

**STRUCTURED ADSORBENT BEDS, METHODS OF
PRODUCING THE SAME AND USES THEREOF**

FIELD

[0001] The present invention relates to structured adsorbent beds for purification of gas feedstreams and methods of making such structured adsorbent beds. The structured adsorbent beds comprise a substrate with a high cell density and a coating on the substrate, wherein the coating comprises adsorbent particles and a binder.

BACKGROUND

[0002] Gas separation is important in many industries for removing undesirable contaminants from a gas stream and for achieving a desired gas composition. For example, natural gas from many gas fields can contain significant levels of H₂O, SO₂, H₂S, CO₂, N₂, mercaptans, and/or heavy hydrocarbons that have to be removed to various degrees before the gas can be transported to market. It is preferred that as much of the acid gases (*e.g.*, H₂S and CO₂) be removed from natural gas as possible to leave methane as the recovered component. Small increases in recovery of methane can result in significant improvements in process economics and also serve to prevent unwanted resource loss. It is desirable to recover more than 80 vol %, particularly more than 90 vol %, of the methane when detrimental impurities are removed.

[0003] Additionally, synthesis gas (syngas) typically requires removal and separation of various components before it can be used in fuel, chemical and power applications because all of these applications have a specification of the exact composition of the syngas required for the process. As produced, syngas can contain at least CO and H₂. Other molecular components in syngas can be

- 2 -

CH₄, CO₂, H₂S, H₂O, N₂, and combinations thereof. Minority (or trace) components in the gas can include hydrocarbons, NH₃, NO_x, and the like, and combinations thereof. In almost all applications, most of the H₂S should typically be removed from the syngas before it can be used, and, in many applications, it can be desirable to remove much of the CO₂.

[0004] Adsorptive gas separation techniques are common in various industries using solid sorbent materials such as activated charcoal or a porous solid oxide such as alumina, silica-alumina, silica, or a crystalline zeolite. Adsorptive separation may be achieved by equilibrium or kinetic mechanisms. A large majority of processes operate through the equilibrium adsorption of the gas mixture where the adsorptive selectivity is primarily based upon differential equilibrium uptake of one or more species based on parameters such as pore size of the adsorbent. Kinetically based separation involves differences in the diffusion rates of different components of the gas mixture and allows different species to be separated regardless of similar equilibrium adsorption parameters.

[0005] Kinetically based separation processes may be operated as pressure swing adsorption (PSA), temperature swing adsorption (TSA), partial pressure swing or displacement purge adsorption (PPSA) or as hybrid processes comprised of components of several of these processes. These swing adsorption processes can be conducted with rapid cycles, in which case they are referred to as rapid cycle thermal swing adsorption (RCTSA), rapid cycle pressure swing adsorption (RCPSA), and rapid cycle partial pressure swing or displacement purge adsorption (RCPPSA) technologies, with the term “swing adsorption” taken to include all of these processes and combinations of them.

[0006] Traditionally, adsorptive separation processes use packed beds of adsorbent particulates. However, the traditional packed beds are not likely to

meet the very stringent requirements for natural gas cleanup. Alternatively, a structured adsorbent bed can be utilized to adsorb certain gas species. The structured adsorbent bed can be a monolith, either in the form of one single block or in the form of extrudates with multiple channels or cells, such as a honeycomb structured monolith. The use of adsorbent monoliths provides one approach to designing an adsorbent bed that has low pressure drop, good flow distribution, and low dispersion. Monoliths have very low flow tortuosity and can also be engineered for almost any user specified void volume to meet a specified pressure drop. Other monolith advantages include avoidance of bed fluidization or lifting. In addition to gas separation processes, these types of monoliths have historically been employed as catalyst supports in automobile catalytic converters, catalytic combustion, electrochemical reactors and biochemical reactors.

[0007] In order to prepare the monoliths for use in gas separation processes or as catalyst supports, the cells are washcoated with layers of catalytic or adsorbent coatings. The cell density of the monolith and the size of the particles in the coating have a significant effect on the ability to successfully coat the cells in the monolith to provide a structured adsorbent bed. It is known that coating difficulty increases as the cell density of the monolith increases (*i.e.*, the channel size of the monolith decreases), as the size of the particles in the coating increases over 2 μm , as the number of coatings increase and as substrate porosity decreases toward zero porosity. For example, Agrafiotis, C. *et al.* report that the size of the suspended particles affects the adhesion of the washcoat on the substrate, namely particles with a diameter of less than 2 μm have increased adhesion to a monolith with a cell density of 400 cells per square inch (cps) than larger diameter particles. J. Mater. Sci. Lett., 18:1421–1424 (1999). Thus, typically the monoliths used in practice have lower cell densities (*e.g.*, 300–900 cps), the coatings contain small particles (*e.g.*, diameter less than 2 μm) and/or

the coating is applied in very thin layers (*e.g.*, 1 μm to 10 μm). For example, while U.S. Patent No. 6,936,561 reports a coating layer thickness above 300 μm on a ceramic honeycomb monolith, the monolith has a low cell density of about 45 cpsi. Similarly, U.S. Patent No. 7,560,154 reports a method of manufacturing a honeycomb structure with a coating particle size of 15 to 75 μm , but the cell density of the structure is 260 cpsi.

[0008] However, kinetic separation processes, specifically rapid cycle kinetic separation processes require structured adsorbent beds with ultra high cell density (*i.e.*, greater than 1000 cpsi) and thicker coating layers. Furthermore, larger particle sizes in the coating are desirable because further milling to reduce the particle size can be avoided, thereby avoiding potential fracturing of the particles which can result in diminished capacity and activity. Therefore, there is a need to provide structured adsorbent beds with ultra high cell density as well as thicker coating layers and larger particles sizes in the coating.

SUMMARY

[0009] It has been found that a structured adsorbent bed for purification of a gas feedstream comprising a substrate having a high cell density (*e.g.*, greater than 1040 cpsi), and a coating on the substrate, wherein the coating comprises large adsorbent particles (*e.g.*, an average diameter greater than 20 μm) and a binder, can be achieved by pretreating the substrate prior to applying the adsorbent particles and binder.

[0010] Thus, in one aspect, embodiments of the invention provide a structured adsorbent bed for purification of a gas feedstream comprising: a substrate having a cell density greater than 1040 cpsi; and a coating on the substrate, wherein the coating comprises adsorbent particles and a binder.

- 5 -

[0011] In still another aspect, embodiments of the invention provide a method of preparing the structured adsorbent bed described herein, the method comprising: pretreating the substrate; preparing an aqueous slurry comprising the adsorbent particles and the binder; and applying the aqueous slurry to the substrate to form the coating on the substrate.

[0012] In still another aspect, embodiments of the invention provide a gas separation process comprising contacting a gas mixture containing at least one contaminant with an adsorbent bed described herein.

[0013] Other embodiments, including particular aspects of the embodiments summarized above, will be evident from the detailed description that follows.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] Figure 1 illustrates an example of the distances used for determining the axis ratio of an adsorbent particle in a scanning electron microscope (SEM) image.

[0015] Figures 2a and 2b illustrate SEM images for a 2700 cpsi ceramic monolith.

[0016] Figure 3 illustrates a Leica Optical scope picture with 40 x magnification of a 1440 cpsi 315 stainless steel monolith after 900°C calcination.

[0017] Figures 4a and 4b illustrate a transmission electron microscopy (TEM) image and size analysis results showing average diameter of the binder, 25 nm colloidal SiO₂.

[0018] Figures 5a and 5b illustrate TEM image and size analysis results showing average diameter of the binder, 100 nm colloidal SiO₂.

[0019] Figures 6a and 6b illustrate a TEM image and size analysis results showing average diameter of the binder, string of pearls colloidal SiO₂.

[0020] Figure 7 illustrates a Leica Optical scope picture (40 x magnification) of a 1440 cpsi metal monolith after 4 coatings with DDR (25-30 μm) and SiO₂ (100 nm).

[0021] Figure 8 illustrates an SEM image of a DDR (25-30 μm) and SiO₂ (100 nm) coating on a 1440 cpsi metal monolith and/or glass slide after 500°C calcination.

[0022] Figure 9 provides photographs of the 25-2-2, 26-6-2, 26-7-3, 26-8-23 and 25-4-23 coupons with coating prior to integrity testing.

[0023] Figure 10 illustrates a 26-8-23C coupon before integrity testing (top photograph) and after integrity testing (bottom photograph).

[0024] Figure 11 illustrates a 25-4-23C coupon before integrity testing (top photograph) and after integrity testing (bottom photograph).

[0025] Figure 12 illustrates a 26-7-3C coupon before integrity testing (top photograph) and after integrity testing (bottom photograph).

[0026] Figure 13 illustrates test button D before (left photograph) and after (right photograph) adsorptive kinetic separation (AKS) integrity testing.

- 7 -

[0027] Figure 14 illustrates weight of test button D as superficial gas velocity increases during AKS integrity test.

[0028] Figure 15 illustrates zero length chromatography (ZLC) results comparing a DDR adsorbent (without binder) to SiO₂ bound DDR samples with a DDR:SiO₂ weight ratio of 85:15 w/w.

[0029] Figure 16 illustrates ZLC results comparing a DDR adsorbent (without binder) to SiO₂ bound DDR samples with a DDR:SiO₂ weight ratio of 90:10 w/w.

DETAILED DESCRIPTION

[0030] In various aspects of the invention, structured adsorbent beds, methods of preparing the structured adsorbent beds and gas separation processes using the structured adsorbent beds are provided.

I. Definitions

[0031] To facilitate an understanding of the present invention, a number of terms and phrases are defined below.

[0032] As used in the present disclosure and claims, the singular forms “a,” “an,” and “the” include plural forms unless the context clearly dictates otherwise.

[0033] Wherever embodiments are described herein with the language “comprising,” otherwise analogous embodiments described in terms of “consisting of” and/or “consisting essentially of” are also provided.

- 8 -

[0034] The term “and/or” as used in a phrase such as “A and/or B” herein is intended to include “A and B”, “A or B”, “A”, and “B”.

[0035] As used herein, the term “adsorption” includes physisorption, chemisorption, and condensation onto a solid support and combinations thereof.

