

BINDERLESS ZEOLITIC ADSORBENTS AND METHODS FOR
PRODUCING BINDERLESS ZEOLITIC ADSORBENTS

PRIORITY CLAIM OF EARLIER NATIONAL APPLICATION

[0001] This application claims priority to U.S. Application No. 62/272,522 filed
5 December 29, 2015.

FIELD

[0002] The present invention generally relates to binderless zeolitic adsorbents and methods for making the binderless adsorbents. More particularly, the invention relates to FAU type binderless zeolitic adsorbents and methods for making the FAU type binderless
10 adsorbents. The FAU type binderless adsorbents may be used for xylene separation and purification in selective adsorptive separation processes using binderless zeolitic adsorbents.

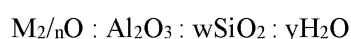
BACKGROUND

[0003] The simulated moving bed (SMB) adsorption process is used commercially in a number of large scale petrochemical separations to recover high purity para-xylene and meta-
15 xylene from mixed xylenes. As used herein, "mixed xylenes" refers to a mixture of C₈ aromatic isomers that includes ethyl benzene, para-xylene, meta-xylene, and ortho-xylene. High purity para-xylene and meta-xylene are used for the production of polyester fibers, resins and films.

[0004] The general technique employed in the performance of simulated moving bed
20 adsorptive separation processes is widely described and practiced. Generally, the process simulates a moving bed of adsorbent with continuous counter-current flow of a liquid feed over the adsorbent. Feed and products enter and leave adsorbent beds continuously, at nearly constant compositions. Separation is accomplished by exploiting the differences in affinity of the adsorbent for meta-xylene relative to the other C₈ aromatic isomers.

[0005] Typical adsorbents used in simulated moving bed adsorption processes generally
25 include crystalline aluminosilicate zeolites and can comprise both the natural and synthetic aluminosilicates. Suitable crystalline aluminosilicate zeolites for use as an adsorbent selective for meta-xylene include those having aluminosilicate cage structures in which alumina and

silica tetrahedra are intimately connected with each other in an open three dimensional crystalline network. The tetrahedra are cross linked by the sharing of oxygen atoms, with spaces between the tetrahedra occupied by water molecules prior to partial or total dehydration of the zeolite. The dehydration results in crystals interlaced with channels having
5 molecular dimensions. In a hydrated form the crystalline aluminosilicate zeolites are generally represented by the formula:



where “M” is a cation that balances the electrovalence of the tetrahedra and is generally referred to as an exchangeable cationic site, “n” represents the valence of the cation, “w”
10 represents the moles of SiO₂, and “y” represents the moles of water. Such crystalline aluminosilicate zeolites that find use as an adsorbent possess relatively well-defined pore structures. The exact type aluminosilicate zeolite is generally identified by the particular silica : alumina molar ratio and the pore dimensions of the cage structures.

[0006] Cations (M) occupying exchangeable cationic sites in the zeolitic adsorbent may
15 be replaced with other cations by ion exchange methods well known to those having ordinary skill in the field of crystalline aluminosilicates. Crystalline aluminosilicates, such as Zeolite Y with cations at the exchangeable cationic sites within the zeolite, are known to selectively adsorb meta-xylene in a mixture comprising at least one other C₈ aromatic isomer.

[0007] Generally, zeolitic adsorbents used in separative processes contain the zeolitic
20 crystalline material dispersed in an amorphous material or inorganic matrix, having channels and cavities therein which enable liquid access to the crystalline material. Silica, alumina or certain clays and mixtures thereof are typical of such inorganic matrix materials, which act as a “binder” to form or agglomerate the zeolitic crystalline particles that otherwise would comprise a fine powder. Agglomerated zeolitic adsorbents may thus be in the form of
25 particles such as extrudates, aggregates, tablets, macrospheres such as beads, granules, or the like.

[0008] The binder is typically inert and does not contribute to any selective adsorption. Efforts have been made to improve adsorbent productivity by increasing the selective part (zeolite volume) within adsorbents by converting the binder into selective zeolite in a
30 conversion process referred to as “zeolitization”, while maintaining the strength and macroporosity of the zeolitic adsorbent. This conversion process results in a “binderless” zeolitic adsorbent. While this conversion process has resulted in an increase in adsorbent

productivity, still further increases in process performance and decreases in operating costs for adsorptive separation processes are sought.

