

MFI ZEOLITE AND ITS USES FOR PRODUCTION OF LIGHT OLEFINS AND/OR
AROMATICS

STATEMENT OF PRIORITY

[0001] This application claims priority to United States Provisional Patent Application Ser. No. 63/315,480, filed on March 01, 2022, the entirety of which is incorporated herein by reference.

FIELD

[0002] The field is zeolites of the MFI structure type having low aluminum occupation at intersection sites and uses in conversion processes.

BACKGROUND

[0003] MFI zeolite is versatile in carrying out a wide array of catalytic processes for petrochemical production such as converting oxygenates to light olefins (methanol to hydrocarbons or propylene, MTH or MTP, respectively), to aromatics (MTA), to co-produce light olefins and aromatics, converting naphtha to light olefin (catalytic cracking) or vacuum gas oil to gasoline and light olefins in fluid catalytic cracking (FCC). In the aforementioned processes, undesirable products such as methane, ethane and propane are typically co-produced. For example, ethane and propane are formed via bi-molecular reaction pathways such as hydrogen transfers between light olefin and heavier paraffin and naphthene. The bimolecular hydrogen transfer reaction is affected by the active site density and geometric constraints around the active sites, and it is controlled typically via active site density for a given zeolite such as MFI.

[0004] Zeolites are a class of crystalline silicates possessing permanent microporosity based on $\text{TO}_{4/2}$ tetrahedra, where T is typically an aluminum or a silicon atom. Replacement of a silicon atom by an aluminum in a T site produces a negative framework charge balanced by a proton or other cation, creating an active site. The locations of the T atoms are unique for each framework and are often referred to as T-sites. As used herein, zeolites may be referred to by an improper name, such as silicalite, a proper name, such as ZSM-5, or by a structure type code, such as MFI. These three letter codes indicate atomic connectivity and hence pore size, shape and connectivity for the various known zeolites. The lists of these codes may be

found in the Atlas of Zeolite Framework Types, which is maintained by the International Zeolite Association Structure Commission at <http://www.iza-structure.org/databases/>. At present, 255 structure types are known and catalogued by the IZA. One such structure type, MFI is described as comprising 3-dimensional 10-ring channels with straight channels along crystallographic axis b and tortuous channels along axis a. Zeolites are distinguished from each other on the basis of their composition, crystal structure, and adsorption properties. One method commonly used in the art to distinguish zeolites is x-ray diffraction.

[0005] In addition to converting feed molecules to olefins, inter-olefin conversions should efficiently convert heavy olefins to lighter olefins by finding means to maximize ethylene, propylene, and/or propylene plus ethylene combined. Efficient and selective inter-olefin conversions are needed in converting butenes, light and heavy catalytic naphtha cracking (LCN and HCN) streams derived from FCC of VGO, and in converting C_4^+ olefins coming off a methanol to olefin (MTO) process through inter-conversion processes such as an olefin cracking process (OCP). In the aforementioned processes, zeolite catalysts repetitively swing between process and regeneration cycles. In the process cycle, the carbonaceous materials deposit on the catalyst, causing catalyst deactivation. The deactivated catalyst is regenerated to restore the activity typically via a carbon burn procedure, before returning to process cycles. During cycles of process and regeneration, zeolite is exposed to hydrothermal environments (particularly in regeneration), causing the degradation of zeolite acidity via de-alumination processes, where aluminum leaves the framework location, and thus loses of catalytic activity. To maintain the production throughput, the process would require constant make-up of fresh catalysts or progressively more severe reaction conditions after each regeneration cycle. Consequently, the economics of operating the processes would be adversely impacted due to the cost of constant fresh catalyst make-up or total catalyst replacement. In some cases, the rate of fresh catalyst make-up or frequency of replacement is too high to make the process economically viable.

[0006] Study of the crystallographic distributions of framework aluminum sites and its impact on zeolitic catalysis is a complex and active area of improvement for MFI zeolite. Literature indicates the majority of aluminum sites are located at the channel intersections for MFI zeolites made using tetra-propylammonium (TPA) structure directing agents (SDAs).

[0007] Crystal size and shape is also important. Increased conversion of butene and selectivity to propylene was observed for small MFI crystallites of a square crystallite shape

and intergrowth on (0,1,0) plane of coffin-shape zeolite crystallites give lower aromatics selectivity due to blockages of straight channel pore mouths and thus higher proportions of sinusoidal channel openings. JP 2011-73913 A shows via direct synthesis of MFI with high crystallization indices, rates of de-alumination are slowed down based on acidity measurements and catalytic tests across the hydrothermal treatments.

[0008] Various modifications have been utilized. In WO 2007/043742, modification via incorporating metal phosphate compound onto MFI zeolite slowed the rate of zeolite de-alumination as characterized by the retention of H-NMR signal after the hydrothermal stability treatment. Modification improved stability for catalytic naphtha cracking to olefins. Others have incorporated phosphorus on H-ZSM-5 for the conversion of methanol and obtained catalysts which switched from aromatics to olefin production modes with increasing phosphorus and with xylene products being significantly rich in para-xylene. However, significant decreases in methanol conversion activities and stability as well as micropore volume and surface area were observed.

[0009] Thus, there is a need for an improved MFI zeolite for the catalytic production of light olefins and/or aromatics with high conversion, selectivity to the desired product(s), and high selectivity to para-xylene.

BRIEF SUMMARY

[0010] We have found that zeolites of the MFI structure type having low aluminum occupation at intersection sites characterized by an ortho-xylene to para-xylene uptake ratio of greater than 0.1 and less than 0.55 possess unique reactivity for conversion of feedstocks comprising hydrocarbon or oxygenate to products comprising light olefins and/or aromatics.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] Figure 1 is a drawing of the MFI zeolite structure. The left side of the figure describes the MFI structure as possessing T-sites in straight channels (alpha), at the channel intersections (beta), and in the tortuous channels (gamma). Straight channels run along the b-axis of the structure. Labeling of the 12 individual T-sites by number is shown on the right side of the figure.

[0012] Figure 2 are plots of ethylene and propylene yield as a function of conversion achieved during the paraffin cracking test of the present disclosure. Open squares are achieved over the MFI of Example 1. Open triangles are achieved over the MFI of Comparative Example

1.1. Plot A is the H⁺ form of the materials, Plot B from materials steamed at 650°C and Plot C after steaming at 760°C.

[0013] Figure 3 are plots of ethylene and propylene yield as a function of conversion achieved during the paraffin cracking test of the present disclosure. Open squares are achieved over the MFI of Example 3. Open triangles are achieved over the MFI of Comparative Example 3.1. Stars are achieved over the MFI of Comparative Example 3.2. Plot A is the H⁺ form of the materials, Plot B from materials steamed at 650°C and Plot C after steaming at 760°C.

[0014] Figure 4 are plots of ethylene and propylene yield as a function of conversion achieved during the modified paraffin cracking test of the present disclosure. Open squares are achieved over the MFI of Example 1. Filled circles are achieved over the MFI of Comparative Examples 1.1 or 1.2. Plot A is the H⁺ form of the materials, Plot B from materials steamed at 650°C and Plot C after steaming at 760°C.

[0015] Figure 5 are plots of the ratio of ethylene to total moles of ethylene, propylene, and butene as a function of the weight percent of ethylene, propylene, and butene achieved during the modified paraffin cracking test of the present disclosure. In Plot A, open circles, squares, and triangles are achieved over the MFI of Example 1 in H⁺ form, after steaming at 650°C, and after steaming at 760°C respectively. Filled circles, squares and triangles are achieved over the MFI of Comparative Examples 1.1 or 1.2 in H⁺ form, after steaming at 650°C, and after steaming at 760°C respectively. In Plot B, open circles, squares, and triangles are achieved over the MFI of Example 2 in H⁺ form, after steaming at 650°C, and after steaming at 760°C respectively. Filled circles, squares and triangles are achieved over the MFI of Comparative Example 2.1 in H⁺ form, after steaming at 650°C, and after steaming at 760°C respectively. Plus, dash, and star symbols are achieved over the MFI of Comparative Example 2.2 in H⁺ form, after steaming at 650°C, and after steaming at 760°C respectively. In Plot C, open circles, squares, and triangles are achieved over the MFI of Example 3 in H⁺ form, after steaming at 650°C, and after steaming at 760°C respectively. Filled circles, squares and triangles are achieved over the MFI of Comparative Example 3.1 in H⁺ form, after steaming at 650°C, and after steaming at 760°C respectively. Plus, dash, and star symbols are achieved over the MFI of Comparative Example 3.2 in H⁺ form, after steaming at 650°C, and after steaming at 760°C respectively.

[0016] Figure 6A shows a plot of the moles of ethylene and propylene to heptane conversion achieved during the modified paraffin cracking test of the present disclosure. Figure

6B shows a plot of the moles of ethylene and propylene to total moles of ethylene, propylene, and butene as a function of the weight percent of ethylene, propylene, and butene achieved during the modified paraffin cracking test of the present disclosure. Figure 6C shows a plot of the ratio of ethylene and propylene to total moles of ethylene, propylene, and butene as a function of the weight percent of ethylene, propylene, and butene achieved during the modified paraffin cracking test of the present disclosure. Filled squares in Figures 6A, B, C are from the material of Comparative Example 1.2. Filled circles in Figures 6A, B, C are from the material of Comparative Example 1.1. Open squares in Figures 6A, B, C are from the material of Example 1.2. Open circles in Figures 6A, B, C are from the material of Example 1.

[0017] Figures 7 and 8 show the impact of zeolite silica to alumina molar ratio on heptane cracking results at 482°C achieved during the modified paraffin cracking test of the present disclosure. Figure 7A shows a plot of heptane conversion against silica to alumina ratio. Figure 7B shows a plot of ethylene weight percent versus silica to alumina ratio. Figure 7C shows a plot of propylene weight percent versus silica to alumina ratio. Figure 8A shows a plot of BTEX (benzene, toluene, ethylbenzene and xylene combined) against silica to alumina ratio. Figure 8B shows a plot of C6-C9 NA (non-aromatics hydrocarbons ranging from 6 to 9 carbon numbers) versus silica to alumina ratio. Open squares in Figures 7A, B, 8A, B are from Examples 3 of the instant invention. Closed circles in Figures 7A, B, 8A, B are from Comparative Examples 3.

