about 4 hours, about 1.25 hours to about 2 hours, about 1.5 hours to about 8 hours, or about 1.5 hours to about 4 hours. For catalysts steamed according to the alternative steaming procedure, after steaming, the alpha value of the catalyst can be about 100 or less, for example about 75 or less, about 50 or less, or about 25 or less. Although this reduction in the number of acidic sites can reduce catalyst activity, the reduced number of acidic sites can also reduce the amount of coke formation. Such a reduction in the amount of coke formation is an alternative option for increasing catalyst lifetime.

Conversion Catalyst

[0027] In various aspects, a zeolite catalyst composition is provided that is steamed to enhance the activity and/or lifetime of the catalyst composition for conversion of methanol (or other oxygenate feeds) to olefins. Optionally, the zeolite catalyst composition can be a transition metal-enhanced zeolite catalyst composition. In some alternative aspects, instead of an aluminosilicate type molecular sieve, the catalyst composition can use an alternative type of molecular sieve, such as a silicoaluminophosphate molecular sieve or an aluminophosphate molecular sieve.

[0028] The zeolite employed in the present catalyst composition generally comprises 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 include zeolites having an MFI or MEL framework, such as ZSM-5 or ZSM-11. ZSM-5 is described in detail in U.S. Patent Nos. 3,702,886 and RE29,948. ZSM-11 is described in detail in U.S. Patent No.

3,709,979. Preferably, the zeolite is ZSM-5. Other useful molecular sieves can include ZSM-12 (U.S. Patent No. 3,832,449); ZSM-22 (U.S. Patent No. 4,556,477); ZSM-23 (U.S. Patent No. 4,076,842); ZSM-34 (U.S. Patent No. 4,079,095) ZSM-35 (U.S. Patent No. 4,016,245); ZSM-48 (U.S. Patent No. 4,397,827); ZSM-57 (U.S. Patent No. 4,046,685); and ZSM-58 (U.S. Patent No. 4,417,780). Non-limiting examples of SAPO and AlPO molecular sieves can include one or a combination of SAPO-5, SAPO-8, SAPO-11, SAPO-16, SAPO-17, SAPO-18, SAPO-20, SAPO-31, SAPO-34, SAPO-35, SAPO-36, SAPO-37, SAPO-40, SAPO-41, SAPO-42, SAPO-44, SAPO-47, SAPO-56, AlPO-5, AlPO-11, AlPO-18, AlPO-31, AlPO-34, AlPO-36, AlPO-37, and AlPO-46.

[0029] Another option for characterizing a zeolite (or other molecular sieve) is based on the nature of the ring channels in the zeolite. The ring channels in a zeolite can be defined based on the number of atoms including in the ring structure that forms the channel. In some aspects, a zeolite can include at least one ring channel based on a 10-member ring. In such aspects, the zeolite preferably does not have any ring channels based on a ring larger than a 10-member ring. Examples of suitable framework structures having a 10-member ring channel but not having a larger size ring channel include EUO, FER, IMF, LAU, MEL, MFI, MFS, MTT, MWW, NES, PON, SFG, STF, STI, TON, TUN, MRE, and PON framework types.

[0030] In some alternative aspects, the molecular sieve can be a molecular sieve that includes an 8-member ring channel (small pore molecular sieves), a 10-member ring channel (as described above), or a 12-member ring channel (large pore molecular sieves), but does not have any ring channels based on a ring larger than a 12-member ring. In such aspects, suitable large pore molecular sieves can include those having AFI, AFS, ATO, ATS, *BEA, BEC, BOG, BPH, CAN, CON, EMT, EON, EZT, FAU, GME, GON, IFR, ISV, -*ITN, IWR, IWW, LTL, MAZ, MEI, MOR, MOZ, MSE, MTW, OFF, OKO, OSI, SAF, SAO, SEW, SFE, SFO, SSF, SSY, and USI framework types. In such aspects, suitable small pore molecular sieves can include those having the AEI, AFT, AFX, ATT, DDR, EAB, EPI, ERI, KFI, LEV, LTA, MER, MON, MTF, PAU, PHI, RHO, and SFW framework types.

[0031] Generally, a zeolite having the desired activity can have a silicon to aluminum molar ratio of about 10 to about 300, for example about 15 to about 100, about 20 to about 80, or about 20 to about 40. In some embodiments, the silicon to aluminum ratio can be at least about 10, for example at least about 20, at least about 30, at least about 40, at least about 50, or at least about 60. Additionally or alternately, the silicon to aluminum ratio can be about 300 or less, for example about 200 or less, about 100 or less, about 80 or less, about 60 or less, or about 50 or less.

[0032] In some preferred aspects, the silicon to aluminum ratio can be at least about 20, for example at least about 30 or at least about 40. In such embodiments, the silicon to aluminum ratio can optionally be about 100 or less, for example about 80 or less, about 60 or less, about 50 or less, or about 40 or less. Typically, reducing the silicon to aluminum ratio in a zeolite can result in a zeolite with a higher acidity, and therefore higher activity for cracking of hydrocarbon or hydrocarbonaceous feeds, such as petroleum feeds. However, with respect to conversion of oxygenates to aromatics, such increased cracking activity due to a decrease in the silicon to aluminum ratio may not be beneficial, and instead may result in increased formation of residual carbon or coke during the conversion reaction. Such residual carbon can deposit on the zeolite catalyst, leading to deactivation of the catalyst over time. Having a silicon to aluminum ratio of at least about 40, for example at least about 50 or at least about 60, can reduce/minimize the amount of additional residual carbon formed due to the acidic or cracking activity of the catalyst.

[0033] It is noted that the molar ratio described herein is a ratio of silicon to aluminum. If a corresponding ratio of silica to alumina were described, the corresponding ratio of silica (SiO_2) to alumina (Al_2O_3) would be twice as large, due to the presence of two aluminum atoms in each alumina stoichiometric unit compare to only one silicon atom in the silica stoichiometric unit. Thus, a silicon to aluminum ratio of 10 corresponds to a silica to alumina ratio of 20.

[0034] When used in the present catalyst composition, the zeolite can be present at least partly in the hydrogen (active) form. Depending on the conditions used to synthesize the zeolite, this may correspond to converting the zeolite from, for example, the sodium form. This can readily be achieved, for example, by ion exchange to convert the zeolite to the ammonium form followed by calcination in air or an inert atmosphere at a temperature of about 400°C to about 700°C to convert the ammonium form to the active hydrogen form. Alternatively, methods for directly converting a sodium form zeolite to a hydrogen form zeolite can also be used.