[0009] Accordingly, it is desirable to provide a binderless zeolitic adsorbent that decreases the amount of adsorbent and desorbent required to process a fixed amount of feed.

5 It is also desirable to provide a method for forming such a binderless adsorbent. Furthermore, other desirable features and characteristics of the present invention will become apparent from the subsequent detailed description of the invention and the appended claims, taken in conjunction with the background of the invention.

SUMMARY

10 **[0010]** The present invention provides a binderless zeolitic adsorbent and a method for producing the binderless zeolitic adsorbent.

[0011] A first embodiment of the invention is a binderless zeolitic adsorbent comprising a first FAU type zeolite having a silica to alumina molar ratio of from 3.0 to 6.0; a binder-converted FAU type zeolite having a silica to alumina molar ratio of from 2.0 to 6.0, wherein
15 the binder-converted FAU type zeolite may be 5-50% of the binderless zeolitic adsorbent; and cationic exchangeable sites within the binderless zeolitic adsorbent. 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 at least 95% of the binderless zeolitic adsorbent is FAU type zeolite. An embodiment of the invention is one, any or all of prior embodiments in
20 this paragraph up through the first embodiment in this paragraph, wherein at least 98% of the binderless zeolitic adsorbent is FAU type zeolite. 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 binder-converted FAU type zeolite may be 10-20% of the binderless zeolitic adsorbent. An embodiment of the invention is one, any or all of prior embodiments in
25 this paragraph up through the first embodiment in this paragraph, wherein the cationic exchangeable sites may be alkali/alkaline earth cations. 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 cationic exchangeable sites may be barium, potassium, sodium, or any combination of barium, potassium, or sodium. An embodiment of the invention is one, any or
30 all of prior embodiments in this paragraph up through the first embodiment in this paragraph, wherein the ion-exchangeable sites of the agglomerates comprises Na at cationic

exchangeable sites within the agglomerated FAU type zeolite adsorbent to at least 95% of the cationic exchangeable sites. 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 non-zeolitic binder comprises silica, alumina, or a combination of silica and alumina. 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 binder-converted FAU type zeolite has a silica to alumina molar ratio of 3.0 to 6.0. 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 binderless zeolitic adsorbent contains 1% to 7% of water.

- 10 **[0012]** A second embodiment of the invention is a method for producing a binderless zeolitic adsorbent comprising forming agglomerates having ion-exchangeable sites, the agglomerates formed from a FAU type zeolite having a silica to alumina molar ratio of from 3.0 to 6.0, a non-zeolitic binder comprising silica, alumina, or a combination of silica and alumina, and a forming aid, wherein agglomerates are formed from greater than 50% of the
- 15 FAU type zeolite; applying a thermal treatment to precondition the binder and dissipate the forming aid; applying a hydrothermal treatment with a solution containing at least one source of hydroxide to convert non-zeolitic material into FAU type zeolite material; and drying the binderless zeolitic adsorbent. 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
- 20 at least 95% of the binderless zeolitic adsorbent is FAU type zeolite. 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 at least 98% of the binderless zeolitic adsorbent is FAU type zeolite. 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 solution
- 25 containing hydroxide further comprises silicon, aluminum, or a mixture of both silicon and aluminum. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph, further comprising exchanging the ion-exchangeable sites. 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 drying the binderless zeolitic adsorbent assures that the binderless zeolitic adsorbent
- 30 contains 1% to 7% of water. 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

forming agglomerates further comprises agglomerates having a particle size in the range of 0.3 mm to 0.8 mm. 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 step of forming agglomerates comprises combining FAU type zeolite and kaolin clay binder in
5 amounts, respectively, of between 80 to 90 weight percent and between 10 and 20 weight percent of the agglomerated binderless FAU type zeolite adsorbent, and mixing with cornstarch in an amount of up to 5% by weight of the combined weight percent of the binder-converted FAU type zeolite and the FAU type zeolite. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in
10 this paragraph, wherein the step of forming agglomerates comprises forming agglomerates with FAU type zeolite having a silica to alumina molar ratio of 4.0 to 6.0. 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 step of exchanging the ion-exchangeable sites of the agglomerates comprises Na at cationic exchangeable sites within the agglomerated FAU
15 type zeolite adsorbent to at least 95% of the cationic exchangeable sites. 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 step of activating the agglomerates comprises heating the agglomerates to at least 625°C and the step of converting the meta-kaolin clay binder into binder-converted zeolite comprises caustic digesting the meta-kaolin clay binder
20 with an aqueous alkali metal hydroxide solution.

