

SELF-SUPPORTING STRUCTURES HAVING ACTIVE MATERIALS

CROSS-REFERENCE TO RELATED APPLICATIONS

5 [0001] This application claims priority to U.S. Provisional Patent Application number 62/437,327 titled "Self-Supporting Structures Having Active Materials," filed on December 21, 2016, and U.S. Provisional Patent Application number 62/585,574 titled "Self-Supporting Structures Having Active Materials," filed on November 14, 2017, having common inventors and assignee, the disclosure of which is incorporated by reference herein in its entirety.

10 [0002] This application is related to U.S. Provisional Patent Application number 62/437,319 titled "Self-Supporting Structures Having Active Materials," filed on December 21, 2016, the disclosure of which is incorporated by reference herein in its entirety.

FIELD

15 [0003] The present techniques relate to fabrication of self-supporting structures being open-celled and including active material. In particular, the self-supporting structures may be used in separation and/or catalysis processes, such as swing adsorption processes and other processes to enhance the recovery of hydrocarbons.

BACKGROUND

20 [0004] Processing techniques are useful in many industries and can typically be accomplished by flowing a mixture of fluids over an active material, such as a catalyst or adsorbent material, to provide the preferred product stream. For adsorption process, the adsorbent materials preferentially adsorbs one or more gas components, while not adsorbing one or more other gas components. The non-adsorbed components are recovered as a separate product. For catalytic processes, the catalyst is configured to interact with the components in the stream to increase the rate of a chemical reaction.

25 [0005] By way of example, one particular type of gas separation technology is swing adsorption, such as temperature swing adsorption (TSA), pressure swing adsorption (PSA), partial pressure purge swing adsorption (PPSA), rapid cycle pressure swing adsorption (RCPSA), rapid cycle partial pressure swing adsorption (RCPPSA), and not limited to but also combinations of the fore mentioned processes, such as pressure and temperature swing
30 adsorption. As an example, PSA processes rely on the phenomenon of gases being more readily adsorbed within the pore structure or free volume of an active material, such as an adsorbent material, when the gas is under pressure. That is, the higher the gas pressure, the

greater the amount of readily-adsorbed gas adsorbed. When the pressure is reduced, the adsorbed component is released, or desorbed from the adsorbent material.

[0006] The swing adsorption processes (e.g., PSA and TSA) may be used to separate gases of a gas mixture because different gases tend to fill the micropore of the adsorbent material to different extents. For example, if a gas mixture, such as natural gas, is passed under pressure through a vessel containing an adsorbent material that is more selective towards carbon dioxide than it is for methane, at least a portion of the carbon dioxide is selectively adsorbed by the adsorbent material, and the gas exiting the vessel is enriched in methane. When the adsorbent material reaches the end of its capacity to adsorb carbon dioxide, it is regenerated in a PSA process, for example, by reducing the pressure, thereby releasing the adsorbed carbon dioxide. The adsorbent material is then typically purged and repressurized. Then, the adsorbent material is ready for another adsorption cycle.

[0007] Typically, the structures used in catalytic processes and adsorption processes have a limited array of physical structure types. The active material are often structured into beads, granules, spheres or pellets using binders and processing techniques like extrusion or spray drying. The beads, granules, spheres or pellets are then packed together within a unit as a packed bed for the catalytic or adsorption processes. As a result, the conventional fabrication of catalysts or adsorbents, involve extrusions of small sphere-like active materials to be used in packed beds (e.g., spheres, pellets, lobes, etc.). However, the packed beds provide tortuous paths through the packed bed, which result in large pressure drops.

[0008] In other configurations, the structure may be an engineered structure, such as a monolith. In engineered structures, the active materials are coated onto substrates, such as a metal or ceramic monolith. The engineered structures provide substantially uniform flow paths, which lessen pressure drops as compared to packed beds. However, with these structures the majority of weight is inactive material that is used to form the underlying support structure.

[0009] As a result, typical fabrication approaches of structures involve extrusions of small sphere-like active materials to be used in packed beds (e.g., spheres, pellets, lobes, etc.), or the application of thin coatings of active material on monolith substrates (e.g., ceramic or metal monoliths). The packed beds have large pressure drops as compared with engineered structures. Also, the engineered structures include additional weight from structural support that is inactive material, which increases the size and weight of the structure.

[0010] Accordingly, there remains a need in the industry for apparatus, methods, and systems that provide enhancements in processes having self-supporting structures that include

active materials and may include complex geometries. Further, the present techniques provide enhancements by integrating self-supporting open-celled structures with adsorption or catalytic processes, such as swing adsorption processes to separate contaminants from a feed stream. Accordingly, the present techniques overcome the drawbacks of conventional structures in separation and/or catalysis processes.

SUMMARY OF THE INVENTION

[0011] In one embodiment, a processing unit is described. The processing unit includes a housing forming an interior region; a self-supporting structure disposed within the interior region, wherein the self-supporting structure has greater than 50% by weight of the active material in the self-supporting structure, wherein the self-supporting structure is an open-celled structure configured to provide one or more defined channels for fluid flow paths through the self-supporting structure; and a plurality of valves secured to the housing, wherein each of the plurality of valves is configured to control fluid flow along a flow path extending between the self-supporting structure and a location external to the housing.

[0012] In one or more embodiment, the processing unit may include various enhancements. For example, the processing unit may include two or more of the plurality of valves are operated via common actuation mechanism; the processing unit may be a cyclical swing adsorbent bed unit configured to remove contaminants from a gaseous feed stream that passes through the self-supporting structure; the self-supporting structure may have greater than 60% by weight of the active material in the self-supporting structure or the self-supporting structure may have greater than 70% by weight of the active material in the self-supporting structure; the self-supporting structure may have an inert support member (e.g., inorganic or inactive support member) coated by the active material in the self-supporting structure (e.g., inert with respect to the stream passing through the self-supporting structure or inert at operating conditions); may include a flow distributor disposed between the adsorbent bed and the plurality of valves; the housing may be configured to maintain a pressure from 5 pounds per square inch absolute (psia) and 1,400 psia; the self-supporting structure may have a layer of active material that is greater than 10 micrometers or may have a layer of active material that is greater than 100 micrometers; wherein the one or more defined channels comprise two or more channels that are substantially parallel and/or the self-supporting structure has a low thermal mass.

[0013] In yet another embodiment, a method for removing contaminants from a feed stream is described. The method comprises: a) performing one or more adsorption steps in an

adsorbent bed unit, wherein each of the one or more adsorption steps comprise: passing a gaseous feed stream through the self-supporting structure disposed in an interior region of a housing of the adsorbent bed unit to remove one or more contaminants from the gaseous feed stream, wherein the self-supporting structure has greater than 50% by weight of the active material in the self-supporting structure, wherein the self-supporting structure is an open-celled structure configured to provide one or more defined channels for fluid flow paths through the self-supporting structure; b) performing one or more regeneration steps, wherein each of the one or more regeneration steps comprise conducting away at least a portion of the one or more contaminants in a contaminant output stream; and c) repeating the steps a) to b) for at least one additional cycle.

[0014] Further, in one or more embodiment, the method for removing contaminants from a feed stream may include various enhancements. For example, the method may be a swing adsorption method and the cycle duration may be for a period greater than 1 second and less than 600 seconds or a period greater than 1 second and less than 300 seconds; wherein the performing one or more regeneration steps comprises performing one or more purge steps, wherein each of the one or more purge steps comprise passing a purge stream through the self-supporting structure to conduct away at least a portion of the one or more contaminants in the contaminant output stream; wherein the gaseous feed stream may be a hydrocarbon containing stream having greater than one volume percent hydrocarbons based on the total volume of the gaseous feed stream; wherein a feed pressure of the gaseous feed stream may be in the range between 400 pounds per square inch absolute (psia) and 1,400 psia; wherein performing the one or more adsorption steps may be configured to lower the carbon dioxide (CO₂) level to less than 50 parts per million volume; wherein performing the one or more adsorption steps may be configured to lower the water (H₂O) level to less than 105 parts per million volume; and/or the self-supporting structure has a low thermal mass.

[0015] In yet another embodiment, a method of manufacturing a processing unit is described. The method may include: creating a template for a self-supporting structure; disposing a mixture within the template, wherein the mixture has greater than 50% by weight of the active material in the self-supporting structure and the remaining mixture includes binder material; curing the template and the mixture to form a self-supporting structure that maintains a solid form; removing the template from the self-supporting structure, wherein the self-supporting structure is an open-celled structure configured to provide one or more defined channels for fluid flow paths through the self-supporting structure based on the template; and disposing the self-supporting structure within housing of a processing unit having an interior

region.

[0016] Moreover, in one or more embodiment, the method of manufacturing a processing unit may include various enhancements. For example, the method may include creating a three-dimensional model of the self-supporting structure having predetermined geometries for one or more defined channels in the through the self-supporting structure; may include creating a model of a template based on the three-dimensional model of the self-supporting structure; may include printing a three-dimensional template based on the model of the template; wherein removing the template from the self-supporting structure may further comprise heating the self-supporting structure and the template to melt or decompose the template and conduct away the melted template; may include vibrating the template and the mixture prior to curing the template and mixture to lessen any voids that may be formed between the template and mixture; wherein curing the template and the mixture may further comprise sintering the binder material and active material into a cohesive solid structure that is the self-supporting structure; and/or may include creating a plurality of valve ports into the housing; and securing a valve to the housing in each of the plurality of valve ports to form a plurality of valves, wherein each of the plurality of valves is configured to control fluid flow between the self-supporting structure and a location external to the housing.

[0017] Further still, in yet another embodiment, a method of manufacturing a processing unit is described. The method comprises: extruding a mixture into a monolith form comprising a plurality of substantially parallel channels, separated by thin walls, wherein the mixture has greater than 50% by weight of the active material in the self-supporting structure and the remaining mixture includes binder material; drying the monolith form; and calcining the monolith form from 400 °C to 800 °C to form a mechanically stable, active monolith form; wherein the plurality of substantially parallel channels have a cross sectional shape of a square, a circle, a triangular, or a hexagonal; wherein the cell density of the monolith form is in a range between 200 cells per square inch and 2,000 cells per square inch; and wherein the walls separating the plurality of substantially parallel channels have a thickness in the range between 40 micron to 1 millimeter.

BRIEF DESCRIPTION OF THE FIGURES

[0018] The foregoing and other advantages of the present disclosure may become apparent upon reviewing the following detailed description and drawings of non-limiting examples of embodiments.

[0019] Figure 1 is a flow diagram of a method for fabricating and using a self-supporting

structure in accordance with an embodiment of the present techniques.

[0020] Figures 2A, 2B and 2C are various diagrams of a mold, combined mold and mixture and resulting self-supporting structure in accordance with an embodiment of the present techniques.

5 [0021] Figures 3A, 3B and 3C are various diagrams of a mold, combined mold and mixture and resulting self-supporting structure in accordance with another embodiment of the present techniques.

[0022] Figures 4A, 4B and 4C are various diagrams of a mold, combined mold and mixture and resulting self-supporting structure in accordance with yet another embodiment of the
10 present techniques.

[0023] Figures 5A and 5B are various diagrams of a combined mold and mixture and resulting self-supporting structure in accordance with still yet another embodiment of the present techniques.

[0024] Figures 6A and 6B are various diagrams of a mold and a self-supporting structure
15 in accordance with another embodiment of the present techniques.

[0025] Figures 7A and 7B are various diagrams of two monolith structures in accordance with an embodiment of the present techniques.

[0026] Figure 8 is an exemplary diagram of an x-ray diffraction scan of the self-supporting structure.

20 [0027] Figure 9 is an exemplary SEM diagram of a self-supporting structure.

[0028] Figures 10A and 10B are exemplary SEM diagrams of a self-supporting structure.

[0029] Figure 11 is an exemplary diagram of overlay patterns that match 5A zeolites.

[0030] Figure 12 is a diagram of the weight loss for 3A, due to loss of adsorbed water, as a function of temperature.

25 [0031] Figures 13A to 13D are diagrams of various profiles.

[0032] Figure 14 is an exemplary diagram of self-supporting structure monolith testing.

[0033] Figures 15A and 15B are exemplary diagrams of polyethylene spheres used in self-supporting structure monoliths.

[0034] Figures 16A to 16D are exemplary diagrams of a permeance measurements in
30 accordance with an embodiment of the present techniques.

[0035] Figure 17 is an exemplary diagram of average pore diameter based on gas permeance measurements in accordance with an embodiment of the present techniques.

[0036] Figure 18 is an exemplary diagram of water breakthrough in accordance with an embodiment of the present techniques.

[0037] Figure 19 is a three-dimensional diagram of the swing adsorption system with six adsorbent bed units and interconnecting piping in accordance with an embodiment of the present techniques.

