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(54) DESULFURIZATION SYSTEM AND METHOD FOR DESULFURIZING A FUEL STREAM

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(57) ABSTRACT

A method for producing a substantially desulfurized hydrocarbon fuel stream at temperatures less than 100° C. including providing a nondesulfurized fuel cell hydrocarbon fuel stream and passing the fuel stream through a sequential sulfur adsorbent system containing calcium exchanged zeolite, hydrated alumina and a selective sulfur adsorbent placed in sequence to produce a substantially desulfurized hydrocarbon fuel stream.

FIGURE 1

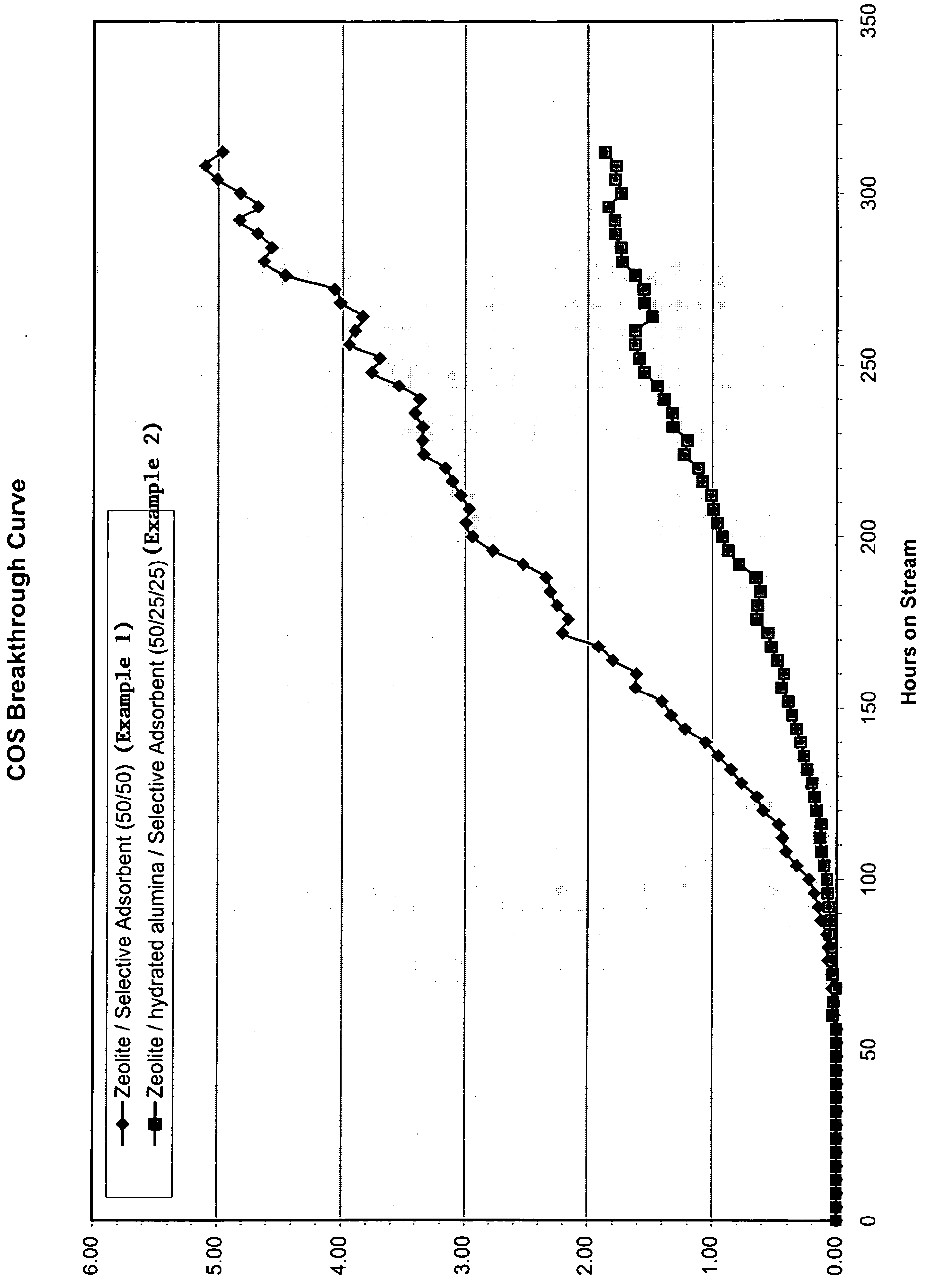
COS Breakthrough Curve
Zeolite / Selective Adsorbent (50/50) (Example 1)
Zeolite / hydrated alumina / Selective Adsorbent (50/25/25) (Example 2)
Exit S (ppm mol)
Hours on Stream
0.00
1.00
2.00
3.00
4.00
5.00
6.00
0
50
100
150
200
250
300
350

FIGURE 2

Desulfurization system containing calcium-exchanged zeolite and selective sulfur adsorbent of Example 1.