[0035] Additionally or alternately, the catalyst composition can include and/or be enhanced by a transition metal. The transition metal can be incorporated into the zeolite by any convenient method, such as by impregnation or by ion exchange. After impregnation or ion exchange, the transition metal-enhanced catalyst can be treated in air or an inert atmosphere at a temperature of about 400°C to about 700°C. The amount of transition metal can be related to the molar amount of aluminum present in the zeolite. Preferably, the molar amount of the transition metal can correspond to about 0.1 to about 1.3 times the molar amount of aluminum in the zeolite. In some embodiments, the molar amount of transition metal can be at least about 0.1 times the molar amount of aluminum in the zeolite, for example at least about 0.2 times, at least about 0.3 times, or at least about 0.4 times. Additionally or alternately, the molar amount of transition metal can be about 1.3 times or less relative to the molar amount of aluminum in the zeolite, for example about 1.2 times or less, about 1.0 times or less, or about 0.8 times or less. Still further additionally or alternately, the amount of transition metal can be expressed as a weight percentage of the bound zeolite catalyst, such as having at least about 0.1 wt% of transition metal, at least about 0.25 wt%, at least about 0.5 wt%, at least about 0.75 wt%, or at least about 1.0 wt%. Additionally or alternately, the amount of transition metal can be about 20 wt% or less, for example about 10 wt% or less, about 5 wt% or less, about 2.0 wt% or less, about 1.5 wt% or less, about 1.2 wt% or less, about 1.1 wt% or less, or about 1.0 wt% or less.

[0036] In some aspects, the catalyst composition can be substantially free of phosphorous. A catalyst composition that is substantially free of phosphorous can contain no more than about 0.01 wt% of phosphorous, for example less than about 0.005 wt% of phosphorous or less than about 0.001 wt% of phosphorous. A catalyst composition that is substantially free of phosphorous can be substantially free of intentionally added phosphorous or substantially free of both intentionally added phosphorous as well as phosphorous present as an impurity in a reagent for forming the catalyst composition. In some aspects, the catalyst composition can contain no added phosphorous, such as containing no intentionally added phosphorous and/or containing no phosphorous impurities to within the detection limits of standard methods for characterizing a reagent and/or a resulting zeolite.

[0037] In other aspects, the catalyst composition can include phosphorus. The total weight of the phosphorous can be from about 0.1 wt% to about 10.0 wt% based on the total weight of the catalyst. Thus, the upper limit on the range of the phosphorous added to the molecular sieve may be 10.0 wt%, 9.0 wt%, 8.0 wt%, 7.0 wt%, 6.0 wt%, 5.0 wt%, 4.0 wt%, 3.0 wt%, 2.0 wt%, or 1.0 wt%; and the lower limit on the range added to the molecular sieve may be 9.0 wt%, 8.0 wt%, 7.0 wt%, 6.0 wt%, 5.0 wt%, 4.0 wt%, 3.0 wt%, 2.0 wt%, 1.0 wt%, or 0.1 wt%. Ranges expressly disclosed include combinations of any of the above-enumerated upper and lower limits, e.g., 0.1 to 10.0 wt%, 0.1 to 8.0 wt%, 0.1 to 6.0 wt%, 0.1 to 5.0 wt%, 0.1 to 4.0 wt%, 0.1 to 3.0 wt%, 0.1 to 2.0 wt%, 0.1 to 1.0 wt%, 1.0 to 10.0 wt%, 1.0 to 9.0 wt%, 1.0 to 8.0 wt%, 1.0 to 7.0 wt%, 1.0 to 6.0 wt%, 1.0 to 5.0 wt%, 1.0 to 4.0 wt%, 1.0 to 3.0 wt%, etc. Of course, the total weight of the phosphorous shall not include amounts attributable to the molecular sieve itself, if the molecular sieve contains any phosphorus.

[0038] Additionally or alternatively, the catalyst composition can include one or more Group 13 and/or Group 14 metals. Group 13 and Group 14 refer to the group columns from the IUPAC periodic table, and thus include the metals Ga, In, and Sn. The total weight of the Group 13 and/or Group 14 metals can be about 0.1 wt% to about 10.0 wt% based on the total weight of the catalyst. Thus, the upper limit on the range of the Group 13 and/or Group 14 metals added to the molecular sieve may be 10.0 wt%, 9.0 wt%, 8.0 wt%, 7.0 wt%, 6.0 wt%, 5.0 wt%, 4.0 wt%, 3.0 wt%, 2.0 wt%, or 1.0 wt%; and the lower limit on the range added to the molecular sieve may be 9.0 wt%, 8.0 wt%, 7.0 wt%, 6.0 wt%, 5.0 wt%, 4.0 wt%, 3.0 wt%, 2.0 wt%, 1.0 wt%, or 0.1 wt%. Ranges expressly disclosed include combinations of any of the above-enumerated upper and lower limits, e.g., 0.1 to 10.0 wt%, 0.1 to 8.0 wt%, 0.1 to 6.0 wt%, 0.1 to 5.0 wt%, 0.1 to 4.0 wt%, 0.1 to 3.0 wt%, 0.1 to 2.0 wt%, 0.1 to 1.0 wt%, 1.0 to 10.0 wt%, 1.0 to 9.0 wt%, 1.0 to 8.0 wt%, 1.0 to 7.0 wt%, 1.0 to 6.0 wt%, 1.0 to 5.0 wt%, 1.0 to 4.0 wt%, 1.0 to 3.0 wt%, etc. Of course, the total weight of the Group 13 and/or Group 14 metals shall not include amounts attributable to the molecular sieve itself, if the molecular sieve contains any phosphorus.

[0039] In some optional aspects, the zeolite catalyst composition employed herein can further be characterized by at least one, at least two, or all three of the following properties: (a) a mesoporosity of greater than about 20 m^2/g, for example greater than about 30 m^2/g, and less than about 120 m^2/g, for example less than about 100 m^2/g or less than about 85 m^2/g; (b) a microporous surface area of at least about 290 m^2/g, for example at least about 300 m^2/g or at least about 310 m^2/g; and (c) a diffusivity for 2,2-dimethylbutane of greater than about 1.0 x 10^{-2} sec^{-1}, for example greater than about 1.25 x 10^{-2} sec^{-1}, when measured at a temperature of about 120°C and a 2,2-dimethylbutane pressure of about 60 torr (about 8 kPa). Additionally or alternately, a bound catalyst composition can have a combined micropore and mesopore surface area of at least about 380 m^2/g, for example at least about 390 m^2/g.

[0040] Of these properties, mesoporosity and diffusivity for 2,2-dimethylbutane can be determined by a number of factors for a given zeolite, including the crystal size of the zeolite. Microporous surface area is 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. It is noted that mesopore or external surface area and micropore surface area can be characterized, for example, using adsorption-desorption isotherm techniques within the expertise of one of skill in the art, such as the BET (Brunauer Emmett Teller) method.