DETAILED DESCRIPTION OF THE INVENTION

[0038] Unless otherwise explained, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this disclosure pertains. The singular terms "a," "an," and "the" include plural referents unless the context clearly indicates otherwise. Similarly, the word "or" is intended to include "and" unless the context clearly indicates otherwise. The term "includes" means "comprises." All patents and publications mentioned herein are incorporated by reference in their entirety, unless otherwise indicated. In case of conflict as to the meaning of a term or phrase, the present specification, including explanations of terms, control. Directional terms, such as "upper," "lower," "top," "bottom," "front," "back," "vertical," and "horizontal," are used herein to express and clarify the relationship between various elements. It should be understood that such terms do not denote absolute orientation (e.g., a "vertical" component can become horizontal by rotating the device). The materials, methods, and examples recited herein are illustrative only and not intended to be limiting.

[0039] As used herein, "majority component" means greater than 50 % by weight.

[0040] As used herein, "open-celled" refers to structures having open channel networks, compared to extruded solid shapes, such as spheres or pellets. The open-celled structures include monoliths or other engineered structures that provide flow paths through channels or passages in the respective structure.

[0041] As used herein, "stream" refers to a fluid (e.g., solids, liquid and/or gas) being conducted through various equipment. The equipment may include conduits, vessels, manifolds, units or other suitable devices.

[0042] As used herein, volume percent is based on standard conditions. The standard conditions for a method may be normalized to the temperature of 0 °C (e.g., 32 °F) and absolute pressure of 100 kiloPascals (kPa) (1 bar).

[0043] The present techniques relate to the fabrication of self-supporting structures from active material, which may have complex geometries and be open-celled structures. In particular, the present techniques relate to enhancements in the self-supporting structures that

contain a majority of active material (e.g., greater than 50% by weight or greater than or equal to 60% by weight) to provide enhanced structures. The enhanced structures may provide flexibility through customizable configurations, which may enhance the flow paths and provide higher volumetric efficiency in the configurations, which are lighter than conventional structures. The self-supporting structures may be configured to have various defined channels to provide fluid flow paths through the structure.

[0044] The self-supporting structures may be useful in various chemical and engineering applications. The self-supporting structures of active material may be referred to engineered into various geometric structures. By way of example, certain methods may be enhanced with the active materials, such as adsorption and catalytic processes. In particular, a self-supporting structure may be used instead of a packed adsorbent bed, which have higher pressure drops and slower mass transfer rates. In the packed bed configurations, the pressure drops and mass transfer limitations do not permit or are inefficient in operating the adsorption or catalytic processes at rapid cycles. Further, large volume gas separation processes, which rely upon pressure swing adsorption and rapid cycling, involve self-supporting structures with low pressure drop and high volumetric efficiency. The present techniques may provide enhancements to the associated structures to enhance the respective method and associated economics.

[0045] The self-supporting structure may be fabricated from various techniques, such as intrusion and extrusion techniques. For example, the techniques may include intrusion processes that employs three-dimensional (3D) printing. The 3D printing approach may use templates to produce custom structures of active material (e.g., a zeolite) that is combined with a binder material. By using the templates, the self-supporting structure may be formed into complex geometries, which may be an open-celled structure configured to provide defined channels for fluid flow paths through the structure. As another example, an extrusion method may be employed to produce monolith structures composed of the active material combined with the binder material. Both fabrication methods may utilize active materials, such as active inorganic materials, that are stable to high temperature calcinations (e.g., equal to or greater than 500 °C) and combination of organic and inorganic binders.

[0046] By way of example, the present techniques may also utilize 3D printing techniques to design and produce custom self-supporting structures made of active materials. The use of 3D printing and intrusion methods provide geometric flexibility in the design of structures that may not be made using conventional extrusion methods. These structures may form an open-

celled structures, which are configured to provide defined channels for fluid flow paths through the respective structure. Further, engineering flexibility in the adsorbent material structures is also provided, which removes the use and reliance on a ceramic or metal substrate, which lessen the cost of fabricating the self-supporting structures, such as adsorbent beds.

- 5 **[0047]** The present techniques may also include an extrusion method to produce bulk monolith structures, which have the active material as the majority component. In contrast, conventional techniques involve applying a thin coating of active material to an inactive substrate, such as an inert ceramic or metal monolith substrates. The inactive substrate, which typically provides mechanical support for the thin coating of active material, is more than 90%
10 of the total weight of the self-supporting structure. Accordingly, the thin coating of active material in conventional self-supporting structures equal to or less than 10% of the total weight of the self-supporting structure.

- [0048]** In certain configurations, the self-supporting structure may include different combinations of active material and binder material. For example, the self-supporting structure
15 may be fabricated from a microporous zeolites, which may be the active material. In certain configurations, the active material may be greater than or equal to 25% by weight of the self-supporting structure; greater than or equal to 40% by weight of the self-supporting structure; greater than or equal to 50% by weight of the self-supporting structure; greater than or equal to 60% by weight of the self-supporting structure; or greater than or equal to 70% by weight of
20 the self-supporting structure; while the remaining portion may include binder material. In other configurations, the binder material may be less than 75% by weight of the self-supporting structure; less than 60% by weight of the self-supporting structure; less than 50% by weight of the self-supporting structure; less than 40% by weight of the self-supporting structure; or less than 30% by weight of the self-supporting structure; while the remaining portion may include
25 active material.

[0049] The self-supporting structure may include higher masses of active material per unit volume that is greater than conventional coating techniques. For example, the layer or thickness of active material that is greater than 10 micrometers, is greater than 100 micrometers or is greater than 200 micrometers.

- 30 **[0050]** The active materials may include one or more adsorbent materials in certain configurations to adsorb contaminants from the stream. By way of example, the active materials may include zeolites, aluminophosphate molecular sieves (e.g., AIPOs and SAPOs), ZIFs (zeolitic imidazolate frameworks (e.g., ZIF-7, ZIF-9, ZIF-8, ZIF-11, etc.) and carbons, as

- well as mesoporous materials, such as the amine functionalized MCM materials, SBA, KIT materials. Other example of active materials may include cationic zeolites, amine-functionalized mesoporous materials, stannosilicates, and/or carbons. In other configurations, the adsorbent materials may include zeolite type A (e.g., LTA structures), such as 3A, 4A, 5A and/or 13X (which are highly porous adsorbents that have a high affinity and high capacity to adsorb water, as well as other molecules that have dimensions small enough to fit into the uniform pores of these structures), 8-member ring zeolite materials (e.g., ZSM 58 and/or DDR).
- 5 [0051] In other configurations, the active material may include one or more catalytic materials that are configured to react with the components in the stream.
- 10 [0052] In addition, various enhancements in macro-pore engineering may be used to provide additional pores and porosity. In particular, polymer spheres may be added to the composition, which may be diminished or removed (e.g., a material that may be burn out) when calcination process is performed on the composition. These polymer spheres may be used to increase the system porosity and enhance the diffusional performance.
- 15 [0053] The binder materials may include organic and inorganic binders. The organic binder may include, for example, 2% aqueous solution of methyl cellulose derivatives. The inorganic binder material may include, for example, SiO₂ and/or clays. Silica particle diameter may be in the range between 25 nanometer and 1,000 nanometer and silica particles in a string of pearls configuration.
- 20 [0054] By way of example, a processing unit may include a housing forming an interior region; a self-supporting structure disposed within the interior region, wherein the self-supporting structure has greater than 50% by weight of the active material in the self-supporting structure, wherein the self-supporting structure is an open-celled structure configured to provide one or more defined channels for fluid flow paths through the self-supporting structure;
- 25 and a plurality of valves secured to the housing, wherein each of the plurality of valves is configured to control fluid flow along a flow path extending between the self-supporting structure and a location external to the housing. In various configurations, the processing unit may include two or more of the plurality of valves are operated via common actuation mechanism; the processing unit may be a cyclical swing adsorbent bed unit configured to remove contaminants from a gaseous feed stream that passes through the self-supporting structure; the self-supporting structure may have greater than 60% by weight of the active material in the self-supporting structure or the self-supporting structure may have greater than 70% by weight of the active material in the self-supporting structure; the self-supporting
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structure may have a support member coated by the active material in the self-supporting structure, for example, a washcoated ceramic or metal structure; may include a flow distributor disposed between the adsorbent bed and the plurality of valves; the housing may be configured to maintain a pressure from 5 pounds per square inch absolute (psia) and 1,400 psia; the self-supporting structure may have a layer of active material that is greater than 10 micrometers or
5 may have a layer of active material that is greater than 100 micrometers; wherein the one or more defined channels comprise two or more channels that are substantially parallel and/or the self-supporting structure has a low thermal mass.

[0055] As yet another example, a method for removing contaminants from a feed stream
10 may include: a) performing one or more adsorption steps in an adsorbent bed unit, wherein each of the one or more adsorption steps comprise: passing a gaseous feed stream through the self-supporting structure disposed in an interior region of a housing of the adsorbent bed unit to remove one or more contaminants from the gaseous feed stream, wherein the self-supporting structure has greater than 50% by weight of the active material in the self-supporting structure,
15 wherein the self-supporting structure is an open-celled structure configured to provide one or more defined channels for fluid flow paths through the self-supporting structure; b) performing one or more regeneration steps, wherein each of the one or more regeneration steps comprise conducting away at least a portion of the one or more contaminants in a contaminant output stream; and c) repeating the steps a) to b) for at least one additional cycle. In certain
20 configurations, the method may be a swing adsorption method and the cycle duration may be for a period greater than 1 second and less than 600 seconds or a period greater than 1 second and less than 300 seconds; wherein the performing one or more regeneration steps comprises performing one or more purge steps, wherein each of the one or more purge steps comprise passing a purge stream through the self-supporting structure to conduct away at least a portion
25 of the one or more contaminants in the contaminant output stream; wherein the gaseous feed stream may be a hydrocarbon containing stream having greater than one volume percent hydrocarbons based on the total volume of the gaseous feed stream; wherein a feed pressure of the gaseous feed stream may be in the range between 400 pounds per square inch absolute (psia) and 1,400 psia; wherein performing the one or more adsorption steps may be configured
30 to lower the carbon dioxide (CO₂) level to less than 50 parts per million volume; wherein performing the one or more adsorption steps may be configured to lower the water (H₂O) level to less than 105 parts per million volume; wherein the one or more defined channels comprise two or more channels that are substantially parallel and/or the self-supporting structure has a low thermal mass.

[0056] As yet another example, a method of manufacturing a processing unit may include: creating a template for a self-supporting structure; disposing a mixture within the template, wherein the mixture has greater than 50% by weight of the active material in the self-supporting structure and the remaining mixture includes binder material; curing the template and the mixture to form a self-supporting structure that maintains a solid form; removing the template from the self-supporting structure, wherein the self-supporting structure is an open-celled structure configured to provide one or more defined channels for fluid flow paths through the self-supporting structure based on the template; and disposing the self-supporting structure within housing of a processing unit having an interior region. In certain configurations, the method may include creating a three-dimensional model of the self-supporting structure having predetermined geometries for one or more defined channels through the self-supporting structure (e.g., the open-celled structure is configured to provide defined channels for fluid flow paths through the structure); may include creating a model of a template based on the three-dimensional model of the self-supporting structure; may include printing a three-dimensional template based on the model of the template; wherein removing the template from the self-supporting structure may further comprise heating the self-supporting structure and the template to melt or decompose the template and conduct away the melted template; may include vibrating the template and the mixture prior to curing the template and mixture to lessen any voids that may be formed between the template and mixture; wherein curing the template and the mixture may further comprise sintering the binder material and active material into a cohesive solid structure that is the self-supporting structure; and/or may include creating a plurality of valve ports into the housing; and securing a valve to the housing in each of the plurality of valve ports to form a plurality of valves, wherein each of the plurality of valves is configured to control fluid flow between the self-supporting structure and a location external to the housing.

[0057] Further still, in yet another configuration, a method of manufacturing a processing unit is described. The method comprises: extruding a mixture into a monolith form comprising a plurality of substantially parallel channels, separated by thin walls, wherein the mixture has greater than 50% by weight of the active material in the self-supporting structure and the remaining mixture includes binder material; drying the monolith form; and calcining the monolith form from 400 °C to 800 °C to form a mechanically stable, active monolith form; wherein the plurality of substantially parallel channels have a cross sectional shape that may be a square, a circle, a triangular, or a hexagonal; wherein the cell density of the monolith form is in a range between 200 cells per square inch and 2,000 cells per square inch (e.g., cross

sectional shape is along a plane that is perpendicular to the primary flow path for the feed stream through the self-supporting structure); and wherein the walls separating the plurality of substantially parallel channels have a thickness in the range between 40 micron to 1 millimeter. Further, the method may include disposing the self-supporting structure within housing of a processing unit having an interior region and/or may include creating a plurality of valve ports into the housing; and securing a valve to the housing in each of the plurality of valve ports to form a plurality of valves, wherein each of the plurality of valves is configured to control fluid flow between the self-supporting structure and a location external to the housing.