[0013] Additional objects, advantages and novel features of the examples will be set forth in part in the description which follows, and in part will become apparent to those skilled in the art upon examination of the following description or may be learned by production or operation of the examples. The objects and advantages of the concepts may be realized and
25 attained by means of the methodologies, instrumentalities and combinations particularly pointed out in the appended claims.

DEFINITIONS

[0014] As used herein, the term “stream” can include various hydrocarbon molecules, such as straight-chain, branched, or cyclic alkanes, alkenes, alkadienes, and alkynes, and
30 optionally other substances, such as gases, e.g., hydrogen, or impurities, such as metals, and sulfur and nitrogen compounds. The stream can also include aromatic and non-aromatic

hydrocarbons. Moreover, the hydrocarbon molecules may be abbreviated C_1 , C_2 , $C_3 \dots C_n$ where “n” represents the number of carbon atoms in the one or more hydrocarbon molecules. Furthermore, a superscript “+” or “-” may be used with an abbreviated one or more hydrocarbons notation, e.g., C_3^+ or C_3^- , which is inclusive of the abbreviated one or more hydrocarbons. As an example, the abbreviation “ C_3^+ ” means one or more hydrocarbon molecules of three and/or more carbon atoms.

[0015] As used herein, the term “zone” can refer to an area including one or more equipment items and/or one or more sub-zones. Equipment items can include one or more reactors or reactor vessels, heaters, exchangers, pipes, pumps, compressors, and controllers.

Additionally, an equipment item, such as a reactor, dryer, or vessel, can further include one or more zones or sub-zones.

[0016] As used herein, the term “weight percent” may be abbreviated “wt%”.

[0017] As used herein, the term “atomic ratio” may be used interchangeably with “mole ratio”.

[0018] As used herein, the term “FAU type” can refer to faujasite zeolites, such as

zeolites X and Y.

DETAILED DESCRIPTION

[0019] The following detailed description of the invention is exemplary in nature and is not intended to limit the invention or the application and uses of the invention. Also, there is no intention to be bound by any theory presented in the preceding background of the invention or the following detailed description of the invention.

[0020] A first embodiment of the invention is a binderless zeolitic adsorbent comprising a first FAU type zeolite having a silica to alumina molar ratio of from 3.0 to 6.0; a binder-converted FAU type zeolite having a silica to alumina molar ratio of from 2.0 to 6.0, wherein the binder-converted FAU type zeolite may be 5-50% of the binderless zeolitic adsorbent; and cationic exchangeable sites within the binderless zeolitic adsorbent. 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 at least 95% of the binderless zeolitic adsorbent is FAU type zeolite. 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 at least 98% of the binderless zeolitic adsorbent is FAU type zeolite. 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 binder-converted FAU type zeolite may be 10-20% of the binderless zeolitic adsorbent. 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 cationic exchangeable sites may be alkali/alkaline earth cations. 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 cationic exchangeable sites may be barium, potassium, sodium, or any combination of barium, potassium, or sodium. 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 ion-exchangeable sites of the agglomerates comprises Na at cationic exchangeable sites within the agglomerated FAU type zeolite adsorbent to at least 95% of the cationic exchangeable sites. 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 non-zeolitic binder comprises silica, alumina, or a combination of silica and alumina. 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 binder-converted FAU type zeolite has a silica to alumina molar ratio of 3.0 to 6.0. 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 binderless zeolitic adsorbent contains 1% to 7% of water.