[0018] Figures 9 and 10 show the impact of zeolite silica to alumina molar ratio on heptane cracking results at 607°C achieved during the modified paraffin cracking test of the present disclosure. Figure 9A shows a plot of heptane conversion against silica to alumina ratio. Figure 9B shows a plot of ethylene weight percent versus silica to alumina ratio. Figure 9C shows a plot of propylene weight percent versus silica to alumina ratio. Figure 10A shows a plot of BTEX against silica to alumina ratio. Figure 10B shows a plot of C6-C9 NA versus silica to alumina ratio. Open squares in Figures 9A, B, 10A, B are from Examples 3 of the instant invention. Closed circles in Figures 9A, B, 10A, B are from Comparative Examples 3.

[0019] Figure 11 are plots of ethylene and propylene yield as a function of time on stream during the methanol conversion test of Example 8 of the present disclosure. Open squares are achieved over the MFI of Example 1. Stars are achieved over the MFI of Comparative Example 1.1. Plot A is the H⁺ form of the calcined materials, Plot B from materials steamed at 650°C.

[0020] Figure 12 are plots of ethylene and propylene yield as a function of time on stream during the methanol conversion test of Example 8 of the present disclosure. Open squares are achieved over the MFI of Example 2. Open triangles are achieved over the MFI of Comparative Example 2.1. Stars were achieved over the MFI of Comparative Example 2.2. Plot A is the H+ form of the materials, Plot B from materials steamed at 650°C and Plot C after steaming at 760°C.

[0021] Figure 13 are plots of ethylene and propylene yield as a function of time on stream during the methanol conversion test of Example 8 of the present disclosure. Open squares are achieved over the MFI of Example 3. Open triangles are achieved over the MFI of Comparative Example 3.1. Stars were achieved over the MFI of Comparative Example 3.2. Plot A is the H+ form of the materials, Plot B from materials steamed at 650°C.

[0022] Figure 14 are plots of aromatics yield as a function of time on stream during the methanol conversion test of Example 8 of the present disclosure. Open squares are achieved over the MFI of Example 2. Open triangles are achieved over the MFI of Comparative Example 2.1. Stars were achieved over the MFI of Comparative Example 2.2. Plot A is the H+ form of the materials, Plot B from materials steamed at 650°C.

[0023] Figure 15 are plots of aromatics yield as a function of time on stream during the methanol conversion test of Example 8 of the present disclosure. Open squares are achieved over the MFI of Example 3. Open triangles are achieved over the MFI of Comparative Example 3.1. Stars were achieved over the MFI of Comparative Example 3.2. Plot A is the H+ form of the materials, Plot B from materials steamed at 650°C.

[0024] Figure 16 are plots of the ratio of para xylene to total xylenes as a function of total xylenes during the methanol conversion test of Example 8 of the present disclosure. Open squares are achieved over the MFI of Example 2. Open triangles are achieved over the MFI of Comparative Example 2.1. Stars were achieved over the MFI of Comparative Example 2.2. Plot A is the H+ form of the materials, Plot B from materials steamed at 650°C.

[0025] Figure 17 are plots of the ratio of para xylene to total xylenes as a function of total xylenes during the methanol conversion test of Example 8 of the present disclosure. Open squares are achieved over the MFI of Example 3. Open triangles are achieved over the MFI of Comparative Example 3.1. Stars were achieved over the MFI of Comparative Example 3.2. Plot A is the H+ form of the materials, Plot B from materials steamed at 650°C.

DEFINITIONS

[0026] The term “communication” means that fluid flow is operatively permitted between enumerated components, which may be characterized as “fluid communication”.

[0027] The term “downstream communication” means that at least a portion of fluid flowing to the subject in downstream communication may operatively flow from the object with which it fluidly communicates.

[0028] As used herein, the term “predominant” or “predominate” or “predominantly” means greater than 50%, suitably greater than 75% and preferably greater than 90%.

[0029] The term “Cx” is to be understood to refer to molecules having the number of carbon atoms represented by the subscript “x”. Similarly, the term “Cx-” refers to molecules that contain less than or equal to x and preferably x and less carbon atoms. The term “Cx+” refers to molecules with more than or equal to x and preferably x and more carbon atoms.

[0030] As used herein, naphtha is to be understood to be a hydrocarbon stream having a boiling point range of from 25°C at initial boiling point to 200°C at final boiling point. Naphthas may be derived from a variety of sources within a refinery and may potentially be split into multiple fractions all of which are understood to be naphtha. The boiling range for a light naphtha typically ranges from 29.4°C (85°F) at the 5% distillation point to 82.2°C (180°F) at the 95% distillation point by ASTM D-2887. This boiling range encompasses the majority of 2-methylbutane as a key component on the light end and benzene as the key component on the heavy end. Heavy naphtha boiling range may typically be from 82.2°C (180°F) at the 5% distillation point up to 198.9°C (390°F) at the 95% point.

[0031] As used herein, the term “gasoline” includes hydrocarbon streams having a T10 boiling point temperature of 70°C (158°F) and a T90 boiling point temperature of 190°C (374°F).

[0032] As used herein, the term “diesel” or “distillate” includes hydrocarbons having a T90 boiling point temperature of 338°C (640.4°F) and with an initial boiling point in the range of 150 to 200°C (302 to 392°F).

[0033] As used herein, the term “vacuum gas oil” (VGO) includes hydrocarbons having an initial boiling point above 343°C (650°F), with a T10 boiling point temperature using ASTM D1160 of 370°C (698°F) and a T90 boiling point temperature using ASTM D1160 of 500°C (932°F).

[0034] As used herein, the terms “xylene” or “xylenes” describe the class of dimethyl benzene molecules comprising one or more of 1,2-dimethylbenzene, 1,3-dimethylbenzene, and 1,4-dimethylbenzene. 1,2-dimethylbenzene is often referred to as ortho-xylene or oX. 1,3-dimethylbenzene is often referred to as meta-xylene or mX. 1,4-dimethylbenzene is often referred to as para-xylene or pX.

DETAILED DESCRIPTION

[0035] The disclosure provides MFI structure type zeolites characterized by high para-xylene and low ortho-xylene uptake as per measurements by Thermal Gravimetric Analysis (TGA). Unlike conventional MFI, characterized by equilibrium ortho-xylene to para-xylene uptake ratio of 0.70 or higher, this class of MFI exhibits equilibrium ortho-xylene to para-xylene (at 240 minutes) uptake ratio of less than 0.55. The disclosure further provides processes for use of the improved MFI zeolites for conversion of feed streams comprising hydrocarbons or oxygenates to products comprising light olefins and/or aromatics.

[0036] In the MFI structure type, adsorption and mass transport takes place primarily along axis b and then permeates through tortuous channels along axis a. The mass transport along the tortuous channels is intrinsically slower than that along straight channels. The mass transport from straight to tortuous channels can be further slowed down by the presence of adsorption sites located at the intersections of straight and tortuous channels. The impact of adsorption sites at intersections on the accessibility to adsorption/active sites in the tortuous channels can be viewed from the effect of framework aluminum densities. The probability of having adsorption sites at the intersections increases as the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios decrease (increased numbers of framework aluminum). Specifically, at 46 $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio, there would be one framework aluminum per intersection, at 94 $\text{SiO}_2/\text{Al}_2\text{O}_3$ half of intersections are occupied by one aluminum, and at 190 $\text{SiO}_2/\text{Al}_2\text{O}_3$, 25% of intersections are occupied by an aluminum assuming adsorption sites are uniformly distributed only among the intersections. The magnitudes of the impact are significantly amplified because reactions taking place at the intersections lead to carbonaceous deposits. Slower mass transport through the blocked intersection reduces the participation of active sites in the tortuous channels as illustrated by the patterns of catalytic performances in responses to $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios and hydrothermal treatment as illustrated in the examples below.

[0037] In this disclosure we tailor the morphology of zeolite MFI independently from altering framework aluminum distributions. The improved MFI zeolite may comprise a

heteroatom Q selected from the group consisting of boron, gallium, indium and iron, and mixtures thereof. Incorporation of heteroatom such as boron in addition to framework aluminum may reduce the effective mass transport path across the zeolite following the work by Hur and et. al. in Ind. Eng. Chem. Res. 2019, 58(27), 11849-11860. The heteroatom Q may be boron and the ratio of Si/B may range from 2 to 50. MFI zeolites of the disclosure may be synthesized by incorporating boron and specific organic structural directing agent (OSDA) including ethylenediamine (EDA) and 1,4 diazobicyclo[2.2.2]octane (DABCO) at $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios ranging from 60 to 1000.

[0038] This group of MFIs may be synthesized using ethylenediamine (EDA) as the primary structural directing agent (SDA) along with tetra-propylammonium (TPA) as the secondary SDA following the work by Hur mentioned previously and Miller, J.T. and et. al. on WO2019028035A2,. This group of MFI's can also be synthesized using DABCO following the procedure described by Nimlos, C. T. and et. al., in Chem. Mater. 2020, 32 (21), 9277-9298. It can also be prepared by the synthesis approach designed by Grose and Flanigen in US 4,257,885.

[0039] Improved MFI zeolites of the present disclosure having low aluminum occupation at intersection sites may be synthesized by mixing together a source of silicon, a source of aluminum, a source of boron, a SDA, and water, forming a homogenous mixture of composition comprising these sources, hydrothermally crystallizing the mixture at a temperature of from 125°C to 200°C or from 150°C to 180°C while continuously mixing for a time of from 75 hours to 100 hours, and recovering a solid product predominantly comprising MFI zeolite.

[0040] Silicon, aluminum, and boron sources may be those commonly known in zeolite synthesis including sodium silicate, tetramethyl orthosilicate, tetraethyl orthosilicate, fumed and/or precipitated silica, aluminum nitrate, aluminum hydroxide, sodium aluminate, boron oxide, boric acid and the like.

[0041] MFIs of the instant disclosure may also be synthesized via controlling aluminum incorporation rate via using amorphous or crystalline silica alumina as sources of aluminum in molecular sieve syntheses as shown in Tables 2 and 3. A preferred aluminum source is previously crystallized LTA zeolite. The improved MFI zeolite may have a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of from 60 to 600 and possess low aluminum occupation at intersection sites characterized by an ortho-xylene to para-xylene uptake ratio of no less than 0.1 and no more than 0.55. The

improved MFI zeolite may be further characterized by a micropore volume as determined by N₂ BET of from 0.11mL/g to 0.135mL/g.