[0041] It is noted that the micropore surface area can be characterized for either zeolite crystals or a catalyst formed from the zeolite crystals. In various aspects, the micropore surface area of a self-bound catalyst or a catalyst formulated with a separate binder can be at least about 340 m^2/g, for example at least about 350 m^2/g, at least about 360 m^2/g, at least about 370 m^2/g, or at least about 380 m^2/g. Typically, a formulation of zeolite crystals into catalyst particles (either self-bound or with a separate binder) can result in some loss of micropore surface area relative to the micropore surface area of the zeolite crystals. Thus, in order to provide a catalyst having the desired micropore surface area, the zeolite crystals can also have a micropore surface area of at least about 340 m^2/g, for example at least about 350 m^2/g, at least about 360 m^2/g, at least about 370 m^2/g, or at least about 380 m^2/g. As a practical matter, the micropore surface area of a zeolite crystal and/or a corresponding self-bound or bound catalyst as described herein can be less than about 1000 m^2/g, and typically less than about 750 m^2/g. Additionally or alternately, the micropore surface area of a catalyst (self-bound or with a separate binder) can be about 105% or less of the micropore surface area of the zeolite crystals in the catalyst, and typically about 100% or less of the micropore surface area of the zeolite crystals in the catalyst, for example from about 80% to 100% of the micropore surface area of the zeolite crystals in the catalyst. In some embodiments, the micropore surface area of a catalyst can be at least about 80% of the micropore surface area of the zeolite crystals in the catalyst, for example at least about 85%, at least about 90%, at least about 95%, at least about 97%, or at least about 98%, and/or about 100% or less, for example about 99% or less, about 98% or less, about 97% or less, or about 95% or less.

[0042] Additionally or alternately, the diffusivity for 2,2-dimethylbutane of a catalyst (self-bound or with a separate binder) can be about 105% or less of the diffusivity for 2,2-dimethylbutane of the zeolite crystals in the catalyst, and typically about 100% or less of the diffusivity for 2,2-dimethylbutane of the zeolite crystals in the catalyst, for example about 80% to 100% of the diffusivity for 2,2-dimethylbutane of the zeolite crystals in the catalyst. In some embodiments, the diffusivity for 2,2-dimethylbutane of a catalyst can be at least about 80% of the diffusivity for 2,2-dimethylbutane of the zeolite crystals in the catalyst, for example at least about 85%, at least about 90%, at least about 95%, at least about 97%, or at least about 98%, and/or about 100% or less, for example about 99% or less, about 98% or less, about 97% or less, or about 95% or less.

[0043] A catalyst composition as described herein can employ a zeolite in its original crystalline form, or the crystals can be formulated into catalyst particles, such as by extrusion. One example of binding zeolite crystals to form catalyst particles is to form a self-bound catalyst. A process for producing zeolite extrudates in the absence of a binder is disclosed in, for example, U.S. Patent No. 4,582,815, the entire contents of which are incorporated herein by reference.

[0044] As another example of forming a self-bound catalyst, the following procedure describes a representative method for forming self-bound ZSM-5 catalyst particles. It is noted that the absolute values in grams provided below should be considered as representative of using an appropriate ratio of the various components. ZSM-5 crystal (such as about 1,400 grams on a solids basis) can be added to a mixer and dry mulled. Then, approximately 190 grams of deionized water can be added during mulling. After about 10 minutes, about 28 grams of about 50 wt% caustic solution mixed with about 450 grams of deionized water can be added to the mixture and mulled for an additional ~5 minutes. The mixture can then be extruded into ~1/10" quadrulobes. The extrudates can be dried overnight (~8-16 hours) at about 250°F (about 121°C) and then calcined in nitrogen for about 3 hours at about 1000°F (about 538°C). The extrudates can then be exchanged twice with an ~1N solution of ammonium nitrate. The exchanged crystal can be dried overnight (~8-16 hours) at about 250°F (about 121°C) and then calcined in air for about 3 hours at about 1000°F (about 538°C). This can result in a self-bound catalyst. Based on the exchange with ammonium nitrate and subsequent calcinations in air, the ZSM-5 crystals in such a self-bound catalyst can correspond to ZSM-5 with primarily hydrogen atoms at the ion exchange sites in the zeolite. Thus, such a self-bound catalyst can sometimes be described as being a self-bound catalyst that includes H-ZSM-5.

[0045] As an alternative to forming self-bound catalysts, zeolite crystals can be combined with an alumina binder to form bound catalysts. Generally, a binder can be present in an amount between about 1 wt% and about 90 wt%, for example between about 3 wt% and about 90 wt% of a catalyst composition, about 3 wt% to about 80 wt%, about 5 wt% to about 90 wt%, about 5 wt% to about 80 wt%, about 5 wt% to about 40 wt%, or about 10 wt% to about 40 wt%. In some aspects, the catalyst can include at least about 5 wt% binder, for example at least about 10 wt%, or at least about 20 wt%. Additionally or alternately, the catalyst can include about 90 wt% or less of binder, for example about 80 wt% or less, about 50 wt% or less, about 40 wt% or less, or about 35 wt% or less. Combining the zeolite and the binder can generally be achieved, for example, by mulling a mixture of the zeolite and binder (optionally an aqueous mixture) and then extruding the mixture into catalyst pellets.

[0046] In some aspects, a binder for formulating a catalyst can be selected so that the resulting bound catalyst has a micropore surface area of at least about 290 m^2/g, for example at least about 300 m^2/g or at least about 310 m^2/g. Optionally but preferably, a suitable binder can be a binder with a surface area of about 200 m^2/g or less, for example about 175 m^2/g or less or about 150 m^2/g or less. Unless otherwise specified, the surface area of the binder is defined herein as the combined micropore surface area and mesopore surface area of the binder.

[0047] As an example of forming a bound catalyst, the following procedure describes a representative method for forming alumina bound ZSM-5 catalyst particles. ZSM-5 crystal and an alumina binder, such as an alumina binder having a surface area of about 200 m^2/g or less, can be added to a mixer and mulled. Additional deionized water can be added during mulling to achieve a desired solids content for extrusion. Optionally, a caustic solution can also be added to the mixture and mulled. The mixture can then be extruded into a desired shape, such as ~1/10" quadrulobes. The extrudates can be dried overnight (~8-16 hours) at about 250°F (about 121°C) and then calcined in nitrogen for about 3 hours at about 1000°F (about 538°C). The extrudates can then be exchanged twice with an ~1N solution of ammonium nitrate. The exchanged crystal can be dried overnight (~8-16 hours) at about 250°F (about 121°C) and then calcined in air for about 3 hours at about 1000°F (about 538°C). This can result in an alumina bound catalyst. Based on the exchange with ammonium nitrate and subsequent calcinations in air, the ZSM-5 crystals in such a bound catalyst can correspond to ZSM-5 with primarily hydrogen atoms at the ion exchange sites in the zeolite. Thus, such a bound catalyst can sometimes be described as being a bound catalyst that includes H-ZSM-5.

[0048] To form a transition metal-enhanced catalyst, a bound (or self-bound) catalyst can be impregnated via incipient wetness with a solution containing the desired metal for impregnation, such as Zn and/or Cd. The impregnated crystal can then be dried overnight at about 250°F (about 121°C), followed by calcination in air for about 3 hours at about 1000°F (about 538°C). More generally, a transition metal can be incorporated into the ZSM-5 crystals and/or catalyst at any convenient time, such as before or after ion exchange to form H-ZSM-5 crystals, or before or after formation of a bound extrudate. In some aspects that are preferred from a standpoint of facilitating manufacture of a bound zeolite catalyst, the transition metal can be incorporated into the bound catalyst (such as by impregnation or ion exchange) after formation of the bound catalyst by extrusion or another convenient method.