[0036] The term “monolith” refers to any three-dimensional material that can contain numerous parallel channels per square inch and can serve as a support for adsorbents or catalysts, such as solid pieces of metal or ceramic materials or honeycomb structures. The term monolith is meant to be distinguished from a collection of individual particles packed into a bed formation, in which the end product comprises individual particles.

[0037] As used herein, the term “average diameter” of the particle refers to the number average of the major axis and minor axis.

[0038] As used herein, the term “porosity” refers to a measure of the void spaces in a material, and is measured herein as percent between zero and 100%.

[0039] As used herein, the term “macroporosity” refers to the percentage of pores in a material that have a diameter greater than 50 nm.

[0040] As used herein, the term “microporous” refers to solid materials having pores with a diameter less than 2 nm.

[0041] As used herein, the term “Si/Al ratio” is defined as the molar ratio of silica to alumina of a zeolitic structure.

II. Structured Adsorbent Bed

[0042] In a first embodiment a structured adsorbent bed for purification of a gas feedstream is provided comprising a substrate and a coating on the substrate.

A. Substrate

[0043] As discussed above, substrates traditionally have a lower cell density because as cell density of the substrate increases and the channels in the bed decrease in size, difficulty in coating the substrates increases. However, substrates, such as monoliths, with higher cell density are provided herein. In various aspects, the substrate has a cell density of greater than or equal to about 900 cpsi, greater than or equal to about 920 cpsi, greater than or equal to about 940 cpsi, greater than or equal to about 960 cpsi, greater than or equal to about 980 cpsi, greater than or equal to about 1,000 cpsi, greater than or equal to about 1,020 cpsi, greater than or equal to about 1,040 cpsi, greater than or equal to about 1,060 cpsi, greater than or equal to about 1,080 cpsi, greater than or equal to about 1,100 cpsi, greater than or equal to about 1,120 cpsi, greater than or equal to about 1,140 cpsi, greater than or equal to about 1,160 cpsi, greater than or equal to about 1,180 cpsi, greater than or equal to about 1,200 cpsi, greater than or equal to about 1,220 cpsi, greater than or equal to about 1,240 cpsi, greater than or equal to about 1,260 cpsi, greater than or equal to about 1,280 cpsi, greater than or equal to about 1,300 cpsi, greater than or equal to about 1,320 cpsi, greater than or equal to about 1,340 cpsi, greater than or equal to about 1,360 cpsi, greater than or equal to about 1,380 cpsi, greater than or equal to about 1,400 cpsi, greater than or equal to about 1,420 cpsi, greater than or equal to about 1,440 cpsi, greater than or equal to about 1,460 cpsi, greater than or equal to about 1,480 cpsi, greater than or equal to about 1,500 cpsi, greater than or equal to about 1,520 cpsi, greater than or equal to about 1,640 cpsi, greater than or equal to about 1,760 cpsi, greater than or equal to about 1,880 cpsi, greater than or equal to about 1,900 cpsi, greater than or equal to about 1,920 cpsi, greater than or equal to about 1,940 cpsi, greater than or equal to

about 1,960 cpsi, greater than or equal to about 1,980 cpsi, greater than or equal to about 2,000 cpsi, greater than or equal to about 2,100 cpsi, greater than or equal to about 2,200 cpsi, greater than or equal to about 2,300 cpsi, greater than or equal to about 2,400 cpsi, greater than or equal to about 2,500 cpsi, greater than or equal to about 2,600 cpsi, greater than or equal to about 2,700 cpsi, greater than or equal to about 2,800 cpsi, greater than or equal to about 2,900 cpsi, greater than or equal to about 3,000 cpsi, greater than or equal to about 3,100 cpsi, greater than or equal to about 3,200 cpsi, greater than or equal to about 3,300 cpsi, greater than or equal to about 3,400 cpsi, greater than or equal to about 3,500 cpsi, greater than or equal to about 3,600 cpsi, greater than or equal to about 3,700 cpsi, greater than or equal to about 3,800 cpsi, greater than or equal to about 3,900 cpsi, greater than or equal to about 4,000 cpsi, greater than or equal to about 4,100 cpsi, greater than or equal to about 4,200 cpsi, greater than or equal to about 4,300 cpsi, greater than or equal to about 4,400 cpsi, greater than or equal to about 4,500 cpsi, greater than or equal to about 4,600 cpsi, greater than or equal to about 4,700 cpsi, greater than or equal to about 4,800 cpsi, greater than or equal to about 4,900 cpsi, or greater than or equal to about 5,000 cpsi. Particularly, the substrate has a cell density greater than about 1,040 cpsi and greater than or equal to about 1,400 cpsi. Additionally or alternatively, the substrate has a cell density of less than or equal to about 900 cpsi, less than or equal to about 920 cpsi, less than or equal to about 940 cpsi, less than or equal to about 960 cpsi, less than or equal to about 980 cpsi, less than or equal to about 1,000 cpsi, less than or equal to about 1,020 cpsi, less than or equal to about 1,040 cpsi, less than or equal to about 1,060 cpsi, less than or equal to about 1,080 cpsi, less than or equal to about 1,100 cpsi, less than or equal to about 1,120 cpsi, less than or equal to about 1,140 cpsi, less than or equal to about 1,160 cpsi, less than or equal to about 1,180 cpsi, less than or equal to about 1,200 cpsi, less than or equal to about 1,220 cpsi, less than or equal to about 1,240 cpsi, less than or equal to about 1,260 cpsi, less than or

equal to about 1,280 cpsi, less than or equal to about 1,300 cpsi, less than or equal to about 1,320 cpsi, less than or equal to about 1,340 cpsi, less than or equal to about 1,360 cpsi, less than or equal to about 1,380 cpsi, less than or equal to about 1,400 cpsi, less than or equal to about 1,420 cpsi, less than or equal to about 1,440 cpsi, less than or equal to about 1,460 cpsi, less than or equal to about 1,480 cpsi, less than or equal to about 1,500 cpsi, less than or equal to about 1,520 cpsi, less than or equal to about 1,640 cpsi, less than or equal to about 1,760 cpsi, less than or equal to about 1,880 cpsi, less than or equal to about 1,900 cpsi, less than or equal to about 1,920 cpsi, less than or equal to about 1,940 cpsi, less than or equal to about 1,960 cpsi, less than or equal to about 1,980 cpsi, less than or equal to about 2,000 cpsi, less than or equal to about 2,100 cpsi, less than or equal to about 2,200 cpsi, less than or equal to about 2,300 cpsi, less than or equal to about 2,400 cpsi, less than or equal to about 2,500 cpsi, less than or equal to about 2,600 cpsi, less than or equal to about 2,700 cpsi, less than or equal to about 2,800 cpsi, less than or equal to about 2,900 cpsi, less than or equal to about 3,000 cpsi, less than or equal to about 3,100 cpsi, less than or equal to about 3,200 cpsi, less than or equal to about 3,300 cpsi, less than or equal to about 3,400 cpsi, less than or equal to about 3,500 cpsi, less than or equal to about 3,600 cpsi, less than or equal to about 3,700 cpsi, less than or equal to about 3,800 cpsi, less than or equal to about 3,900 cpsi, less than or equal to about 4,000 cpsi, less than or equal to about 4,100 cpsi, less than or equal to about 4,200 cpsi, less than or equal to about 4,300 cpsi, less than or equal to about 4,400 cpsi, less than or equal to about 4,500 cpsi, less than or equal to about 4,600 cpsi, less than or equal to about 4,700 cpsi, less than or equal to about 4,800 cpsi, less than or equal to about 4,900 cpsi, or less than or equal to about 5,000 cpsi. Ranges expressly disclosed include combinations of the above-enumerated upper and lower limits, e.g., about 900 cpsi to about 5,000 cpsi, about 1,500 cpsi to about 3,000 cpsi, about 1,500 cpsi to about 4,000 cpsi, about 1,400 cpsi to about 3,300

cpsi, etc. Particularly, the substrate has a cell density of about 1,500 cpsi to about 4,000 cpsi.

[0044] Exemplary channel geometries in the substrate include, but are not limited to a trapezoidal geometry and a square geometry.

[0045] In various aspects, the substrate can be a porous solid. Exemplary porous solids include, but are not limited to a metal oxide, a mixed-metal oxide, a ceramic, a zeolite and combinations thereof. Metal oxides that can be used include, but are not limited to alumina, silica, zirconia and titania. An example of a suitable mixed-metal oxide ceramic includes cordierite. Examples of suitable zeolites include, but are not limited to ZSM-5 and ZSM-58.

[0046] In various aspects, the substrate has a porosity of less than or equal to about 40%, less than or equal to about 35%, less than or equal to about 30%, less than or equal to about 25%, less than or equal to about 20%, less than or equal to about 15%, less than or equal to about 10%, less than or equal to about 9%, less than or equal to about 8%, less than or equal to about 7%, less than or equal to about 6%, less than or equal to about 5%, less than or equal to about 4%, less than or equal to about 3%, less than or equal to about 2%, less than or equal to about 1% or less than or equal to about 0.5%. Particularly, the substrate has a porosity of less than or equal to about 30%. Additionally or alternatively, the substrate has a porosity of greater than or equal to about 40%, greater than or equal to about 35%, greater than or equal to about 30%, greater than or equal to about 25%, greater than or equal to about 20%, greater than or equal to about 15%, greater than or equal to about 10%, greater than or equal to about 9%, greater than or equal to about 8%, greater than or equal to about 7%, greater than or equal to about 6%, greater than or equal to about 5%, greater than or equal to about 4%, greater than or equal to about 3%, greater than or equal to about 2%,

greater than or equal to about 1% or greater than or equal to about 0.5%. Ranges expressly disclosed include combinations of the above-enumerated upper and lower limits, e.g., about 0.5% to about 40%, about 1% to about 10%, about 2% to about 30%, etc.

[0047] Additionally or alternatively, the substrate can be a non-porous solid having a porosity of about 0.0%. Exemplary non-porous solids include, but are not limited to a metal, a glass, and a plastic. The metal can comprise stainless steel and/or aluminum.