[0058] Beneficially, the present techniques provide self-supporting structures that may be utilized to provide various enhancements over conventional approaches. For example, the present techniques may provide structures that provide geometric design flexibility and provide custom structures and flow paths. The custom structures may be an open-celled structure configured to provide defined channels for fluid flow paths through the structure, which enhance the interaction of the active material with the fluid passing through the channels. Further, by utilizing the active material to form the self-supporting structure, the working capacity may be increased and volumetric efficiency may be enhanced, which may further lessen the size of the structure and associated weight of the structure. The lessening of the size and weight may also lessen the associated size of the equipment utilized with the housing that contains the self-supporting structure. The present techniques may be further understood with reference to the Figures 1 to 14 below.

[0059] Figure 1 is a flow diagram **100** of a method for fabricating and using a self-supporting structure in accordance with an embodiment of the present techniques. In this diagram **100**, the method includes fabricating a self-supporting structure including active material along with using the self-supporting structure. In particular, the method may include determining a configuration for the self-supporting structure, as shown in block **102**, creating a mold or template for the self-supporting structure, as shown in block **104**, producing the self-supporting structure as shown in blocks **106** and **108**, and forming a processing unit with the self-supporting structure and utilizing the self-supporting structure in processing of feeds, as shown in blocks **110** and **112**.

[0060] The method begins at block **102**. In block **102**, a configuration for a self-supporting structure is determined. This determination may involve modeling and identifying various aspects of the self-supporting structure to enhance process engineering selections, such as determining the mechanical features of the self-supporting structure, determining flow paths

(e.g., the level of tortuosity of the flow path) through the self-supporting structure, determining the cell size within the self-supporting structure, determining the pressure drop for flow through the self-supporting structure, determining the operating conditions that the self-supporting structure may be subject to during process operations (e.g., pressures, temperatures and stream compositions) and/or determining the contaminants to be adsorbed by the active material in the self-supporting structure .

5 [0061] Once the configuration for the self-supporting structure is determined, a mold is created for the self-supporting structure, as shown in block 104. The creation of the self-supporting structure may involve modeling the desired structure and then three-dimensional
10 (3D) printing the mold or template from a specific material. The template material utilized in the three-dimensional printing may include materials that may be dissolved as part of the self-supporting structure fabrication process, or may be materials that may be removed from the resulting self-supporting structure. For example, the template may include plastics, such as Acrylonitrile Butadiene Styrene (ABS), polylactide (PLA), and/or other suitable plastics and/or
15 waxes.

[0062] Once the mold is created, the self-supporting structure is produced, as shown in blocks 106 and 108. At block 106, the self-supporting structure is created. The creation of the self-supporting structure may involve mixing an active material with organic and/or inorganic binders to provide a specific formulation. The mixture, which may be an aqueous slurry, may
20 be provided to the mold directly, or may be combined with the mold inside a container or vessel. The container or vessel may be used to vibrate the mold and mixture to lessen any voids that may be formed between the mold and mixture. Then, the mold and mixture may be processed to cure the mixture into a solid form. The processing may include heating the mold and mixture to dry and/or cure the mixture and melt or decompose the mold. At block 108, the
25 created self-supporting structure may be verified. The verification of the created self-supporting structure may include using sensors to obtain measurements on the created self-supporting structure to identify voids, fractures and/or non-homogeneous sections of the created self-supporting structure. The verification may include performing a high temperature x-ray diffraction on the self-supporting structure. For example, a high temperature x-ray
30 diffraction scan indicates that an active component of 5A zeolite is stable at 860 °C for several minutes and then loses stability, as shown by decreasing peak heights. This analysis may be used to determine maximum temperatures and time for calcination of the self-supporting structures. The mechanical strength of the self-supporting structures is related to calcination temperatures greater than 500 °C.

[0063] Once the self-supporting structure is produced, the self-supporting structure is formed into a processing unit, as shown in block 110. The forming the processing unit, may involve disposing the self-supporting structure within a housing, coupling a head to the housing, coupling one or more valves (e.g., poppet valves) to the housing and coupling one or more conduits to the housing and/or one or more of the valves. The processing unit may be an adsorbent bed unit that includes a housing, which may include a head portion coupled to one or more body portions, that forms a substantially gas impermeable partition. The housing may include the self-supporting structure (e.g., formed as an adsorbent bed) disposed within an interior region enclosed by the housing. Various valves may be configured to provide fluid flow passages through openings in the housing between the interior region of the housing and locations external to the housing. Then, the self-supporting structure may be utilized in processing of fluids, as shown in block 112. For example, the processing of feeds may include performing swing adsorption method (e.g., rapid cycle processes) for the removal of one or more contaminants from a feed stream. Other examples may include utilizing the self-supporting structure in a catalytic process.

[0064] One method for forming the self-supporting structure may involve the use of 3D molds or templates. By way of example, the self-supporting structure, which may include complex geometries, may be prepared by modeling techniques (e.g., modeling software) to model the shape of the three dimensional objects that are used as templates. The modeling software may produce sets of location coordinates (e.g., x, y, z coordinates), which may be used by a 3D printer to construct a plastic mold or template, in a layer-by-layer method. A high solids aqueous slurry of active material, organic and inorganic binders and other additives may be processed and added to the mold. The organic binder acts as a temporary binder to facilitate particle cohesion during low temperature processing and drying. The slurry is dried and calcined in the template (e.g., the plastic 3D printed mold). During the calcination process, which may be performed at 500 °C or higher, the plastic mold melts or decomposes, the inorganic binder and active material particles sinter into a cohesive, self-supporting structure with a geometric form derived from the mold. As a result, the self-supporting structure may be an open-celled structure configured to provide defined channels for fluid flow paths through the structure, which are based on the template. Various different templates or molds are shown in Figures 2A to 7B, as examples of the different self-supporting structure that may be created.

[0065] Figures 2A, 2B and 2C are various diagrams 200, 220 and 240 of a mold, combined mold and mixture and resulting self-supporting structure in accordance with an embodiment of the present techniques. In Figure 2A, a plastic mold 202 is shown, which may be a 3D printed

sacrificial template or mold having a circular prism shape. In Figure 2B, the mold **202** is combined with the mixture **222**, which includes active material and binder. The resulting self-supporting structure **242** is shown in Figure 2C. The resulting self-supporting structure **242** is a laminar sheet structure of 3A/SiO₂ (e.g., about a 70:30 ratio of active material by weight to binder by weight for the self-supporting structure (w/w)) formed by intrusion. The self-supporting structure **242** has a 1 inch diameter by 2 inch length, total weight of 19.02 grams, which includes 13.3 grams of 3A zeolite and 5.7 grams of SiO₂ binder.

[0066] Figures 3A, 3B and 3C are various diagrams **300**, **320** and **340** of a mold, combined mold and mixture and resulting self-supporting structure in accordance with another embodiment of the present techniques. In Figure 3A, a plastic mold **302** is shown, which may be a 3D printed sacrificial mold having a rectangular prism shape. In Figure 3B, the mold **302** is combined with the mixture **322** of binder and active material. The resulting self-supporting structure **342** is shown in Figure 3C. The resulting self-supporting structure **342** is a fractal-type structure of 3A/SiO₂ (e.g., about 70:30 w/w) formed by intrusion. The self-supporting structure **342** has a 2.25 inch width by 2 inch length.

[0067] Figures 4A, 4B and 4C are various diagrams **400**, **420** and **440** of a mold, combined mold and mixture and resulting self-supporting structure in accordance with yet another embodiment of the present techniques. In Figure 4A, a plastic mold **402** is shown, which may be a 3D printed sacrificial mold having a rectangular prism shape. In Figure 4B, the mold **402** is combined with the mixture **422** of binder and active material. The resulting self-supporting structure **442** is shown in Figure 4C. The resulting self-supporting structure **442** is a cross-flow structure of 3A/SiO₂ (e.g., about 70:30 w/w) formed by intrusion. The self-supporting structure **442** has a 2.25 inch width by 2 inch length, which has six faces of interconnecting channels.

[0068] Figures 5A and 5B are various diagrams **500** and **520** of a combined mold and mixture and resulting self-supporting structure in accordance with still yet another embodiment of the present techniques. In Figure 5A, a plastic mold **502** is shown with a mixture **504** of active material and binder. The mold **502** may be a 3D printed sacrificial mold having a circular prism shape. The resulting self-supporting structure **522** is shown in Figure 5B. The resulting self-supporting structure **522** is a crescent structure of 3A/SiO₂ (e.g., 70:30 w/w) formed by intrusion. The self-supporting structure **522** has a 2.25 inch diameter by 2 inch length, which may be formed by a calcination process.

[0069] Figures 6A and 6B are various diagrams **600** and **620** of a mold and a self-

supporting structure in accordance with another embodiment of the present techniques. In Figure 6A, a plastic mold **602** is shown, which may be a 3D printed sacrificial mold having a hexagonal prism shape. The resulting self-supporting structure **622** is shown in Figure 6B. The resulting self-supporting structure **622** is a hexagonal structure of ZSM 58/SiO₂ (e.g., 70:30 w/w) formed by intrusion. The self-supporting structure **622** has a 2.25 inch width by 2 inch length, which may be formed by a calcination method heating the mixture to about 500 °C.

[0070] Figures 7A and 7B are various diagrams **700** and **720** of two monolith structures in accordance with an embodiment of the present techniques. In Figure 7A, the self-supporting structure **702** is a circular structure of 5A/SiO₂ (e.g., 70:30 w/w) formed by an extrusion process. The self-supporting structure **622** has a 1 inch diameter by 3 inch length, and has cells that are triangular shaped. In Figure 7B, the self-supporting structure **722** is a circular structure of 5A/SiO₂ (e.g., 70:30 w/w) formed by an extrusion process. The self-supporting structure **722** has a 1 inch diameter by 3 inch depth and has cells that are square shaped.

[0071] To cure the mixture into the self-supporting structure, the thermal stability of active material by high temperature may be assessed. As noted above, one of the final steps in creating a self-supporting structure may include calcination. Calcination at high temperatures, which may include temperatures equal to or greater than 500 °C, dehydrates the zeolite and SiO₂ particle mixture and coalesces the mixture into more dense structures that result in enhanced mechanical strength. To assess the high temperature stability of the active material (e.g., adsorbent or catalyst material) for calcination purposes, a high temperature x-ray diffraction may be performed on the self-supporting structure. For example, a high temperature x-ray diffraction scans may provide a representation to indicate that the 5A zeolite (e.g., active material) was stable at a specific temperature for a certain period of time (e.g., about 860 °C for several minutes) and then loses stability, which may be shown by decreasing peak heights. Accordingly, this type of analysis may be used to determine the maximum temperatures and time for calcination of the structures. The mechanical strength of the self-supporting structures is related to calcination temperatures greater than 500 °C.

[0072] Figure 8 is an exemplary diagram **800** of an x-ray diffraction scan of the self-supporting structure. In the diagram **800**, the x-ray diffraction scan of the self-supporting structure is performed at 860 °C that monitored the first 2-theta peaks of 5A zeolite on the two-theta axis **802** in degrees versus the number of scans axis **804**. The scans may be performed using an x-ray diffractometer with a high temperature environmental cell. The scans may be performed every minute, which includes the 48 second scan time and 12 second reset time.

The scans may be conducted in the 2° to 12° 2 theta region at 860 °C for six hours.

[0073] By way of example, the preparation scheme for producing self-supporting structures resulting from processing the materials in 3D printed plastic molds or templates. A high solids aqueous mixture of adsorbent zeolite or catalyst powder and organic and inorganic binder materials was prepared. The well-mixed slurry was added into 3D printed plastic mold, while vibrating the mold and slurry. The mixture was dried and calcined to 500 °C or higher inside the plastic mold producing an active, mechanically stable structure with a geometry derived from the mold. The channels are defined channels for fluid flow paths through the structure based on the plastic mold.

[0074] For example, 118.3 grams of 3A zeolite powder may be added to a container (e.g., a plastic bowl or cup). Then, 126.75 grams of colloidal silica (40 wt. % solution with 25 nanometers (nm) suspended SiO₂ particles) may be added to the 3A zeolite powder in the container. The mixture rapidly heats to 65 °C (e.g., self-heated), due to heat of adsorption of the water into the 3A zeolite. Then, the sample may be cooled to room or ambient temperatures, which results in the mixture being a damp solid. Then, it is mixed well for 1 to 2 minutes at 2,000 revolutions per minute (rpm). In a separate container, 15.02 grams of water and 10.3 grams of 1.5% methylcellulose polymer (used as organic binder) may be mixed and once mixed, added to the container containing the 3A zeolite along with the colloidal silica. The combined mixture was mixed at 2,000 rpm for 2 minutes. The resulting viscous, pourable slurry may be decanted into a 3D printed plastic mold.