Conversion Conditions

[0049] In various aspects, catalysts described herein can be used for conversion of oxygenate feeds to aromatics and/or olefins products, such as oxygenates containing at least one C_1-C_4 alkyl group and/or oxygenate. Examples of suitable oxygenates include feeds containing methanol, dimethyl ether, C_1-C_4 alcohols, ethers with C_1-C_4 alkyl chains, including both asymmetric ethers containing C_1-C_4 alkyl chains (such as methyl ethyl ether, propyl butyl ether, or methyl propyl ether) and symmetric ethers (such as diethyl ether, dipropyl ether, or dibutyl ether), or combinations thereof. It is noted that oxygenates containing at least one C_1-C_4 alkyl group are intended to explicitly identify oxygenates having alkyl groups containing about 4 carbons or less. Preferably the oxygenate feed can include at least about 50 wt% of one or more suitable oxygenates, for example at least about 75 wt%, at least about 90 wt%, or at least about 95 wt%. Additionally or alternately, the oxygenate feed can include at least about 50 wt% methanol, for example at least about 75 wt% methanol, at least about 90 wt% methanol, or at least about 95 wt% methanol. The oxygenate feed can be derived from any convenient source. For example, the oxygenate feed can be formed by reforming of hydrocarbons in a natural gas feed to form synthesis gas (H_2, CO, CO_2), and then using the synthesis gas to form alcohols.

[0050] In some aspects, the feedstock can be a feed that includes methanol, dimethyl ether, or a combination thereof. The feed may also include other hydrocarbons or hydrocarbonaceous compounds (i.e., compounds similar to hydrocarbons that also contain one or more heteroatoms). Additionally or alternately, the feed can be diluted with liquid water and/or steam at any convenient time, such as prior to entering a conversion reactor or after entering a conversion reactor. Examples of suitable feeds (excluding the presence of water and/or any optional dilution with steam) include feeds that are substantially methanol, feeds that are substantially dimethyl ether, feeds that are substantially methanol and dimethyl ether, or feeds that include at least about 30 wt% of methanol and/or dimethyl ether, or at least about 50 wt%, or at least about 60 wt%, or at least about 75 wt%. A feed that is substantially composed of a compound (or compounds) is a feed that is at least 90 wt% of the compound (or compounds), for example at least 95 wt% of the compound, at least 98 wt% of the compound, or at least 99 wt% of the compound, on a water-/steam- free basis. For a feed that is less than 100 wt% methanol and/or dimethyl ether (excluding the presence of water and/or any optional dilution with steam), other hydrocarbon compounds (and/or hydrocarbonaceous compounds) in the feed can include paraffins, olefins, aromatics, and mixtures thereof.

[0051] The feed can be exposed to the conversion catalyst in any convenient type of reactor. Suitable reactor configurations include fixed bed reactors, moving bed reactors, fluidized bed reactors (such as ebullating bed reactors), riser reactors, and other types of reactors where the feed can be exposed to the catalyst in a controlled manner.

[0052] A suitable feed can be converted to aromatics (including para-xylene) and olefins by exposing the feed to a conversion catalyst under effective conversion conditions. General conversion conditions for conversion of methanol and/or dimethyl ether (and/or other oxygenates) to aromatics and olefins include a pressure of about 100 kPaa to about 3000 kPaa, for example about 100 kPaa to about 2500 kPaa, about 100 kPaa to about 2000 kPaa, about 100 kPaa to about 1500 kPaa, or about 100 kPaa to about 1200 kPaa. The amount of feed (weight) relative to the amount of catalyst (weight) can be expressed as a weight hourly space velocity (WHSV). Suitable weight hourly space velocities can include a WHSV of about 0.1 hr^{-1} to about 20 hr^{-1}, for example about 1.0 hr^{-1} to about 10 hr^{-1}.

[0053] The temperature for the conversion reaction can vary depending on the nature of the catalyst used for the conversion and/or the desired type of conversion reaction. Suitable reaction temperatures for conversion of methanol to gasoline or other aromatics and olefins can include a temperature of about 200°C to about 450°C, for example about 200°C to about 400°C, about 200°C to about 375°C, about 200°C to about 350°C, about 250°C to about 450°C, about 250°C to about 400°C, about 250°C to 375°C, about 250°C to about 350°C, about 275°C to about 450°C, about 275°C to about 400°C, about 275°C to about 375°C, or about 300°C to about 450°C.

[0054] In some alternative aspects, the reaction conditions can be selected for conversion of methanol and/or dimethyl ether to aromatics (such as benzene, toluene, and/or xylene) and olefins. Suitable reaction temperatures include a temperature of about 350°C to about 700°C, for example about 350°C to about 600°C, about 350°C to about 550°C, about 350°C to about 500°C, about 375°C to about 600°C, about 375°C to about 550°C, about 375°C to about 500°C, about 400°C to about 600°C, about

400°C to about 550°C, about 400°C to about 500°C, about 425°C to about 600°C, about 425°C to about 550°C, about 450°C to 600°C, about 450°C to about 550°C, about 475°C to about 600°C, or about 475°C to about 550°C, about 500°C to about 600°C, or about 500°C to about 550°C.

[0055] In still other alternative aspects, suitable reaction temperatures can include a temperature of about 200°C to about 700°C, for example about 450°C to about 700°C, about 450°C to about 650°C, about 450°C to about 600°C, about 475°C to about 700°C, about 475°C to about 650°C, about 475°C to 600°C, about 500°C to about 700°C, about 500°C to about 650°C, about 500°C to about 600°C, about 525°C to about 700°C, about 525°C to about 650°C, or about 550°C to about 700°C.

[0056] As an example, during a conversion process, a feed comprising methanol, dimethyl ether, or a combination thereof can be introduced into a reactor containing a conversion catalyst. Alternatively, other oxygenates can be used in addition to or in place of the methanol and/or dimethyl ether. Liquid water and/or steam can optionally also be introduced into the reactor. After performing the conversion reaction, the reactor effluent can be quenched to facilitate separation of the effluent. The quench can be sufficient to allow removal of water from the effluent as a liquid. Light organics containing 4-5 carbons or less can be removed as a gas phase stream. Ethylene and propylene can subsequently be separated from this light ends stream. The remaining portion of the effluent can substantially correspond to hydrocarbons that are liquids at standard temperature and pressure. In some aspects, at least a portion of the liquid product (i.e., liquid at standard temperature and pressure) can correspond to a naphtha boiling range product (gasoline).