Percent S in form of COS removed at breakthrough	0.45%
Hours on stream before breakthrough (1 ppm)	136 Hours

Desulfurization system containing calcium-exchanged zeolite/hydrated alumina/selective sulfur adsorbent of Example 2.

Percent S in form of COS removed at breakthrough	0.66%
Hours on stream before breakthrough (1 ppm)	204 Hours

DESULFURIZATION SYSTEM AND METHOD FOR DESULFURIZING A FUEL STREAM

CROSS REFERENCED TO RELATED APPLICATIONS

[0001] This application is a continuation-in-part application based on application Ser. No. 11/207,154, filed on Aug. 18, 2005, which is a continuation-in-part application based on application Ser. No. 10/923,177, which was filed on Sep. 1, 2004.

BACKGROUND OF INVENTION

[0002] The present invention relates to a novel method for producing a substantially desulfurized hydrocarbon fuel stream, particularly for hydrogen generation, and more particularly for use within a fuel cell processing train, by passing a nondesulfurized hydrocarbon fuel stream, particularly natural gas, propane or liquefied petroleum gas (LPG), through a sequential sulfur adsorbent system at temperatures less than 100° C., wherein the sequential sulfur adsorbent system contains in sequence a zeolite sulfur adsorbent, a hydrated alumina adsorbent, and a selective sulfur adsorbent. The present invention further relates to a process for producing hydrogen within a fuel cell processing train from a substantially desulfurized hydrocarbon fuel stream, particularly desulfurized natural gas, propane or LPG, wherein the hydrocarbon fuel stream is desulfurized using the above-described sequential sulfur adsorbent system. The present invention further includes the desulfurization system described above utilized for hydrogen generation, particularly within a fuel cell processing train, which system desulfurizes hydrocarbon fuel streams, particularly comprising natural gas, propane or LPG, at temperatures as low as ambient temperature, even when the level of water or other hydrolyzing agents within that fuel stream is less than 500 ppm.

[0003] For hydrogen generation, particularly for use in a conventional low temperature fuel cell processing train, such as a proton exchange membrane (PEM) fuel cell, which is suitable for use in a stationary application or in a vehicle, such as an automobile, the hydrocarbon fuel stream can be derived from a number of conventional fuel sources with the preferred fuel sources including natural gas, propane and LPG. In a conventional hydrogen generation system, particularly a fuel cell processing train, the hydrocarbon fuel stream is passed over and/or through a desulfurization system to be desulfurized. The desulfurized hydrocarbon fuel stream for such fuel cell processing train then flows into a reformer wherein the fuel stream is converted into a hydrogen-rich fuel stream. From the reformer the fuel stream passes through one or more heat exchangers to a shift converter where the amount of CO in the fuel stream is reduced. From the shift converter the fuel stream again passes through various heat exchangers and then through a selective oxidizer or selective methanizer having one or more catalyst beds, after which the hydrogen rich fuel stream flows to the fuel cell stack where it is utilized to generate electricity.

[0004] Raw fuels, in gaseous or liquid phase, particularly natural gas, propane and LPG, are useful as a fuel source for hydrogen generation, particularly for fuel cell processing trains. Unfortunately, virtually all raw fuels of this type contain relatively high levels, up to as high as 1,000 ppm or so, but typically in the range of 20 to 500 ppm, of various naturally occurring sulfur compounds, such as, but not limited to, carbonyl sulfide, hydrogen sulfide, thiophenes, such as tetra hydro thiophene, dimethyl sulfide, various mercaptans, disulfides, sulfoxides, other organic sulfides, higher molecular weight organic sulfur compounds, and combinations thereof. In addition, because hydrocarbon fuel streams, particularly natural gas, propane and LPG, may have different sources of origin, the quantity and composition of the sulfur compounds that may be present in the fuel streams can vary substantially. Further, these fuel stream sources generally contain low quantities of water and other hydrolyzing agents, generally at a level that may be as low as 500 ppm or lower.

[0005] The presence of sulfur-containing compounds, particularly carbonyl sulfide, in a hydrocarbon fuel stream can be very damaging to components of the fuel cell processing train, including the fuel cell stack itself, and such compounds must therefore be substantially removed. If not substantially removed, the sulfur compounds may shorten the life expectancy of the components of the fuel cell processing train.