[0021] A second embodiment of the invention is a method for producing a binderless zeolitic adsorbent comprising forming agglomerates having ion-exchangeable sites, the agglomerates formed from a FAU type zeolite having a silica to alumina molar ratio of from 3.0 to 6.0, a non-zeolitic binder comprising silica, alumina, or a combination of silica and alumina, and a forming aid, wherein agglomerates are formed from greater than 50% of the FAU type zeolite; applying a thermal treatment to precondition the binder and dissipate the forming aid; applying a hydrothermal treatment with a solution containing at least one source of hydroxide to convert non-zeolitic material into FAU type zeolite material; and drying the binderless zeolitic adsorbent. 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 at least 95% of the binderless zeolitic adsorbent is FAU type zeolite. 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 at least 98% of the binderless zeolitic adsorbent is FAU type zeolite. 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 solution containing hydroxide further comprises silicon, aluminum, or a mixture of both silicon and aluminum. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph, further comprising

5 exchanging the ion-exchangeable sites. 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 drying the binderless zeolitic adsorbent assures that the binderless zeolitic adsorbent contains 1% to 7% of water. An embodiment of the invention is one, any or all of prior

10 embodiments in this paragraph up through the second embodiment in this paragraph, wherein forming agglomerates further comprises agglomerates having a particle size in the range of 0.3 mm to 0.8 mm. 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 step of forming agglomerates comprises combining FAU type zeolite and kaolin clay binder in amounts, respectively, of between 80 to 90 weight percent and between 10 and 20 weight

15 percent of the agglomerated binderless FAU type zeolite adsorbent, and mixing with cornstarch in an amount of up to 5% by weight of the combined weight percent of the binder-converted FAU type zeolite and the FAU type zeolite. 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 step of forming agglomerates comprises forming agglomerates

20 with FAU type zeolite having a silica to alumina molar ratio of 4.0 to 6.0. 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 step of exchanging the ion-exchangeable sites of the agglomerates comprises Na at cationic exchangeable sites within the agglomerated FAU type zeolite adsorbent to at least 95% of the cationic exchangeable sites. An embodiment of

25 the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph, wherein the step of activating the agglomerates comprises heating the agglomerates to at least 625°C and the step of converting the meta-kaolin clay binder into binder-converted zeolite comprises caustic digesting the meta-kaolin clay binder with an aqueous alkali metal hydroxide solution.

30 **[0022]** The preferred class of zeolite of the instant invention is faujasite, including both synthetic X and Y types. Most preferred is the Y type as disclosed generally in U.S. Pat. No. 3,130,007, incorporated herein by reference. The crystals of zeolite Y are basically three

dimensional frameworks of SiO_4 and AlO_4 tetrahedra crosslinked by sharing of oxygen atoms. The electrovalence of each tetrahedron containing aluminum is balanced by the presence in the aluminosilicate framework of a cation such as an alkali metal ion. The void spaces in the framework are occupied by water molecules.

5 **[0023]** In one embodiment, the method for preparing the FAU-type zeolite begins with the formation of adsorbent agglomerates comprised of the Zeolite Y and inert binder. The Zeolite Y is agglomerated into adsorbent beads using the inert binder by mixing at ambient temperature with water. In a preferred embodiment, the inert binder comprises kaolin clay with a silica: alumina molar ratio in the range of 2.0 to 2.2, preferably 2.0. Kaolin clay is
10 available from U.S. Silica Co., Berkeley Springs, WV, for example. The beads may be comprised of from 80 to 90 wt% of Zeolite Y and 10 to 20 wt% of kaolin clay binder (on a volatile-free basis). The kaolin clay binder holds the starting zeolite powder together to form adsorbent beads with a particle size in the range of 0.3 mm to 0.8 mm and having increased mechanical strength as shown by water attrition tests as hereinafter described. While
15 agglomerates in the form of beads have been described, the invention is not so limited. The Zeolite Y may be agglomerated into other forms of particles such as extrudates, aggregates, tablets, macrospheres, granules, or the like.

[0024] In an exemplary embodiment, additives, such as cornstarch, may also be mixed with the Zeolite Y and inert binder during the agglomerate-forming step. Cornstarch may be
20 added in an amount from 0 to 5.0 wt% (on a volatile-free basis) of the total combined weight of the binder-converted zeolite portion and the starting Zeolite Y for purposes as hereinafter described. Other additives may include polymers and fibers.