[0057] Alternatively, if individual aromatic products are desired, a series of separations can then be performed to separate out desired products. For example, a first separation on the liquid effluent can separate C_7- (lower boiling) compounds from C_8+ (higher boiling) compounds. In the first separation, para-xylene and other C_8+ molecules are included in the higher boiling fraction, while C_7- compounds (benzene, toluene) and other lower boiling compounds such as oxygenates form the lower boiling fraction. In this discussion, a C_7- product stream is defined as a product stream where at least 50 wt% of the hydrocarbons correspond to hydrocarbons having 7 carbons or less. Similarly, a C_8+ product stream is defined as a product stream where at least 50 wt% of the hydrocarbons correspond to hydrocarbons having at least 8 carbons. This lower boiling fraction may also contain a variety of non-aromatic compounds. The lower boiling compounds from this first separation are one suitable source, if desired, for a recycle stream to provide hydrogen-lean molecules to the conversion reaction.

[0058] The C_8+ fraction can then be further separated into a C_8 fraction and a C_9+ fraction. The C_9+ fraction will typically be primarily aromatics and is another suitable fraction for recycle, if desired. In this discussion, a C_8 product stream is defined as a product stream where at least 50 wt% of the hydrocarbons correspond to hydrocarbons having 8 carbons. Similarly, a C_9+ product stream is defined as a product stream where at least 50 wt% of the hydrocarbons correspond to hydrocarbons having at least 9 carbons. In some aspects, if a distillation column is used, the first separation and second separation can be combined to form the C_7-, C_8, and C_9+ fractions in a single distillation or fractionation process. In some aspects, the separations to form the C_7-, C_8, and C_9+ fractions can correspond to any convenient number of distillation steps in order to improve recovery of the desired C_8 fraction.

[0059] The C_8 fraction of the liquid effluent from conversion will typically include at least a portion of xylene isomers other than para-xylene. The ortho- and meta-xylene isomers can be separated from the para-xylene isomers by any convenient method, such as by using crystallization to separate the isomers or by selective adsorption. Optionally, the C_8 fraction can be treated in a xylene isomerization unit prior to recovery of the para-xylene. This can increase the concentration of para-xylene in the C_8 fraction relative to the concentration prior to the xylene isomerization. Optionally, the separated ortho- and meta-xylenes can be recycled back to the distillation step(s) for further recovery of any remaining para-xylene and/or for further isomerization to form more para-xylene.

Additional Embodiments

[0060] Embodiment 1. A method of converting a feed to form olefins and aromatics, comprising: steaming a catalyst in the presence of at least 0.01 atm (1 kPa) of water at a temperature of about 450°F (about 221°C) to about 700°F (about 371°C) for at least about 0.25 hours to form a steamed catalyst, the catalyst comprising a molecular sieve having at least one 10-member ring channel and having no ring channels larger than a 10-member ring channel; and subsequently exposing a feed comprising at least about 30 wt% (for example at least about 50 wt%, at least about 75 wt%, or at least about 90 wt%) of methanol, dimethyl ether, or a combination thereof to the steamed catalyst under effective conversion conditions to form a conversion effluent comprising ethylene, propylene, and at least one aromatic (preferably para-xylene), the effective conversion conditions including a temperature of about 200°C to about 700°C, for example about 350°C to about 600°C or about 450°C to about 550°C, the steamed catalyst having a cycle length under the effective conversion conditions that is at least about 15% greater than a cycle length under the effective conversion conditions for the catalyst prior to steaming, and/or the steamed catalyst having an alpha value that is at least about 10 greater than an alpha value for the catalyst prior to steaming.

[0061] Embodiment 2. A method of converting an oxygenate feed to form hydrocarbons, comprising: steaming a catalyst in the presence of at least 0.9 atm (91 kPa) of water at a temperature of about 450°F (about 221°C) to about 650°F (about 343°C) for at about 0.25 hours to about 16 hours to form a steamed catalyst, the catalyst comprising a molecular sieve having at least one 8-member ring channel, 10-member ring channel, or 12-member ring channel and having no ring channels larger than a 12-member ring channel; and subsequently exposing a feed comprising at least about 50 wt% of methanol, dimethyl ether, or a combination thereof to the steamed catalyst under effective conversion conditions to form a conversion effluent comprising one or more hydrocarbons, the effective conversion conditions including a temperature of about 200°C to about 700°C, the steamed catalyst having a cycle length under the effective conversion conditions that is at least about 15% greater than a cycle length under the effective conversion conditions for the catalyst prior to steaming, and/or the steamed catalyst having an alpha value that is at least about 10 greater than an alpha value for the catalyst prior to steaming.

[0062] Embodiment 3. The method of any one of the previous embodiments, wherein the catalyst further comprises about 3 wt% to about 90 wt%, based on a total weight of the catalyst, for example about 3 wt% to about 80 wt%, about 5 wt% to about 90 wt%, about 5 wt% to about 80 wt%, about 5 wt% to about 40 wt%, about 10 wt% to about 90 wt%, about 10 wt% to about 80 wt%, or about 10 wt% to about 40 wt%, of a binder comprising alumina and/or silica.

[0063] Embodiment 4. The method of any of the above embodiments, wherein the catalyst is steamed at a temperature of about 650°F (about 343°C) or less, for example about 625°F (about 329°C) or less or about 600°F (316°C) or less; wherein the catalyst is steamed in the presence of partial pressure of at least about 0.5 atm (about 50 kPag) of water, for example at least about 0.9 atm (about 90 kPag) of water, the catalyst optionally being steamed in the presence of about 5 atm (about 510 kPag) of water or less, for example about 2 atm (about 200 kPag) of water or less; wherein the catalyst is steamed for about 16 hours or less, for example about 8.5 hours or less or about 4.5 hours or less, the catalyst optionally being steamed for at least about 0.75 hours; or a combination thereof.

[0064] Embodiment 5. The method of any one of the previous embodiments, wherein the catalyst has an alpha value of at least about 20, at least about 50, or at least about 200 prior to the steaming of the catalyst and optionally an alpha value prior to the steaming of the catalyst of about 1000 or less.

[0065] Embodiment 6. The method of any one of the previous embodiments, wherein the steamed catalyst has an alpha value that is greater than the alpha value of the catalyst prior to the steaming of the catalyst by at least about 10, at least about 25, or at least about 50.

[0066] Embodiment 7. The method of any one of the previous embodiments, wherein the steamed catalyst has an alpha value of at least about 250, at least about 300, or at least about 350, and optionally an alpha value of about 2000 or less.

[0067] Embodiment 8. The method of any one of the previous embodiments, wherein exposing a feed to the steamed catalyst comprises exposing the feed to the steamed catalyst in a fixed bed reactor, a fluidized bed reactor, a moving bed reactor, or a riser reactor; wherein exposing a feed to the steamed catalyst comprises exposing the feed to the steamed catalyst in the presence of steam and/or a hydrogen-lean stream; or a combination thereof.

[0068] Embodiment 9. The method of any of the above embodiments, further comprising separating at least a portion of the converted effluent to form a naphtha boiling range product.

[0069] Embodiment 10. The method of any of the above embodiments, further comprising separating at least a portion of the converted effluent to form a light ends product comprising ethylene, propylene, or a combination thereof and a liquid effluent.