[0042] At low SiO₂/Al₂O₃ (i.e., SiO₂/Al₂O₃) ratios of around 40-50, MFI zeolites with ortho-xylene to para-xylene uptake ratio of between 0.1 and 0.55 show lower cracking activity and are less stable than MFIs with ortho-xylene to para-xylene uptake ratios of greater than 0.7. However, increasingly higher and more stable paraffin cracking and light olefin yields are observed for MFI zeolites with ortho-xylene to para-xylene uptake ratio of no less than 0.1 and no more than 0.55 during catalyzed cracking as SiO₂/Al₂O₃ increases from 50, to 100 and then to 168 ratios. Calculations on the diffusion and uptake process of ortho-xylene and para-xylene in MFI framework show the change of equilibrium uptake ratio is caused by interactions of xylene molecules with aluminum atoms at different framework locations. Therefore, the adsorption characteristics may suggest a substantial amount of active sites are located in the tortuous channels.

[0043] The improved MFI zeolite may also be subjected to hydrothermal and/or steaming treatment to enhance catalytic properties. Hydrothermal conditions may comprise a temperature of from 500°C to 850°C or from 600°C to 800°C. Hydrothermal conditions may further comprise a steam level of from 5% to 100% or from 20% to 80%. Steam levels may be calculated for specific temperature, pressure, and diluent compositions from thermodynamic properties of water such as the steam tables. Hydrothermal conditions may further comprise a period of from 30 minutes to 24 hours or from 2 hours to 18 hours. Following hydrothermal treatment, paraffin cracking activities to olefin may increase and become more stable than those with equilibrium ortho-xylene to para-xylene uptake ratios of greater than 0.7.

[0044] Such transition on cracking activity and selectivity after hydrothermal treatment suggests that, without being bound by theory, the adsorption/active sites in the tortuous channels may be more efficient at converting hydrocarbons to olefins (in terms of higher olefin yields and selectivity) and perhaps more hydrothermally stable. It is further noted that distributions among C₂ – C₄ olefins are shifted toward lighter olefin, and most pronouncedly to ethylene, in contrast to conventional MFI zeolites, where ethylene is typically below equilibrium due to significant energetic barriers in olefin interconversions to produce ethylene.

[0045] The improved MFI zeolite may be formulated into a catalyst. Forming processes such as extrusion, pelletization, marumerization, oil dropping, and/or spray drying may be used to produce catalysts within specific size and density range to meet fluid dynamic and contact

time requirement pertaining to respective processes. The catalyst may comprise zeolite contents of between 5 and 80% zeolite or between 10% and 50% zeolite. The catalyst may comprise between 20 and 95% of binders comprising silica, alumina, magnesia, zirconia, clay and mixtures of thereof. The catalyst may be steam modified prior to use. Steam modification conditions may comprise a temperature in the range of from 500°C to 850°C and may further comprise a steam level of from 5% to 100%, and/or a treatment time in the range of from 30 minutes to 24 hours. The catalyst can optionally be modified further via treatment with alkali earth elements, rare earth elements, phosphate, and combinations thereof.

[0046] In another embodiment MFI zeolite having less than 0.55 and preferably less than 0.4 oX to pX uptake ratios may be mixed with MFI zeolite having greater than 0.55 oX to pX ratio. In such case, the MFI of low oX to pX ratios may comprise greater than 60% or preferably greater than 70% or most preferably greater than 80% of the total amount of MFI zeolite comprising the catalyst. Catalysts comprising mixtures of MFI zeolites with high and low oX to pX uptake ratios may be formulated into a single formed particle through forming processes previously mentioned. Alternatively, MFI zeolites of low oX/pX and high oX/pX ratios may be in separate formed catalysts following the aforementioned processes before introduction into the hydrocarbon or oxygenate conversion processes. By employing a mixtures of two respective catalyst particles, one can tailor the product compositions, for example, propylene versus ethylene, according to the respective demands at a given time.

[0047] Accordingly, an embodiment of the disclosure is a hydrocarbon conversion process comprising contacting a feedstream comprising hydrocarbon with a catalyst wherein the catalyst comprises an improved MFI zeolite comprising in the calcined and ion-exchanged form a molar $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of from 60 to 600 and having low aluminum occupation at intersection sites characterized by an ortho-xylene to para-xylene uptake ratio of greater than 0.1 and less than 0.55. The feedstream may be converted to a product at reaction conditions, and a product comprising light olefins, aromatics, or mixtures thereof may be recovered.

[0048] Hydrocarbon conversion processes may comprise reactor and/or process designs of fixed bed design, moving beds such as continuous catalyst regeneration (CCR), and/or fluidized beds for converting hydrocarbon feeds to light olefins comprising ethylene and propylene and/or aromatics. The hydrocarbon feed may comprise at least 50 wt% paraffin. The feed may be straight run naphtha or hydrocracked naphtha or catalytically cracked naphtha as are commonly found in refineries. The feed can optionally be hydrotreated to saturate

aromatics. In some instances, the feed may contain at least 5 wt% C4+ olefins. The hydrocarbon feed may comprise distillate and/or vacuum gas oil.

[0049] Reaction conditions may comprise a pressure of from 10 to 3000 kPa, and/or a temperature of from 500°C to 800°C, and/or a WHSV of from 0.5 to 25. The feedstream may comprise a diluent selected from the group consisting of nitrogen, steam, methane, hydrogen, and mixtures thereof. The diluent may comprise steam and/or methane. The diluent may comprise steam and/or nitrogen. Diluents may be used to lower the partial pressures of feeds to favor the catalytic cracking to olefin, to introduce the heat required for the endothermic reaction and/or to impart the catalyst sufficient velocity to pass through the reactor section in specific fluidization regions as defined by volumetric catalyst fractions. For fluidized bed hydrocarbon conversion processes, the catalyst to feed ratios (w/w) may be in the range of from 10 to 100 and diluent to feed ratios (w/w) may be from 1 to 10 or less.

[0050] Accordingly, an embodiment of the disclosure is an oxygenate conversion process comprising contacting a feedstream comprising oxygenate with a catalyst. MFI zeolites characterized by ortho-xylene to para-xylene uptake ratios of no less than 0.1 and no more than 0.55 may comprise the catalyst. Oxygenates may be converted to light olefins (ethylene and propylene) and/or aromatics. Improved relative activity of MFI zeolites of the instant disclosure may increase with increasing SiO₂/Al₂O₃ ratios and with hydrothermal treatment versus those of ortho-xylene to para-xylene uptake ratios greater than 0.7, in terms of higher light olefin production and increased stability. Improved catalytic properties may be observed on increasing the SiO₂/Al₂O₃ ratio to no greater than 200 or no greater than 300, or no greater than 400 or potentially no greater than 600, and even possibly to no greater than 800. The participation of active sites in the constrained environment (tortuous channels) may be further manifested in higher and stable total aromatics productions, higher xylene and higher para-xylene selectivity out of total xylenes produced.

[0051] The oxygenate may comprise methanol, dimethyl ether, dimethyl carbonate, ethanol, and mixtures thereof.

[0052] An oxygenate conversion process may comprise passing an oxygenate feedstream to an oxygenate conversion reactor operated at oxygenate conversion reaction conditions, wherein the reactor includes a catalyst, to generate a process stream comprising light olefins and/or aromatics. Oxygenate conversion reaction conditions may comprise a temperature in the range of from 300°C to 600°C or from 400°C to 500°C, and/or a pressure which allows an

absolute oxygenate partial pressure in the range from 20 kPa to 800 kPa or from 100 kPa to 400 kPa, and/or a WHSV from 0.1 to 20 or from 1 to 10. The process may further comprise separating the product stream comprising light olefins and/or aromatics into an ethylene stream, a propylene stream, a C4 stream, a C5 stream, a C5+ heavies stream, an aromatics stream, and combinations thereof. Separated portions of the product stream may be used as feed streams for further process units.

[0053] The consistently low and slow ortho-xylene uptakes going from 50 to 168 $\text{SiO}_2/\text{Al}_2\text{O}_3$ as shown below, without being bound by theory, suggest the adsorption sites are located in the tortuous channels, where adsorption energetics are not favorable under measurement conditions. Rates of adsorptions can slow down further when the adsorption sites located at the intersections of straight and tortuous channels become occupied after initial uptake of ortho-xylene. This interpretation of experimental observations is corroborated with Density Functional Theory (DFT) calculations. DFT calculated diffusion pathways and energetics indicate, the diffusion barriers from T1 aluminum to T1 aluminum (located at intersections) along the straight channels and from non-aluminum T1 (intersection) to T4 (located in tortuous channel) aluminum sites remain low with ortho-xylene being 24-30 kJ/mol more difficult than para-xylene, see Table 1, Figure 1 and Table 1 below. However, diffusion barrier for translation of molecules when aluminum is located at T1 site versus aluminum located at the T4 site increase appreciably with ortho-xylene being 20 kJ/mol higher than para-xylene. Furthermore, when both T1 and T4 sites are occupied with aluminum, diffusion barriers from intersection to tortuous channel are significantly increased for both para-xylene and ortho-xylene with access barrier for ortho-xylene elevated to a level greater than 100 kJ/mol. It suggests that the occupation of T1 by aluminum (located at intersection) would significantly impact the accessibility to a T4 aluminum site in the tortuous channels especially for a bulky molecule such as ortho-xylene, while a less bulky molecule such as para-xylene is not affected. Apparently favorable adsorption at aluminum T1 site makes the diffusion to non-aluminum T4 and aluminum T4 sites a great deal more difficult especially for bulky molecule.

Table 1: The MFI crystal structure and definition of the crystallographically unique T sites

Cell Symmetry	Space Group Name H-M	International Tables Number	Setting
	Pnma	62	Orthorhombic

Cell Dimensions (Å)		20.0900	19.7380	13.1420
Cell Angle (°)		90	90	90
T-Sites	Label	Fractional Coordinate X	Fractional Coordinate Y	Fractional Coordinate Z
	T1	0.4214	0.0711	0.6898
	T2	0.3259	0.0336	0.8500
	T3	0.2792	0.0536	0.0655
	T4	0.1246	0.0514	0.0481
	T5	0.0721	0.036	0.8233
	T6	0.2034	0.0687	0.7197
	T7	0.4195	0.8274	0.6805
	T8	0.3152	0.8765	0.8361
	T9	0.2733	0.8278	0.0402
	T10	0.1185	0.8279	0.0183
	T11	0.0657	0.8794	0.8087
	T12	0.1947	0.8288	0.7092

Table 2. Adsorption Energetics and Diffusion Barriers of Para- and Ortho-Xylene in MFI

	Adsorption {kJ/mol}	Adsorption {kJ/mol}	Adsorption {kJ/mol}	Diffusion barrier {kJ/mol}	Diffusion barrier {kJ/mol}	Diffusion barrier {kJ/mol}	Diffusion barrier {kJ/mol}
	T1 ^ξ	T4 ^ξ	T1 ^η	T1 ^ξ -to-T1 ^ξ	T1 ^ξ -through-T4 ^η	T1 ^ξ -through-T4 ^ξ	T1 ^η -through-T4 ^ξ
pX	-134	-102	-96	45	71	78	46
oX	-127	-96	-100	69	89	107	76
{ ^ξ : T site with Al; ^η : T site without Al}							

[0054] This indicates that para-xylene should have comparable amounts and uptake rates to ortho-xylene, when aluminum occupies T1 sites, consistent with experimental observations for conventional MFI. On the other hand, the diffusion barriers and thus accessibility of ortho-xylene to aluminum T4 site from intersections would depend on whether T1 sites are occupied with aluminum or not. Therefore, the relative adsorption amounts and uptake rate of ortho-

xylene to para-xylene are rationalized by distinct aluminum distributions among crystallographic distinct sites.