B. Coating

[0048] In various aspects, the coating can comprise adsorbent particles. The adsorbent particles can have an average diameter of greater than or equal to about 1 μm , greater than or equal to about 2 μm , greater than or equal to about 4 μm , greater than or equal to about 6 μm , greater than or equal to about 8 μm , greater than or equal to about 10 μm , greater than or equal to about 12 μm , greater than or equal to about 14 μm , greater than or equal to about 16 μm , greater than or equal to about 18 μm , greater than or equal to about 20 μm , greater than or equal to about 21 μm , greater than or equal to about 22 μm , greater than or equal to about 23 μm , greater than or equal to about 24 μm , greater than or equal to about 25 μm , greater than or equal to about 26 μm , greater than or equal to about 27 μm , greater than or equal to about 28 μm , greater than or equal to about 29 μm , greater than or equal to about 30 μm , greater than or equal to about 32 μm , greater than or equal to about 34 μm , greater than or equal to about 36 μm , greater than or equal to about 38 μm , greater than or equal to about 40 μm , greater than or equal to about 42 μm , greater than or equal to about 44 μm , greater than or equal to about 46 μm , greater than or equal to about 48 μm or greater than or equal to about 50 μm . Particularly, the adsorbent particles have an average diameter greater than about

20 μm . Additionally or alternatively, the adsorbent particles can have an average diameter of less than or equal to about 1 μm , less than or equal to about 2 μm , less than or equal to about 4 μm , less than or equal to about 6 μm , less than or equal to about 8 μm , less than or equal to about 10 μm , less than or equal to about 12 μm , less than or equal to about 14 μm , less than or equal to about 16 μm , less than or equal to about 18 μm , less than or equal to about 20 μm , less than or equal to about 21 μm , less than or equal to about 22 μm , less than or equal to about 23 μm , less than or equal to about 24 μm , less than or equal to about 25 μm , less than or equal to about 26 μm , less than or equal to about 27 μm , less than or equal to about 28 μm , less than or equal to about 29 μm , less than or equal to about 30 μm , less than or equal to about 32 μm , less than or equal to about 34 μm , less than or equal to about 36 μm , less than or equal to about 38 μm , less than or equal to about 40 μm , less than or equal to about 42 μm , less than or equal to about 44 μm , less than or equal to about 46 μm , less than or equal to about 48 μm or less than or equal to about 50 μm . Ranges expressly disclosed include combinations of the above-enumerated upper and lower limits, e.g., about 1 μm to about 50 μm , about 2 μm to about 40 μm , about 10 μm to about 36 μm , etc. Particularly, the adsorbent particles can have an average diameter of about 2 μm to about 50 μm and/or about 20 μm to about 40 μm .

[0049] Additionally or alternatively, the adsorbent particles described herein can generally have a hexagonal disc shape where the particles have hexagonal faces. The top and bottom hexagonal faces can generally correspond to larger hexagonal faces, with a smaller depth dimension (roughly) perpendicular to the top and bottom faces. The hexagonal disc shape of the adsorbent particles can be seen in Figure 8.

[0050] Additionally or alternatively, the adsorbent particles described herein can generally have a rounded or circular disc shape with top and bottom rounded or circular disc faces. The depth dimension for the rounded discs can be smaller than the lateral dimension of the rounded faces of the disc.

[0051] One way to characterize the difference between the hexagonal disc shape and the rounded disc shape can be based on the difference between the vertex-to-vertex distance and the edge-to-edge distance in a hexagonal face of a crystal. To perform this type of characterization, an initial step can be to identify the correct face(s) of the particle for performing the characterization. For a hexagonal disc particle, the combination of a vertex-to-vertex line and an edge-to-edge line can roughly define a plane. The dimension perpendicular to this plane can then correspond to the depth of the crystal. For the hexagonal disc shape, this depth dimension can generally be shorter than either the vertex-to-vertex distance or the edge-to-edge distance. If the depth distance is longer than either of the other two distances, then either a different hexagonal face should be selected for this calculation, or the crystal may not correspond to a hexagonal disc shape or round disc shape. After determining that the correct type of hexagonal (or rounded) face has been selected for characterizing the crystal, the vertex-to-vertex distance and the edge-to-edge distance for the hexagonal face can be compared in order to calculate an axis ratio. Additionally or alternatively, the adsorbent particles described herein can be a prismatic shape.

[0052] Figure 1 shows a schematic example of this type of calculation. In Figure 1, line 110 corresponds to the vertex-to-vertex distance for a hexagon. Line 120 corresponds to the edge-to-edge distance. For a hexagonal face with well defined edges and vertices, the vertex-to-vertex distance, by definition, is typically larger than the edge-to-edge distance. As the angles and edges of the hexagon become smoothed toward forming a circle, to the degree that the

vertices and edges can still be identified, the vertex-to-vertex distance and the edge-to-edge distance can become increasingly closer. In the limiting case of a circle, the axis ratio of vertex-to-vertex distance and edge-to-edge distance becomes 1, with the caveat that the location of a “vertex” and an “edge” in the limiting case may be somewhat arbitrary.

[0053] For adsorbent particles of the type shown in Figure 8, the ratio of vertex-to-vertex distance versus edge-to-edge distance can be determined based on measuring distances in an SEM micrograph. The adsorbent particles shown in Figure 8 can be used herein in the coating and the axis ratio of the vertex-to-vertex distance versus the edge-to-edge distance was observed to be at least about 1.15, such as at least about 1.2.

[0054] The characterization of the rounded disc shape particles can be performed in a similar manner. The depth dimension can be identified in relation to the rounded (approaching circular) face(s) of the crystal. In some embodiments, a ratio of the depth dimension to the edge-to-edge distance can be about 0.9 or less, e.g., about 0.85 or less. In such embodiments, particles with a ratio of depth dimension to edge-to-edge distance of greater than about 0.95 were identified to correspond to a roughly spherical morphology. The rounded face of the rounded discs can then be characterized using the axis ratio. Additionally or alternatively, the round disc particles can have an axis ratio of the vertex-to-vertex distance versus edge-to-edge distance of about 1.1 or less, e.g., about 1.05 or less, or a still lower value that can approach the limiting axis ratio value of 1.0.

[0055] Additionally or alternatively, the adsorbent particles comprise a microporous material, such as a zeolite. The zeolite can have a Si/Al ratio of at least about 200:1, at least about 300:1, at least about 400:1, at least about 500:1,

at least about 600:1, at least about 700:1, at least about 800:1, at least about 900:1 or at least about 1,000:1. Particularly, the zeolite can have a Si/Al ratio of about 600:1. Examples of suitable zeolites include, but are not limited to the following zeolite frameworks: CDO, FAU, MFI, DOH, DDR and combinations thereof. Particularly, the zeolite can be DDR. Examples of DDR framework zeolites include, but are not limited to Sigma-1, ZSM-58 and SSZ-28. A person of ordinary skill in the art knows how to make the aforementioned zeolites. For example, see the references provided in the International Zeolite Association's database of zeolite structures found at www.iza-structure.org/databases. Particularly, the DDR framework zeolite can be ZSM-58. For example, ZSM-58 can be formed according to the methods described in U.S. Patent Application Publication No. 2014/0161717, the entirety of which is incorporated by reference. Additionally or alternatively, the DDR framework zeolite can include DDR frameworks formed according to the methods described in U.S. Provisional Patent Application Serial No. 62/082,210, the entirety of which is incorporated by reference.

[0056] Additionally or alternatively, the coating can also comprise a binder. The binder particles are capable of binding the adsorbent particles together to form an aggregate of binder particles and adsorbent particles in the coating. The binder can comprise particles having an average diameter of greater than or equal to about 10 nm, greater than or equal to about 15 nm, greater than or equal to about 20 nm, greater than or equal to about 25 nm, greater than or equal to about 30 nm, greater than or equal to about 35 nm, greater than or equal to about 45 nm, greater than or equal to about 50 nm, greater than or equal to about 55 nm, greater than or equal to about 60 nm, greater than or equal to about 65 nm, greater than or equal to about 70 nm, greater than or equal to about 75 nm, greater than or equal to about 80 nm, greater than or equal to about 85 nm, greater than or equal to about 90 nm, greater than or equal to about 95 nm,

greater than or equal to about 100 nm, greater than or equal to about 110 nm, greater than or equal to about 120 nm, greater than or equal to about 130 nm, greater than or equal to about 140 nm, greater than or equal to about 150 nm, greater than or equal to about 160 nm, greater than or equal to about 170 nm, greater than or equal to about 180 nm, greater than or equal to about 190 nm, greater than or equal to about 200 nm, greater than or equal to about 210 nm, greater than or equal to about 220 nm, greater than or equal to about 230 nm, greater than or equal to about 240 nm or greater than or equal to about 250 nm. Additionally or alternatively, the binder can comprise particles can have an average diameter of less than or equal to about 10 nm, less than or equal to about 15 nm, less than or equal to about 20 nm, less than or equal to about 25 nm, less than or equal to about 30 nm, less than or equal to about 35 nm, less than or equal to about 45 nm, less than or equal to about 50 nm, less than or equal to about 55 nm, less than or equal to about 60 nm, less than or equal to about 65 nm, less than or equal to about 70 nm, less than or equal to about 75 nm, less than or equal to about 80 nm, less than or equal to about 85 nm, less than or equal to about 90 nm, less than or equal to about 95 nm, less than or equal to about 100 nm, less than or equal to about 110 nm, less than or equal to about 120 nm, less than or equal to about 130 nm, less than or equal to about 140 nm, less than or equal to about 150 nm, less than or equal to about 160 nm, less than or equal to about 170 nm, less than or equal to about 180 nm, less than or equal to about 190 nm, less than or equal to about 200 nm, less than or equal to about 210 nm, less than or equal to about 220 nm, less than or equal to about 230 nm, less than or equal to about 240 nm or less than or equal to about 250 nm. Ranges expressly disclosed include combinations of the above-enumerated upper and lower limits, e.g., about 10 nm to about 250 nm, about 25 nm to about 200 nm, about 100 nm to about 200 nm, etc. Particularly, the binder particles can have an average diameter of about 100 nm to about 200 nm.