[0070] Embodiment 11. The method of any of the above embodiments, further comprising separating at least a portion of the liquid effluent to form a C_8 product stream and one or more of a C_7- stream and a C_9+ stream.

[0071] Embodiment 12. The method of any of the above embodiments, wherein the catalyst is steamed for about 1 hour to about 16 hours.

[0072] Embodiment 13. The method of any of the above embodiments, wherein the molecular sieve comprises ZSM-5, ZSM-11, or a combination thereof, preferably ZSM-5.

[0073] Embodiment 14. The method of any of the above embodiments, wherein the molecular sieve has a silicon to aluminum ratio of about 20 to about 100, for example about 20 to about 80.

[0074] Embodiment 15. The method of any of the above embodiments, wherein the steamed catalyst further comprises about 0.1 wt% to about 10 wt% of phosphorus, about 0.1 wt% to about 10 wt% of a transition metal, about 0.1 wt% to about 10 wt% of a Group 13 metal or Group 14 metal, or a combination thereof.

[0075] Embodiment 16. The method of any of the above embodiments, wherein a) the effective conversion conditions comprise a pressure of about 100 kPaa to about 2500 kPaa, for example about 100 kPaa to about 1200 kPaa; and a WHSV of about 0.1 hr^{-1} to about 20 hr^{-1}, for example about 1.0 hr^{-1} to about 10 hr^{-1}; b) the feed substantially comprises methanol, dimethyl ether, or a combination thereof; or c) a combination thereof.

EXAMPLE

Example 1 – Cracking Activity of Steamed Conversion Catalyst

[0076] A series of steamed and unsteamed catalysts were investigated to determine the n-hexane cracking activity of the catalysts. The catalysts were bound ZSM-5 catalysts composed of ~65 wt% ZSM-5 (in the H+ form) and ~35 wt% of a binder. The catalysts were bound with either an alumina binder or a silica binder. The steamed catalysts were generated by one of two types of steam treatments. Some catalysts were steamed by treating the catalyst in ~1 atm (~100 kPa) of flowing steam at ~650°F

(~343°C) for about 12 hours. This is referred to as “Steaming method 1” in Table 1. Other catalysts were steamed by treating the catalyst in ~1 atm (~100 kPa) of flowing steam at ~650°F (~343°C) for about 4.5 hours. This is referred to as “Steaming method 2” in Table 1. The ZSM-5 crystals used in the silica-bound sample were made using n-propylamine as the organic template. The alumina-bound samples were made using tetrapropylammonium bromide as the organic template.

[0077] After forming the bound catalysts, the catalysts were used for conversion of a substantially pure methanol feed to form products. During conversion, the space velocity of the methanol feed, defined as grams of methanol per gram of catalyst per hour, was maintained at a constant value. The bound catalysts were contacted with the substantially pure methanol feed in an isothermal (~440°C), fixed-bed reactor at about 30 psig (about 210 kPag) and a weight hourly space velocity of about 6 (grams methanol/grams catalyst/hour). The conversion temperature and pressure were selected so that at least 99% of the feed was converted. The conversion process was then performed until the methanol conversion dropped below 99%. The cycle length for the catalyst for the conversion process was measured based on the time from the start of the conversion process until the conversion dropped below 99%.

[0078] Table 1 below shows representative examples of the cycle length for steamed and unsteamed versions of bound ZSM-5 catalysts. Catalysts A and B correspond to alumina bound ZSM-5 catalysts, while Catalyst C is a silica bound catalyst. In Table 1, the reactivity of each steamed catalyst is expressed as a relative value in comparison with the unsteamed version of the catalyst. As shown in Table 1, for the two different types of alumina bound ZSM-5 catalysts, steaming of the catalyst provided a cycle length that was at least about twice as long as the cycle length for the corresponding unsteamed catalyst. This is in contrast to silica bound Catalyst C, which had roughly the same cycle length for the steamed and unsteamed versions of the catalyst.

[0079] Table 1 also shows the relative activities of the steamed and unsteamed catalysts, based on the activity of the catalysts for cracking of n-hexane. The n-hexane activities were measured using a method similar to the alpha test method described above. It is believed that n-hexane cracking activity can be an indicator of activity for methanol conversion. As shown in Table 1, steaming of all of the catalysts resulted in an increase in the n-hexane cracking activity, although the amount of increase varied. It is noted that the shorter steaming time period resulted in an increase of about 90% in n-hexane cracking activity, while the longer protocol provided increases in activity from about 10% to about 50%.

Table 1 – Catalyst Cycle Length and Cracking Activity

	Binder	Cycle Length (days)	% improvement in cycle length	Relative n-hexane cracking activity
Catalyst A	Al_2O_3	2.6		1
Steamed Catalyst A (Steaming method 1)	Al_2O_3	5.5	112	1.3
Steamed Catalyst A (Steaming method 2)	Al_2O_3	4.2	61	1.9
Catalyst B	Al_2O_3	3.8		1
Steamed Catalyst B (Steaming method 1)	Al_2O_3	8.0	111	1.1
Catalyst C	SiO_2	3.2		1
Steamed Catalyst C (Steaming method 1)	SiO_2	3.1	<none>	1.5

[0080] It is noted that for the catalyst steamed according to “Steaming method 2”, the pressure (in atm) multiplied by the time (in hours) results in a value of ~4.5. It is also noted that $0.01*F_T$, where F_T is defined as $2.6x10^{-9}e^{16000/T}$, results in a value of ~4.65 using “Steaming method 2”.

[0081] FIG. 1 shows additional investigation of the n-hexane cracking activity for alumina bound ZSM-5 catalyst samples that were steamed at various temperatures in ~1 atm (~100 kPa) of steam for about 12 hours. The alpha value for the “fresh” ZSM-5 prior to steaming was about 400. FIG. 1 shows the relative n-hexane cracking activity in comparison with an unsteamed sample of the catalyst. As shown in FIG. 1, for temperatures less than about 700°F (about 371°C), steaming of the catalyst appeared to result in an increase in the relative n-hexane cracking activity. It is noted that the samples showing improved activity in FIG. 1 had conditions roughly overlapping with the conditions shown in Table 1 for providing improved catalyst cycle length. It is also noted that, for a temperature of ~600°F (~589°K), the value of $0.01*F_T$, where F_T is defined as $2.6x10^{-9}e^{16000/T}$, resulted in a value of ~16.5. For steaming at temperatures of about 700°F (about 371°C) or greater, such as about 800°F (about 427°C) or about 900°F (about 482°C), the relative n-hexane activity appeared to decrease below the activity of the corresponding unsteamed catalyst. It is believed that these lower activity samples did not have the increased catalyst lifetime benefit, as the steaming conditions at temperatures greater than about 700°F (about 371°C) can correspond to conventional steaming conditions that result in a reduced number of acidic sites on the catalyst.