[0055] To enhance the participation of aluminum sites along the tortuous channels and thus improve catalytic performance, one would like to deploy optimized syntheses using choices of SDA, $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios, and modification methods such as steam, chemical extractions (acid, base or combination) designed to result in adsorption/reaction sites located along the tortuous channels in the gamma position and to have the channel intersections (beta position) void of such sites.

EXAMPLES

[0056] Prior to subjecting the samples below to catalytic tests and xylene uptakes by TGA, they were worked up to remove organic SDA and ammonium ion exchanged to lower sodium contents to part per millions on a weight basis. For EDA/TPA-MFI syntheses, the as-synthesized zeolite was first ammonium exchanged four times, each time using 14 ml of 1M NH_4NO_3 solution per gram zeolite at 80°C for 1 hour, and then calcined in a flowing air to lower sodium contents to levels of part per million on a weight basis. As for TPA-MFI samples, the as-synthesized zeolite was first calcined at 580°C for 6 hours in a flowing air, then ammonium ion exchanged using 25 ml 1 M NH_4NO_3 solution per gram zeolite at 80°C , followed by activation.

EXAMPLE 1

[0057] An alumina-boro-silicate solution was prepared by first mixing 43.48 g of aluminum nitrate nonahydrate, 68.11 g boric acid, 66.19 g of ethylenediamine, 29.47 g of TPAOH (40wt% solution) and 762.07 g of water, while stirring vigorously. After thorough mixing, 430.67 g Ludox HS-40 (SiO_2 , mass-40 %). The reaction mixture was homogenized for 20 minutes with a high-speed mechanical stirrer, transferred to a 2-L Parr Hastelloy stir autoclave. The mixture was crystallized at 175°C with stirring at 300 RPM for 90 hours. The solid product was recovered by filtration, washed with de-ionized water, and dried at 100°C . The product was identified as MFI by XRD. Chemical analysis gave a product composition of $\text{Si}/\text{Al}=24.75$, $\text{Si}/\text{B}=27.1$. The sample was calcined at 580°C for 6 hours and the BET surface area was $296 \text{ m}^2/\text{g}$ with a micropore volume of 0.119 cc/g and a total pore volume of 0.179 cc/g .

Example 1.2

Example 1.2 was synthesized following the same procedure described for Example 1 but targeting a product Si/Al ratio of 20. The zeolite was analyzed to have 18 Si/Al.

COMPARATIVE EXAMPLE 1.1

[0058] An alumina-boro-silicate solution was prepared by first mixing 29.59 g of aluminum nitrate nonahydrate, 46.35 g boric acid, 300.8 g of TPAOH (40% solution), 9.47 g NaOH and 720.7 g of water, while stirring vigorously. After thorough mixing, 293.06 g Ludox HS-40 (SiO₂, mass-40 %). The reaction mixture was homogenized for 20 minutes with a high-speed mechanical stirrer, transferred to a 2-L Parr Hastelloy stir autoclave. The mixture was crystallized at 175°C with stirring at 300 RPM for 72 hours. The solid product was recovered by filtration, washed with de-ionized water, and dried at 100°C. The product was identified as MFI by XRD. Chemical analysis gave a product composition of Si/Al=24.92, Si/B=83.17. The sample was calcined at 580°C for 6 hours and the BET surface area was 343 m²/g with a micropore volume of 0.159 cc/g and a total pore volume of 0.212 cc/g.

COMPARATIVE EXAMPLE 1.2

[0059] A similar preparation to Example 1.1 was performed with the use of TPAOH as SDA. In this case, the synthesis was performed without boron and yielded MFI-40 as Comparative Example 1.2.

EXAMPLE 2

[0060] An alumina-boro-silicate solution was prepared by first mixing 22.14 g of aluminum nitrate nonahydrate, 69.36 g boric acid, 53.21 g of ethylenediamine, 45.01 g of TPAOH (40% solution) and 771.76 g of water, while stirring vigorously. After thorough mixing, 438.53 g Ludox HS-40 (SiO₂, mass-40 %). The reaction mixture was homogenized for 20 minutes with a high-speed mechanical stirrer, transferred to a 2-L Parr Hastelloy stir autoclave. The mixture was crystallized at 175°C with stirring at 300 RPM for 90 hours. The solid product was recovered by filtration, washed with de-ionized water, and dried at 100°C. The product was identified as MFI by XRD. Chemical analysis gave a product composition of Si/Al=49.91, Si/B=15.99. The sample was calcined at 580°C for 6 hours and the BET surface

area was 301 m²/g with a micropore volume of 0.124 cc/g and a total pore volume of 0.179 cc/g.

COMPARATIVE EXAMPLE 2.1

[0061] An alumina-boro-silicate solution was prepared by first mixing 14.91 g of aluminum nitrate nonahydrate, 46.71 g boric acid, 323.38 g of TPAOH (40% solution) and 719.63 g of water, while stirring vigorously. After thorough mixing, 295.37 g Ludox HS-40 (SiO₂, mass-40 %). The reaction mixture was homogenized for 20 minutes with a high-speed mechanical stirrer, transferred to a 2-L Parr Hastelloy stir autoclave. The mixture was crystallized at 175°C with stirring at 300 RPM for 90 hours. The solid product was recovered by filtration, washed with de-ionized water, and dried at 100°C. The product was identified as MFI by XRD. Chemical analysis gave a product composition of Si/Al=49.67, Si/B=52.6. The sample was calcined at 580°C for 6 hours and the BET surface area was 355 m²/g with a micropore volume of 0.129 cc/g and a total pore volume of 0.233 cc/g.

COMPARATIVE EXAMPLE 2.2

[0062] MFI-80 was acquired from Zeolyst.

EXAMPLE 3

[0063] An alumina-boro-silicate solution was prepared by first mixing 11.33 g of aluminum nitrate nonahydrate, 70.09 g boric acid, 53.77 g of ethylenediamine, 30.32 g of TPAOH (40% solution) and 791.35 g of water, while stirring vigorously. After thorough mixing, 443.14 g Ludox HS-40 (SiO₂, mass-40 %). The reaction mixture was homogenized for 20 minutes with a high-speed mechanical stirrer, transferred to a 2-L Parr Hastelloy stir autoclave. The mixture was crystallized at 175°C with stirring at 300 RPM for 88 hours. The solid product was recovered by filtration, washed with de-ionized water, and dried at 100°C. The product was identified as MFI by XRD. Chemical analysis gave a product composition of Si/Al=84, Si/B=21.71. The sample was calcined at 580°C for 6 hours and the BET surface area was 290 m²/g with a micropore volume of 0.129 cc/g and a total pore volume of 0.165 cc/g.

COMPARATIVE EXAMPLE 3.1

[0064] An alumina-boro-silicate solution was prepared by first mixing 7.49 g of aluminum nitrate nonahydrate, 46.91 g boric acid, 324.73 g of TPAOH (40% solution) and 724.27 g of water, while stirring vigorously. After thorough mixing, 296.6 g Ludox HS-40 (SiO₂, mass-40 %). The reaction mixture was homogenized for 20 minutes with a high-speed mechanical stirrer, transferred to a 2-L Parr Hastelloy stir autoclave. The mixture was crystallized at 175°C with stirring at 300 RPM for 88 hours. The solid product was recovered by filtration, washed with de-ionized water, and dried at 100°C. The product was identified as MFI by XRD. Chemical analysis gave a product composition of Si/Al=80.5, Si/B=35.47. The sample was calcined at 580°C for 6 hours and the BET surface area was 348 m²/g with a micropore volume of 0.171 cc/g and a total pore volume of 0.195 cc/g.

COMPARATIVE EXAMPLE 3.2

[0065] Zeolite silicalite of target SiO₂/Al₂O₃ ratio of 95 was synthesized using tetrapropylammonium (TPA) as organic structure directing agent (OSDA). The resulting zeolite after calcination to remove the organic template has Si/Al ratio of 100 and a BET surface area of 358 m²/gm with a micropore volume of 0.184 cc/g and a total pore volume of 0.208 cc/g.

EXAMPLE 3.3

An alumina-boro-silicate solution was prepared by first mixing 11.19 g of aluminum nitrate nonahydrate, 70.09 g boric acid, 53.77 g of ethylenediamine, 30.33 g of TPAOH (40% solution) and 791.45 g of water, while stirring vigorously. After thorough mixing, 443.18 g
5 Ludox™ HS-40 (SiO₂, mass-40 %) was added to the aforementioned mixture. The reaction mixture was homogenized for 20 minutes with a high-speed mechanical stirrer, and then transferred to a 2-L Parr Hastelloy stir autoclave. The mixture was crystallized at 175°C with stirring at 300 RPM for 88 hours. The solid product was recovered by filtration, washed with de-ionized water, and dried at 100°C. The product was identified as MFI by XRD. The
10 chemical analysis gave a product composition of Si/Al₂=221.47, Si/B₂=42.73. The sample was calcined at 580°C for 6 hrs and the BET surface area was 287 m²/g with a micropore volume of 0.143 cc/g and a total pore volume of 0.164 cc/g.