[0057] Additionally or alternatively, the binder is basic. The binder can have a pH of greater than or equal to about 7, greater than or equal to about 7.5, greater than or equal to about 8, greater than or equal to about 8.5, greater than or equal to about 9, greater than or equal to about 9.5, greater than or equal to about 10, greater than or equal to about 10.5, greater than or equal to about 11, greater than or equal to about 11.5, greater than or equal to about 12, greater than or equal to about 12.5, greater than or equal to about 13, greater than or equal to about 13.5 or greater than or equal to about 14. Particularly, the binder can have a pH greater than about 7, particularly about 10. Additionally or alternatively, the binder has a pH of less than or equal to about 7, less than or equal to about 7.5, less than or equal to about 8, less than or equal to about 8.5, less than or equal to about 9, less than or equal to about 9.5, less than or equal to about 10, less than or equal to about 10.5, less than or equal to about 11, less than or equal to about 11.5, less than or equal to about 12, less than or equal to about 12.5, less than or equal to about 13, less than or equal to about 13.5 or less than or equal to about 14. Ranges expressly disclosed include combinations of the above-enumerated upper and lower limits, e.g., about 7 to about 14, about 10 to about 12, about 11 to about 13.5, about 11 to about 12.5, etc. Particularly, the pH can be from about 7 to about 11.

[0058] Exemplary materials suitable for use as the binder include but are not limited to silica (SiO_2) and alumina (Al_2O_3). Particularly, the binder can comprise SiO_2 .

[0059] Additionally or alternatively, the coating can be present on the substrate in a thickness of greater than or equal to about 20 μm , greater than or equal to about 30 μm , greater than or equal to about 40 μm , greater than or equal to about 50 μm , greater than or equal to about 60 μm , greater than or equal to about 70 μm , greater than or equal to about 80 μm , greater than or equal to about

90 μm , greater than or equal to about 100 μm , greater than or equal to about 110 μm , greater than or equal to about 120 μm , greater than or equal to about 130 μm , greater than or equal to about 140 μm , greater than or equal to about 150 μm , greater than or equal to about 160 μm , greater than or equal to about 170 μm , greater than or equal to about 180 μm , greater than or equal to about 190 μm , greater than or equal to about 200 μm , greater than or equal to about 210 μm , greater than or equal to about 220 μm , greater than or equal to about 230 μm , greater than or equal to about 240 μm , greater than or equal to about 250 μm , greater than or equal to about 260 μm , greater than or equal to about 270 μm , greater than or equal to about 280 μm , greater than or equal to about 290 μm , or greater than or equal to about 300 μm . Particularly, the coating can be present on the substrate in a thickness of greater than or equal to about 100 μm . Additionally or alternatively, the coating can be present on the substrate in a thickness of less than or equal to about 20 μm , less than or equal to about 30 μm , less than or equal to about 40 μm , less than or equal to about 50 μm , less than or equal to about 60 μm , less than or equal to about 70 μm , less than or equal to about 80 μm , less than or equal to about 90 μm , less than or equal to about 100 μm , less than or equal to about 110 μm , less than or equal to about 120 μm , less than or equal to about 130 μm , less than or equal to about 140 μm , less than or equal to about 150 μm , less than or equal to about 160 μm , less than or equal to about 170 μm , less than or equal to about 180 μm , less than or equal to about 190 μm , less than or equal to about 200 μm , less than or equal to about 210 μm , less than or equal to about 220 μm , less than or equal to about 230 μm , less than or equal to about 240 μm , less than or equal to about 250 μm , less than or equal to about 260 μm , less than or equal to about 270 μm , less than or equal to about 280 μm , less than or equal to about 290 μm , or less than or equal to about 300 μm . Ranges expressly disclosed include combinations of the above-enumerated upper and lower limits, e.g., about 20 μm to about 300 μm , about 30 μm to about

200 μm , about 50 μm to about 100 μm , etc. Particularly, the coating on the substrate can have a thickness of about 30 μm to about 200 μm .

[0060] Additionally or alternatively, the coating can comprise one or more layers of adsorbent particles and binder particles. The coating can comprise two or more layers, three or more layers, four or more layers, five or more layers, six or more layers, seven or more layers, eight or more layers, nine or more layers, or ten or more layers of adsorbent particles and binder particles. Additionally or alternatively, the coating can comprise two or fewer layers, three or fewer layers, four or fewer layers, five or fewer layers, six or fewer layers, seven or fewer layers, eight or fewer layers, nine or fewer layers, or ten or fewer layers of adsorbent particles and binder particles. Ranges expressly disclosed include combinations of the above-enumerated upper and lower limits, e.g., one to ten layers, two to eight layers, three to seven layers, etc.

[0061] Additionally or alternatively, the coating on the substrate can have a macroporosity of at least about 5%, at least about 10%, at least about 15%, at least about 20%, at least about 25%, at least about 30%, at least about 35%, at least about 40%, at least about 45% or at least about 50%. The coating on the substrate can have a macroporosity of less than about 5%, less than about 10%, less than about 15%, less than about 20%, less than about 25%, less than about 30%, less than about 35%, less than about 40%, less than about 45% or less than about 50%. Ranges expressly disclosed include combinations of the above-enumerated upper and lower limits, e.g., about 5% to about 50%, about 10% to about 40%, about 20% to about 35%, etc. Particularly, the coating on the substrate can have a macroporosity of about 10% to about 40%.

C. Primer Layer

[0062] Additionally or alternatively, the adsorbent bed may further comprise a primer layer on the substrate. The primer layer can be present between the substrate and the coating. The primer layer can increase surface roughness of the substrate and/or provide a surface more similar in composition to the adsorbent particles in the coating for increased adhesion and improved bonding of the coating to the substrate. Additionally, when the substrate is a metal, the primer layer can reduce exposure of potentially reactive species on the metal surface and also diminish thermal expansion differences between the metal surface and the coating. The primer layer can be a zirconium-containing layer. Particularly, the zirconium-containing layer can comprise zirconium oxide, zirconium silicate or a combination thereof.

III. Methods of Preparing the Structured Adsorbent Bed

[0063] In various aspects, a method of preparing a structured adsorbent bed described herein is provided. The method can comprise pretreating the substrate, preparing an aqueous slurry comprising the adsorbent particles and the binder and applying the aqueous slurry to the substrate to form the coating on the substrate.

[0064] Additionally or alternatively, pretreating the substrate can comprise applying a primer layer, such as the zirconium-containing layer described herein. Additionally or alternatively, the substrate can be cleaned prior to application of the primer layer.

[0065] Additionally or alternatively, pretreating the substrate can comprise heating the substrate and applying a primer layer, such as the zirconium-containing layer described herein. When the substrate is a metal having no porosity, heating the substrate prior to application of the primer layer results in a

micron-thin metal oxide skin, which roughens the metal surface and creates anchoring sites on the metal surface thereby improving adhesion and bonding of the coating. In pretreating the substrate, the substrate can be heated at a temperature of greater than or equal to about 500°C, greater than or equal to about 550°C, greater than or equal to about 600°C, greater than or equal to about 650°C, greater than or equal to about 700°C, greater than or equal to about 750°C, greater than or equal to about 800°C, greater than or equal to about 850°C, greater than or equal to about 900°C, greater than or equal to about 950°C, greater than or equal to about 1,000°C, greater than or equal to about 1,050°C, greater than or equal to about 1,100°C, greater than or equal to about 1,150°C, greater than or equal to about 1,200°C, greater than or equal to about 1,250°C, or greater than or equal to about 1,300°C. Additionally or alternatively, the substrate can be heated at a temperature of less than or equal to about 500°C, less than or equal to about 550°C, less than or equal to about 600°C, less than or equal to about 650°C, less than or equal to about 700°C, less than or equal to about 750°C, less than or equal to about 800°C, less than or equal to about 850°C, less than or equal to about 900°C, less than or equal to about 950°C, less than or equal to about 1,000°C, less than or equal to about 1,050°C, less than or equal to about 1,100°C, less than or equal to about 1,150°C, less than or equal to about 1,200°C, less than or equal to about 1,250°C, or less than or equal to about 1,300°C. Ranges expressly disclosed include combinations of the above-enumerated upper and lower limits, e.g., about 500°C to about 1,300°C, about 600°C to about 1,100°C, about 900°C to about 1050°C, etc. The substrate can be heated at a temperature of about 600°C to about 1,100°C, particularly about 900°C.

[0066] Additionally or alternatively, the substrate can be pre-treated by heating the substrate for at least about 1 hour, at least about 2 hours, at least about 3 hours, at least about 4 hours, at least about 5 hours, at least about 6

hours, at least about 7 hours, at least about 8 hours, at least about 9 hours or at least about 10 hours, particularly at least about 6 hours. Alternatively or additionally, the substrate can be heated for less than about 1 hour, less than about 2 hours, less than about 3 hours, less than about 4 hours, less than about 5 hours, less than about 6 hours, less than about 7 hours, less than about 8 hours, less than about 9 hours or less than about 10 hours. Ranges expressly disclosed include combinations of the above-enumerated upper and lower limits, e.g., about 1 hour to about 10 hours, about 1 hour to about 2 hours, about 2 hours to about 6 hours, etc.

[0067] Additionally or alternatively, the aqueous slurry can comprise the adsorbent particles and the binder, both as described herein, in a weight ratio from about 70:30 w/w to about 90:10 w/w. Particularly, the weight ratio of adsorbent particles to binder in the aqueous slurry can be about 80:20 w/w or about 90:10 w/w. Particularly, the binder in the aqueous slurry can be SiO₂. Additionally or alternatively, the aqueous slurry can include viscosity modifiers, water and/or dispersants.

[0068] Coating adhesion, particle cohesion and uniformity depend on slurry properties. Further, the size of the suspended particles has a great influence on the stability of the suspension and adhesion to the substrate. In one aspect, the adsorbent particles in the slurry have an average diameter of greater than or equal to about 25 μ m. Additionally or alternatively, the binder particles in the slurry have an average diameter of from about 100 nm to about 200 nm. The aqueous slurry as described herein can be stable for many hours, for example about 5, about 10, about 15, about 20, about 25, about 30 hours if stirred and minutes if not stirred. Further, the aqueous slurry can have a pH of about 7 to about 10 and an approximate viscosity of 14.4 cP. Additionally or alternatively,

the aqueous slurry can also include organic additives for controlling rheology of the slurry and/or to act as temporary binding aids.

