

METHOD AND APPARATUS FOR REMOVING CONTAMINANT FROM FLUID

FIELD

[0001] The presently disclosed subject matter relates to methods and apparatus for removing contaminants from fluids, such as petrochemical and chemical gas streams.

BACKGROUND

[0002] In many petrochemical and chemical processes, removal of contaminant provides process control and ensures compliance with environmental regulations. For example, syngas generated by gasification of coal or biomass, natural gases, gases generated from petroleum refining and processing can contain harmful and toxic gases such as H₂S, COS, etc., which need be removed to control catalyst poisoning in the downstream processing and for regulatory compliance. In general, this removal is carried out by adsorbing the contaminant on the surface of sorbent materials in reactors, such as fluidized bed or moving bed reactors. In these reactors, the sorbent materials are normally in the form of pellets of sizes on the order of a few hundred microns to few thousand microns. To achieve an adequate removal capacity, sorbent materials with high surface area are normally used. For example, for the removal of H₂S from a gas stream by adsorption, various porous materials such as activated carbon, modified clay, or modified zeolites have been used.

[0003] However, the available adsorption sites of the sorbent materials in a fluidized bed reactor or a fixed bed reactor are predominately located on the internal surfaces of the pellets. With this approach the gases must diffuse into the internal porosities of the pellets, which in turn, limits the removal rate. In addition, due to the interaction of gases with the internal surfaces and repeated expansion and contraction of the pellets in adsorption-regeneration cycles, the pellets become physically unstable. Due to this physical instability, the pellets can lose integrity, i.e., break apart mechanically, causing costly clean up and lost materials. To keep the operation running efficiently, new sorbent pellets must be added to the system and the disintegrated pellets must be removed from the reactors. Therefore, the current gas cleanup techniques suffer from this costly drawback arising from the aggregate forms of the absorbent materials used.

[0004] U.S. Patent No. 5,494,880 describes the preparation of pellets with improved physical stability using a mixture of sorbent oxide, such as ZnO, a stabilizing amount of an inert refractory oxide and porous silica, held together with binders. However, the use of large amounts of materials other than the active sorbents can reduce the absorbing efficiency.

[0005] Recent developments in the removal of contaminant have involved utilizing nanostructures of absorbent materials. For example, Lee et al. ("Desulfurization Using ZnO Nanostructure Prepared by Matrix Assisted Method" Korean J. Chem. Eng., 26(2), 582-586) describes purported methods for removing H₂S by a fixed-bed reactor containing nanosized ZnO, which are synthesized by the matrix-assisted method. Wang et al. ("Low-temperature H₂S Removal From Gas Streams With SBA-15 Supported ZnO Nanoparticles," Chem. Eng. J., 142 (2008) 48-55.) describes a purported mesoporous silica gel SBA-15 functionalized by ZnO nanoparticle for H₂S removal from a gas stream. U.S. Patent Application Publication No. 20090114093 describes desulfurization of warm fuel gases by metal-based sorbents attached to a porous substrate. In addition, Sayyadnejad et al. ("Removal of Hydrogen Sulfide by Zinc Oxide Nanoparticles in Drilling Fluid" Int. J. Environ. Sci. Tech., 5(4), 565-569, 2008) describes purported removal of H₂S gas in drilling fluid by ZnO nanoparticles prepared by spray pyrolysis. The disclosure of each of these publications is incorporated herein by reference in its entirety.

[0006] As such, there is a need for methods and apparatus that overcome the drawbacks of the existing technologies and remove contaminant in a more efficient and economical manner.

SUMMARY

[0007] The disclosed subject matter provides methods, apparatus, and systems for removing contaminant in a fluid (e.g., chemical and petrochemical gas streams) using nanostructures of a sorbent material, such as ZnO nanostructures. The nanostructures of the sorbent materials are prepared, for example, as a thin coating on one or more plates. Such coated plates can be mounted closely, and in one particular embodiment, substantial parallel to each other, thereby forming channels between the plates for the fluid to flow through. The plate-supported nanostructures provide sorption sites

substantially located on the exposed surface of the aggregation of the nanostructures for removing the contaminant, for example H_2S , in a fluid passing across the surface of the plates. After sorption, the nanostructures can be regenerated using heat or other methods.