[0075] Self-supporting structure may be fabricated from a 3D template intrusion structures. The intruded adsorbent zeolite structures, after calcination, consist of 70:30 weight/weight of zeolite adsorbent to SiO₂ binder. The zeolite particles may be in the range between 2 micron diameter and 25 micron diameter. The SiO₂ binder particles used were either 25 nanometer (nm) or 100 nm monodisperse particles. The particle size distribution of the Linde Type A (LTA) adsorbent powders indicates that the particle size ranges are 2 micrometer (μm) to 5 μm, with a mean value of 4 μm (e.g., Zeolite A (Linde Division, Union Carbide)). The particle size distribution of the ZSM-58 adsorbent powders indicates that the particle size ranges are 20 μm to 30 μm, with a mean value of 25 μm. Zeolite or other inorganic catalytic particles are not inherently cohesive after a high temperature calcination processes. The organic binder materials used were a 1% aqueous solution of methyl cellulose derivatives.

[0076] Also, the aqueous slurry sample was prepared at 65 weight percentage (wt.%) solids in aqueous slurry. The ratio of adsorbent zeolite to SiO₂ (e.g., 25 nm) binder was about a 70:30

(w/w). On a dry basis, the 3A zeolite and SiO₂ are solids, which has formulation targets of a 70:30 dry weight ratio. The organic binder (e.g., methyl cellulose and/or methyl cellulose derivatives) target was 0.06 wt.% organic binder solid in total slurry weight, or 6 wt.% as a 1 wt.% organic binder solution in total slurry weight.

5 [0077] The aqueous slurry was well mixed using an asymmetric mixer for one to three minutes at 1,000 to 2,500 revolutions per minute (rpm). Further, small alumina agates were added to reduce any solid agglomerates, if needed.

[0078] The resulting viscous, pourable slurry was decanted into a 3D printed plastic mold. The structure was vibrated for fifteen to twenty minutes during addition and afterwards, using
10 a vibrating table.

[0079] The LTA zeolite self-supporting structures involved a modified slurry preparation method because of the rapid temperature increase, as a result of high H₂O adsorption. The slurry temperatures increase quickly from room temperature to 70 °C within seconds. The 70 °C temperature can decompose common aqueous organic binders, such as methyl cellulose,
15 which cause them to become irreversibly insoluble. Thus, with LTA slurry preparations, the aqueous organic binder was added to a slurry of LTA and colloidal SiO₂ after the LTA zeolite/SiO₂ mixture had cooled to room temperature to avoid damaging the aqueous organic binder properties.

[0080] As an example, the self-supporting structure may include an example of 3A/SiO₂
20 (25 nm) slurry and fractal-type structure preparation. In forming the mixture, 118.33 grams of 3A zeolite, a white fine powder, was added to a tared plastic jar. Then, 126.75 grams of colloidal silica was added to the 3A in the jar and contents were mixed with a spatula. The colloidal silica is 40 wt.% SiO₂ solution, while the diameter size of the SiO₂ particles in the solution are 25 nanometers (nm). There was a rapid temperature rise to 65 °C as the 3A
25 material adsorbed much of the water in the colloidal solution. After the sample cooled to room temperature, the jar was capped and the contents were placed inside an asymmetric mixer for one to two minutes at 1,500 to 2,000 rpms to mix the sample, resulting in a gritty, damp solid. In a separate jar, 15.02 grams of water were added, followed by 10.32 grams of a 1.5 wt.% methylcellulose organic binder solution. The sample was mixed and the resulting viscous
30 solution was added to the 3A/SiO₂ mixture. The combined mixture was mixed using the mixer at 2,000 rpm for two minutes, resulting in a moldable, cohesive sand-like solid. Then, 10.3 grams of additional water was added to the solid mixture, along with 8 alumina agates to eliminate any agglomerated solids. The sample was mixed using the mixer at 2,000 rpm for

two minutes resulting in a viscous, pourable white slurry. In other embodiments, the organic binder solution may include methyl cellulose and/or methyl cellulose derivatives.

[0081] The resulting slurry was added to a fractal-type 3D printed plastic mold, such as the mold 302 in Figure 3A, while vibrating the structure on a vibration table for fifteen minutes to
5 degas and densify (e.g., vibration procedure that serves to compact the slurry material, and bring solid particles closer together). The vibration of the slurry is performed to remove trapped air bubbles in the mixture by bringing the air bubbles to the top of slurry. The sample was air dry overnight in the mold in an oven at 80 °C. The sample and mold were then dried at 120 °C for ten hours. For example, samples may be gently dried at a temperature, such as
10 80 °C, which is lower than the boiling point temperature of water (e.g., 120 °C) for twelve to sixteen hours. This method is performed in a manner to remove the water slowly. Once dried, the sample and mold were removed from the oven and the plastic walls were removed from the mold. The exposed walls of 3A/SiO₂ were smooth and crack-free. The plastic mold base remained attached to 3A/SiO₂ structure. The structure was then calcined to 500 °C using a
15 programmable furnace. The sample was exposed to temperatures around 120 °C for six hours, exposed to temperatures increasing from 120 °C to 350 °C for in ten hours, thermally soaked at 350 °C for four hours to decompose the plastic mold, exposed to temperatures increasing from 350 °C to 500 °C for six hours, thermally soaked at 500 °C for six hours, and then cooled to 120 °C. Following calcination process, the resulting self-supporting structure has a weight
20 of 121.283 grams of 70:30 w/w 3A/SiO₂. The self-supporting structure had a fractal-type geometric form (e.g., Figure 3C), with dimensions of 2.25 inch width by 2 in length. The surfaces of the structure were in very good condition, with only some minor hair-line cracks in the top of the structure.

[0082] Various SEM images of a self-supporting structure is shown in Figure 9. Figure 9
25 is exemplary SEM diagrams 900 and 920 of the self-supporting structure. In these diagrams 900 and 920, the self-supporting structure is calcined ZSM 58/SiO₂ 100 nm (70:30 w/w), which shows high temperature binding. In diagram 900, the edge of a zeolite particle is shown by the light line indicated by arrow 902, while the SiO₂ particles are shown by 904. Further, as indicated by region 906, which is expanded into the diagram 920, various 100 nm SiO₂ spheres.

30 [0083] SEM diagrams 900 and 920 in Figure 9 show that smaller 100 nm SiO₂ spheres act as an inorganic particle glue to bind the 20 micron diameter zeolite particles together into a cohesive composite of zeolite and SiO₂ particles after 500 °C calcination. The SiO₂ binder particles are too large to enter the zeolite pores, but small enough to form a dense-packed

surface layer on the much larger (e.g., 15 μm to 20 μm) zeolite crystals. High temperature calcination (500 $^{\circ}\text{C}$ to 800 $^{\circ}\text{C}$) sinters the zeolite and inorganic particles together to form a connected solid network that is still porous. The 30 nm to 50 nm diameter space (pores) between the spherical binder particles is large enough for reactant gases to access the zeolite particles where catalytic and/or separation processes can occur.

[0084] Colloidal silicas, when used as binders for adsorbent or catalyst powders, are a very weak bonding agent at low temperatures. However, the bonding strength of the Colloidal silicas increase dramatically with 500 $^{\circ}\text{C}$ to 800 $^{\circ}\text{C}$ calcination temperatures, if there are enough silica particles to make point-to-point contact and also bridge the interstitial spaces between the larger adsorbent particles, as shown in Figure 9. During drying, prior to the 500 $^{\circ}\text{C}$ to 800 $^{\circ}\text{C}$ calcination process, the slurry shrinks during water loss and the adsorbent particles are pulled closer together, surrounded by a thin layer of SiO_2 particles.

[0085] As another example, SEM images of a self-supporting structure is shown in Figures 10A and 10B. Figures 10A and 10B are exemplary SEM diagrams **1000** and **1020** of a self-supporting structure. In these diagrams **1000** and **1020**, the self-supporting structures are monoliths, such as monolith **1002** in diagram **1000** and monolith **1022** in diagram **1020**. These monoliths **1002** and **1022** are 5A/ SiO_2 25 nm (70:30 w/w) extruded monoliths (e.g., include 70 wt.% active 5A zeolite and 30 wt.% SiO_2 binder, which are 25 nm diameter SiO_2 particles). The diagram **1000** in Figure 10A has the square cell structure from Figure 7B, while the diagram **1020** in Figure 10B has the triangular cell structure from Figure 7A. The two monoliths, a square-celled monolith **1002** and a triangular-celled monolith **1022**, were extruded using the same formulation that was used to produce the intrusion structures above that utilized 3D printed molds. The monoliths were calcined to 750 $^{\circ}\text{C}$. The square-celled monolith **1002** has cell wall thickness **1004** of about 280 μm , and the square-shaped channels are approximately 700 μm by 700 μm . Specifically, the square-shaped channels have a cell length **1006** of 700 μm and cell width **1008** of 700 μm . The resulting structure yields a cell density of approximately 650 cells per square inch (cps). The triangular-celled monolith **1022** has cell wall thickness **1024** of about 200 μm , a side length **1026** of about 1.274 μm and a height **1028** of about 1,060 μm .

[0086] In this example, the same formulation utilized to produce a self-supporting structure having custom and complex geometries for the flow passages or channels, as shown in monoliths **1002** and **1022**, was also applied to a ceramic extrusion method to produce active material monoliths instead of inactive ceramic monoliths. The resulting structure may be an

open-celled structure configured to provide predefined channels for fluid flow paths through the respective monoliths **1002** and **1022**.

[0087] Extruded ceramic monoliths involve very high “firing” temperatures (e.g., 1,200 °C to 1,500 °C) to achieve mechanical strength. After firing, these ceramic monoliths are typically used as inert support structure (e.g., inorganic support material or inactive support material with the streams passing through the monolith or the environmental conditions the monolith is exposed to during operations). These monoliths, after firing, are usually post-coated with a thin layer of active material. So, the purpose of the ceramic monolith is to act as a substrate/support that provides mechanical strength for the active coating. The ceramic monolith structure, because of its open channel geometry, provides laminar flow and low pressure drop.

[0088] The extruded active material monoliths formed by the present techniques are made to be formed from 70% by weight of active material, calcined to much lower temperatures than ceramics (e.g., calcined to 500 °C to 650 °C). The lower temperatures are utilized to maintain activity of the zeolite. The strength for the resulting self-supporting structures is provided by the inorganic SiO₂ and/or clay binders. However, the self-supporting structures, while mechanically stable, are not nearly as strong as ceramic monoliths. While clay may be used as a binder for zeolites, it does not provide the strength of sintered SiO₂.

[0089] Figure 11 is an exemplary diagram **1100** of powder x-ray diffraction overlay patterns **1106** and **1108** of samples from inner and outer walls of extruded 5A/SiO₂ monoliths that match 5A zeolites. As shown in this diagram **1100**, the 5A zeolite structure survived the extrusion and calcination method and the outer co-extruded wall and inner cells are the same formulation. The patterns **1106** and **1108** of the interior cells and exterior wall of the sample indicate that the material in the interior walls and exterior walls is the substantially similar, which are shown along a two-theta axis **1102** in degrees (deg) against intensity counts axis **1104**.

[0090] As a selection for the active material, the zeolite type A (e.g., LTA structures), such as 3A, 4A and/or 5A, are highly porous adsorbents that have a high affinity and high capacity to adsorb water, as well as other molecules that have dimensions small enough to fit into the uniform pores of these structures. Accordingly, processes that involve drying and purification of gases and liquids rely on the adsorption capacity and efficiency of LTA-type zeolites, such as swing adsorption methods. These 3A, 4A, 5A LTA- type zeolites have the ability to readily adsorb water over a wide range of conditions. They also release the adsorbed water when

heated, without the zeolite structure degrading. Thus, they have the ability to cycle between releasing water when heated and re-adsorbing water upon cooling.

[0091] The use of 3A in water desorption is shown in relation to a thermogravimetric analysis (TGA). The TGA was performed by starting with a 3A zeolite powder without binder additives. The TGA experiment yields data on weight loss to the sample versus temperature, as shown in Figure 12.