[0006] An especially efficient desulfurization system is necessary for use in such fuel cell processing trains as they generally only contain a single desulfurization system. Further, desulfurization systems for such uses must have high capacity, as they may need to be in use for an extended period of time before replacement.

[0007] Several processes, conventionally termed "desulfurization," have been employed for the removal of sulfur from gas and liquid fuel streams for hydrogen generation. Adsorption of sulfur-contaminated compounds from these hydrocarbon streams using a "physical" sulfur adsorbent is the most common method for removal of sulfur compounds from such hydrocarbon fuel streams because of their relatively low capital and operational costs. (For purposes of this specification, the terms "adsorption" and "absorption" as well as "adsorbents" and "absorbents" each have the same, all inclusive meaning.) While physical adsorbents are useful, they can desorb the sulfur compounds from the adsorbent under certain operating conditions. In addition, there are often limits on the quantity of sulfur compounds which can be adsorbed by such physical sulfur adsorbents.

[0008] An additional type of adsorbent that has been useful as a desulfurization agent is a "chemical" sulfur adsorbent. However, chemical desulfurization normally requires the desulfurization system to be heated to temperatures of 150° C. to 400° C. before the nondesulfurized hydrocarbon fuel streams can be effectively desulfurized by the chemical adsorbent desulfurization system. In addition, other operational problems may occur when such chemical desulfurization processes are utilized.

[0009] While many different desulfurization processes have been suggested for hydrocarbon fuel streams, there is still a need for improved processes for desulfurization to achieve enhanced adsorption of sulfur components, especially carbonyl sulfide, over an extended range of sulfur concentrations, especially at relatively low operating temperatures and pressures, and for extended periods of time. In addition, these improved processes for desulfurization must be able to achieve enhanced adsorption of sulfur compounds even when the quantity of water or other hydrolyzing agents in the feed stream is low, i.e. less than 500 ppm. Further, there is a need for improved desulfurization system to adsorb substantial quantities of a wide range of sulfur compounds, including particularly hydrogen sulfide, carbonyl sulfide, tetra hydro thiophene, dimethyl sulfide, various mercaptans, disulfides, sulfoxides, other organic sulfides, various higher molecular weight sulfur-containing compounds and combinations thereof, especially carbonyl sulfide without addition of hydrolyzing agents. Further, it is important that these improved desulfurization systems absorb this broad range of sulfur compounds effectively for an extended period of time to delay "breakthrough" of sulfur compounds as long as possible. "Breakthrough" occurs when the amount of any sulfur compound remaining in the feed stream after desulfurization is above a predetermined level. Typical "breakthrough" levels for sulfur compounds occur at less than 1 ppm. Breakthrough by virtually any of the sulfur compounds present in the hydrocarbon fuel stream is disadvantageous as substantially all sulfur compounds can cause damage to components of a hydrogen generation system, particularly for a fuel cell processing train. Further, some sulfur compounds, particularly carbonyl sulfide, are quite difficult to remove from such fuel streams, especially without the addition of hydrolyzing agents.

[0010] In addition, some prior art adsorbents, while effective as adsorbents for some sulfur compounds, can synthesize the production of sulfur compounds even as they are removing some of the naturally occurring sulfur compounds that are present in the hydrocarbon fuel stream. (These newly produced sulfur compounds are referred to herein as "synthesized sulfur compounds.") It is important that the desulfurization system avoid the production of synthesized sulfur compounds to the greatest extent possible and for the longest period of time possible.

[0011] The foregoing description of preferred embodiments of the invention provides processes, systems and products that address some or all of the issues discussed above.

SUMMARY OF INVENTION

[0012] One of the inventions disclosed is a process for supplying a substantially desulfurized hydrocarbon fuel stream, particularly for hydrogen generation, and most particularly for use in a fuel cell processing train, comprising providing a nondesulfurized hydrocarbon fuel stream, preparing a desulfurization system comprising a sequential sulfur adsorbent system comprising, in sequence, a calcium exchanged zeolite sulfur adsorbent, a hydrated alumina adsorbent, and a selective sulfur adsorbent, and passing the nondesulfurized hydrocarbon fuel stream through or over the desulfurization system at a temperature optimally less than about 100° C. to produce a substantially desulfurized hydrocarbon fuel stream with desulfurization levels as low as about 50 ppb or so. Preferably, this level of desulfurization is accomplished even when the level of water and other hydrolyzing agents that are present in the feed stream are less than 500 ppm. One feature of one embodiment of this invention is that effective sulfur removal, particularly for the removal of carbonyl sulfide, can be achieved without the addition of conventional hydrolyzing agents to the feed stream. The composition and choice of the selective sulfur adsorbent within the desulfurization system depends on the composition of the sulfur compounds which are present in that fuel stream and the extent of sulfur removal and time before breakthrough occurs that are required.