[0025] To convert the kaolin clay binder to a binder-converted zeolite, the agglomerates are activated at 625°C or higher to convert the kaolin clay binder into meta-kaolin clay
25 binder. The kaolin clay binder undergoes an endothermic dehydroxylation reaction and converts to a disordered meta-kaolin phase. If cornstarch was previously added, it burns off during this step.

[0026] Next, the meta-kaolin clay binder is then caustic-digested at a temperature of 88°C by a solution containing sodium silicate and sodium hydroxide and the meta-kaolin binder is
30 converted to binder-converted zeolite having a silica: alumina molar ratio in the range of from 2.0 to 6.0. The conversion results in an increase in selective pore volume as determined through McBain O_2 capacity measurements at liquid O_2 temperature. Such measurement is

described in ZEOLITE MOLECULAR SIEVES: STRUCTURE, CHEMISTRY AND USE by Donald W. Breck, John Wiley & Sons, 1974. Thus, the adsorbent beads comprise substantially 100% zeolite with negligible inert binder, forming “binderless” zeolitic adsorbent beads. The adsorbent beads comprise a Zeolite Y portion (from the starting Zeolite Y) with a silica:

5 alumina molar ratio in the range of 3.0 to 6.0, and the binder-converted zeolite portion with a silica: alumina molar ratio in the range of 2.0 to 6.0. While the conversion of a kaolin clay binder to binder-converted zeolite has been described, the invention is not so limited. For example, other clay binders may be converted to a binder-converted zeolite. Non-limiting examples include clays belonging to the halloysite family. In addition, while the use of a
10 sodium hydroxide solution has been described as the caustic solution for binder conversion, the invention is not so limited. In addition to sodium hydroxide, other aqueous alkali metal hydroxide solutions may be used for conversion. Non-limiting examples include a solution of potassium hydroxide or a mixture of sodium hydroxide and potassium hydroxide.

[0027] Next, the FAU type binderless zeolitic adsorbent is dried to fix its water content.
15 In this regard, the FAU type binderless zeolitic adsorbent is activated by washing and drying the beads to 1 to 7% Loss on Ignition (LOI at 900°C). The drying is generally carried out by thermal activation, preferably at temperatures of from 175°C to 250 °Celsius. The water content of the adsorbent is expressed herein in terms of the recognized LOI test at 900°C. The LOI test is described in UOP Test Method No. UOP954-03 (available through ASTM
20 International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA, 19428-2959 USA).

[0028] As noted above, cornstarch may be added to the Zeolite Y and the clay binder mixture during the bead-forming stage. The addition of cornstarch increases the meso- and macro- porosity of the adsorbent beads, as explained in more detail below. As used herein
25 and conventionally, “macro-pores” are defined as pores having a pore diameter greater than 50 nm and “meso-pores” are defined as pores having a pore diameter between 2 and 50 nm. Macro- and meso-porosity facilitates conversion of the binder by permitting the sodium hydroxide conversion solution to flow throughout the binder. The macro- and meso-pores also help improve the mass transfer rate of the FAU type binderless zeolitic adsorbent.

30 **[0029]** The binderless adsorbents may be used for xylene separation and purification in selective adsorptive separation processes using binderless zeolitic adsorbents, such as purifying high purity paraxylene or meta-xylene. Non-limiting examples include: batch and

continuous operating modes; liquid phase and gas phase operations; fix-bed, moving bed, and simulated moving bed operations; and counter-current and co-current flows. In an exemplary embodiment, the binderless zeolitic adsorbent is used in counter-current, liquid phase, simulating moving bed, adsorptive separation processes for the recovery of meta-xylene from mixed xylenes. The adsorbent is selective for meta-xylene. The desorbent used for the SMB
5 process may comprise para-diethylbenzene, toluene, benzene, or indane.

EXAMPLES

[0030] The following example is intended to further illustrate the subject adsorbent. This illustration of an embodiment of the present disclosure is not meant to limit the claims of this
10 present disclosure to the particular details of these examples. These examples are based on engineering calculations and actual operating experience with similar processes. The following table illustrates five different compositions that were tested.