[0092] Figure 12 is a diagram 1200 of the weight loss for 3A, due to loss of adsorbed water, as a function of temperature. In this diagram 1200, a first response 1208 and a second response 1210 are shown along a time axis 1202 in minutes (min), a weight percentage axis 1204 in percent and a temperature axis 1206 in °C. The sample was heated in air from 30 °C to 600 °C, at a rate of 10 °C per minute, as shown along the second response 1210. The first response 1208 represents a total weight loss of 15.3%, indicating that the 3A powder had adsorbed 15.3% by weight of water at ambient conditions. The adsorbed water was removed from the sample at 280 °C (e.g., 25 minutes times 10 °C/minute plus 30 °C starting temperature).

[0093] Further enhancements may be described by comparing H₂O desorption in 3A powder with H₂O adsorption in a 500 °C calcined 3A/SiO₂ intrusion structure. As noted below, Table 1 compares the water adsorption in a calcined 3A/SiO₂ (e.g., 70:30 w/w) structure, to the water desorption results in response 1208 of Figure 12 on the 3A powder.

Table 1

3A/SiO ₂ structure wt. after 500 °C (grams)	3A wt. (%) in 3A/SiO ₂ structure	3A wt. calcd. (grams)	SiO ₂ wt calcd (grams)	Structure wt. after 3 days RT (grams)	Wt increase due to H ₂ O uptake (grams)	Wt.% increase in 3A/SiO ₂ structure	3A in structure (dry, 500°C) + H ₂ O uptake (grams)	3A wt.% increase due to H ₂ O uptake (%)	3A powder TGA result (above) wt. loss due to H ₂ O desorption (%)	Agreement between TGA wt. loss and structure H ₂ O uptake (% of agreement)
20.560	70%	14.392	6.168	22.837	2.217	11.07%	16.609	15.4%	15.3%	99.3%

20

[0094] In Table 1, the 3A/SiO₂ structure used in the comparison is similar to that in Figure 2C, which is a 70:30 w/w 3A:SiO₂ laminar sheet monolith obtained by the method described above. The structure was calcined to 500 °C to decompose the 3D printed plastic mold and organic binder and sinter the 3A and SiO₂ 25 nm particles together. The 3A/SiO₂ laminar sheet structure was stored in a 120 °C furnace, after 500 °C calcination process. The 3A component of the structure was expected to have no adsorbed water. The 3A/SiO₂ structure, which is 1 inch *d* by 2 inch length, was weighed at 120 °C from the furnace and its weight, as recorded in Table 1 was 20.560 grams, which has 70% of the 20.560 gram total weight, or 14.392 grams is

the 3A component. The remaining 30% of the 20.560 grams of total weight, or 6.168 grams, is the 25 nm diameter SiO₂ binder particles.

[0095] After weighing the 3A/SiO₂ structure devoid of water (H₂O), the structure was exposed on a lab bench for seventy-two hours to ambient conditions. After seventy-two hours of being exposed to ambient conditions, the 3A/SiO₂ structure was re-weighed, and its weight was 22.837 grams. This increase in weight was 11.07%, which is a result of adsorbing 2.217 grams of water from the ambient air. The majority of the water could only be adsorbed by the 3A component in the 3A/SiO₂ structure. When determining the water uptake for the 3A component of the structure, it corresponds to a 15.4% weight increase. This weight increase is similar to the 15.3% weight loss in 3A powder, due to water desorption in response **1210** of Figure 12. As a result, the weight increase in the 3A/SiO₂ laminar sheet structure indicates that the 3A component in the structure is accessible to the water molecules, but this ambient moisture test does not provide information about the rate of access.

[0096] In recent tests, the rate of access to 3A, by adsorbing gas molecules, may be hindered by the 25 nm SiO₂ binder, especially at elevated calcination temperatures (700 C +). Accordingly, the method may include adjustments to the binder to enhance access to the pores.

[0097] For examples, the 3A component in the 3A/SiO₂ structure is porous. The “windows” or pores of the 3A structure have openings of 3 angstroms size. Water molecules have a diameter of about 2.8 angstroms and may fit into the 3A structure or “adsorbed” to the inside of the 3A structure. The SiO₂ binder is non-porous. The SiO₂ spheres do not have pores and thus, do not adsorb water into its structure. The water can wet the surface of the SiO₂ spheres, but that amount of water may be a very small fraction of the total amount of water that could be adsorbed by a 3A zeolite (70 wt.%)/ SiO₂ (30 wt.%) structure. Thus, the 3A zeolite component is the primary material to adsorb water in the 3A/SiO₂ composite structure. TGA (thermal gravimetric analysis) measures weight loss versus temperature. Figure 12 is the TGA analysis of 3A zeolite only. It shows that the 3A powder lost 15.3% of weight, which is due to desorbing the water that it adsorbed under ambient conditions.

[0098] From the example above, this TGA result on 3A zeolite powder is approximately equal to the 15.4 % weight gain in the 3A/SiO₂ structure in the example due to adsorption of water under ambient conditions. The nearly identical TGA desorption (weight loss) result and adsorption (weight gain) result in the 3A/SiO₂ structure shows that the 3A zeolite component was accessible to the water.

[0099] As an additional enhancement, gas adsorption break-through test were also

performed on the self-supporting structures. A gas adsorption break-through unit, which is referred to as NatGas Unit, was used to measure gas adsorption and break-through profiles of coated substrates. A sample of known weight is wrapped to prevent gas bypass and inserted into a tube in the gas adsorption break-through unit. The samples are exposed to a total 1,000
5 standard cubic centimeters per minute (sccm) gas flow rate, comprised of 300 sccm N₂ saturated with H₂O at 25 °C, 100 sccm He and 600 sccm N₂. The gas break-through is monitored by a mass spectrometry. The gas flow measurement term of sccm represents cm³/min at standard temperature and pressure.

[00100] As part of this testing, an aqueous slurry with 35 wt.% solids, comprised of 3A/SiO₂
10 (70:30) and methyl cellulose (temporary organic binder), was formulated, as described above in the example 3A/SiO₂ slurry preparation. The slurry was applied to an Al₂O₃ ceramic monolith, which has dimensions suitable for testing in the gas adsorption break-through unit. The washcoat on the ceramic monolith had a similar composition to the self-supported structures after calcination. Thus, the 3A/SiO₂ washcoated monolith was used as a suitable
15 surrogate for the self-supporting intrusion and extrusion structures and, hence, breakthrough results should be and are expected to be comparable.

[0100] In this testing, the 900 cpsi Al₂O₃ monoliths had dimensions of 0.5 inch d by 1 inch L, 30% wall porosity and 55% open frontal area. The starting, uncoated weight of the monolith was 4.099 gram. Two coatings of the slurry were applied by conventional
20 washcoating techniques and the sample was dried and calcined to 500 °C. The sample weight after calcination was 4.893 grams. The resulting 3A/SiO₂ (25 nm d) washcoated monolith contained approximately 0.556 gram of 3A adsorbent and was a representative sample for formulations used in self-supporting intrusion and extrusion structures. Prior to break-through testing, the 3A/SiO₂ coated monolith was dried for twelve hours at 150 °C and 100 sccm He
25 flow.

[0101] Figures 13A and 13B are diagrams **1300** and **1320** of break-through profiles. The breakthrough profile is reasonably sharp. In Figure 13A, the He response **1306** and H₂O response **1308** are shown along a time axis **1302** in minutes versus a mass spectrometer axis **1304** in counts per second to water. The estimated rate of water feed is 5.48 milligrams (mg)
30 per minutes (min). The estimated time for 0.55 grams of 3A in the 3A/SiO₂ washcoat to adsorb water before break-through is 25 minutes (e.g., 30 minutes at uptake level off minus 5 minutes at beginning of uptake). The response **1306** represents a blank trace (e.g., no sample), which from time 0 to 50 minutes of dry He purge and the response **1306** is flat and near the baseline,

indicating no counts for H₂O. Then, after 50 minutes, the valve switches to feed humidified stream, which may be primary a nitrogen stream N₂. The response **1306** rises vertically as the mass spectrometer shows increasing counts per second of H₂O, until the H₂O is removed at 300 minutes. Then, the response **1306** returns to the baseline indicating no counts of H₂O. The response **1308** shows a similar experiment through a sample of 3A/SiO₂ coated onto Al₂O₃ ceramic monolith. As indicated by this response **1308**, it is about 5 minutes longer for the response **1308** to rise as compared to the response **1306** for the blank sample, which indicates that H₂O breakthrough is being slowed by the adsorption of H₂O in the 3A component until the sample reaches water saturation and equilibrium.

[0102] In Figure 13B, the He response **1326** and H₂O response **1328** are shown along a time axis **1322** in minutes versus a normalized fractional concentration of H₂O axis **1324** in C/Co, which expresses the normalized fractional concentration of H₂O being measured by a mass spectrometer as a function of time axis **1322**. In this diagram **1320**, the 3A adsorbs water for about 25 minutes, indicating that the 3A adsorbent particles are accessible without signs of major diffusional hindrance. The response **1326** represents a dry He purge passing through an empty cell for 5 minutes, which is flat and near the baseline. Once a valve is switched to feed humidified He stream, the mass spectrometer indicates a breakthrough of the Helium (He) at time 0 minutes. In comparison, the response **1328** represents a sample cell with 3A/SiO₂ washcoated ceramic monolith responding to a humidified He flow. The response **1328** indicates the normalized H₂O concentration versus time. Accordingly, it indicates that it takes several minutes (e.g., about 25 minutes) until the 3A component in the sample is saturated with H₂O and the full concentration (100%) of H₂O is indicated by the mass spectrometer.

[0103] Figures 13C and 13D are diagrams **1340** and **1360** of transition feed versus purge temperature profiles. In this diagrams **1340** and **1360**, ceramic monoliths perform significantly better to thermal transitions than the metal monoliths. The ceramic materials should perform similar to the self-supported active structures, which have a low thermal mass structures similar to ceramics and should exhibit similar thermal swing advantages. Further, the self-supported structures of the present techniques are composed of a majority of active material, which is the material that the thermal swing process is attempting heat and cool rapidly.

[0104] In the diagrams **1340** and **1360**, a cyclic process was used that involved fluid flows for 20 seconds each for feed and purge steps of the cycle. The gas flow rates were 14 standard cubic feet per minute (scfm) for feed gas and 22 scfm for purge gas. Nitrogen gas was used for feed and purge streams, which were introduced at opposite ends of the monoliths or bed.

The feed stream was at ambient temperature, while the purge stream was at 180 °C. To monitor the temperature, fast response thermocouples were used to measure and store the temperatures, which had a first thermocouple positioned to measure temperatures at the feed gas inlet side of the structure and a second thermocouple positioned to measure temperatures at the purge gas inlet side of feed gas.

[0105] In Figure 13C, the temperature responses **1346** and **1348** are shown along a time axis **1342** in seconds versus a temperature axis **1344** in °C. The metal monolith used as a sample bed were three monoliths of 0.75 inches in diameter by 2 inches in length, made of stainless steel, with cell density greater than 1,000 cell per square inch (cpsi), with 50 micron thick cell walls and a center steel arbor of 3/8 inch diameter. The monolith cells were coated with thin layer of adsorbent and the monoliths were wrapped with fibrous insulation to prevent gas bypass. The resulting structure was loaded into a sample tube. The diagram **1340** with temperature responses **1346** and **1348** for the metal monoliths indicate a large temperature gap of approximately 70 °C in responding to temperature transitions between 180 °C purge gas and ambient temperature feed gas. This indicates that the metal monolith is adsorbing significant heat into the structure.

[0106] In Figure 13D, the temperature responses **1366** and **1368** are shown along a time axis **1362** in seconds versus a temperature axis **1364** in °C. The ceramic monolith used as a sample bed includes the monoliths of 0.75 inch diameter and 2 inch length, made of alumina ceramic, with cell density of 900 cpsi, with 100 micron thick cell walls, no center arbor. Ceramic monoliths were wrapped with fibrous insulation to prevent gas bypass. The resulting structure was loaded into a sample tube. The diagram **1360** with the temperature responses **1366** and **1368** for the alumina ceramic monoliths indicate that the temperature transitions during the temperature cycle has a smaller temperature change than the metal monolith, as shown in Figure 13C. The temperature gap in the responses **1366** and **1368** for the ceramic monoliths is approximately 20 °C during cycling process. This indicates that the ceramic monoliths adsorb less heat into the structure than the metal monoliths, as shown in Figure 13C.

[0107] Testing may be performed on the self-supporting structure. For example, an ambient air exposure test may be performed, which is a passive test. There is no driving force to add water to the 3A/SiO₂ structure. It slowly adsorbs water from the air and it is affected by conditions of relative humidity and temperature, which are measured. This test delivers a calibrated flow of gas in sccm with known concentration of water and monitors the time until the 3A/SiO₂ structure has adsorbed water to its capacity. There is a mass spectrometer

instrument monitoring the exit gas stream from the structure. The mass spectrometer instrument is monitoring water in the gas versus time. When water is detected, which is referred to as “breakthrough”, it indicates that the 3A component of structures is saturated with water at these specific conditions and cannot adsorb more water.