COMPARATIVE EXAMPLE 3.4

An alumina-boro-silicate solution was prepared by first mixing 7.53 g of aluminum nitrate nonahydrate, 47.18 g boric acid, 306.21 g of TPAOH (40% solution) and 740.74 g of water, while stirring vigorously. After thorough mixing, 298.33 g Ludox™ HS-40 (SiO₂, mass-40 %) was added. The reaction mixture was homogenized for 20 minutes with a high-speed mechanical stirrer, and then transferred to a 2-L Parr Hastelloy stir autoclave. The mixture was crystallized at 175°C with stirring at 300 RPM for 88 hours. The solid product was recovered by filtration, washed with de-ionized water, and dried at 100°C. The product was identified as MFI by XRD. The chemical analysis gave a product composition of Si/Al₂=186.16, Si/B₂=70.15. The sample was calcined at 580°C for 6 hrs and the BET surface area was 344 m²/g with a micropore volume of 0.171 cc/g and a total pore volume of 0.190 cc/g.

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EXAMPLE 3.5

An alumina-boro-silicate solution was prepared by first mixing 5.61 g of aluminum nitrate nonahydrate, 70.31 g boric acid, 53.94 g of ethylenediamine, 30.42 g of TPAOH (40% solution) and 795.15 g of water, while stirring vigorously. After thorough mixing, 444.57 g Ludox™ HS-40 (SiO₂, mass-40 %) was added. The reaction mixture was homogenized for 20 minutes with a high-speed mechanical stirrer, and then transferred to a 2-L Parr Hastelloy stir autoclave. The mixture was crystallized at 175°C with stirring at 300 RPM for 88 hours. The solid product was recovered by filtration, washed with de-ionized water, and dried at 100°C. The product was identified as MFI by XRD. The chemical analysis gave a product composition of Si/Al₂=400, Si/B₂=40.13. The sample was calcined at 580°C for 6 hrs and the BET surface area was 273 m²/g with a micropore volume of 0.137 cc/g and a total pore volume of 0.153 cc/g.

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COMPARATIVE EXAMPLE 3.6

An alumina-boro-silicate solution was prepared by first mixing 3.02 g of aluminum nitrate nonahydrate, 47.3 g boric acid, 306.99 g of TPAOH (40% solution) and 743.6 g of water, while stirring vigorously. After thorough mixing, 299.09 g Ludox™ HS-40 (SiO₂, mass-40 %) was added.

30

was added. The reaction mixture was homogenized for 20 minutes with a high-speed mechanical stirrer, and then transferred to a 2-L Parr Hastelloy stir autoclave. The mixture was crystallized at 175°C with stirring at 300 RPM for 88 hours. The solid product was recovered by filtration, washed with de-ionized water, and dried at 100°C. The product was identified as MFI by XRD. The chemical analysis gave a product composition of Si/Al₂=441, Si/B₂=63.06. The sample was calcined at 580°C for 6 hrs and the BET surface area was 342 m²/g with a micropore volume of 0.173 cc/g and a total pore volume of 0.184 cc/g.

EXAMPLE 3.7

10 An alumina-boro-silicate solution was prepared by first mixing 3.74 g of aluminum nitrate nonahydrate, 70.39 g boric acid, 54.0 g of ethylenediamine, 30.45 g of TPAOH (40% solution) and 796.39 g of water, while stirring vigorously. After thorough mixing, 445.03 g LudoxTM HS-40 (SiO₂, mass-40 %) was added. The reaction mixture was homogenized for 20 minutes with a high-speed mechanical stirrer, and then transferred to a 2-L Parr Hastelloy stir autoclave.

15 The mixture was crystallized at 175°C with stirring at 300 RPM for 88 hours. The solid product was recovered by filtration, washed with de-ionized water, and dried at 100°C. The product was identified as MFI by XRD. The chemical analysis gave a product composition of Si/Al₂=590.6, Si/B₂=37.7. The sample was calcined at 580°C for 6 hrs and the BET surface area was 285 m²/g with a micropore volume of 0.144 cc/g and a total pore volume of 0.154 cc/g.

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COMPARATIVE EXAMPLE 4

[0066] Example 4 follows Example 8 of US4257885 by Grose and Flanigen. It was prepared by using Zeolite silicalite with organic template removed as a seed using a synthesis gel that does not contain organic SDA.

EXAMPLE 5

[0067] In this series, MFI zeolites were synthesized with different ratios of liquid sodium aluminate (LSA) and Linde Type A (LTA) zeolite 4A as an aluminum source.

EXAMPLE 5.1

[0068] An alumina-silicate gel was prepared by first mixing 33.35 g of LTA zeolite (4A), 18.7 g of NaOH, 23.41 g of diethanolamine, 3.95 g of TPABr (50wt% solution) and 808.96 g of water, while stirring vigorously. After thorough mixing, 502.06 g Ludox HS-40 (SiO₂, mass-40 %). The reaction mixture was homogenized for 20 minutes with a high-speed mechanical stirrer, transferred to a 2-L Parr Hastelloy stir autoclave. The mixture was crystallized at 160°C with stirring at 300 RPM for 72 hours. The solid product was recovered by filtration, washed with de-ionized water, and dried at 100°C. The product was identified as MFI by XRD. Chemical analysis gave a product composition of Si/Al=20.31. A small sample was calcined at 580°C x 6 hrs and the BET surface area was 317 m²/g with a micropore volume of 0.159 cc/g and a total pore volume of 0.189 cc/g.

[0069] The MFI made with LTA was ammonium ion exchanged to exchange Na for NH₄. The MFI was ammonium ion-exchanged by contacting 2000 mL of 1 M NH₄NH₂ solution with 160 g MFI at 80°C and stirring for 1 hour, filtered and washed. The procedure was repeated four times.

EXAMPLE 5.2

[0070] An alumina-silicate gel was prepared by first mixing 8.14 g LSA, 33.35 g of LTA zeolite (4A), 17.96 g NaOH, 23.41 g of diethanolamine, 3.95 g of TPABr (50% solution) and 813.99 g of water, while stirring vigorously. After thorough mixing, 507.53 g Ludox HS-40 (SiO₂, mass-40 %). The reaction mixture was homogenized for 20 minutes with a high-speed mechanical stirrer, transferred to a 2-L Parr Hastelloy stir autoclave. The mixture was crystallized at 160°C with stirring at 300 RPM for 72 hours. The solid product was recovered by filtration, washed with de-ionized water, and dried at 100°C. The product was identified as MFI by XRD. Chemical analysis gave a product composition of Si/Al=20.33. A small sample was calcined at 580°C x 6 hrs and the BET surface area was 327 m²/g with a micropore volume of 0.16 cc/g and a total pore volume of 0.198 cc/g.

[0071] The MFI made was ammonium ion-exchanged following the same procedure as described in (example 5.1)

COMPARATIVE EXAMPLE 5.3

[0072] An alumina-silicate gel was prepared by first mixing 16.28 g of liquid sodium aluminate (LSA), 16.67 g of LTA zeolite (4A), 17.95 g of NaOH, 23.4 g of diethanolamine,

3.95 g of TPABr (50% solution) and 808.96 g of water, while stirring vigorously. After thorough mixing, 512.79 g Ludox HS-40 (SiO₂, mass-40 %). The reaction mixture was homogenized for 20 minutes with a high-speed mechanical stirrer, transferred to a 2-L Parr Hastelloy stir autoclave. The mixture was crystallized at 160°C with stirring at 300 RPM for 72 hours. The solid product was recovered by filtration, washed with de-ionized water, and dried at 100°C. The product was identified as MFI by XRD. Chemical analysis gave a product composition of Si/Al=20.17. A small sample was calcined at 580°C x 6 hrs and the BET surface area was 330 m²/g with a micropore volume of 0.159 cc/g and a total pore volume of 0.211 cc/g.

[0073] The MFI made was ammonium ion-exchanged following the same procedure as described in (example 5.1)

COMPARATIVE EXAMPLE 5.4

[0074] An alumina-silicate gel was prepared by first mixing 24.42 g of liquid sodium aluminate (LSA), 8.33 grs of LTA zeolite (4A), 17.21 g of NaOH, 23.4 g of diethanolamine, 3.95 grs g of TPABr (50% solution) and 808.96 g of water, while stirring vigorously. After thorough mixing, 518.26 g Ludox HS-40 (SiO₂, mass-40 %). The reaction mixture was homogenized for 20 minutes with a high-speed mechanical stirrer, transferred to a 2-L Parr Hastelloy stir autoclave. The mixture was crystallized at 160°C with stirring at 300 RPM for 72 hours. The solid product was recovered by filtration, washed with de-ionized water, and dried at 100°C. The product was identified as MFI by XRD. Chemical analysis gave a product composition of Si/Al=19.98. A small sample was calcined at 580°C x 6 hrs and the BET surface area was 321 m²/g with a micropore volume of 0.157 cc/g and a total pore volume of 0.198 cc/g.

[0075] The MFI made was ammonium ion-exchanged following the same procedure as described in example 5.1.

COMPARATIVE EXAMPLE 5.5

[0076] An alumina-silicate gel was prepared by first mixing 32.57 g of liquid sodium aluminate (LSA), 16.32 g of NaOH, 23.4 g of diethanolamine, 3.95 grs g of TPABr (50% solution) and 808.96 g of water, while stirring vigorously. After thorough mixing, 523.77 g Ludox HS-40 (SiO₂, mass-40 %). The reaction mixture was homogenized for 20 minutes with a high-speed mechanical stirrer, transferred to a 2-L Parr Hastelloy stir autoclave. The mixture was crystallized at 160°C with stirring at 300 RPM for 72 hours. The solid product was

recovered by filtration, washed with de-ionized water, and dried at 100°C. The product was identified as MFI by XRD. Chemical analysis gave a product composition of Si/Al=20.17. A small sample was calcined at 580°C x 6 hrs and the BET surface area was 297 m²/g with a micropore volume of 0.136 cc/g and a total pore volume of 0.239 cc/g.

[0077] The MFI made was ammonium ion-exchanged following the same procedure as described in example 5.1.

Table 3.1. Composition of MFI made from Zeolite LTA and LSA (Liquid Sodium Aluminate).

Examples	<u>LTA /</u> <u>(LTA+LSA)</u>	<u>Si</u>	<u>Al</u>	<u>Na</u>	<u>SiO₂/Al₂O₃</u>
Example 5.1	1	44.19	2.09	1.22	40.61
Example 5.2	0.75	44.15	2.11	1.24	40.66
Comparative Example 5.3	0.5	44.3	2.11	1.01	40.34
Comparative Example 5.4	0.25	44.09	2.12	1.32	39.97
Comparative Example 5.5	0	44.05	2.04	1.49	41.45

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Table 3.2. Surface Areas of MFI made from Zeolite LTA and LSA (Liquid Sodium Aluminate).