[0013] Another of the inventions is a process for generating hydrogen for use in a fuel cell processing train by use of a substantially desulfurized hydrocarbon fuel stream comprising preparing a fuel cell processing train containing the desulfurization system described above, passing a non-desulfurized hydrocarbon fuel cell fuel stream through the desulfurization system at a temperature, preferably less than about 100° C., and introducing the substantially desulfurized hydrocarbon fuel stream to the remaining components of the fuel cell processing train.

[0014] Another of the inventions is a desulfurization system, particularly for hydrogen generation and most particularly for use in a fuel cell processing train, comprising an inlet for receiving a nondesulfurized hydrocarbon fuel stream, particularly natural gas, propane and/or LPG, the sequential adsorbent system described above, and an outlet for passing a substantially desulfurized hydrocarbon fuel stream downstream to the remaining components of the hydrogen generation system.

[0015] A further invention is a sequential sulfur adsorbent system, particularly for hydrogen generation and most particularly for use in a fuel cell processing train, comprising, in sequence, a calcium exchanged zeolite, a hydrated alumina adsorbent, and a selective sulfur adsorbent. The choice of the specific selective sulfur adsorbent that is used within the sequential sulfur adsorbent system depends upon the composition and quantity of the sulfur compounds that are present in the hydrocarbon fuel stream and the level of sulfur removal and time for breakthrough that are required. One particularly preferred selective sulfur adsorbent comprises one or more manganese compounds, copper oxide and a binder. A further alternative preferred selective sulfur adsorbent comprises copper oxide, zinc oxide and alumina. An additional alternative preferred selective sulfur adsorbent comprises one or more manganese compounds, iron oxide and a high surface area carrier, particularly alumina.

BRIEF DESCRIPTION OF DRAWINGS

[0016] **FIG. 1** is a graph showing a comparison of the performance of two sequential adsorbent systems of Example 1 and Example 2 for the removal of carbonyl sulfide from a synthetic natural gas feed stream.

[0017] **FIG. 2** comprises the performance of the desulfurization systems of Example 1 and Example 2 for the removal of carbonyl sulfide from a fuel stream.

DISCLOSURE OF A PREFERRED EMBODIMENT OF THE INVENTION

[0018] The invention includes, but is not limited to, a method for supplying a substantially desulfurized hydrocarbon fuel stream, particularly for a hydrogen generation system and most particularly for a fuel cell processing train. Raw fuel, for use in such hydrogen generation systems, particularly a fuel cell processing train, such as natural gas, propane and LPG, must be desulfurized prior to use because such fuel streams contain relatively high levels of sulfur compounds, such as, but not limited to, hydrogen sulfide, carbonyl sulfide, thiophenes, such as tetra hydro thiophene, dimethyl sulfide, mercaptans (including ethyl, methyl, propyl and tertiary butyl mercaptan), other sulfides, various higher molecular weight organic sulfur compounds and combinations thereof. In addition, some sulfur compounds, particularly carbonyl sulfide can be quite difficult to remove from such raw fuel. These sulfur compounds can damage components of the hydrogen generation system and the fuel cell processing train. While numerous combinations and quantities of these sulfur compounds may be present in the fuel stream, in some situations the sulfur compounds present in the fuel stream may be limited to only one or two of such sulfur compounds. Such raw fuels, particularly natural gas, generally contain limited amounts of water and other common hydrolyzing agents, such as ethanol or methane, generally 500 ppm or less. It is one feature of this invention that effective removal of sulfur compounds, particularly carbonyl sulfide, can be achieved without the addition of a hydrolyzing agent, such as water, ethanol or methanol to the fuel stream.

[0019] Where the raw fuel stream comprises natural gas, which is in a gaseous state at operating temperatures below 100° C., particularly below 60° C., the level of sulfur compounds, such as carbonyl sulfide, hydrogen sulfide, tetra hydro thiophene, dimethyl sulfide, mercaptans, other organic sulfur compounds, and combinations thereof may be as high as 100 ppm or so. The presence of such high levels of sulfur compounds, if not removed, results in the poisoning of components of the fuel cell processing train and may foul the fuel cell stack itself. Substantially complete removal of all of the sulfur compounds is necessary as the presence of even modest quantities of even a single sulfur compound can damage components of the fuel cell processing train.