- 5 **[0108]** As yet another example, the self-supporting structure may be formed through an extrusion process. For example, a mixture may be formed into a monolith form comprising defined channels (e.g., substantially parallel channels), separated by thin walls, wherein the mixture has greater than 50% by weight of the active material in the self-supporting structure and the remaining mixture includes binder material. Then, the monolith form may be dried
10 and the monolith form may be calcined within a temperature range between 400 °C and 800 °C to form a mechanically stable, active monolith form. The monolith form may include the defined channels have a cross sectional shape (e.g., cross sectional shape that is along a plane that is perpendicular to direction of primary flow through the respective channel) that may be a square, a circle, a triangular, a hexagonal or any other suitable shape. The cell density of the
15 monolith form may be in a range between 200 cells per square inch and 2,000 cells per square inch. The walls separating the channels may have a thickness in the range between 40 micron and 1 millimeter.

- [0109]** Once formed, the monolith form, which is the self-supporting structure, may be disposed within a housing of a processing unit having an interior region. The housing may
20 have a plurality of valve ports created into the housing (e.g., drilled or formed into the housing); and valves may be secured to the housing in each of the valve ports to form the valves, wherein each of the valves is configured to control fluid flow between the self-supporting structure and a location external to the housing.

- [0110]** In certain configurations, the present techniques may be utilized in a swing adsorption method (e.g., a rapid cycle process) for the removal of one of more contaminants
25 from a feed stream. In particular, the present techniques involve a one or more adsorbent bed units to perform a swing adsorption method or groups of adsorbent bed unit configured to perform a series of swing adsorption methods. Each adsorbent bed unit is configured to perform a specific cycle, which may include an adsorption step and a regeneration step. By
30 way of example, the steps may include one or more feed steps, one or more depressurization steps, one or more purge steps, one or more recycle steps, and one or more re-pressurization steps. The adsorption step may involve passing a feed stream through the adsorbent bed to remove contaminants from the feed stream. The regeneration step may include one or more

purge steps, one or more blowdown steps, one or more heating steps and/or one or more repressurization steps.

[0111] The present techniques may also include active materials that are configured to perform at various operating conditions. For example, the feed pressure may be based on the preferred adsorption feed pressure, which may be in the range from 400 pounds per square inch absolute (psia) to 1,400 psia, or in the range from 600 psia to 1,200 psia. Also, the purge pressure may be based on the sales pipeline pressure, which may be in the range from 400 psia to 1,400 psia, in the range from 600 psia to 1,200 psia.

[0112] In addition, other configurations may involve enhancements for adsorption structures that may be formed primarily from active component. Beneficially, the use of primarily active components may provide significantly cheaper, higher working capacity potential in smaller volume, cell uniformity, increased geometric and engineering flexibility, and/or lower thermal mass. For example, the self-supporting structures may be formed into self-supporting structure monoliths, self-supporting 3D structures (e.g., indirect from 3D printing), and/or self-supporting structure foams. The self-supporting structure monoliths may be preferred for applications, such as pressure swing adsorption, which involves low pressure drop.

[0113] By way of example, the compositions of the self-supporting structure monoliths may include thin films that are used with natural gas stream, which indicate that the compositions are beneficial. One configuration includes extruded self-supporting structure monoliths. This configuration may lack a preferred breakthrough front because gas diffusion hindrance issues and/or damaged adsorbent crystals.

[0114] Figure 14 is an exemplary diagram **1400** of self-supporting structure monolith test results. As shown in Figure 14, an extruded self-supporting structure monolith may be formed of a composition of 5A/SiO₂ to 25 nm (70:30) and may be calcinated at 750 °C. As shown in the diagram **1400**, a plot of a natural gas test is shown. In the diagram **1400**, a first response **1408** of Helium and a second response **1406** of Water (H₂O) are shown along a time axis **1402** in minutes (min) and a normalized fractional concentration of H₂O axis **1404** in normalized concentration (C/Co). The first response **1408** is a breakthrough curve increases at an angle to the right, which may preferably be vertical. Gas permeance testing may be performed to determine if extrusion pressures (e.g., 2000 pounds per square inch gauge (psig) to 4,000 psig) needed to form self-supported extruded monoliths, have diminished the macro pore system, thus increasing diffusional hindrance. Similarly, a H₂O breakthrough test may be performed

to determine whether the extrusion pressure damaged the adsorbent crystals. This testing may include using the same sample and/or the sample holder, which may be performed after gas permeance test completed. The gas permeance testing, may involve using a carver press to compress disks of self-supporting structures monoliths compositions to 5,000 psig to simulate monolith extrusion pressures.

[0115] In one or more configurations, measurements of the effects on gas permeance are obtained in disk structures of self-supporting structure monolith compositions. For example, the effects on gas permeance may be compared with extrusion-type pressures, such as disks compressed to 5,000 psig before drying and/or calcination or may be compared with various polyethylene sphere additives. The gas permeation results indicate that a method of using polyethylene spheres as an approach to enhance gas transport in self-supported compositions, appears to be effective. The effects of macro-pore additive may include greater impact with smaller (e.g., 25 nm) binder system than in 100 nm binder system. The larger effect on average pore size of 25 nm binder system is enhanced because 25 nm particles (e.g., 25 nm SiO₂ particles) are smaller than 100 nm particles (e.g., 100 nm SiO₂ particles) and there are more 25 nm particles for same composition of 5A/SiO₂ w/w ratio than 100 nm particles. By way of example, the self-supported structures may utilize pore engineering methods, which may involve using polyethylene spheres. The adsorbent (e.g., 5A) may be a combination of macro-pore additives (polyethylene spheres dimensions of 2 to 4 micrometer spherical) and an inorganic binder (e.g., SiO₂ particles colloidal solution of 40 weight percent (wt.%) of 25 nm SiO₂ or 40 wt.% of 100 nm SiO₂).

[0116] Figures 15A and 15B are exemplary diagrams **1500** and **1520** of polyethylene spheres, which may be used in self-supporting structure monoliths. Figure 15A is a diagram **1500** of spheres, which includes a first diameter **1502** and a second diameter **1504**. The first diameter **1502** and second diameter **1504** may be in the range between 2 micrometers and 4 micrometers. Figure 15B is a diagram **1520** of spherical macro-porous holes after burnout after 500 °C calcination in a 5A/SiO₂ sample (with 5% polyethylene spheres).

[0117] To assess self-supporting structure monolith compositions, testing may be performed to determine porosity (e.g., gas permeance and/or mercury porosimetry testing) and capacity (e.g., H₂O uptake by adsorbent). By way of example, the testing may include gas permeance testing, water uptake testing and mercury porosimetry testing. For the gas permeance testing, the gas permeance is compared with the feed pressure. The probing porosity system of self-supporting structure monolith disks may involve deriving information about

permeability, connected porosity, pore diameter, and any combination thereof. The gas permeance configuration of the test unit may include a housing having an interior region configured to hold a disk, a pressure meter at the inlet side of the housing, and a flow meter at the outlet side of the housing. The formulated disks may be compressed to 5,000 psig, which
5 is used to mimic the monolith extrusion pressure in the range between 2,000 psig and 4,000 psig. The gas permeance testing may include passing various streams through the self-supporting structure monolith disks, such as Helium (He) to provide a non-adsorbing trace line and other gases having mass and viscosity (e.g., four other compositions, which are run separately through the disks). These different streams may include Helium (He), Nitrogen
10 (N₂), carbon dioxide (CO₂), methane (CH₄) and Argon (Ar). The gas permeance testing may include measuring the gas pressure on an inlet side of the test unit and measuring the fluid flow on the outlet side of the test unit. The associated measurements provide insights of the open pore system.

[0118] In addition, the testing may include water uptake testing, which may be performed
15 after the gas permeance testing. This testing may involve determining H₂O breakthrough. The water uptake testing configuration of the test unit may include a housing having an interior region configured to hold a disk and a humidity sensor at the outlet side of the housing. The water uptake testing may involve probing working capacity of zeolite adsorbent in self-supporting structure monoliths, disks or films. The testing may include 40% relative humidity
20 (RH) water on gas feed side to be used for measuring breakthrough humidity versus time on outlet side. The weight of disk with adsorbent composition is known and is used to calculate and compare breakthrough time. This indicates the amount of the adsorbent (e.g., zeolite) is accessible (e.g., working capacity) as compared to the known amount of adsorbent.

[0119] Further still, the testing may include Mercury (Hg) porosimetry testing, which may
25 be performed after the gas permeance testing and water uptake testing. The Hg porosimetry testing may include determining the Hg intrusion. The Hg porosimetry testing configuration of the test unit may include a housing having an interior region configured to hold a disk. The testing may include probing porosity system of the disks using Hg liquid and pressures (e.g., ambient to 60,000 psig). This testing may be used to determine pore diameter and/or pore
30 volume. Portions or pieces of formulated disks may be used in permeance and breakthrough tests are sent to Micromeritics Analytical Services Company for testing.

[0120] Various observations are shown in Figures 16A to 16D. In particular, Figures 16A, 16B, 16C and 16D are exemplary diagrams **1600**, **1620**, **1640** and **1660** of a permeance

measurements in accordance with embodiments of the present techniques. In these diagrams **1600**, **1620**, **1640** and **1660**, the gas permeances of extrusion-type samples tested are high (e.g., 10^{-6} to 10^{-5} moles/s m² Pa). The self-supporting structure monolith disks have a composition that is an adsorbent zeolite to SiO₂ (e.g., 25 nm) binder having about a 80:20 (w/w) ratio. The disks are compressed at 5,000 psig.

[0121] Figure 16A is an exemplary diagram **1600** of permeance measurements for Helium (He) gas passing through the self-supporting structure monolith disks. In this diagram **1600**, various response points, such as points **1606**, **1607**, **1608** and **1609**, are shown along a permeance axis **1604** in moles per second meter squared Pascal (moles/s m² Pa) against a pressure axis **1602** in kilo-Pascal (kPa). In particular, the points, such as points **1606**, shown by x's represent the disk made of 5A/SiO₂ 100 nm having 10% w/w macropore additive before calcination, while the points, such as points **1607**, shown by the squares represent the disk made of 5A/SiO₂ 25 nm having 5% w/w macropore additive before calcination, and the points, such as points **1608**, shown by the triangles represent the disk made of 5A/SiO₂ 100 nm having 0% w/w macropore additive before calcination, and the points, such as points **1609**, shown by the diamonds represent the disk made of 5A/SiO₂ 25 nm having 0% w/w macropore additive before calcination.

[0122] Figure 16B is an exemplary diagram **1620** of permeance measurements for Nitrogen (N₂) gas passing through the self-supporting structure monolith disks. In this diagram **1620**, various response points, such as points **1626**, **1627**, **1628** and **1629**, are shown along a permeance axis **1624** in moles per second meter squared Pascal (sm²Pa) against a pressure axis **1622** in kilo-Pascal (kPa). In particular, the points, such as points **1626**, shown by x's represent the disk made of 5A/SiO₂ 100 nm having 10% w/w macropore additive before calcination, while the points, such as points **1627**, shown by the squares represent the disk made of 5A/SiO₂ 25 nm having 5% w/w macropore additive before calcination, and the points, such as points **1628**, shown by the triangles represent the disk made of 5A/SiO₂ 100 nm having 0% w/w macropore additive before calcination, and the points, such as points **1629**, shown by the diamonds represent the disk made of 5A/SiO₂ 25 nm having 0% w/w macropore additive before calcination.

[0123] Figure 16C is an exemplary diagram **1640** of permeance measurements for methane (CH₄) gas passing through the self-supporting structure monolith disks. In this diagram **1640**, various response points, such as points **1646**, **1647**, **1648** and **1649**, are shown along a permeance axis **1644** in moles per second meter squared Pascal (sm²Pa) against a pressure axis

1642 in kilo-Pascal (kPa). In particular, the points, such as points **1646**, shown by x's represent the disk made of 5A/SiO₂ 100 nm having 10% w/w macropore additive before calcination, while the points, such as points **1647**, shown by the squares represent the disk made of 5A/SiO₂ 25 nm having 5% w/w macropore additive before calcination, and the points, such as points **1648**, shown by the triangles represent the disk made of 5A/SiO₂ 100 nm having 0% w/w macropore additive before calcination, and the points, such as points **1649**, shown by the diamonds represent the disk made of 5A/SiO₂ 25 nm having 0% w/w macropore additive before calcination.