Examples	<u>LTA/(LTA+LSA)</u>	<u>SA</u> <u>m²/g</u>	<u>MSA</u> <u>m²/g</u>	<u>uPV</u> <u>cc/g</u>	<u>TPV cc/g</u>
Example 5.1	1	317	10	0.159	0.189
Example 5.2	0.75	324	25	0.155	0.216
Comparative Example 5.3	0.5	330	23	0.159	0.211
Comparative Example 5.4	0.25	321	17	0.157	0.198
Comparative Example 5.5	0	297	34	0.136	0.239

EXAMPLE 6

[0078] Procedure for xylene vapor uptake measurement by Thermal Gravimetric Analysis (TGA). A loading of 25 mg of zeolite sized to 40x60 mesh is placed onto the weighing pan of the instrument. The sample is pretreated at 350°C for 60 minutes in a flowing N₂, and its weight

recorded after pretreatment. Thereafter, the sample temperature is lowered to the adsorption temperature of 120°C. The uptake experiment is performed by passing a flow of N₂ at 72 ml/min through a para-xylene or ortho-xylene saturator controlled at 18°C, which is then combined with a separate N₂ flow set at 127 ml/min, before contacting the sample. The time of adsorption for para-xylene is 40 to 100 minutes and for ortho-xylene is 200 to 240 minutes. The experiment is performed separately for para-xylene adsorption and for ortho-xylene adsorption. Net weight gain of sample is defined as the difference between 1) sample weight upon reaching adsorption equilibrium (and stable weight) or at the end of adsorption experiment, and 2) the sample weight after pretreatment step. The uptake weight percentage of each xylene isomer is defined as the ratio of net weight gain to the weight after pretreatment, and the ortho-xylene to para-xylene uptake ratio is defined as the ratio of ortho-xylene uptake weight percentage to para-xylene uptake weight percentage. The results are summarized in Tables 4 and 5. The results showed that a higher level of xylenes uptake is achieved when the MFI structure has a lower SiO₂/Al₂O₃ ratio, and also MFIs in examples 1-5 with specific synthesis protocol showed a lower equilibrium uptake ratio of ortho-/para-xylene than the comparative examples.

Table 4. Uptake Characteristics of Examples and Comparative Examples 1 through 4

Example	Material Description	SiO ₂ /Al ₂ O ₃	SiO ₂ /B ₂ O ₃	pX uptake wt % at equil or 240 min	oX uptake wt % at equil or 240 min	oX to pX uptake ratio
Example 1	MFI EDA/TPA	49.4	54.2	4.926	1.45	0.29
Comparative 1.1	MFI TPA	49.7	166.1	5.895	5.063	0.86
Example 1.2	MFI EDA/TPA	36				
Comparative 1.2	MFI-TPA	40		6.1	5.06	0.83
Example 2	MFI EDA/TPA	99.6	32.0	4.443	1.23	0.28
Comparative 2.1	MFI TPA	99.1	105.0	4.555	3.631	0.80
Comparative 2.2	Zeolyst MFI-80	80		4.463	3.814	0.85
Example 3	MFI EDA/TPA	168.0	43.5	3.27	1.16	0.35
Comparative 3.1	MFI TPA	160.7	70.8	3.75	2.728	0.73
Comparative 3.2	MFI-TPA	190		3.012	1.735	0.58
Example 3.3	MFI EDA/TPA	221	42.7	3.14	0.90	0.29
Comparative 3.4	MFI TPA	186	70.2	3.68	2.52	0.68
Example 3.5	MFI EDA/TPA	400	40.1	2.51	0.95	0.38
Comparative 3.6	MFI TPA	441	63.1	3.17	1.49	0.47
Example 3.7	MFI EDA/TPA	591	37.3	2.42	0.40	0.17

Comparative 3.8	MFI TPA	500		2.50	1.29	0.52
Comparative Example 4	US4257885	44		6.339	3.064	0.48

Table 5. Uptake Characteristics of Examples and Comparative Examples 5

Examples	$\frac{LTA}{(LTA+LSA)}$	pX uptake wt% at equil	oX uptake wt% at equil or 240 min	oX to pX uptake ratio
Example 5.1	1	6.059	1.83	0.30
Example 5.2	0.75	6.266	3.112	0.50
Comparative Example 5.3	0.5	5.812	4.665	0.80
Comparative Example 5.4	0.25	5.642	4.988	0.88
Comparative Example 5.5	0	5.195	4.53	0.87

EXAMPLE 7

[0079] Procedure for normal heptane (nC7) cracking tests. A catalyst loading of 250 mg sized to 40x60 mesh is first pretreated at 625°C in a flowing N₂ for 60 minutes. The catalytic performance is evaluated at one atmosphere pressure and at variable temperatures of 483, 533, 608 (sequentially) and then return to 483°C with a constant N₂ flow at 125 ml/minute passing through normal heptane saturator controlled at 0°C. GC method is set up to capture light paraffin and olefin, benzene, toluene, xylene isomers/ethylbenzene and C₅-C₉ non-aromatics.

[0080] MFIs prepared as per Examples 1-3 and Comparative Examples 1-4 are ion-exchanged as previously described to be in NH₄⁺/H⁺ (c) form prior to catalytic tests. In separate nC7 cracking experiments, MFIs are also hydrothermally treated at 650 and 760°C at 40% steam over a period of 12 hours, respectively, prior to gauging catalytic performance.

[0081] As shown in Figures 2 to 5, At SiO₂/Al₂O₃ ratios of 40-50, EDA-MFI exhibits significantly lower activities across the entire range of temperatures. Unlike TPA-MFI, its activities exhibit near zero or negative responses to increased temperatures. Furthermore, when returning the initial condition, its activity drops to zero, suggesting severe deactivation. As SiO₂/Al₂O₃ ratios increase from 50, to 100 and then 160-170, the activity and light olefin yield

gaps first narrows and then reverses. The activity and light olefin yield responses to temperatures of EDA-MFI turns from negative, linear and then exponential. The same transformation of performance ranking with respect to $\text{SiO}_2/\text{Al}_2\text{O}_3$ is also observed, when MFIs are subject to hydrothermal treatment, designed to mimic the hydrothermal environments the zeolite would be exposed to process and regeneration conditions. The higher productivity of light olefin and improved response to temperatures, with increased $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios and/or hydrothermal treatment, is illustrated in Figures 2-5, suggesting that, without being bound by theory, active sites in the tortuous channels have higher intrinsic activity and/or better hydrothermal stability.

[0082] To further illustrate the utility of active sites located in the constraint environment, the paraffin cracking test is modified to obtained performance at earlier times on stream comparable to the contacts representative of processes such as fluidized beds, riser and etc. The modified paraffin cracking test involves the same 625°C, 1-hour N_2 pretreatment procedure and measures performances at temperatures of 500, 550, 625, and 500°C sequentially (483, 533, 608 and 483°C reactor temperatures). Normal heptane feed is still introduced via flowing N_2 at 125 ml/minute through a saturator of liquid normal heptane controlled at 0°C, but at each temperature, the catalyst is only exposed to paraffin vapor feed for 5 minutes before GC sampling of product and flow is switched to pure N_2 immediately afterwards, and catalyst stays in pure N_2 flow at 125ml/min during transition to the next condition. The contact in the modified paraffin cracking test corresponds to a catalyst to feed ratios on a wight basis from 1 to 10.

[0083] As shown in Figures 2-5, paraffin cracking to light olefin (C2-C4) are becoming more favorable for MFIs containing active sites in constrained environments, with increased $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios and/or hydrothermal treatment, and especially pronounced for converting paraffin to lighter olefin (C2-C3) as shown in Figures 2-5. It is further observed that the active sites located in the constraint environment favorably produce ethylene as shown in Figure 5, the levels of which are below thermodynamically allowable levels due to high energetic barriers for olefin interconversions from higher olefins to ethylene. Conceivably, for catalytic processes such as oxygenates to light olefin, hydrocarbon cracking to light olefin, olefin interconversion to lighter olefins, it is useful to deploy MFI zeolite containing active sites located in the constraint environment to co-produce ethylene and propylene, and especially to co-produce ethylene and propylene at high proportions of ethylene. Conversely, one would limit

the active sites located in the constraint environment to minimize ethylene production if the process objective is to maximize propylene production or propylene/butylene co-production.

[0084] To further assess the hydrothermal severity impact on catalyst performance, such as that occurring in fluid catalytic cracking processes, zeolites of Example 1 were subjected to 100% steam at 796°C for 16 hours. As shown in Figure 6, zeolite of Examples 1 of the instant invention exhibited higher ethylene and propylene percentages and higher ethylene and propylene percentages at given heptane conversions than those of Comparative Examples 1. Furthermore, ethylene to propylene ratios (w/w) for materials of the instant invention are approximately double those of Comparative Examples 1 at ethylene plus propylene weight percentages (Figure 6C).

[0085] It is noted that TPA-MFI (Comparative Examples 5) is directed toward propylene and butylene production. Its activity to produce C2-C4 olefin was adversely impacted, when exposed to hydrothermal exposure incurred during conversion and regeneration unit operations in olefin producing processes. Furthermore, its activity to produce light olefins is greatly impacted by Si/Al₂ ratio as shown in Figures 7 through 10. With increasing Si/Al₂ ratios from 80 to 600, the activities in producing ethylene and propylene are adversely impacted, requiring significantly higher temperature to trigger the light olefin production.

[0086] On the other hand, EDA/TPA MFI materials of the instant invention are geared toward ethylene and propylene production. They have distinctly higher activity in producing ethylene and propylene, are relatively insensitive to Si/Al₂ of 100 to 600 as shown in Figures 7 and 9. We conceive that ethylene and propylene may be maximized by combining EDA/TPA-MFI materials of the instant invention with TPA-MFI of Comparative Examples. Without being bound by theory, it appears an increased amount of ethylene and propylene is attained by converting butylene and higher olefin to ethylene and propylene on active sites pertaining to EDA/TPA MFI as shown in Tables 6 to attain ethylene to propylene ratios greater than 0.4 ratio on a weight basis. Preferably, greater than 20% and less than 95% of TPA-MFI of Si/Al₂ less than 2500 is employed with the balance being EDA/TPA-MFI of Si/Al₂ ratios greater than 100. Most preferably, greater than 40% and less than 90% of TPA-MFI of Si/Al₂ less than 200 is employed with the balance being EDA/TPA-MFI of Si/Al₂ ratios greater than 200.