TABLE 1

NB #	Target Synthesis Composition (not including Y-54)	Target Converted Binder Si/Al ₂	XRD Crystallinity (%)	SF ₆ Capacity (wt%)	SF ₆ Crystallinity (%)	ICP Si/Al ₂
35709-82-3	Y-54 Powder		100	33.0	100	4.96
35709-91-UC	Unconverted extrudates		84	26.4	80	4.24
35709-91-3	Al ₂ O ₃ : 4.0 Na ₂ O : 9.65 SiO ₂ : 500 H ₂ O	5	96	32.2	98	
35709-91-4	Al ₂ O ₃ : 4.5 Na ₂ O : 10.45 SiO ₂ : 500 H ₂ O	5	99	32.0	97	4.98
35709-91-5	Al ₂ O ₃ : 3.0 Na ₂ O : 5.85 SiO ₂ : 500 H ₂ O	4	98	33.0	100	
35709-91-6	Al ₂ O ₃ : 3.0 Na ₂ O : 4.74 SiO ₂ : 500 H ₂ O	3.5	97	33.6	102	
35709-91-7	Al ₂ O ₃ : 3.0 Na ₂ O : 3.66 SiO ₂ : 500 H ₂ O	3	94	34.0	103	

[0031] 85 wt% Y-54 powder and 15 wt% kaolin clay were first extruded as 1/16" cylinders using 3 wt% CMC as extrusion aid. Extrudates were dried in an oven overnight at 100°C. Next, the extrudates were activated using the following steps: 2°C/minute ramp to 300°C and held for two hours followed with a 5°C/minute ramp to 675°C and held for three hours, and finally cool
5 down to 100°C at 10°C/minute. After the extrudates cooled to room temperature they were crushed and sized to 20/40 mesh. 10g of meshed extrudates were next treated with a solution that was prepared by targeting the following gel molar oxide ratio: Al_2O_3 : 10.45 SiO_2 : 4.5 Na_2O : 500 H_2O (including the binder composition but not the Y-54 powder). The solution was made up with 11.82g sodium silicate; 2.09g 50% NaOH solution; and 52.13g H_2O , and added to a glass
10 flask, covered and brought up to digestion temperature, 88 °C in a hot water bath. Once the solution was at temperature the meshed extrudates were added to the flask, which was again covered and placed back into the water bath. Finally, the water bath was covered, the shaker component started, and the program was set to remain at temperature for 20 hours and programmed to shut off automatically. Once cooled to room temperature, the flask's mother
15 liquor was decanted and the converted solid was washed with deionized water at ambient temperature until the wash water pH was <11. Samples were air-dried overnight at room temperature.

[0032] From the foregoing, it is to be appreciated that by converting the binder to zeolite, the gravimetric capacity of the adsorbent increases which allows more feed to be processed with a
20 given mass of adsorbent. Further, by converting a binder which is low in silica content, e.g. kaolin clay or alumina, to a zeolite that has a relatively high silica content, a large increase in volumetric capacity can be realized. This is due to the addition of the mass of silica and charge balancing cations while maintaining a constant volume of the formed adsorbent body. This increase in volumetric capacity allows significantly more feed to be processed with the same
25 volume of adsorbent.

TABLE 2

Adsorbent	MX/EB Sel	MX/PX Sel	MX/OX Sel	Delta W	Capacity	MX/OX Breathrough test Sel
35709-91 – UC (unconverted extrudate)	4.1	1.84	1.84	7.9	8.4	1.52
35709-94 (converted extrudate)	4.01	1.8	1.79	12.5	11.52	1.46

[0033] Pulse/dynamic test results of lab prepared sample is shown in Table 2. The data illustrates that the converted extrudate has surprisingly high capacity increase, by 37% over unconverted sample. This will translate to significant capacity and productivity improvement over existing MXSorbex product.

[0034] While at least one exemplary embodiment has been presented in the foregoing detailed description of the invention, it should be appreciated that a vast number of variations exist. It should also be appreciated that the exemplary embodiment or exemplary embodiments are only examples, and are not intended to limit the scope, applicability, or configuration of the invention in any way. Rather, the foregoing detailed description will provide those skilled in the art with a convenient road map for implementing an exemplary embodiment of the invention, it being understood that various changes may be made in the function and arrangement of elements described in an exemplary embodiment without departing from the scope of the invention as set forth in the appended claims and their legal equivalents.

SPECIFIC EMBODIMENTS

[0035] 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.