[0124] Figure 16D is an exemplary diagram **1660** of permeance measurements for carbon dioxide (CO₂) gas passing through the self-supporting structure monolith disks. In this diagram **1660**, various response points, such as points **1666**, **1667**, **1668** and **1669**, are shown along a permeance axis **1664** in moles per second meter squared Pascal (sm²Pa) against a pressure axis **1662** in kilo-Pascal (kPa). In particular, the points, such as points **1666**, shown by x's represent the disk made of 5A/SiO₂ 100 nm having 10% w/w macropore additive before calcination, while the points, such as points **1667**, shown by the squares represent the disk made of 5A/SiO₂ 25 nm having 5% w/w macropore additive before calcination, and the points, such as points **1668**, shown by the triangles represent the disk made of 5A/SiO₂ 100 nm having 0% w/w macropore additive before calcination, and the points, such as points **1669**, shown by the diamonds represent the disk made of 5A/SiO₂ 25 nm having 0% w/w macropore additive before calcination.

[0125] As shown by the diagrams **1600**, **1620**, **1640** and **1660**, the permeance improves between the addition of 0% polyethylene spheres, 5% polyethylene spheres and 10% polyethylene spheres to the composition. Further, the differences between 25 nm binder and 100 nm binder samples are shown in these diagrams **1600**, **1620**, **1640** and **1660**. Accordingly, the addition of 5% polyethylene spheres to disk composition having 25 nm diameter yield similar permeance to disk compositions for 100 nm diameter (100 nm) binder with 0% polyethylene spheres.

[0126] The average pore diameter may be determined from the gas permeance measurements and/or Knudsen and Poiseuille models, as shown in Figure 17. Figure 17 is an exemplary diagram **1700** of average pore diameter based on gas permeance measurements in accordance with an embodiment of the present techniques. In the diagram **1700**, the effect of the macropore additive in disks for the 25 nm binder material versus 100 nm binder materials. In this diagram **1700**, various disks, which have various compositions are shown along a pore

diameter axis **1704** in micrometers (μm) against a sample identification (ID) axis **1702**. The disk may have a composition of 5A/25 nm SiO_2 particles having 0% polyethylene spheres, as shown by response **1706**, while the disk may have a composition of 5A/25 nm SiO_2 particles having 5% polyethylene spheres, as shown by responses **1708**. The disk may have a composition of 5A/100 nm SiO_2 particles having 0% polyethylene spheres, as shown by response **1710**, while the disk may have a composition of 5A/100 nm SiO_2 particles having 5% polyethylene spheres, as shown by responses **1712**, and the disk may have a composition of 5A/100 nm SiO_2 particles having 10% polyethylene spheres, as shown by responses **1714**.

[0127] As shown by the responses **1706**, **1708**, **1710**, **1712** and **1714**, the average pore diameters may indicate the effects of pore engineering macro-pore additives. In the model, the calculations indicates the average pore diameter sizes between 0.6 micrometers to 2.0 micrometers. The addition of macropore additives have a greater impact on increasing average pore diameters of 5A compositions containing smaller diameter binder materials (e.g., 25 nm) as compared to the larger diameter binder materials (e.g., 100 nm). The larger effect on average pore size of 5A compositions containing smaller diameter binder materials (e.g., 25 nm) is attributed to differences in binder particle diameter sizes (e.g., 25 nm SiO_2 particles are smaller than 100 nm SiO_2 particles) and/or the larger number of particles for volume (e.g., more 25 nm particles for same 5A/ SiO_2 w/w ratio than 100 nm particles).

[0128] The water uptake testing may be used to generate qualitative results of water breakthrough on a self-supporting structure monolith disks. Figure 18 is an exemplary diagram **1800** of water breakthrough in accordance with an embodiment of the present techniques. In the diagram **1800**, the composition of the self-supporting structure monolith disks may include 5A/ SiO_2 in a ratio of 80:20 (w/w), wherein the SiO_2 are 25 nm and the composition include 5% polyethylene spheres. The water uptake testing may be performed after gas permeance testing. For example, a disk that was tested in a gas permeance test unit has approximately 1.943 grams mass with a composition of approximately 80:20 5A/ SiO_2 . In the diagram **1800**, a first response **1808** of Helium and a second response **1810** of water (H_2O) are shown along a time axis **1802** in seconds (s), a relative humidity axis **1804** in percentage (%) and a concentration axis **1806** in parts per million (ppm). In this diagram **1800**, the flow rate is about 90 sccm, 38% relative humidity (RH), and 0.00088 grams water per minute (g $\text{H}_2\text{O}/\text{min}$). The estimated breakthrough time for 15% uptake capacity is about 15,311 seconds. The response **1810** has an initial sharp, vertical breakthrough portion, which is followed by a portion of the response **1810** flattens to a nearly horizontal line. As a result, the water uptake and breakthrough graph result indicates that the 5A crystals are functional after 5,000 psig

compression.

[0129] Beneficially, the gas permeation results indicate that the method of using polyethylene spheres as one approach to pore engineering is effective. The use of polyethylene spheres to enhance gas transport in self-supported monolith disk compositions is also effective.

- 5 In addition, pore engineering using macro-pore additives appears to provide greater advantage to compositions with smaller (25 nm) binder materials than in 100 nm binder materials at a similar w/w of binder material. These effects may include having a larger effect on average pore size of 25 nm binder materials because 25 nm SiO₂ particles are smaller than 100 nm SiO₂ particles and there are more 25 nm particles for same volume of material than 100 nm particles.
- 10 Accordingly, the pore engineering may improve gas transport in self-supported structures, which may be specifically be used with polyethylene spheres, as an example approach to pore engineering.

- [0130]** Further enhancements in the self-supported structures may be used to enhance the fabrication processes and/or resulting structure. For example, the present techniques may
- 15 include optimizing the order of components that are added, may include additives to enhance porosity and diffusional performance, and/or may include additives to enhance formulation processing (e.g., extruded monolith structures). As a first enhancement, the order of addition may be used to enhance the self-supported monolith. In this method, the pre-condition adsorbent may be filled to capacity with water. The order of addition may prevent fouling of
- 20 adsorbent, which may include adding a sodium cation stabilizer in colloidal silica solutions. Also, the order of addition may involve preventing agglomeration and poor distribution of SiO₂ binder particles, as a result of adsorbing the H₂O from the binder solution. As a second enhancement, the addition of macro pore additives to the composition. The addition of macro pore additives may improve macro porosity and reduce diffusional hindrance issues and may
- 25 involve using polyethylene spheres (e.g., between 2 μm and 4 μm in diameter). As a third enhancement, the addition of plasticizing additive to the composition. The addition of plasticizing additive, such as clay materials, to the composition may be used to enhance material workability for processing by extrusion or intrusion or other methods. Also, the addition of plasticizing additive may improve structure defect issues that may result from
- 30 drying and calcining.

[0131] By way of example, Figure 19 is a three-dimensional diagram of the swing adsorption system **1900** having six adsorbent bed units and interconnecting piping. While this configuration is a specific example, the present techniques broadly relate to adsorbent bed units

that can be deployed in a symmetrical orientation, or non-symmetrical orientation and/or combination of a plurality of hardware skids. Further, this specific configuration is for exemplary purposes as other configurations may include different numbers of adsorbent bed units. In this configuration, the adsorbent bed units may include self-supporting structures.

- 5 [0132] In this system, the adsorbent bed units, such as adsorbent bed unit **1902**, may be configured for a cyclical swing adsorption method for removing contaminants from feed streams (e.g., fluids, gaseous or liquids). For example, the adsorbent bed unit **1902** may include various conduits (e.g., conduit **1904**) for managing the flow of fluids through, to or from the adsorbent bed within the adsorbent bed unit **1902**. These conduits from the adsorbent bed units
- 10 **1902** may be coupled to a manifold (e.g., manifold **1906**) to distribute the flow of the stream to, from or between components. The adsorbent bed within an adsorbent bed unit may separate one or more contaminants from the feed stream to form a product stream. As may be appreciated, the adsorbent bed units may include other conduits to control other fluid streams as part of the process, such as purge streams, depressurizations streams, and the like. Further,
- 15 the adsorbent bed unit may also include one or more equalization vessels, such as equalization vessel **1908**, which are dedicated to the adsorbent bed unit and may be dedicated to one or more step in the swing adsorption process.

- [0133] In certain configurations, the self-supporting structure may be utilized in an adsorbent bed unit that includes a housing, which may include a head portion and other body
- 20 portions, that forms a substantially gas impermeable partition. The housing may include the self-supporting structure (e.g., formed as an adsorbent bed) disposed within the housing and a plurality of valves (e.g., poppet valves) providing fluid flow passages through openings in the housing between the interior region of the housing and locations external to the interior region of the housing. Each of the poppet valves may include a disk element that is seatable within
- 25 the head or a disk element that is seatable within a separate valve seat inserted within the head (not shown). The configuration of the poppet valves may be any variety of valve patterns or configuration of types of poppet valves. As an example, the adsorbent bed unit may include one or more poppet valves, each in flow communication with a different conduit associated with different streams. The poppet valves may provide fluid communication between the
- 30 adsorbent bed and one of the respective conduits, manifolds or headers. The term "in direct flow communication" or "in direct fluid communication" means in direct flow communication without intervening valves or other closure means for obstructing flow. As may be appreciated, other variations may also be envisioned within the scope of the present techniques.

[0134] The adsorbent bed comprises adsorbent material formed into the self-supporting structure, which is capable of adsorbing one or more components from the feed stream. Such adsorbent materials are selected to be durable against the physical and chemical conditions within the adsorbent bed unit and can include metallic, ceramic, or other materials, depending on the adsorption process.

[0135] In certain configurations, the swing adsorption system, which includes the active material, may process a feed stream that predominately comprises hydrocarbons along with one or more contaminants. For example, the feed stream may be a hydrocarbon containing stream having greater than one volume percent hydrocarbons based on the total volume of the feed stream. Further, the feed stream may include hydrocarbons along with H₂O, H₂S, and CO₂. By way of example, the stream may include H₂O as one of the one or more contaminants and the gaseous feed stream may comprise H₂O in the range of 50 parts per million (ppm) molar to 1,500 ppm molar; or in the range of 500 ppm to 1,500 ppm molar. Moreover, the feed stream may include hydrocarbons and H₂O, wherein the H₂O is one of the one or more contaminants and the feed stream comprises H₂O in the range of two ppm molar to saturation levels in the feed stream.

[0136] In addition, the present techniques may provide an adsorption system that utilizes a rapid cycle swing adsorption method to separate acid gas contaminants from feed streams, such as acid gas from hydrocarbon streams. Acid gas removal technology may be useful for gas reserves exhibit higher concentrations of acid gas (e.g., sour gas resources). Hydrocarbon feed streams vary widely in amount of acid gas, such as from several parts per million acid gas to 90 volume percent (vol. %) acid gas. Non-limiting examples of acid gas concentrations from exemplary gas reserves include concentrations of at least: (a) 1 vol.% H₂S, 5 vol.% CO₂, (b) 1 vol.% H₂S, 15 vol.% CO₂, (c) 1 vol.% H₂S, 60 vol.% CO₂, (d) 15 vol.% H₂S, 15 vol.% CO₂, and (e) 15 vol.% H₂S, 30 vol.% CO₂. Accordingly, the present techniques may include equipment to remove various contaminants, such as H₂S and CO₂ to desired levels. In particular, the H₂S may be lowered to levels less than 4 ppm, while the CO₂ may be lowered to levels less than 1.8 molar percent (%) or, preferably, less than 50 ppm. As a further example, the acid gas removal system may remove CO₂ to LNG specifications (e.g., less than or equal to 50 parts per million volume (ppmv) CO₂).