Tables 6.1. Modified n-Heptane Cracking Test of a Physical Mixture of EDA- and TPA-MFI

	C7 Conv			C2 to C4 olefins selectivity		
% EDA MFI / Temp °C	482.96	532.95	607.99	482.96	532.95	607.99
0	8.06	20.32	63.18	67.46	67.10	71.78
5	9.01	21.74	59.53	69.10	68.81	70.33
10	9.93	21.74	54.85	70.86	69.22	69.17
25	11.85	23.48	55.11	72.49	69.77	66.97
50	12.23	22.81	48.51	72.97	68.57	63.36
75	15.44	26.45	49.28	72.34	67.85	60.49
100	16.41	25.93	38.47	70.06	65.59	59.12

Tables 6.2. Modified n-Heptane Cracking Test of a Physical Mixture of EDA- and TPA-MFI

	C2= plus C3= selectivity			C2= to C3= w/w ratios		
% EDA MFI / Temp °C	482.96	532.95	607.99	482.96	532.95	607.99
0	34.39	36.78	44.26	0.08	0.12	0.22
5	39.56	43.02	48.88	0.24	0.34	0.49
10	41.78	44.87	50.13	0.28	0.41	0.61
25	45.83	49.30	52.76	0.40	0.60	0.93
50	49.78	52.46	53.04	0.56	0.85	1.36
75	52.95	55.89	53.45	0.73	1.16	1.95
100	54.86	56.96	53.84	0.92	1.49	2.55

[0087] When applying the modified paraffin cracking test to LTA-MFI of the Example 5 series, it was noted that at elevated temperatures of 600°C, materials of the instant invention (LTA-derived MFIs) in Examples 5.1, 5.2 exhibited higher C₂-C₄ olefin and lower methane, lower C₆-C₉ non-aromatics and lower aromatics than materials of Comparative Examples 5.3, 5.4, 5.5, see Table 7. The constraint active sites derived by using zeolite LTA as the aluminum

source in the syntheses appear to lower the cracking activities at lower temperatures consistent with lower ortho- to para-xylene uptake ratios. However, at elevated temperatures of around 600°C, cracking to olefin activities have caught up, while H₂ transfer reactions for light paraffin and aromatics remained suppressed.

Table 7. Modified n-Heptane Cracking Test of LTA-MFIs

	Example 5.1			Comparative Ex. 5.3			Comparative Ex. 5.4			Comparative Ex. 5.5		
Temperature °C	482	532	607	482	532	607	482	532	607	482	532	607
C1	2.4	3.8	6.0	4.4	6.7	8.0	4.6	6.5	7.9	4.0	5.6	7.1
C2=	9.2	14.1	24.9	14.0	20.3	29.2	13.9	20.2	29.3	12.4	18.1	28.1
C3=	20.4	27.7	29.1	22.1	25.0	21.0	22.4	25.0	20.3	22.6	26.9	23.6
C4=	9.5	11.0	6.1	8.6	6.6	2.3	8.9	6.8	2.2	9.6	8.7	3.1
C2-C3=	29.5	41.8	53.9	36.1	45.3	50.2	36.3	45.1	49.6	35.0	45.0	51.7
C2-C4=	39.1	52.8	60.0	44.7	51.9	52.5	45.2	51.9	51.7	44.5	53.7	54.8
C2=C3= sel,%	40.9	46.4	54.1	39.7	45.6	50.3	39.6	45.5	49.6	40.1	46.2	51.7
n-heptane conv, %	72.2	90.2	99.8	91.0	99.2	99.8	91.7	99.0	100.0	87.2	97.3	100.0
C2-C5P	22.5	22.6	15.4	28.2	22.4	13.6	27.4	21.3	12.4	26.1	21.5	12.8
C6-C9 NA	3.5	5.0	8.2	4.5	7.3	11.4	5.2	8.1	12.6	4.5	6.9	11.4
Aromatics	4.2	5.4	9.3	8.4	10.2	13.6	8.7	10.5	14.5	7.3	8.9	13.0

EXAMPLE 8

[0088] Procedure for methanol conversion tests. A catalyst loading of 325 mg sized to 40x60 mesh is first pretreated at 500°C in a flowing N₂ for 30 minutes. The catalytic performance is evaluated at one atmosphere pressure and a constant temperature of 450°C with a constant N₂ flow at 135 ml/minute passing through a methanol saturator controlled at 15°C. GC method is set up to capture light paraffin and olefin, benzene, toluene, xylene isomers/ethylbenzene and heavier aromatics.

[0089] As shown in Table 8, during methanol conversion, MFIs of the instant invention in the calcined state have consistently higher initial ethylene and aromatics versus comparative examples, despite having in general lower total olefin (C₂=-C₅=). Among the Examples of the instant invention, C₂-C₅ olefin yields increase and the stability improves with increased Si/Al ratios. However, total C₂-C₅ olefin yields and the total olefin stability are in general no better than those of comparative examples. Conversely, upon steaming, MFIs of the instant invention exhibited higher total olefin (C₂=-C₅=) selectivity with comparable lighter olefins (C₂=-C₃=), aromatics, along with comparable to higher ethylene yields and activity for hydrocarbons formation as shown in Table 9. Furthermore, the stability is vastly improved. The performance

is further illustrated in Figures 11-17. For MFIs of the instant invention, the stability of methanol conversion to lighter olefins (C2-C3) reaction improves as $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios increase or with hydrothermal (steam) treatments, and the MFIs of the instant invention at high $\text{SiO}_2/\text{Al}_2\text{O}_3$ (by 160 or higher) or after hydrothermal treatment have comparable stability and C2-C3 olefin yield in MTO reaction to that of comparative examples.

[0090] The same observation on stability improvement is also found on the conversion of methanol to aromatics (MTA) in the same evaluation test, but samples showed difference on aromatic yield. As shown in Figures 14 and 15, the MTA reaction by MFIs of the instant invention becomes stable as $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios increase or after the samples are subject to hydrothermal treatment, but the amounts of aromatics exceed those of comparative examples at high $\text{SiO}_2/\text{Al}_2\text{O}_3$ (by 160 or higher) or at medium-to-high $\text{SiO}_2/\text{Al}_2\text{O}_3$ (above 80) after hydrothermal treatment. Among the aromatics produced, the amounts of xylenes produced by MFIs of the instant invention are higher and strikingly contain a significantly higher proportion of para-xylene above 60% of xylenes as shown in Figures 16-17. The increasing participation of active sites in tortuous via straight channels controlling the location of active sites and by reducing carbonaceous deposition at the interactions may result in the desirable stable para-xylene production.

Table 8. EDA/TPA MFIs vs. TPA-MFI (580°C calcination) - Methanol to Olefin and Aromatics

	Example 1		comparative EX 1.1		Example 2		comparative EX 2.1		Example 3		comparative EX 3.1	
HOS	1.2	5.3	1.2	5.3	1.2	5.3	1.2	5.3	1.2	5.3	1.2	5.3
MeOH	0.0	23.6	0.0	0.0	2.9	14.2	0.0	0.0	0.1	0.4	0.0	0.0
DME	0.0	72.1	0.0	0.0	1.0	23.9	0.0	0.0	0.0	0.0	0.0	0.0
C1	5.8	1.7	2.3	3.6	4.7	4.1	0.4	0.7	1.3	1.7	0.4	0.5
C2=	16.2	0.5	13.6	14.6	13.0	7.6	10.1	10.2	9.6	9.4	5.0	6.0
C3=	29.0	0.2	17.4	18.5	31.8	19.5	44.6	44.4	44.2	42.6	47.8	46.7
C2-C5=	58.7	0.6	42.8	44.3	64.9	41.1	79.3	78.3	78.6	77.0	80.5	79.0
NA unknown	2.1	0.0	2.3	2.9	7.3	6.4	4.4	4.2	5.1	6.4	5.4	5.1
C2-C5P	12.2	0.0	31.4	28.6	7.8	4.3	14.4	14.0	10.4	9.7	12.5	13.8
Aromatics	21.3	0.3	21.2	20.6	11.1	6.6	1.5	2.7	4.3	4.4	0.9	1.5

Table 9. EDA/TPA MFIs vs. TPA-MFI (40% steam/650°C) - Methanol to Olefin and Aromatics

	Example 1		comparative EX 1.1		Example 2		Example 3		comparative EX 3.1	
HOS	1.2	5.3	1.2	5.3	1.2	5.3	1.2	5.3	1.2	5.3
MeOh	3.3	1.5	1.9	0.1	0.4	0.1	0.5	0.6	5.7	6.5
DME	0.9	0.2	0.4	0.0	0.0	0.0	0.0	0.0	2.6	3.0
C1	2.4	1.9	0.8	0.6	2.9	2.6	0.5	0.4	0.3	0.3
C2=	10.6	10.5	10.4	11.3	13.1	13.1	6.0	5.7	4.8	4.6
C3=	32.0	33.4	29.4	28.3	34.2	34.4	41.3	41.1	39.3	38.6
C2=C3=	42.6	43.9	39.8	39.6	47.3	47.5	47.3	46.8	44.1	43.2
C2=C5=	63.8	65.4	57.2	54.5	67.3	67.3	72.3	71.7	70.4	69.0
NA										
unknown	9.4	8.6	8.9	7.8	5.9	5.1	7.8	8.3	11.9	12.2
C2-C5P	12.1	13.0	23.2	26.5	13.3	13.8	14.5	14.4	8.0	7.7
Aromatics	7.5	9.1	7.3	10.1	10.0	10.8	4.0	4.1	0.9	0.9

[0091] To further illustrate the utility of active sites located in the constrained environment, the methanol conversion test is modified to obtained performance at earlier times on stream comparable to contact times representative of processes such as fluidized beds, riser and etc. The modified methanol conversion test involves the same 500°C, 30-minutes N₂ pretreatment procedure and measures performances at temperatures of 450°C. Methanol feed is still introduced via flowing N₂ at 135 ml/minute through a saturator of liquid normal heptane controlled at 15°C, but the catalyst is only exposed to methanol vapor feed for 5 minutes before GC sampling of product and flow is switched to pure N₂ immediately afterwards, and catalyst stays in pure N₂ flow at 135ml/min during transition to the next sampling and GC injection. The contact in the modified methanol conversion test corresponds to a catalyst to feed ratios on a wight basis from 1 to 10. As shown in Table 10, example MFIs of the instant invention made using zeolite LTA as the aluminum source gave stable methanol conversion activity, higher total olefin, higher ethylene, higher propylene, comparable methane but lower aromatics and lower C2-C5 paraffin in comparison with comparative example MFIs made using liquid sodium aluminate.