[0008] In accordance with another aspect of the disclosed subject matter, a sorbent structure to remove contaminant from a fluid is provided. The sorption structure includes a vessel having an inlet and an outlet, the vessel defining a chamber therein, and a plurality of plates disposed within the vessel between the inlet and the outlet. The plurality of plates are arranged in spaced relationship to define at least one channel therebetween, in which at least one plate has a surface coated with nanostructures of a sorbent material for sorption of contaminant from fluid passing through the at least one channel across the surface of the at least one plate.

[0009] In yet another aspect of the disclosed subject matter, a sorption system is provided to remove contaminant from a petrochemical fluid. The sorption system includes a feed of petrochemical fluid containing a contaminant; a sorption structure fluidly coupled to the feed of petrochemical fluid. The sorption structure includes an inlet to receive the feed of petrochemical fluid and at least one plate having a surface coated with nanostructures of a sorbent material. The contaminant in the petrochemical fluid is subject to sorption by the sorbent material. An outlet is provided a discharge of the petrochemical fluid after passing across the surface of the plate, wherein the petrochemical fluid has a reduced amount of contaminant after passing across the surface of the plate.

[0010] The methods, sorption structure and systems provided herein will be described in conjunction with each other for purpose of understanding and enablement.

[0011] The contaminant removal approach disclosed herein utilizes nanostructures with high external surface area and an intrinsically low diffusion time, which allows high fluid flow rate and high processing capacity. In one embodiment, the nanostructures are tightly aggregated structures forming a compact layer on a substrate that has very low amount of inter-particle spaces (or pores) to allow a fluid to diffuse therein. In such a case, the sorption of contaminant occurs predominantly at the external or exposed

surface of the compact layer. Using external surface area as the sorption site also eliminates the physical instability that exists with pellets used in many reactors today.

[0012] The various features and the advantages of the disclosed subject matter are described herein and will become readily apparent to those skilled in the art from the following detailed description, including the accompanied figures as well as the claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] Figure 1 illustrates a perspective view of an exemplary configuration of a sorption structure including a plurality of nanostructure-coated plates according to one embodiment of the disclosed subject matter;

[0014] Figure 2 is a microscope image of the nanostructures of ZnO for contaminant removal according to one embodiment of the disclosed subject matter;

[0015] Figure 3 is a microscope image of the nanostructures of ZnO having a columnar structure for contaminant removal according to one embodiment of the disclosed subject matter;

[0016] Figure 4 illustrates an enlarged side view of the sorption structure illustrated in Figure 1 according to one embodiment of the disclosed subject matter; and

[0017] Figure 5 illustrates a top view of another exemplary configuration of a sorption structure including a plurality of nanostructure-coated plates according to one embodiment of the disclosed subject matter.

DETAILED DESCRIPTION

[0018] In accordance with one aspect of the disclosed subject matter, a method of removing contaminant from a fluid is provided. The method includes introducing a feed of fluid to a sorption structure, wherein the sorption structure includes at least one plate having a surface coated with nanostructures of a sorbent material, wherein the fluid containing a contaminant is subject to sorption by the sorbent material. The method further includes passing the fluid across the surface of the plate for sorption of the contaminant by the sorbent material, wherein the fluid has a reduced amount of contaminant after passing across the surface of the plate, and discharging the fluid from the sorption structure after passing across the surface of the plate. The sorption structure

can further include a vessel that houses the at least one plate, where the vessel includes an inlet and outlet.

[0019] Figure 1 illustrates an exemplary configuration of a sorption structure including plurality of nanostructure-coated plates according to one embodiment of the disclosed subject matter. The sorption structure 100 includes a plurality of generally planar plates 110 that are coated with nanostructures of a sorbent material. The plates are arranged in a substantially parallel fashion, forming gaps or channels 120. A frame 130 is used to support the plurality of the plates. A feed of fluid 140, which contains a contaminant subject to sorption by the sorbent material, is introduced to the sorption structure 100, e.g., via an inlet. As the feed of fluid is directed to pass through the channels 120 and across the surface of the sorbent material-coated plates 110, at least a portion of the contaminant is removed by the sorbent material. Thereafter, the fluid is discharged, e.g., via an outlet, wherein the amount of contaminant in the fluid is reduced.

[0020] The fluid that is subject to removal of contaminants can be a chemical or petrochemical gas process stream. It is contemplated that the method and system according to the present invention are suitable for use with various process streams. For example, the method and system according to the present invention may be used as a desulfurization approach for a gas stream. The gas stream may include, but is not limited to, coal gases, flue gases, methanol synthesis gas, H_2/N_2 mixture, carbon monoxide and natural gas. The method and system may be used to remove contaminants such as sulfur compounds such as, but not limited to, carbonyl sulfide (COS), carbon disulfide (CS_2), hydrogen sulfide (H_2S) and mercaptan.