[0069] Additionally or alternatively, the aqueous slurry can be applied to the substrate by dip coating techniques, pulling the slurry into the substrate with a vacuum and/or pumping the slurry into the substrate. Multiple coatings of the aqueous slurry can be applied to the substrate, for example, at least one coating, at least two coatings, at least three coatings, at least four coatings, at least five coatings, at least six coatings, at least seven coatings, at least eight coatings, at least nine coatings or at least ten coatings.

[0070] Additionally or alternatively, the method further comprises removing excess coating from the coated substrate, drying the coated substrate and/or heating the coated substrate.

[0071] Removing the excess coating in a high cell density substrate (e.g., monoliths) can be difficult due to the high capillary forces within the cells as result of the smaller channel diameter (e.g., 400 μm) of the high cell density substrates. To remove excess coating from the channels in the substrate, the pressure drop across the substrate must be greater than the capillary force through the channel. Thus, in one aspect, the excess coating can be removed from the substrate by flowing a gas, such as nitrogen, through the coated substrate at a rate greater than or equal to about 100 L/min, greater than or equal to about 150 L/min, greater than or equal to about 200 L/min, or greater than or equal to about 250 L/min. Particularly, the gas can be flowed through the substrate at a rate greater than or equal to about 100 L/min. Additionally or alternatively, the gas can be flowed through the substrate at a rate lesser than or equal to about 100 L/min, lesser than or equal to about 150 L/min, lesser than or equal to about 200 L/min, or lesser than or equal to about 250 L/min. Ranges

expressly disclosed include combinations of the above-enumerated upper and lower limits, e.g., about 100 L/min to about 250 L/min, about 100 L/min to about 200 L/min, etc.

[0072] Additionally or alternatively, drying the coated substrate can comprise flash drying the coated substrate. The gas flowed through the substrate at a high flow rate to remove excess coating can result in rapid evaporative cooling of the slurry in the channels. This can lead to slower water evaporation and drying of the slurry, which can contribute to “bridging,” resulting in channels being blocked by unstable, mobile slurry particles bridging the cell diameter in the monoliths and drying into plugs. Flash drying the coated substrate may stabilize the coating films and prevent “bridging” and size segregation of the zeolite and binder particles upon vertical standing. The flash drying can comprise heating a gas purge, such as the same gas used to remove the excess coating, to about 40°C, about 45°C, about 50°C, about 55°C, about 60°C, about 65°C or about 70°C, particularly between about 50°C and about 60°C. The heated gas purge can be flowed through the coated substrate at a rate of at least about 100 L/min, at least about 150 L/min, at least about 200 L/min, or at least about 250 L/min. Particularly, the heated purge gas can be flowed through the substrate at a rate of at least about 100 L/min. Additionally or alternatively, the heated gas purge can be flowed through the coated substrate at a rate of no greater than about 100 L/min, no greater than about 150 L/min, no greater than about 200 L/min, or no greater than about 250 L/min. Ranges expressly disclosed include combinations of the above-enumerated upper and lower limits, e.g., about 100 L/min to about 250 L/min, about 100 L/min to about 200 L/min, etc.

[0073] Additionally or alternatively, the method further comprises calcining the coated substrate, which optionally, can be performed after the coated substrate is dried. The calcining can be performed in air. The calcining can be

performed at a temperature suitable for degrading and/or removing substantially all of the volatile organic components and water in the structured adsorbent bed, for example, at least about 300°C, at least about 350°C, at least about 400°C, at least about 450°C, about 500°C, at least about 550°C or at least about 600°C. Additionally or alternatively, the calcining can be performed at a temperature of less than about 300°C, less than about 350°C, less than about 400°C, less than about 450°C, less than about 500°C, less than about 550°C or less than about 600°C. Ranges expressly disclosed include combinations of the above-enumerated upper and lower limits, e.g., about 300°C to about 600°C, about 350°C to about 450°C, about 300°C to about 500°C, etc. Particularly, the calcining is performed at a temperature of about 500°C, optionally using a heating ramp, such as: a) drying at about 120°C for about 8 hours; b) increasing the temperature to about 500°C over about 4 hours; c) holding at about 500°C for about 2 hours; and d) cooling to about 120°C over about 2 hours.

IV. Gas Separation Processes

[0074] In various aspects, a gas separation process is provided herein. The gas separation process comprises contacting a gas mixture containing at least one contaminant with a structured adsorbent bed as described herein.

[0075] In various aspects, the gas separation process can be achieved by swing adsorption processes, such as pressure swing adsorption (PSA) and temperature swing adsorption (TSA). All swing adsorption processes have an adsorption step in which a feed mixture (typically in the gas phase) is flowed over an adsorbent that preferentially adsorbs a more readily adsorbed component relative to a less readily adsorbed component. A component may be more readily adsorbed because of kinetic or equilibrium properties of the adsorbent. The adsorbent can typically be contained in a contactor that is part of the swing adsorption unit. The contactor can typically contain an engineered structured

- 28 -

adsorbent bed or a particulate adsorbent bed. The bed can contain the adsorbent and other materials such as other adsorbents, mesopore filling materials, and/or inert materials used to mitigate temperature excursions from the heat of adsorption and desorption. Other components in the swing adsorption unit can include, but are not necessarily limited to, valves, piping, tanks, and other contactors.

[0076] PSA processes rely on the fact that gases under pressure tend to be adsorbed within the pore structure of the adsorbent materials. Typically, the higher the pressure, the greater the amount of targeted gas component that will be adsorbed. When the pressure is reduced, the adsorbed targeted component is typically released, or desorbed. PSA processes can be used to separate gases of a gas mixture, because different gases tend to fill the pores or free volume of the adsorbent to different extents due to either the equilibrium or kinetic properties of the adsorbent. In many important applications, to be described as "equilibrium-controlled" processes, the adsorptive selectivity is primarily based upon differential equilibrium uptake of the first and second components. In another important class of applications, to be described as "kinetic-controlled" processes, the adsorptive selectivity is primarily based upon the differential rates of uptake of the first and second components.

[0077] If a gas mixture, such as natural gas, is passed under pressure through a vessel containing a polymeric or microporous adsorbent that is more selective towards carbon dioxide than it is for methane, at least a portion of the carbon dioxide can be selectively adsorbed by the adsorbent, and the gas exiting the vessel can be enriched in methane. When the adsorbent reaches the end of its capacity to adsorb carbon dioxide, it can be regenerated by reducing the pressure, thereby releasing the adsorbed carbon dioxide. The adsorbent can then typically be purged and repressurized and ready for another adsorption cycle.

[0078] TSA processes also rely on the fact that gases under pressure tend to be adsorbed within the pore structure of the adsorbent materials. When the temperature of the adsorbent is increased, the adsorbed gas is typically released, or desorbed. By cyclically swinging the temperature of adsorbent beds, TSA processes can be used to separate gases in a mixture when used with an adsorbent selective for one or more of the components in a gas mixture. Partial pressure purge displacement (PPSA) swing adsorption processes regenerate the adsorbent with a purge. Rapid cycle (RC) swing adsorption processes complete the adsorption step of a swing adsorption process in a short amount of time. For kinetically selective adsorbents, it can be preferable to use a rapid cycle swing adsorption process. If the cycle time becomes too long, the kinetic selectivity can be lost. These swing adsorption protocols can be performed separately or in combinations. Examples of processes that can be used herein either separately or in combination are PSA, TSA, pressure temperature swing adsorption (PTSA), partial purge displacement swing adsorption (PPSA), PPTSA, rapid cycle PSA (RCPSA), RCTSA, vacuum pressure swing adsorption (VPSA), RCPPSA and RCPTSA.

[0079] In PSA processes, a feed gas mixture containing the first and second gas components is separated by cyclic variations of pressure coordinated with cyclic reversals of flow direction in a flow path contacting a fixed bed of the adsorbent material in an adsorber vessel. In the case of TSA or PPSA processes, cyclic variations of temperature and/or partial pressure of the gas components may be coordinated with gas flow through a flow path to perform a separation. The process in any specific PSA application operates at a cyclic frequency characterized by its period, and over a pressure envelope between a first relatively higher pressure and a second relatively lower pressure. Separation in PSA is achieved by coordinating the pressure variations with the flow pattern

within the flow path, so that the gas mixture in the flow path is enriched in the second component (owing to preferential adsorptive uptake of the first component in the adsorbent material) when flowing in a first direction in the flow path, while the gas mixture is enriched in the first component (which has been desorbed by the adsorbent material) when flowing in the opposite direction in the flow path. In order to achieve separation performance objectives (i.e. product gas purity, recovery and productivity), process parameters and operating conditions should be designed to achieve a sufficiently high adsorptive selectivity of the first and second components over the adsorbent material, at the cyclic frequency and within the pressure envelope.

[0080] Swing adsorption processes can be applied to remove a variety of target gases, also referred to as a “contaminant gas” from a wide variety of gas mixtures. The “light component” as utilized herein is taken to be the species or molecular component(s) not preferentially taken up by the adsorbent in the adsorption step of the process. Conversely, the “heavy component” as utilized herein is taken to be the species or molecular component(s) preferentially taken up by the adsorbent in the adsorption step of the process.

[0081] An example of a gas mixture that can be separated in the methods described herein is a gas mixture comprising CH_4 , such as a natural gas stream. A gas mixture comprising CH_4 can contain significant levels of contaminants such as H_2O , H_2S , CO_2 , N_2 , mercaptans, and/or heavy hydrocarbons. Additionally or alternatively, the gas mixture can comprise NO_x and/or SO_x species as contaminants, such as a waste gas stream, a flue gas stream and a wet gas stream. As used herein, the terms “ NO_x ,” and “ NO_x species” refers to the various oxides of nitrogen that may be present in waste gas, such as waste gas from combustion processes. The terms refer to all of the various oxides of nitrogen including, but not limited to, nitric oxide (NO), nitrogen dioxide (NO_2),

nitrogen peroxide (N_2O), nitrogen pentoxide (N_2O_5), and mixtures thereof. As used herein, the terms “ SO_x ,” and “ SO_x species” refers to various oxides of sulfur that may be present in waste gas, such as waste gas from combustion processes. The terms refer to all of the various oxides of sulfur including, but not limited to, SO , SO_2 , SO_3 , SO_4 , S_7O_2 and S_6O_2 . Thus, examples of contaminants include, but are not limited to H_2O , H_2S , CO_2 , N_2 , mercaptans, heavy hydrocarbons, NO_x and/or SO_x species.