Table 10. Modified Methanol Conversion Tests of LTA-MFIs

	Example 5.1		Example 5.2		Comparative Ex. 5.4		Comparative Ex. 5.5	
HOS	1.4	6.9	1.4	6.9	1.4	6.9	1.4	6.9
MeOH	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0
DME	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C1	1.3	1.6	1.2	1.7	0.8	1.3	0.9	2.1
C2=	18.1	18.2	16.1	15.6	14.9	14.3	14.0	13.4
C3=	23.8	23.8	23.8	24.0	19.1	18.4	18.2	17.5
C2-C5=	55.3	54.9	52.4	52.2	46.6	44.7	44.6	42.8
NA unknown	2.0	2.0	2.2	2.5	2.2	2.5	2.6	2.5
C2-C5P	25.4	25.3	27.8	27.0	31.9	31.6	32.7	32.1
Aromatics	15.8	16.0	16.2	16.2	18.4	19.8	19.0	20.5

EXAMPLE 9

[0092] DFT calculations were carried out in the Vienna ab initio Simulation Package (G. Kresse and J. Hafner, “Ab initio molecular dynamics for liquid metals”, Phys. Rev. B, 47, 558 (1993); G. Kresse and J. Furthmüller, “Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set”, Comput. Mat. Sci., 6, 15 (1996)). The MFI framework was modeled by a supercell of $20.09 \text{ \AA} \times 17.74 \text{ \AA} \times 13.14 \text{ \AA}$ with 192 O and 96 Si atoms. The acid site was created by replace one Si atom with Al. The PBE density functional (J. P. Perdew, K. Burke, and M. Ernzerhof, “Generalized gradient approximation made simple”, Phys. Rev. Lett., 77, 3865 (1996)) with the Van der Waals correction in the D2 method of Grimme (S. Grimme, “Semiempirical GGA-type density functional constructed with a long-range dispersion correction”, J. Comp. Chem., 27, 1787 (2006)) was used to model electronic exchange and correlation. Vanderbilt pseudo-potentials constructed within the projected augmented wave framework were used for core electrons (G. Kresse and D. Joubert, “From ultrasoft pseudopotentials to the projector augmented-wave method”, Phys. Rev. B, 59, 1758 (1999)), with a plane wave basis set with an energy cutoff of 400 eV for the valence electrons, implemented in a $1 \times 1 \times 1$ k-point sampling of the Brillouin zone that is be sufficient. Geometry optimization were considered converged when the force dropped below $0.01 \text{ eV/\AA}$ on each atom. A Gaussian type of smearing in the amount of 0.05 eV was applied to speed up

the convergence in the electronic state optimization. The projection operators are evaluated in real-space, with fully automatic optimization of projection operators. The adsorption (or binding) energy, E_{ads} , for a xylene molecule on a site is calculated as follows in Eq. 1.

$$\text{Equation 1: } E_{\text{ads}} = E_{(\text{xylene/surface})} - E_{(\text{surface})} - E_{(\text{xylene})}$$

[0093] The diffusion pathway was optimized with the nudged elastic band method (G. Henkelman and H. Jónsson, "Improved tangent estimate in the nudged elastic band method for finding minimum energy paths and saddle points", J. Chem. Phys., 113, 9978 (2000)) with a force tolerance of 0.01 eV/Å. The diffusion barrier is calculated as the energy gap between the transition state of diffusion with the highest energy and the adsorption state with the lowest energy along the diffusion pathway. Results of the calculation is listed in Table 2 previously.

SPECIFIC EMBODIMENTS

[0094] While the following is described in conjunction with specific embodiments, it will be understood that this description is intended to illustrate and not limit the scope of the preceding description and the appended claims.

- 5 [0095] A first embodiment of the invention is an improved MFI zeolite composition in the calcined and ion-exchanged form comprising a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of from 60 to 600 and having low aluminum occupation at intersection sites characterized by an ortho-xylene to para-xylene uptake ratio of no less than 0.1 and no more than 0.55. The ortho-xylene to para-xylene uptake ratio of no less than 0.1 and no more than 0.50. An embodiment of the invention is one, any or
- 10 all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the ortho-xylene to para-xylene uptake ratio is less than 0.4. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the ortho-xylene to para-xylene uptake ratio is less than 0.3. An embodiment of the invention is one, any or all of prior embodiments in this paragraph
- 15 up through the first embodiment in this paragraph further comprising a micropore volume as determined by N_2 BET of from 0.11 mL/g to 0.135 mL/g. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio is from 90 to 600. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this
- 20 paragraph further comprising post-synthetic hydrothermally treatment at temperature of from 650°C to 800°C at 40 to 100% steam for a time of 12 to 20 hours. An embodiment of the

invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph further characterized by a heptane conversion of greater than 10 wt% and a selectivity to ethylene and propylene of greater than 40 wt% in the modified paraffin cracking test. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph further characterized by an ethylene molar percentage of greater than 40% out of the combined ethylene, propylene and butylenes formed in the modified paraffin cracking test. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph further characterized by a selectivity to ethylene and propylene of greater than 5% in the modified paraffin cracking test wherein the hydrothermal treatment temperature was greater than 750°C. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph further characterized by an ethylene to light olefin ratio of greater than 0.4 in the modified paraffin cracking test. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph further comprising formulating the improved MFI zeolite into a catalyst via a forming process comprising extrusion, pelletization, marumerization, oil dropping, spray drying, and mixtures thereof.

[0096] A second embodiment of the invention is a process for conversion of hydrocarbon to product comprising contacting a feedstream comprising hydrocarbon with a catalyst; converting the feedstream to a product at reaction conditions, and recovering a product comprising light olefins, aromatics, or mixtures thereof, wherein the catalyst comprises an improved MFI zeolite comprising in the calcined and ion-exchanged form a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of from 60 to 600, and having low aluminum occupation at intersection sites characterized by an ortho-xylene to para-xylene uptake ratio of no less than 0.1 and no more than 0.55. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the product comprises one or more xylenes. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the product comprises para-xylene. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the para-xylene is greater than 24% of the xylenes. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the

improved MFI zeolite further comprises a micropore volume as determined by N₂ BET of from 0.11mL/g to 0.135mL/g. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the product comprises ethylene and propylene. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the feedstream comprises a diluent selected from the group consisting of nitrogen, steam, methane, ethane, hydrogen, and mixtures thereof. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the hydrocarbon comprises naphtha. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the hydrocarbon comprises vacuum gas oil. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the contacting occurs in a fluidized bed reactor. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the ortho-xylene to para-xylene uptake ratio is less than 0.4. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the ortho-xylene to para-xylene uptake ratio is less than 0.3.

[0097] A third embodiment of the invention is a process for conversion of oxygenate to product comprising contacting a feedstream comprising oxygenate with a catalyst; converting the feedstream to a product at reaction conditions, and recovering a product comprising light olefins, aromatics, or mixtures thereof, wherein the catalyst comprises an improved MFI zeolite comprising in the calcined and ion-exchanged form a SiO₂/Al₂O₃ ratio of from 60 to 600, and having low aluminum occupation at intersection sites characterized by an ortho-xylene to para-xylene uptake ratio of no less than 0.1 and no more than 0.55. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph wherein the product comprises one or more xylenes. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph wherein the product comprises para-xylene. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph wherein the para-xylene is greater than 24% of the xylenes. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up

through the second embodiment in this paragraph wherein the product comprises ethylene and propylene. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph wherein the feedstream comprises a diluent selected from the group consisting of nitrogen, steam, methane, ethane, hydrogen, and mixtures thereof. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph wherein the contacting occurs in a fluidized bed reactor. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph wherein the oxygenate comprises methanol. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph wherein the ortho-xylene to para-xylene uptake ratio is less than 0.4. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph wherein the ortho-xylene to para-xylene uptake ratio is less than 0.3. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph wherein the improved MFI zeolite further comprises a micropore volume as determined by N₂ BET of from 0.11mL/g to 0.135mL/g.

[0098] Without further elaboration, it is believed that using the preceding description that one skilled in the art can utilize the present invention to its fullest extent and easily ascertain the essential characteristics of this invention, without departing from the spirit and scope thereof, to make various changes and modifications of the invention and to adapt it to various usages and conditions. The preceding preferred specific embodiments are, therefore, to be construed as merely illustrative, and not limiting the remainder of the disclosure in any way whatsoever, and that it is intended to cover various modifications and equivalent arrangements included within the scope of the appended claims.

[0099] In the foregoing, all temperatures are set forth in degrees Celsius and, all parts and percentages are by weight, unless otherwise indicated.

CLAIMS:

1. An improved MFI zeolite composition in the calcined and ion-exchanged form comprising:
 - 5 a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of from 60 to 600, and
having low aluminum occupation at intersection sites characterized by an ortho-xylene to para-xylene uptake ratio of no less than 0.1 and no more than 0.55.
 2. The zeolite of claim 1 further comprising a micropore volume as determined by N_2 BET of from 0.11 mL/g to 0.135 mL/g.
 - 10 3. The zeolite of claim 1 wherein the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio is from 90 to 600.
 4. The zeolite of claim 1 further comprising post-synthetic hydrothermal treatment at a temperature of from 650°C to 800°C at 40% steam for a time of 12 hours.
 5. The zeolite of claim 1 further characterized by a heptane conversion of greater than 10 wt% and a selectivity to ethylene and propylene of greater than 40 wt% in the
15 modified paraffin cracking test.
 6. The zeolite of claim 5 further characterized by an ethylene molar percentage of greater than 40% out of the combined ethylene, propylene and butylenes formed in the modified paraffin cracking test.
 7. The zeolite of claim 1 further comprising formulating the improved MFI zeolite
20 into a catalyst via a forming process comprising extrusion, pelletization, marumerization, oil dropping, spray drying, and mixtures thereof.
 8. The zeolite of claim 1 wherein the low aluminum occupation at intersection sites is characterized by an ortho-xylene to para-xylene uptake ratio of no less than 0.1 and no more than 0.50.
 - 25 9. The zeolite of claim 1 wherein the ortho-xylene to para-xylene uptake ratio is less than 0.4.
 10. The zeolite of claim 4 further characterized by a selectivity to ethylene and propylene of greater than 5% in the modified paraffin cracking test wherein the hydrothermal treatment temperature was greater than 750°C.

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