[0082] Although the present invention has been described in terms of specific embodiments, it is not so limited. Suitable alterations/modifications for operation under specific conditions should be apparent to those skilled in the art. It is therefore intended that the following claims be interpreted as covering all such alterations/modifications as fall within the true spirit/scope of the invention.

CLAIMS:

1. A method of converting a feed to form olefins and aromatics, comprising:

teaming a catalyst in the presence of at least 0.01 atm (1 kPa) of water at a temperature of about 450°F (about 221°C) to about 700°F (about 371°C) for at least about 0.25 hours to form a steamed catalyst, the catalyst comprising a molecular sieve having at least one 10-member ring channel and having no ring channels larger than a 10-member ring channel; and

subsequently exposing a feed comprising at least about 30 wt% (for example at least about 50 wt%, at least about 75 wt%, or at least about 90 wt%) of methanol, dimethyl ether, or a combination thereof to the steamed catalyst under effective conversion conditions to form a conversion effluent comprising ethylene, propylene, and at least one aromatic (preferably para-xylene), the effective conversion conditions including a temperature of about 200°C to about 700°C, for example about 350°C to about 600°C or about 450°C to about 550°C,

the steamed catalyst having a cycle length under the effective conversion conditions that is at least about 15% greater than a cycle length under the effective conversion conditions for the catalyst prior to steaming, and/or the steamed catalyst having an alpha value that is at least about 10 greater than an alpha value for the catalyst prior to steaming.

2. A method of converting an oxygenate feed to form hydrocarbons, comprising:

steaming a catalyst in the presence of at least 0.9 atm (91 kPa) of water at a temperature of about 450°F (about 221°C) to about 650°F (about 343°C) for at about 0.25 hours to about 16 hours to form a steamed catalyst, the catalyst comprising a molecular sieve having at least one 8-member ring channel, 10-member ring channel, or 12-member ring channel and having no ring channels larger than a 12-member ring channel; and

subsequently exposing a feed comprising at least about 50 wt% of methanol, dimethyl ether, or a combination thereof to the steamed catalyst under effective conversion conditions to form a conversion effluent comprising one or more hydrocarbons, the effective conversion conditions including a temperature of about 200°C to about 700°C, the steamed catalyst having a cycle length under the effective conversion conditions that is at least about 15% greater than a cycle length under the effective conversion conditions for the catalyst prior to steaming, and/or the steamed catalyst having an alpha value that is at least about 10 greater than an alpha value for the catalyst prior to steaming.

3. The method of any one of the previous claims, wherein the catalyst further comprises about 3 wt% to about 90 wt%, based on a total weight of the catalyst, for example about 3 wt% to about 80 wt%, about 5 wt% to about 90 wt%, about 5 wt% to about 80 wt%, about 5 wt% to about 40 wt%, about 10 wt% to about 90 wt%, about 10 wt% to about 80 wt%, or about 10 wt% to about 40 wt%, of a binder comprising alumina and/or silica.

4. The method of any of the above claims, wherein the catalyst is steamed at a temperature of about 650°F (about 343°C) or less, for example about 625°F (about 329°C) or less or about 600°F (316°C) or less; wherein the catalyst is steamed in the presence of partial pressure of at least about 0.5 atm (about 50 kPag) of water, for example at least about 0.9 atm (about 90 kPag) of water, the catalyst optionally being steamed in the presence of about 5 atm (about 510 kPag) of water or less, for example about 2 atm (about 200 kPag) of water or less; wherein the catalyst is steamed for about 16 hours or less, for example about 8.5 hours or less or about 4.5 hours or less, the catalyst optionally being steamed for at least about 0.75 hours;

or a combination thereof.

5. The method of any one of the previous claims, wherein the catalyst has an alpha value of at least about 20, at least about 50, or at least about 200 prior to the steaming of the catalyst and optionally an alpha value prior to the steaming of the catalyst of about 1000 or less.

6. The method of any one of the previous claims, wherein the steamed catalyst has an alpha value that is greater than the alpha value of the catalyst prior to the steaming of the catalyst by at least about 10, at least about 25, or at least about 50.

7. The method of any one of the previous claims, wherein the steamed catalyst has an alpha value of at least about 250, at least about 300, or at least about 350, and optionally an alpha value of about 2000 or less.

8. The method of any one of the previous claims, wherein exposing a feed to the steamed catalyst comprises exposing the feed to the steamed catalyst in a fixed bed reactor, a fluidized bed reactor, a moving bed reactor, or a riser reactor; wherein exposing a feed to the steamed catalyst comprises exposing the feed to the steamed catalyst in the presence of steam and/or a hydrogen-lean stream; or a combination thereof.

9. The method of any of the above claims, further comprising separating at least a portion of the converted effluent to form a naphtha boiling range product.

10. The method of any of the above claims, further comprising separating at least a portion of the converted effluent to form a light ends product comprising ethylene, propylene, or a combination thereof and a liquid effluent.

11. The method of any of the above claims, further comprising separating at least a portion of the liquid effluent to form a C_8 product stream and one or more of a C_7- stream and a C_9+ stream.

12. The method of any of the above claims, wherein the catalyst is steamed for about 1 hour to about 16 hours.

13. The method of any of the above claims, wherein the molecular sieve comprises ZSM-5, ZSM-11, or a combination thereof, preferably ZSM-5.

14. The method of any of the above claims, wherein the molecular sieve has a silicon to aluminum ratio of about 20 to about 100, for example about 20 to about 80.

15. The method of any of the above claims, wherein the steamed catalyst further comprises about 0.1 wt% to about 10 wt% of phosphorus, about 0.1 wt% to about 10 wt% of a transition metal, about 0.1 wt% to about 10 wt% of a Group 13 metal or Group 14 metal, or a combination thereof.

16. The method of any of the above claims, wherein a) the effective conversion conditions comprise a pressure of about 100 kPaa to about 2500 kPaa, for example about 100 kPaa to about 1200 kPaa; and a WHSV of about 0.1 hr^{-1} to about 20 hr^{-1}, for example about 1.0 hr^{-1} to about 10 hr^{-1}; b) the feed substantially comprises methanol, dimethyl ether, or a combination thereof; or c) a combination thereof.