[0021] As used herein, the term “contaminant” refers to a substance to be removed from a fluid subject to treatment of the methods of the disclosed subject matter. The contaminant can include, for example, H_2S , CS_2 , carbonyl sulfide gases, mercaptan, etc. The concentration of the contaminant in the fluid to be treated can be on the order of hundreds of ppm or less. The present invention may be effective in treating higher amounts of contaminant in the fluid to be treated.

[0022] The sorbent material used for removing the contaminant can be selected based on the contaminant. Various types of sorption mechanisms between the sorbent material and the contaminant can be used. For example, the sorbent material can include metals,

metal alloys, or metal oxides. In some embodiments, the sorption of the contaminant is based on an acid-base reaction. In one specific embodiment, the sorption nanostructures include ZnO nanostructures, which are particularly useful for adsorbing H₂S due to the large equilibrium constant of the chemical reaction between ZnO and H₂S at low temperature. The ZnO and H₂S react to form ZnS and H₂O.

[0023] The nanostructures of the disclosed subject matter are prepared as a coating on a substrate plate. As embodied herein and by way of example, the substrate is a non-porous solid material. For example and not limitation, the nanostructures can be fabricated using chemical vapor deposition (CVD) or metal organic chemical vapor deposition (MOCVD) on a substrate silicon wafer. The MOCVD process is described, for example, in greater detail in US Patent No. 6,710,515 to Lu et al., entitled "Integrated Tunable Surface Acoustic Wave Technology and Sensors Provided Thereby," which is incorporated herein in its entirety by reference. It is contemplated that the silicon wafer can be used as a plate 110 or it can be attached to another substrate or plate to form plate 110. The thickness of wafer is less than 2 mm and preferably less than 1 mm. The thickness of the plate is preferably less than 2 mm. Other suitable plates for growing the nanostructures are glass and sapphire.

[0024] Figure 2 is an exemplary electronic microscope image of ZnO nanostructures coated on a silicon wafer (top-view) in accordance with aspects of the present invention, prepared by MOCVD. The nanostructures are preferably formed as nanotips having a structure as disclosed, for example, in Muthukumar et al, "Selective MOCVD Growth of ZnO Nanotips", IEEE Transactions on Nanotechnology, Vol 2., No. 1, March 2003, which is incorporated herein in its entirety by reference. The nanostructures coated on the plate can have a thickness of less than about 1000 nm, and more particularly, between 800 nm to about 50 nm. These nanostructures may have a columnar structure (as shown in Figure 3), a spherical structure or any other geometry that is capable of being formed or deposited on a flat surface.

[0025] Referring back to Figure 1, the plurality of plates can be arranged in a spaced relationship to each other, e.g., at an average distance of about 100 nm to about 1 mm and preferably 1000 nm between the opposing surfaces of adjacent plates. The surface area of one of the plates (without a coating of nanostructures) can be from about 1 cm² and about 5000 cm². The provision of the nanostructures can dramatically increase the reactive surface area of the plates. In particular, surface area of the plate with nanostructures can be 2 to 100 times greater than the surface area of the plate without nanostructures.

[0026] Figure 4 illustrates an enlarged side view of the sorption structure illustrated in Figure 1, which is arranged in an overall cubic shape with a rectangular cross section. The plurality of coated plates 320 are mounted on the holders 310, which are installed on the support frame 340, forming channels 340 between adjacent plates. The present invention is not intended to be limited to the arrangement shown in Fig. 1; rather, other arrangements of the spaced plates are suitable provided the plates are arranged such that the reactive gas can flow over or across the plates such that the gas stream contacts the nanostructures. For example, the sorption structure can be arranged in an overall cylindrical structure, with a circular cross-section, as shown in Figure 5. This structure includes a combination of a plurality of structures, such as illustrated in Fig. 1, with varying sizes within the determined space. The diameter of the cylinder can be selected to fit in conventional or existing flow tubes for transporting the fluid, e.g., gas flow tubes for retrofit purposes. The cylinder can be divided into several portions in the diameter direction, each of the portions being fitted with plate support frames 420, on which a plurality of nanoparticles-coated plates are mounted. The plurality of plates can have a number of different sizes, depending the locations in which they are mounted. In turn, the plate support frames 420 are installed on the cylindrical wall 410. The empty areas such as 430 in Figure 4 can be filled with smaller size plates.