[0036] A first embodiment of the invention is a binderless zeolitic adsorbent comprising a first FAU type zeolite having a silica to alumina molar ratio of from 3.0 to 6.0; a binder-

converted FAU type zeolite having a silica to alumina molar ratio of from 2.0 to 6.0, wherein the binder-converted FAU type zeolite may be 5-50% of the binderless zeolitic adsorbent; and cationic exchangeable sites within the binderless zeolitic adsorbent. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first

5 embodiment in this paragraph, wherein at least 95% of the binderless zeolitic adsorbent is FAU type zeolite. 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 at least 98% of the binderless zeolitic adsorbent is FAU type zeolite. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph,

10 wherein the binder-converted FAU type zeolite may be 10-20% of the binderless zeolitic adsorbent. 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 cationic exchangeable sites may be alkali/alkaline earth cations. 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

15 the cationic exchangeable sites may be barium, potassium, sodium, or any combination of barium, potassium, or sodium. 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 ion-exchangeable sites of the agglomerates comprises Na at cationic exchangeable sites within the agglomerated FAU type zeolite adsorbent to at least 95% of the cationic exchangeable sites.

20 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 non-zeolitic binder comprises silica, alumina, or a combination of silica and alumina. 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 binder-converted FAU type zeolite has a silica to alumina molar ratio of 3.0 to 6.0.

25 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 binderless zeolitic adsorbent contains 1% to 7% of water.

[0037] A second embodiment of the invention is a method for producing a binderless zeolitic adsorbent comprising forming agglomerates having ion-exchangeable sites, the agglomerates

30 formed from a FAU type zeolite having a silica to alumina molar ratio of from 3.0 to 6.0, a non-

zeolitic binder comprising silica, alumina, or a combination of silica and alumina, and a forming aid, wherein agglomerates are formed from greater than 50% of the FAU type zeolite; applying a thermal treatment to precondition the binder and dissipate the forming aid; applying a hydrothermal treatment with a solution containing at least one source of hydroxide to convert

5 non-zeolitic material into FAU type zeolite material; and drying the binderless zeolitic adsorbent. 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 at least 95% of the binderless zeolitic adsorbent is FAU type zeolite. An embodiment of the invention is one, any or all of prior

10 embodiments in this paragraph up through the second embodiment in this paragraph, wherein at least 98% of the binderless zeolitic adsorbent is FAU type zeolite. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second

15 embodiment in this paragraph, wherein the solution containing hydroxide further comprises silicon, aluminum, or a mixture of both silicon and aluminum. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second

20 embodiment in this paragraph, wherein drying the binderless zeolitic adsorbent assures that the binderless zeolitic adsorbent contains 1% to 7% of water. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this

25 paragraph, wherein forming agglomerates further comprises agglomerates having a particle size in the range of 0.3 mm to 0.8 mm. 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 step of forming agglomerates comprises combining FAU type zeolite and kaolin clay binder in

30 amounts, respectively, of between 80 to 90 weight percent and between 10 and 20 weight percent of the agglomerated binderless FAU type zeolite adsorbent, and mixing with cornstarch in an amount of up to 5% by weight of the combined weight percent of the binder-converted FAU type zeolite and the FAU type zeolite. 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 step of forming agglomerates comprises forming agglomerates with FAU type zeolite having a silica to alumina molar ratio of 4.0 to 6.0. 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 step of exchanging the ion-exchangeable sites of the agglomerates comprises Na at cationic exchangeable sites within the agglomerated FAU type zeolite adsorbent to at least 95% of the cationic exchangeable sites. An embodiment of the invention is one, any or all of prior
5 embodiments in this paragraph up through the second embodiment in this paragraph, wherein the step of activating the agglomerates comprises heating the agglomerates to at least 625°C and the step of converting the meta-kaolin clay binder into binder-converted zeolite comprises caustic digesting the meta-kaolin clay binder with an aqueous alkali metal hydroxide solution.

[0038] Without further elaboration, it is believed that using the preceding description that
10 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
15 that it is intended to cover various modifications and equivalent arrangements included within the scope of the appended claims.

[0039] In the foregoing, all temperatures are set forth in degrees Celsius and, all parts and percentages are by weight, unless otherwise indicated.