[0082] In the practice of the present invention, it may be desirable to operate with a multiplicity of structured adsorbent beds, with several coupled in a heating/cooling operation and others involved in adsorption (and/or desorption). In such an operation, the adsorbent bed can be substantially cooled by a circulating heat transfer medium before it is switched into service for adsorption. One advantage of such an operation can be that the thermal energy used to swing the bed is retained in the heat transfer medium. If adsorption were to proceed simultaneously with cooling, then a substantial part of the heat in the bed could be lost to the adsorbate-free feed, and a higher heat load could be needed to restore the high temperature of the heat transfer medium.

[0083] Adsorptive kinetic separation (AKS) processes, as described above, are useful for development and production of hydrocarbons, such as gas and oil processing. Particularly, as described in U.S. Patent Application Publication No. 2013/032716, which is herein incorporated by reference in its entirety, the AKS processes described herein can use one or more kinetic swing adsorption process, such as pressure swing adsorption (PSA), thermal swing adsorption (TSA), calcination, and partial pressure swing or displacement purge adsorption (PPSA), including combinations of these processes; each swing adsorption process may be utilized with rapid cycles, such as using one or more rapid cycle pressure swing adsorption (RC-PSA) units, with one or more rapid cycle

temperature swing adsorption (RC-TSA) units or with one or more rapid cycle partial pressure swing adsorption (RC-PPSA) units; exemplary kinetic swing adsorption processes are described in U.S. Patent Nos. 7,959,720; 8,545,602; 8,529,663; 8,444,750; and 8,529,662 and U.S. Provisional Application Nos. 61/448,121; 61/447,848; 61/447,869; and 61/447,877, which are each herein incorporated by reference in its entirety. The provided processes, can be useful for rapid, large scale, efficient separation of a variety of target gases from gas mixtures.

[0084] The provided processes and apparatuses may be used to prepare natural gas products by removing contaminants. The provided processes and apparatuses can be useful for preparing gaseous feed streams for use in utilities, including separation applications such as dew point control, sweetening/detoxification, corrosion protection/control, dehydration, heating value, conditioning, and purification. Examples of utilities that utilize one or more separation applications can include generation of fuel gas, seal gas, non-potable water, blanket gas, instrument and control gas, refrigerant, inert gas, and hydrocarbon recovery. Exemplary “not to exceed” product (or “target”) acid gas removal specifications can include: (a) 2 vol % CO₂, 4 ppm H₂S; (b) 50 ppm CO₂, 4 ppm H₂S; or (c) 1.5 vol % CO₂, 2 ppm H₂S.

[0085] The provided processes and apparatuses may also be used to remove acid gas from hydrocarbon streams. Acid gas removal technology becomes increasingly important as remaining gas reserves exhibit higher concentrations of acid (sour) gas resources. Hydrocarbon feed streams can vary widely in amount of acid gas, such as from several parts per million to 90 vol %. Non-limiting examples of acid gas concentrations from exemplary gas reserves can 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; or (e) 15 vol % H₂S, 30 vol % CO₂.

[0086] One or more of the following may be utilized with the processes and apparatuses provided herein, to prepare a desirable product stream, while maintaining relatively high hydrocarbon recovery:

(a) removing acid gas with RC-TSA using advanced cycles and purges as described in U.S. Provisional Application No. 61/447,854, filed Mar. 1, 2011, as well as the U.S. Patent No. 8,784,533, which are together incorporated by reference herein in their entirety;

(b) using a mesopore filler to reduce the amount of trapped methane in the adsorbent bed and increase the overall hydrocarbon recovery, as described in U.S. Patent Nos. 7,959,720; 8,444,750; and 8,529,663, each of which is herein incorporated by reference in its entirety;

(c) depressurizing one or more RC-TSA units in multiple steps to intermediate pressures so that the acid gas exhaust can be captured at a higher average pressure, thereby decreasing the compression required for acid gas injection; pressure levels for the intermediate depressurization steps may be matched to the interstage pressures of the acid gas compressor to optimize the overall compression system;

(d) using exhaust or recycle streams to minimize processing and hydrocarbon losses, such as using exhaust streams from one or more RC-TSA units as fuel gas instead of re-injecting or venting;

(e) using multiple adsorbent particles in a single bed to remove trace amounts of first contaminants, such as H₂S, before removal of a second contaminant, such as CO₂; such segmented beds may provide rigorous acid gas removal down to ppm levels with RC-TSA units with minimal purge flow rates;

(f) using feed compression before one or more RC-TSA units to achieve a desired product purity;

- 34 -

(g) contemporaneous removal of non-acid gas contaminants such as mercaptans, COS, and BTEX; selection processes and materials to accomplish the same;

(h) selecting a cycle time and cycle steps based on adsorbent material kinetics; and

(i) using a process and apparatus that uses, among other equipment, two RC-TSA units in series, wherein the first RC-TSA unit cleans a feed stream down to a desired product purity and the second RC-TSA unit cleans the exhaust from the first unit to capture methane and maintain high hydrocarbon recovery; use of this series design may reduce the need for a mesopore filler.

[0087] The processes, apparatuses, and systems provided herein can be useful in large gas treating facilities, such as facilities that process more than five million standard cubic feet per day (MSCFD) of natural gas, for example more than 15 MSCFD, more than 25 MSCFD, more than 50 MSCFD, more than 100 MSCFD, more than 500 MSCFD, more than one billion standard cubic feet per day (BSCFD), or more than two BSCFD.

V. Further Embodiments

[0088] The invention can additionally or alternately include one or more of the following embodiments.

[0089] Embodiment 1. A structured adsorbent bed for purification of a gas feedstream comprising: a substrate having a cell density greater than 1040 cpsi; and a coating on the substrate, wherein the coating comprises adsorbent particles and a binder.

[0090] Embodiment 2. The structured adsorbent bed of embodiment 1, wherein the adsorbent particles have an average diameter of about 2 μm to about 40 μm .

[0091] Embodiment 3. The structured adsorbent bed of embodiment 1, wherein the adsorbent particles have an average diameter greater than about 20 μm .

[0092] Embodiment 4. The structured adsorbent bed of any of the previous embodiments, wherein the adsorbent particles have an axis ratio of at least 1.2.

[0093] Embodiment 5. The structured adsorbent bed of any of the previous embodiments, wherein the adsorbent particles comprise a microporous material.

[0094] Embodiment 6. The structured adsorbent bed of embodiment 5, wherein the microporous material comprises a zeolite, such as DDR (e.g., Sigma-1 and ZSM-58).

[0095] Embodiment 7. The structured adsorbent bed of any of the previous embodiments, wherein the binder comprises particles having an average diameter of about 25 nm to about 200 nm, particularly 100 nm to about 200 nm.

[0096] Embodiment 8. The structured adsorbent bed of any of the previous embodiments, wherein the binder has a pH greater than 7.

[0097] Embodiment 9. The structured adsorbent bed of any of the previous embodiments, wherein the binder comprises SiO_2 .

- 36 -

[0098] Embodiment 10. The structured adsorbent bed of any of the previous embodiments, wherein the substrate has a cell density of about 1400 cpsi or greater.

[0099] Embodiment 11. The structured adsorbent bed of any of the previous embodiments, wherein the substrate has a cell density of about 1500 cpsi to about 4000 cpsi.

[00100] Embodiment 12. The structured adsorbent bed of any of the previous embodiments, wherein the coating on the substrate has a thickness of at least 100 μm or greater.

[00101] Embodiment 13. The structured adsorbent bed of embodiment 1, wherein the coating on the substrate has a thickness of about 30 μm to about 200 μm .

[00102] Embodiment 14. The structured adsorbent bed of any of the previous embodiments, wherein the substrate is a porous solid selected from the group consisting of a metal oxide, a mixed-metal oxide, a ceramic and a zeolite and/or has a porosity of about 30% or less, or alternatively the substrate is a non-porous solid selected from the group consisting of a metal (e.g., stainless steel), a glass and a plastic.

[00103] Embodiment 15. The structured adsorbent bed of any of the previous embodiments further comprising a zirconium-containing layer (e.g., zirconium oxide, zirconium silicate and/or a combination thereof).

[00104] Embodiment 16. A method of preparing the structured adsorbent bed of any of the previous embodiments, the method comprising: pretreating the

substrate; and/or preparing an aqueous slurry comprising the adsorbent particles and the binder; and/or applying the aqueous slurry to the substrate to form the coating on the substrate.

[00105] Embodiment 17. The method of embodiment 16, wherein pretreating the substrate comprises: (i) applying the zirconium-containing layer (e.g., zirconium oxide, zirconium silicate and/or a combination thereof) to the substrate; or (ii) heating the substrate, particularly at about 600°C to about 1100 °C, and applying the zirconium-containing layer to the substrate.

[00106] Embodiment 18. The method of embodiment 16 or 17, wherein the binder is SiO₂.

[00107] Embodiment 19. The method of embodiment 16, 17, or 18 wherein the weight ratio of the adsorbent particles to the binder is from about 70:30 w/w to about 90:10 w/w.

[00108] Embodiment 20. The method of embodiment 16, 17, 18, or 19 further comprising: removing excess coating from the coated substrate; and/or drying the coated substrate; and/or heating the coated substrate.

[00109] Embodiment 21. The method of embodiment 20, wherein the excess coating is removed from the substrate by flowing a gas through the coated substrate at a rate equal to or greater than about 100 L/min.

[00110] Embodiment 22. The method of embodiment 20, wherein drying the coated substrate comprises flash drying the coated substrate wherein a gas purge heated from about 50°C to about 60°C is flowed through the coated substrate at rate of at least 100 L/min.

- 38 -

[00111] Embodiment 23. The method of embodiments 16, 17, 18, 19, 20, 21, or 22 wherein the coating has about 10% to about 40% macroporosity.

[00112] Embodiment 24. A gas separation process comprising contacting a gas mixture containing at least one contaminant with the structured adsorbent bed of embodiments 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, or 15.

[00113] Embodiment 25. The gas separation process of embodiment 24, wherein the gas mixture comprises CH₄ and/or the at least one contaminant is selected from the group consisting CO₂, H₂O, H₂S, NO_x and SO_x.