[0137] In certain configurations, the active material may be used in a rapid cycle swing adsorption method, such as a rapid cycle PSA process, to remove moisture from the feed stream. The specific level may be related to dew point of desired output product (e.g., the water

- content should be lower than the water content required to obtain a dew point below the lowest temperature of the stream in subsequent process and is related to the feed pressure). As a first approximation, and not accounting for fugacity corrections as a function of pressure, the water concentration in ppm that yields a certain dew point varies inversely with the pressure. For
- 5 example, the output stream from the adsorbent bed may be configured to be the cryogenic processing feed stream, which satisfies the cryogenic processing specifications (e.g., approximately -150 °F (-101.1 °C) dew point for NGL processes or approximately -60 °F (-51.1 °C) for Controlled Freeze Zone (CFZ) processes. The cryogenic processing feed stream specification may include a water content in the stream (e.g., output stream from the adsorbent
- 10 bed or feed stream to the to be cryogenic processing) to be in the range between 0.0 ppm and 10 ppm, in the range between 0.0 ppm and 5.0 ppm, in the range between 0.0 ppm and 2.0 ppm, or in the range between 0.0 ppm and 1.0 ppm. The resulting output stream from the adsorbent beds during the purge step may include a water content in the stream to be in the range between 0.0 ppm and 7 pounds per standard cubic feet (lb/MSCF).
- 15 **[0138]** In one or more embodiments, the present techniques can be used for any type of swing adsorption method. Non-limiting swing adsorption methods for which the present techniques may include pressure swing adsorption (PSA), vacuum pressure swing adsorption (VPSA), temperature swing adsorption (TSA), partial pressure swing adsorption (PPSA), rapid cycle pressure swing adsorption (RCPSA), rapid cycle thermal swing adsorption (RCTSA),
- 20 rapid cycle partial pressure swing adsorption (RCPPSA), as well as combinations of these methods, such as pressure and/or temperature swing adsorption. Exemplary kinetic swing adsorption methods are described in U.S. Patent Application Publication Nos. 2008/0282892, 2008/0282887, 2008/0282886, 2008/0282885, 2008/0282884 and 2014/0013955 and U.S. Serial Nos. 15/233617, 15/233623, 15/233631 and 15/233640, which are each herein
- 25 incorporated by reference in their entirety. However, rapid cycle may be preferred to process the stream. However, the self-supporting structures may be preferably utilized with rapid cycle swing adsorption methods.
- [0139]** Further, in certain configurations of the system, the present techniques may include a specific process flow to remove contaminants, such as water (H₂O) or acid gas, in the swing
- 30 adsorption system. For example, the method may include an adsorbent step and a regeneration step, which form the cycle. The adsorbent step may include passing a feed stream at a feed pressure and feed temperature through an adsorbent bed unit having an active material structure to separate one or more contaminants from the feed stream to form a product stream. The feed stream may be passed through the adsorbent bed in a forward direction (e.g., from the feed end

of the adsorbent bed to the product end of the adsorbent bed). Then, the flow of the feed stream may be interrupted for a regeneration step. The regeneration step may include one or more depressurization steps, one or more purge steps and/or one or more re-pressurization steps. The depressurization steps may include reducing the pressure of the adsorbent bed unit by a predetermined amount for each successive depressurization step, which may be a single step and/or may be a blowdown step. The depressurization step may be provided in a forward direction or may preferably be provided in a countercurrent direction (e.g., from the product end of the adsorbent bed to the feed end of the adsorbent bed). The purge step may include passing a purge stream into the adsorbent bed unit, which may be a once through purge step and the purge stream may be provided in countercurrent flow relative to the feed stream. The purge product stream from the purge step may be conducted away and recycled to another system or in the system. Then, the one or more re-pressurization steps may be performed, wherein the pressure within the adsorbent bed unit is increased with each re-pressurization step by a predetermined amount with each successive re-pressurization step. Then, the cycle may be repeated for additional feed streams and/or the cycle may be adjusted to perform a different cycle for a second configuration. The cycle duration may be for a period greater than 1 second and less than 600 seconds, for a period greater than 2 second and less than 300 seconds, for a period greater than 2 second and less than 200 seconds, or for a period greater than 2 second and less than 90 seconds.

[0140] Also, the present techniques may be integrated into a various configurations, which may include a variety of compositions for the streams. Adsorptive separation methods, apparatus, and systems, as described above, are useful for development and production of hydrocarbons, such as gas and oil processing. Particularly, the provided methods, apparatus, and systems are useful for the rapid, large scale, efficient separation of a variety of target gases from gas mixtures. In particular, the methods, apparatus, and systems may be used to prepare feed products (e.g., natural gas products) by removing contaminants and heavy hydrocarbons (e.g., hydrocarbons having at least two carbon atoms). The provided methods, apparatus, and systems are useful for preparing gaseous feed streams for use in utilities, including separation applications. The separation applications may include dew point control; sweetening and/or detoxification; corrosion protection and/or control; dehydration; heating value; conditioning; and/or purification. Examples of utilities that utilize one or more separation applications include generation of fuel gas; seal gas; non-potable water; blanket gas; instrument and control gas; refrigerant; inert gas; and/or hydrocarbon recovery.

[0141] To provide fluid flow paths through the self-supporting structure in an adsorbent

bed unit, valve assemblies may include poppet valves, which each may include a disk element connected to a stem element which can be positioned within a bushing or valve guide. The stem element may be connected to an actuating means, such as actuating means, which is configured to have the respective valve impart linear motion to the respective stem. As may be appreciated, the actuating means may be operated independently for different steps in the method to activate a single valve or a single actuating means may be utilized to control two or more valves. Further, while the openings may be substantially similar in size, the openings and inlet valves for inlet manifolds may have a smaller diameter than those for outlet manifolds, given that the gas volumes passing through the inlets may tend to be lower than product volumes passing through the outlets. Further, while this configuration has valve assemblies, the number and operation of the valves may vary (e.g., the number of valves) based on the specific cycle being performed.

[0142] In one or more embodiments, the rapid cycle swing adsorption method that utilize the self-supporting structures in the present techniques may include rapid cycle temperature swing adsorption (RCTSA) and/or rapid cycle pressure swing adsorption (RCPSA). For example, the total cycle times may be less than 600 seconds, less than 300 seconds, preferably less than 200 seconds, more preferably less than 90 seconds, and even more preferably less than 60 seconds.

[0143] In view of the many possible embodiments to which the principles of the disclosed invention may be applied, it should be recognized that the illustrative embodiments are only preferred examples of the invention and should not be taken as limiting the scope of the invention.

CLAIMS

What is claimed is:

1. A processing unit comprising:
a housing forming an interior region;
5 a self-supporting structure disposed within the interior region, wherein the self-supporting structure has greater than 50% by weight of the active material in the self-supporting structure, wherein the self-supporting structure is an open-celled structure configured to provide one or more defined channels for fluid flow paths through the self-supporting structure;
a plurality of valves secured to the housing, wherein each of the plurality of valves is
10 configured to control fluid flow along a flow path extending between the self-supporting structure and a location external to the housing.
2. The processing unit of claim 1, wherein the processing unit is a cyclical swing adsorbent bed unit configured to remove contaminants from a gaseous feed stream that passes through
15 the one or more defined channels in the self-supporting structure.
3. The processing unit of any one of claims 1 to 2, wherein the self-supporting structure has greater than 60% by weight of the active material in the self-supporting structure.
- 20 4. The processing unit of any one of claims 1 to 2, wherein the self-supporting structure has greater than 70% by weight of the active material in the self-supporting structure.
5. The processing unit of any one of claims 1 to 4, wherein the self-supporting structure has an inert support member coated by the active material in the self-supporting structure.
25
6. The processing unit of any one of claims 1 to 5, wherein the adsorbent bed unit further comprises a flow distributor disposed between the adsorbent bed and the plurality of valves.
7. The processing unit of any one of claims 1 to 6, wherein the housing is configured to

maintain a pressure from 5 pounds per square inch absolute (psia) and 1,400 psia.

8. The processing unit of any one of claims 1 to 7, wherein the self-supporting structure has a layer of active material that is greater than 10 micrometers.

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9. The processing unit of any one of claims 1 to 7, wherein the self-supporting structure has a layer of active material that is greater than 100 micrometers.

10. The processing unit of any one of claims 1 to 7, wherein the self-supporting structure has a low thermal mass.

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11. The processing unit of any one of claims 1 to 10, wherein the one or more defined channels comprise two or more channels that are substantially parallel.

12. The processing unit of any one of claims 1 to 11, wherein the self-supporting structure has a plurality of pores formed in the active material by removing a plurality of polyethylene spheres from the active material to form the plurality of pores.

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13. A method for removing contaminants from a feed stream, the method comprising:

- 20 a) performing one or more adsorption steps in an adsorbent bed unit, wherein each of the one or more adsorption steps comprise: passing a gaseous feed stream through the self-supporting structure disposed in an interior region of a housing of the adsorbent bed unit to remove one or more contaminants from the gaseous feed stream, wherein the self-supporting structure has greater than 50% by weight of the active material in the
- 25 self-supporting structure, wherein the self-supporting structure is an open-celled structure configured to provide one or more defined channels for fluid flow paths through the self-supporting structure;
- b) performing one or more regeneration steps, wherein each of the one or more regeneration steps comprise conducting away at least a portion of the one or more
- 30 contaminants in a contaminant output stream; and

c) repeating the steps a) to b) for at least one additional cycle.

14. The method of claim 13, wherein the method is a swing adsorption method and the cycle duration is for a period greater than 1 second and less than 600 seconds.

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15. The method of claim 13, wherein the cycle duration is for a period greater than 1 second and less than 300 seconds to separate one or more contaminants from the gaseous feed stream to form the product stream.

10 16. The method of any one of claims 13 to 15, wherein the performing one or more regeneration steps comprises performing one or more purge steps, wherein each of the one or more purge steps comprise passing a purge stream through the self-supporting structure to conduct away at least a portion of the one or more contaminants in the contaminant output stream.

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17. The method of any one of claims 13 to 16, wherein the gaseous feed stream is a hydrocarbon containing stream having greater than one volume percent hydrocarbons based on the total volume of the gaseous feed stream.

20 18. The method of any one of claims 13 to 17, wherein a feed pressure of the gaseous feed stream is in the range between 400 pounds per square inch absolute (psia) and 1,400 psia.

19. The method of any one of claims 13 to 18, wherein performing the one or more adsorption steps is configured to lower the carbon dioxide (CO₂) level to less than 50 parts per
25 million volume.

20. The method of any one of claims 13 to 19, wherein performing the one or more adsorption steps is configured to lower the water (H₂O) level to less than 105 parts per million volume.

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21. The method of any one of claims 13 to 20, wherein the self-supporting structure has a low thermal mass.
- 5 22. The method of any one of claims 13 to 21, wherein the one or more defined channels comprise two or more channels that are substantially parallel.
23. The method of any one of claims 13 to 21, wherein the self-supporting structure has a plurality of pores formed in the active material by removing a plurality of polyethylene spheres
10 from the active material to form the plurality of pores.
24. A method of manufacturing a processing unit, the method comprising:
creating a template for a self-supporting structure;
disposing a mixture within the template, wherein the mixture has greater than 50% by
15 weight of the active material in the self-supporting structure and the remaining mixture includes binder material;
curing the template and the mixture to form a self-supporting structure that is maintains a solid form;
removing the template from the self-supporting structure, wherein the self-supporting
20 structure is an open-celled structure configured to provide one or more defined channels for fluid flow paths through the self-supporting structure, which are based on the template; and
disposing the self-supporting structure within housing of a processing unit having an interior region.
- 25 25. The method of claim 24, further comprising creating a three-dimensional model of the self-supporting structure having predetermined geometries for the one or more defined channels through the self-supporting structure.
26. The method of claim 25, further comprising creating a model of a template based on
30 the three-dimensional model of the self-supporting structure.

27. The method of claim 26, further comprising printing a three-dimensional template based on the model of the template.
- 5 28. The method of any one of claims 24 to 27, wherein removing the template from the self-supporting structure further comprises heating the self-supporting structure and the template to decompose or melt the template and conduct away the melted template.
- 10 29. The method of any one of claims 24 to 28, further comprising vibrating the template and the mixture prior to curing the template and mixture to lessen any voids that may be formed between the template and mixture.
- 15 30. The method of any one of claims 24 to 29, wherein curing the template and the mixture further comprises sintering the binder material and active material into a cohesive solid structure that is the self-supporting structure.
31. The method of any one of claims 24 to 30, further comprising:
creating a plurality of valve ports into the housing; and
securing a valve to the housing in each of the plurality of valve ports to form a plurality
20 of valves, wherein each of the plurality of valves is configured to control fluid flow between the self-supporting structure and a location external to the housing.
32. The method of any one of claims 24 to 31, wherein the mixture comprises a plurality of polyethylene spheres; and
25 wherein the curing the template and the mixture to form the self-supporting structure comprises removing the plurality of polyethylene spheres from the mixture to form the plurality of pores in the self-supporting structure.
33. The method of claim 32, wherein the mixture comprises at least 5% polyethylene

spheres.

34. A method of manufacturing a processing unit, the method comprising:
- extruding a mixture into a monolith form comprising a plurality of substantially parallel
- 5 channels, wherein each of the plurality of substantially parallel channels are separated by thin walls, wherein the mixture has greater than 50% by weight of the active material in the self-supporting structure and the remaining mixture includes binder material;
- drying the monolith form; and
- calcining the monolith form with temperatures in the range between 400 °C and 800 °C to form
- 10 a mechanically stable, active monolith form;
- wherein each of the plurality of substantially parallel channels have a cross sectional shape of one of a square, a circle, a triangular, or a hexagonal;
- wherein the cell density of the monolith form is in a range between 200 cells per square inch and 2,000 cells per square inch; and
- 15 wherein the walls separating the plurality of substantially parallel channels have a thickness in the range between 40 micron to 1 millimeter.