[0027] For purpose of illustration and not limitation, reference is made to certain parameters of a representative embodiment of the method and system. For example, the fluid is a gas stream and the contaminant is H₂S, and the sorption occurs as adsorption at a temperature between about 100 C and about 900 C and a pressure between about 15 psig and about 1500 psig. The flow rate of the gas will vary based upon the size of the sorption structure. Lower flow rates are required for smaller sorption structures, while

higher flow rates can be employed for larger sorption structures. The flow rate is determined such that the gas has similar contact times with the nanostructures. The present invention may result in a significant reduction in H₂S content. The discharged gas containing 10 ppb of H₂S as compared with the feed gas containing 100 ppm of H₂S.

[0028] The sorption sites of the sorbent material can be depleted after prolonged use for removing contaminants, and the sorbent material can turn into an inert compound no longer reactive to the contaminant. To reuse the sorbent material, the plates coated with nanoparticles can be regenerated to the original sorbent material. For example and with reference to the embodiment herein, ZnO nanoparticles will convert to ZnS after adsorbing H₂S. The ZnS nanoparticles can be heated in a temperature range of 500 – 1000°C in air or an oxygen rich atmosphere to revert back to ZnO nanoparticles, accompanied by the release of SO₂ gas, which can be collected or absorbed by suitable media, e.g., a basic solution.

[0029] While various embodiments of the disclosed subject matter are shown and described, it is to be understood that the invention is not limited thereto and may be variously embodied to practice within the scope of the following claims. It will be apparent to those skilled in the art that various changes may be made without departing from the spirit and scope of the invention as defined by the following claims.

Claims

1. A method of removing contaminants from a fluid, comprising:
introducing a feed of fluid to a adsorption structure, the adsorption structure comprising a plurality of plates of a non-porous solid material having thickness less than 2 mm and a surface coated with nanostructures of a metal oxide adsorption material having a thickness less than 1000 nm deposited on the non-porous solid material by metal organic vapor deposition, the plates being in spaced relationship to one another defining channels between the plates, the fluid containing a contaminant subject to sorption by the adsorption material;
passing the fluid through the channels and across the surface of the plates for adsorption of the contaminant on the adsorption material, the fluid having a reduced amount of contaminant after passing across the surface of the plates;
and
discharging the fluid from the adsorption structure after passing across the surface of the plates.
2. The method of claim 1, wherein the plurality of plates have generally planar configurations.
3. The method of claim 2, wherein adjacent plates are arranged substantially in parallel.
4. The method according to anyone of the preceding claims, wherein the plate is formed of silicon.
5. The method of claim 1, wherein the metal oxide is ZnO.
6. The method according to anyone of the preceding claims, wherein the nanostructures as coated on the plate have a thickness of less than 700 nm.
7. The method according to anyone of the preceding claims, wherein the nanostructures have an average diameter of less than 100 nm.
8. The method according to anyone of the preceding claims, wherein the fluid is a gas.

9. The method according to anyone of the preceding claims, wherein the contaminant includes hydrogen sulfide.

10. The method according to anyone of the preceding claims, wherein sorption of the contaminant with the adsorbent material is based on an acid-base reaction.

11. The method according to anyone of the preceding claims, further comprising regenerating the adsorbent material by heating the used adsorbent material.

12. The method according to claim 11 in which the plates are formed of silicon, the metal oxide nanostructures are ZnO, and the contaminant is hydrogen sulfide which is adsorbed at a temperature of 100 to 900°C and the ZnO adsorbent material is regenerated at a temperature of 500 to 1000°C in air or an oxygen rich atmosphere .

13. A sorption structure to remove contaminant from a fluid, comprising:
a vessel having an inlet and an outlet, the vessel defining a chamber therein;
and
a plurality of plates disposed within the vessel between the inlet and the outlet, the plurality of plates of a non-porous solid material having a thickness of less than 2mm and a surface coated with nanostructures of a metal oxide adsorption material having a thickness less than 1000 nm deposited on the non-porous solid material by metal organic vapor deposition, the plates being arranged in spaced relationship to define channels between the plates.

14. A sorption structure according to claim 13 in which the plates are formed of silicon, the metal oxide nanostructures are ZnO.

15. . A sorption structure according to claim 13 or 14 in which the plates are planar and parallel to one another with a distance of 100 nm to 1 mm between the surfaces of adjacent plates.