[00114] Embodiment 26. The gas separation process of embodiment 24 or 25, wherein the process comprises PSA, TSA, PPSA, PTSA, RCPSA, RCTSA, RCPPSA or RCPTSA.

EXAMPLES

[00115] The following examples are merely illustrative, and do not limit this disclosure in any way.

Example 1 - Synthesis

1. Materials

Substrates

[00116] High cell density metal and ceramic substrates were obtained as follows:

- Spiral-wound 316 stainless steel monoliths were obtained from Catacel Corporation. The metal monoliths were ~6 inches long and had diameters of ~1.1 inches. Cell densities of the metal monoliths included ~1440 cpsi and ~2918 cpsi. The monoliths were a corrugated foil matrix which consisted of flat-on-

corrugated sheets that were wound around a central pin. The structures were brazed and tack welded for mechanical strength. The individual cells within the monolith had a trapezoidal geometry. The cell dimensions of the ~1440 cpsi monoliths were approximately 0.55 mm x 0.55 mm. The cell dimensions of the ~2918 cpsi monoliths were approximately 0.38 x 0.42 mm.

- Very low porosity ceramic monoliths (<6% wall porosity) consisting of pure Al_2O_3 were obtained from Applied Ceramics Company. The ceramic monoliths were ~6 inches long with diameters of ~1.1 inches. The cell densities of the ceramic monoliths included ~1500 cpsi and ~2700 cpsi. The individual cells had a square geometry. The cell dimensions of the ~1500 cpsi monoliths were approximately 0.55 mm x 0.55 mm. The cell dimensions of the ~2700 cpsi monoliths were approximately 0.40 x 0.40 mm. Scanning electron microscope (SEM) images of the ~2700 cpsi ceramic monolith is shown in Figures 2a and 2b.

Adsorbent materials:

[00117] DDR zeolites prepared according to the methods described in U.S. Patent Application Publication No. 2014/0161717 with a Si/Al ratio of ~600:1 and a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of ~300:1 were used in the coating formulations. The particle sizes of the DDR zeolites were very large, with the average particle diameter in the range of ~25 μm to ~30 μm .

2. Pre-treatment of substrate

[00118] Two pre-treatment options were used:

- (i) A Zr-based primer layer was applied as a first layer to the metal and the ceramic monoliths. The metal structures were first cleaned with a phosphate solution (i.e., ~1% trisodium

phosphate solution) to remove any processing oils. The ceramic structures were pre-cleaned with acetone, ethanol and water separately to remove any processing materials; or

- (ii) A high temperature thermal oxidation treatment was performed on the metal monoliths followed by an application of the Zr-based primer.

[00119] The metal monoliths, with 0% wall porosity, and the ceramic substrates, with very low wall porosity, were pre-treated before coating to increase adhesion of the adsorbent layer and, thus, increase the lifetime of the structured adsorbent.

[00120] The surface of the metal monoliths were modified by a high temperature (i.e., $\sim 900^{\circ}\text{C}$ – $\sim 1050^{\circ}\text{C}$, for ~ 6 hours) thermal treatment in air to develop a micron-thin metal oxide skin, useful for roughening the surface and creating anchoring sites. An SEM image of the ~ 1440 cpsi metal monolith after pre-treatment at $\sim 900^{\circ}\text{C}$ is shown in Figure 3. Following this process, a thin coating of a Zr-based oxide (Aremco 644-N, diluted with 12% H_2O), was applied by a dip-coating process to apply the primer layer.

[00121] The surface of the ceramic monoliths were primed with the Aremco 644-N to increase surface roughness and anchoring sites on the glass-like, very low porosity walls to improve adhesion of the adsorbent layer.

3. Coating

Slurry Preparation

[00122] An aqueous slurry was prepared with ~ 35 weight % solids content by adding deionized water (~ 40.413 g), colloidal SiO_2 (Nissan Chemicals US, MP-1040, ~ 100 nm diameter SiO_2 , ~ 40 wt% solids, ~ 5.942 g), DDR adsorbent

(prepared according to the methods described in U.S. Patent Application Publication No. 2014/0161717) ($\sim 25\ \mu\text{m}$ to $\sim 30\ \mu\text{m}$ average diameter particles, $\sim 22.050\ \text{g}$), $\sim 0.5\%$ sodium silicate solution (EMD Corp., $\sim 29\%$ SiO_2 , $\sim 9\%$ Na_2O , $\sim 0.253\ \text{g}$), $\sim 2\ \text{wt}\%$ of 2% aqueous methyl cellulose solution (Dow Methocel $\sim 240\ \text{S}$, $\sim 1.422\ \text{g}$) and $\sim 3\ \text{mole}\ \%$ methanol ($\sim 2.43\ \text{gm}$ methanol). Figures 4-6 provide transmission electron microscopy (TEM) images and particle diameter graphs of the $\sim 100\ \text{nm}$ colloidal SiO_2 binder used as well as other binders utilized, specifically $\sim 25\ \text{nm}$ colloidal SiO_2 , and string of pearls colloidal SiO_2 .

[00123] The methyl cellulose was used for viscosity control, slurry stabilization, to aid in uniform film formation, and as a lubricity agent to improve removal of excess slurry in ultra-fine channels that have associated very high capillary forces. Methanol was used to aid particle dispersion (to avoid particle agglomeration) due to its surface activity. The ratio of DDR adsorbent to total SiO_2 added was $\sim 90:10$ weight/weight. The slurry was mixed using a FlackTek asymmetric centrifugal lab mixer for ~ 1 minute at $\sim 2200\ \text{rpm}$ to obtain a homogeneously dispersed mixture. The prepared slurry had a viscosity of $\sim 14\ \text{cP}$ and a final pH of approximately 11.

Coating

[00124] The ultra-high density monoliths were dipped into a well-mixed slurry of approximately $35\ \text{wt}\%$ solids for less than a minute. Other techniques that can be used to immerse the monolith cells in slurry can include mild vacuum technique, pulling slurry up into the cells, and pumping the slurry into the monolith cells from above, inside a closed plastic vessel.

[00125] Excess slurry was removed from the cells using a high velocity nitrogen gas flow (approximately $200\ \text{L/min}$ flow rate) for several minutes. The

- 42 -

high flow gas purge resulted in rapid evaporative cooling of the slurry in the channels. Plugging of the channels by dried slurry was observed. Without being bound by theory, it is believed that the evaporative cooling led to slower water evaporation and drying of the residual coating on the monolith wall. After discontinuing the gas purge, the monoliths statically air dried for hours (~3 to ~6 hours) in a vertical position.

[00126] After removal of excess slurry in the monolith channels, the monoliths were flash dried, to stabilize the films and prevent “bridging” and size segregation of the zeolite and binder particles on vertical standing. After the channels were initially cleared with a high flow gas purge, the gas stream was then heated with an in-line Osram heater to 50-60°C to rapidly dry and stabilize films on the cell walls. The coating was dried in-situ for several minutes. The monoliths were then calcined in air to 500°C using a heating ramp: a) 120°C drying for 8 hrs, b) increase temperature to 500°C over 4 hours, c) holding at 500°C for 2 hours, and d) cooling to 120°C in 2 hours. Figure 7 shows a Leica Optical scope picture (40 x magnification) of the 1440 cpsi metal monolith after 4 coatings with DDR (25-30 μm) and SiO_2 (100 nm), after removal of excess slurry and 500°C calcination. Figure 8 provides an SEM image of the DDR (25-30 μm) and SiO_2 (100 nm) coating on the 1440 cpsi metal monolith and/or a glass slide after 500°C calcination.

Example 2 - Integrity Testing of Coupons

[00127] Samples of test coupons were prepared and sent to Southwest Research Institute (SWRI), an independent lab, for coating integrity testing. The objective was to test the integrity of a washcoat coating on several test coupons under conditions of rapid pressurization and depressurization. During the testing, each coupon was individually installed into a test rig capable of rapid

pressurization and depressurization. During the testing, a total of 24 pressure cycle tests were performed on six test coupons at five pressure conditions.

Sample Preparation

[00128] The substrate coupons used were polished 316 stainless steel (# 8 finish), ~3.25" L x ~0.5" W x ~0.060" thick strips with 2 holes measuring ~0.12 inches in diameter drilled into each coupon for mounting to the test rig.

[00129] A ~69 wt % solids aqueous slurry was made by mixing ~1.4 grams of DDR zeolite (~10 μm to ~15 μm) prepared according to the methods described in U.S. Patent Application Publication No. 2014/0161717) and 1.526 grams of colloidal silica (~25 nm, 40 wt % solids, Aremco 644 S) to form a semi-paste. The paste, representative of the active components in a washcoating slurry, were applied to the coupons with a doctor-blade technique. The coated coupons were air dried at room temperature overnight. They were subsequently dried at ~120°C for ~1 day.

[00130] Four sets (A-D) of duplicate samples were prepared by applying slurry above to coupons. Descriptions of the final coupons and labels are below:

- NB 26027-25-2-2 samples: no pre-thermal oxidation treatment + Zr-silicate primer coating (Aremco 644-N material);
- 26-6-2 samples: ~900°C oxidized coupon + Zr-silicate primer coating (Aremco 644-N material);
- 26-7-3 samples: ~900°C oxidized coupon + no Zr primer coat + DDR/SiO₂ (~25 nm) having a ration of ~70:30 w/w.
- 26-8-23 samples: ~900°C oxidized coupon + Zr-silicate primer coating + DDR/SiO₂ (~25 nm) having a ratio of ~70:30 w/w;
- 25-4-23 samples: no pre-thermal oxidation treatment + Zr-silicate primer coating + DDR/SiO₂ (~25 nm) having a ratio of ~70:30 w/w.

A picture of the samples as prepared is shown in Figure 9. The circled letter indicates which samples were tested.