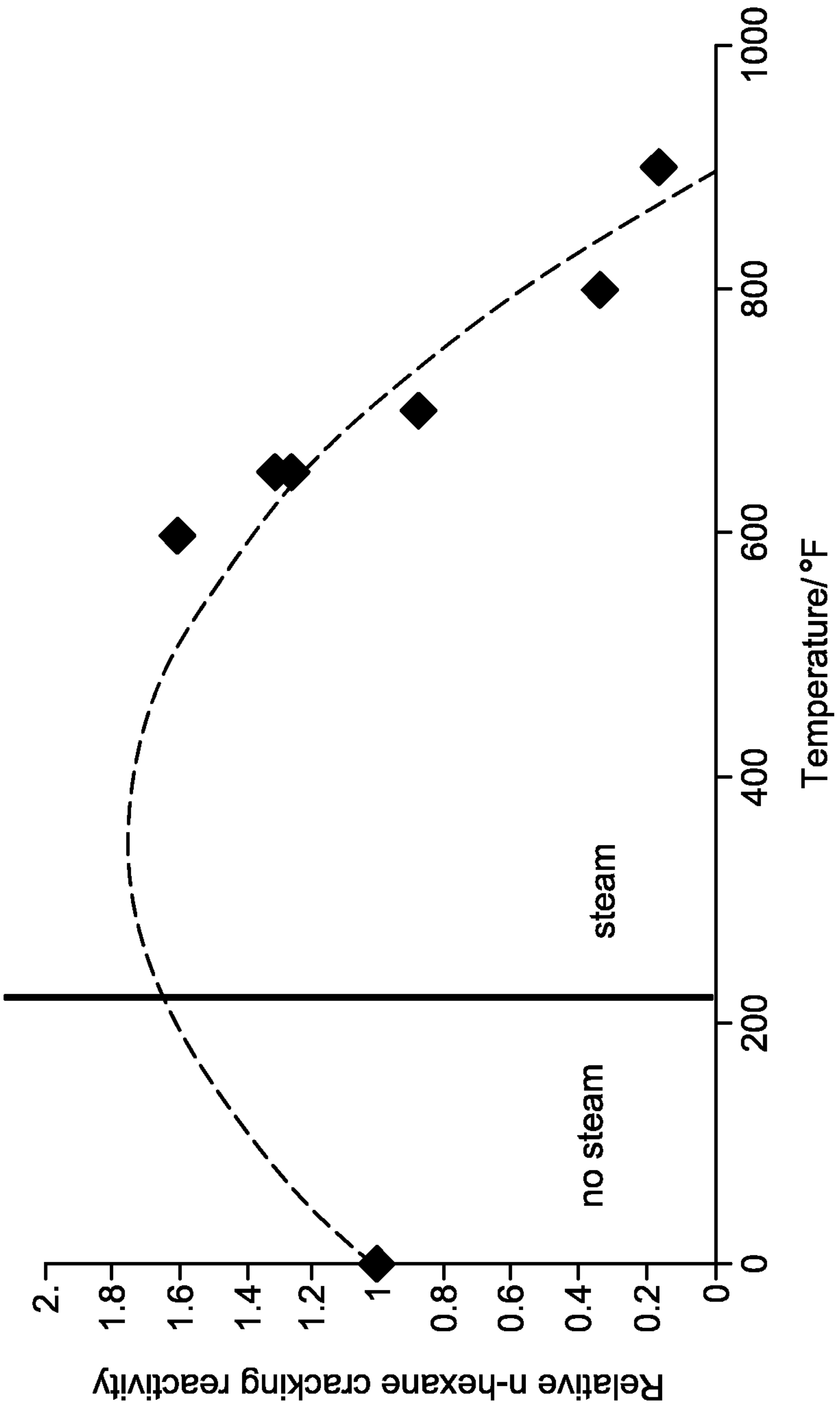
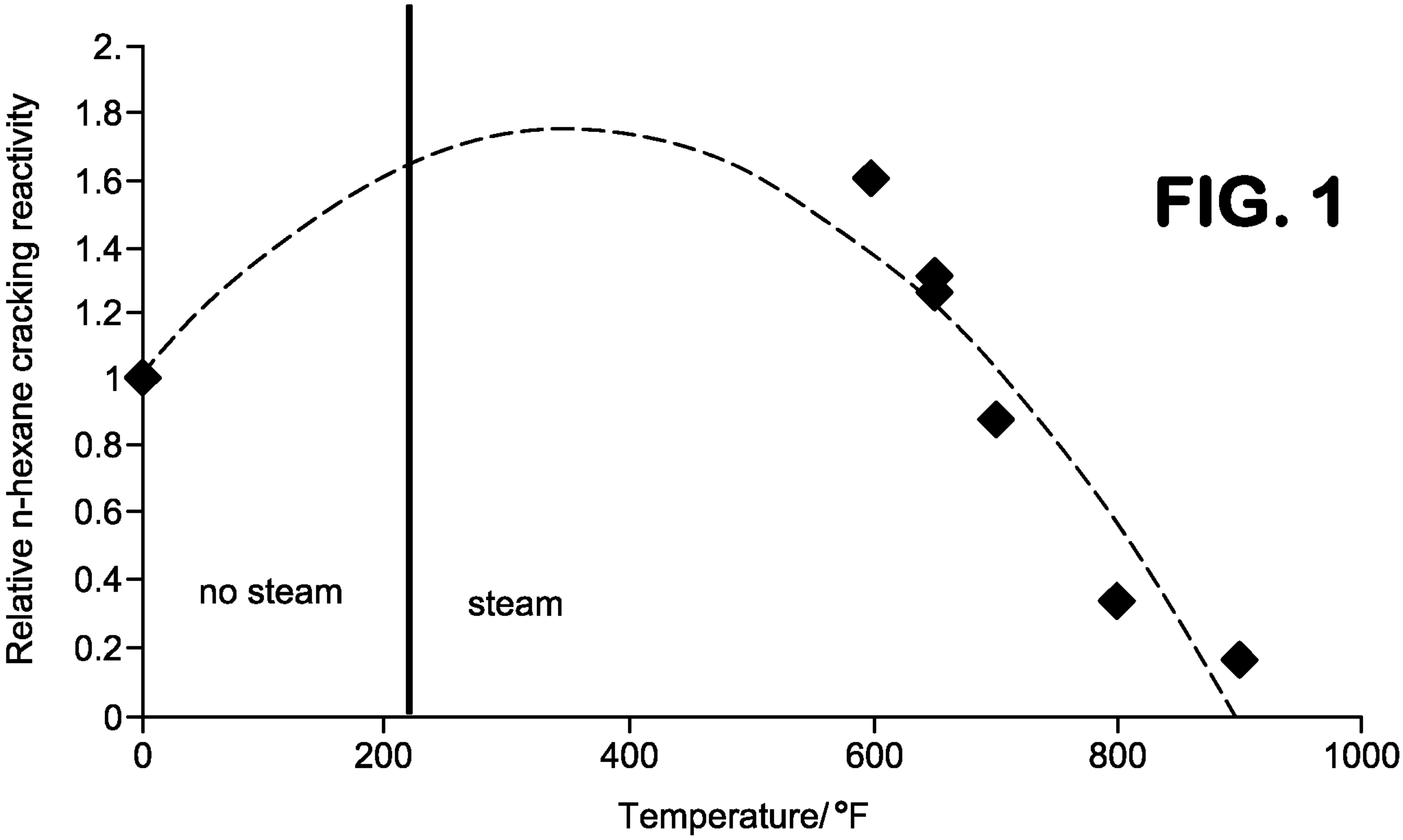

Relative n-hexane cracking reactivity
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
2.
Temperature/°F
0
200
400
600
800
1000
no steam
steam

FIG. 1



Relative n-hexane cracking reactivity
2.
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
no steam
steam
0
200
400
600
800
1000
Temperature/ °F

FIG. 1