Test procedure (SwRI)

[00131] The following test procedure was performed on the coupons:

1. The initial weight of the each coupon was recorded.
2. The coupons were loaded into the test rig and the following conditions were tested on each coupon in Table 1:

Table 1 - Test Summary

TEST CONDITION	NUMBER OF CYCLES PER COUPON	HIGH PRESSURE (psia)	LOW PRESSURE (psia)
Base 1	250	783	653
Base 2	250	783	435
Base 3	250	783	218
Stepout 1	250	943	218
Stepout 2	20	1230	218

3. After each test condition was complete, each coupon was removed from the rig and allowed to sit for at least 5 minutes to allow equilibration with room humidity. The mass of the coupons were taken by leaving the coupons on the scale for about 30 seconds to determine if the coupon was gaining mass through water absorption. Once mass gain had ceased, the mass for the coupons was recorded.

[00132] There was no significant weight loss for any of the coupons during the course of testing as shown in Tables 2 and 3 below.

Table 2 - Weight after Testing

TEST COUPON	RECORDED WEIGHT (g)					
	INITIAL WEIGHT	AFTER BASE 1	AFTER BASE 2	AFTER BASE 3	AFTER STEPOUT 1	AFTER STEPOUT 2
26-8-23C	12.0983	12.0983	12.0985	12.0995	12.0990	12.0992
25-4-23C	11.9207	11.9210	11.9211	11.9225	--	--
26-7-3C	12.1812	12.1812	12.1816	12.1827	--	--

Table 3 - Change in Test Coupon Weight

TEST COUPON	INITIAL WEIGHT (g)	INITIAL WEIGHT RANGE (g)	WEIGHT CHANGE FROM INITIAL (g)				
			AFTER BASE 1	AFTER BASE 2	AFTER BASE 3	AFTER STEPOUT 1	AFTER STEPOUT 2
26-8-23C	12.0983	0.0010	0.0000	0.0002	0.0012	0.0007	0.0008
25-4-23C	11.9207	0.0010	0.0003	0.0004	0.0018	--	--
26-7-3C	12.1812	0.0009	0.0000	0.0004	0.0015	--	--

Variation in coupon weight was observed, but these variances were on the same order of magnitude as those observed during the initial four weights obtained on each untested coupon.

[00133] No visual indications of coating damage or loss were seen during the course of these experiments, as can be seen Figures 10–12, which provides comparison photographs of the coupons take before (top photograph) and after testing (bottom photograph).

Example 3 - Integrity Testing of Coatings on Coated Monoliths

[00134] A ~2390 cpsi 316 stainless steel monolith (1.1" d x 3" L) was oxidized at ~900°C for ~6 hr, primed with a Zr-silicate coating and dip coated multiple times in a slurry of DDR (~25 µm) prepared according to the methods described in U.S. Patent Application Publication No. 2014/0161717 (25 nm

Aremco 644-S colloidal SiO₂). After 500°C calcination, the adsorbent coating matrix, was 20% by total weight and the resultant coated monolith was mounted on metal disc resulting in test button D.

[00135] Pressure swing cycles were conducted on the washcoated monolith using the Test Rig for adsorptive kinetic separation (TRAKS). These tests were done at a adsorptive kinetic separation (AKS) pilot plant with gas velocities up to ~20 ft/s and pressure drops up to ~15 bar-a. As shown in Figure 13 (pictures of test button D before and after testing) and Figure 14 (weight of test button D as superficial gas velocity increases), no significant amount of wash-coat was lost during testing. The results indicate that the washcoat matrix on the monolith is robust enough to withstand AKS operating conditions.

Example 4 - Activity Testing of Coatings

[00136] Samples of the washcoating matrix were processed for activity testing. Aqueous slurries were prepared with ~50 weight % solids content, as described in Example 1 above. The slurries were cast onto glass plates (~12" x ~12") and air dried overnight (~8 to ~16 hours) to form a white colored film on the glass. The sample was then dried at ~120°C for ~8 hours. The samples were removed from the glass plates and the shards of samples were calcined to ~500°C for ~4 hours. A portion of the samples were then ground to a powder and sieved to ~75 – ~150 µm for activity testing by Zero Length Chromatography (ZLC) substantially according to the method described in U.S. Patent Application Serial No. 14/573,177.

[00137] The samples tested are summarized below in Table 4.

Table 4 - Samples for Activity Testing

13-86	1	DDR (25 um avg) 13-48 * 25 nm Aremco SiO2 + 0.5% Na-Silicate + no viscosifier	1 prep
13-86	2	DDR (25 um avg) 13-48 * 25 nm Aremco SiO2 + 0.0% Na-Silicate + no viscosifier	5 prep
13-86	3	DDR (25 um avg) 13-48 * 100 nm nm SiO2 + 0.5% Na-Silicate + viscosifier	1 prep
13-86	4	DDR (25 um avg) 13-48 * string of pearls SiO2 + 0.5% Na-Silicate + viscosifier	1 prep
13-86	5	DDR (25 um avg) 13-48 * 25 nm Aremco SiO2 + 0.0% Na-Silicate + no viscosifier	0 prep
13-86	6	DDR (25 um avg) 13-48 * 100 nm nm SiO2 + 0.5% Na-Silicate + viscosifier	1 prep
13-86	7	DDR (25 um avg) 13-48 * string of pearls SiO2 + 0.5% Na-Silicate + viscosifier	1 prep

ZLC Measurement

[00138] Samples were tested by ZLC to determine if the additives in the coating matrix (e.g., SiO2 binders and other additives) affected the kinetics of the adsorbent. As shown in Figures 15 and 16, there was minimal effect on methane diffusivity due to the diameter or amount of silica binder in the coating matrix samples compared to a DDR adsorbent (“parent DDR”) which was steamed at 1050°C. As determined from Figures 15 and 16, the parent DDR had a diffusivity of 4.4 E-14 m2/s and the coating matrix samples with DDR bound with SiO2 had a diffusivity of 4.0-4.6 E-14 m2/s.

- 48 -

[00139] Samples made with “string of pearls” (i.e., 4 and 7) exhibit a slightly lower methane diffusivity, suggesting a slight selectivation effect by this type of binder.

CLAIMS:

1. A structured adsorbent bed for purification of a gas feedstream comprising:
a substrate having a cell density greater than 1040 cpsi; and
a coating on the substrate, wherein the coating comprises adsorbent particles and a binder.
2. The structured adsorbent bed of claim 1, wherein the adsorbent particles have an average diameter of about 2 μm to about 40 μm .
3. The structured adsorbent bed of claim 1, wherein the adsorbent particles have an average diameter greater than about 20 μm .
4. The structured adsorbent bed of claim 1, wherein the adsorbent particles have an axis ratio of at least 1.2.
5. The structured adsorbent bed of claim 1, wherein the adsorbent particles comprise a microporous material.
6. The structured adsorbent bed of claim 5, wherein the microporous material comprises a zeolite.
7. The structured adsorbent bed of claim 6, wherein the zeolite is DDR.
8. The structure adsorbent bed of claim 7, wherein the zeolite is selected from the group consisting of Sigma-1 and ZSM-58.

- 50 -

9. The structured adsorbent bed of claim 1, wherein the binder comprises particles having an average diameter of about 25 nm to about 200 nm.

10. The structured adsorbent bed of claim 1, wherein the binder comprises particles having an average diameter of about 100 nm to about 200 nm.

11. The structured adsorbent bed of claim 1, wherein the binder has a pH greater than 7.

12. The structured adsorbent bed of claim 1, wherein the binder comprises SiO₂.

13. The structured adsorbent bed of claim 1, wherein the substrate has a cell density of about 1500 cpsi to about 4000 cpsi.

14. The structured adsorbent bed of claim 1, wherein the substrate has a cell density of about 1400 cpsi or greater.

15. The structured adsorbent bed of claim 1, wherein the coating on the substrate has a thickness of about 30 μm to about 200 μm.

16. The structured adsorbent bed of claim 1, wherein the coating on the substrate has a thickness of at least 100 μm or greater.

17. The structured adsorbent bed of claim 1, wherein the coating comprises one or more layers of adsorbent particles and binder particles.

- 51 -

18. The structured adsorbent bed of claim 1, wherein the substrate is a porous solid selected from the group consisting of a metal oxide, a mixed-metal oxide, a ceramic and a zeolite.

19. The structured adsorbent bed of claim 18, wherein the substrate has a porosity of about 6% or less.

20. The structured adsorbent bed of claim 1, wherein the substrate is a non-porous solid selected from the group consisting of a metal, a glass and a plastic.

21. The structured adsorbent bed of claim 20, wherein the metal is stainless steel.

22. The structured adsorbent bed of claim 1 further comprising a zirconium-containing layer on the substrate.

23. A method of preparing the structured adsorbent bed of claim 1, the method comprising:

pretreating the substrate;

preparing an aqueous slurry comprising the adsorbent particles and the binder; and

applying the aqueous slurry to the substrate to form the coating on the substrate.

24. The method of claim 23, wherein pretreating the substrate comprises: (i) applying the zirconium-containing layer to the substrate; or (ii) heating the substrate and applying the zirconium-containing layer to the substrate.

- 52 -

25. The method of claim 24, wherein (ii) heating the substrate is performed at about 600°C to about 1100 °C.

26. The method of claim 24, wherein the zirconium-containing layer comprises zirconium oxide, zirconium silicate or a combination thereof.

27. The method of claim 23, wherein the binder is SiO₂.

28. The method of claim 23, wherein the weight ratio of the adsorbent particles to the binder is from about 70:30 w/w to about 90:10 w/w.

29. The method of claim 23, further comprising:
removing excess coating from the coated substrate;
drying the coated substrate; and
heating the coated substrate.

30. The method of claim 29, wherein the excess coating is removed from the substrate by flowing a gas through the coated substrate at a rate equal to or greater than 100 L/min.

31. The method of claim 29, wherein drying the coated substrate comprises flash drying the coated substrate wherein a gas purge heated from about 50°C to about 60°C is flowed through the coated substrate at rate of at least about 100 L/min.

32. The method of claim 23, wherein the coating has about 10% to about 40% macroporosity.

- 53 -

33. A gas separation process comprising contacting a gas mixture containing at least one contaminant with the structured adsorbent bed of claim 1.

34. The process of claim 33, wherein the gas mixture comprises CH₄.

35. The process of claim 33, wherein the at least one contaminant is selected from the group consisting CO₂, H₂O, H₂S, NO_x and SO_x.

36. The gas separation process of claim 33, wherein the process comprises PSA, TSA, PPSA, PTSA, RCPSA, RCTSA, RCPPSA or RCPTSA.