[0020] While the desulfurization system of one embodiment of the invention can be utilized for a number of different hydrogen generation processes, one particularly preferred utilization is within a fuel cell processing train. For purposes of this specification while the use of this desulfurization system with all hydrogen generation systems is included, one preferred embodiment is the use of this system within a fuel cell processing train.

[0021] The inventors have surprisingly discovered that substantial desulfurization of a hydrocarbon fuel stream down to levels as low as 50 ppb or so can be achieved when a sequential sulfur adsorbent system is used for desulfurization which comprises, in sequence, a zeolite adsorbent, particularly a calcium exchanged zeolite, more particularly a calcium exchanged zeolite X or LSX, a hydrated alumina, and a selective sulfur adsorbent. In a preferred embodiment the sequence of use of the components in the desulfurization system is first the zeolite adsorbent, then the hydrated alumina, and finally the selective sulfur adsorbent. The composition of the components of the sequential sulfur adsorbent system can be modified depending on the composition and quantity of the sulfur compounds that are present in the hydrocarbon feed stream, the extent of removal of sulfur that is required and the time that is required before breakthrough occurs.

[0022] While not a preferred embodiment, it is possible to achieve effective sulfur removal from a feed stream where two or more of the components of the desulfurization system are partially or completely blended together before placement in the desulfurization system. For example, some portion or all of the hydrated alumina may be blended with either or both of the calcium exchanged zeolite and the selective sulfur adsorbent. It is preferred, however, to separate the three components from each other even though minimal blending may occur at the border between two components when those components are placed together in a desulfurization system, for example, when the components are introduced in layers without any physical separation therebetween.

[0023] The selective sulfur adsorbent(s) of the invention may be selected from a wide variety of adsorbents. As used herein a “selective sulfur adsorbent” is a material that preferentially absorbs at least one of the sulfur compounds that are commonly present in hydrocarbon fuel cell fuel streams, particularly natural gas, propane or LPG, such as hydrogen sulfide, carbonyl sulfide, tetra hydro thiophene, dimethyl sulfide, mercaptans, particularly ethyl, methyl, propyl, and tertiary butyl mercaptans and combinations thereof, particularly carbonyl sulfide, at a temperature below about 100° C., particularly below 60° C., and at pressures of about 1 bar to 18 bar. These fuel streams also commonly contain less than 500 ppm of water and other hydrolyzing agents, such as ethanol and methanol. Because of the choice of the components of the sequential bed, it is not necessary to add a hydrolyzing agent to the feed stream, to hydrolyze one or more of the sulfur compounds contained therein, particularly COS, before they are removed therefrom.

[0024] Each selective sulfur adsorbent selectively adsorbs one or more of the sulfur compounds that are commonly present in the hydrocarbon fuel cell fuel stream, preferably natural gas. However, each of these adsorbents may be less or more effective than other of the selective sulfur adsorbents for the adsorption of particular sulfur compounds or combinations of these compounds. Further, problems can be created in the feed stream when some of the selective sulfur adsorbents are used, as these selective sulfur adsorbents can synthesize existing sulfur compounds into different, higher molecular weight sulfur compounds that are not removable from the fuel stream by the particular selective sulfur adsorbent that is utilized.

[0025] It has been surprisingly discovered that a desulfurization system can be substantially enhanced by utilizing a zeolite adsorbent, particularly a calcium exchanged zeolite, and more particularly a calcium exchanged zeolite X or LSX, and a hydrated alumina adsorbent in sequence before the selective sulfur adsorbent. In particular, the combination of a selective sulfur adsorbents with the calcium exchanged zeolite adsorbent and hydrated alumina adsorbent in sequence performs surprisingly better than any of the individual selective sulfur adsorbents, the hydrated alumina adsorbent or the calcium exchanged zeolite, when used individually, or even the selective sulfur adsorbent utilized with the calcium exchanged zeolite, without also using the hydrated alumina adsorbent. The preferred choice and arrangement of the selective sulfur adsorbent(s), the hydrated alumina adsorbent, and the zeolite within the sequential sulfur adsorbent system also reduces the likelihood of the production of synthesized sulfur compounds that are sometimes created when a selective sulfur adsorbent is used with or without the calcium exchanged zeolite in a desulfurization system.

[0026] It has been further surprisingly discovered that the removal of various combinations of sulfur compounds can be enhanced by the specific arrangement and choice of the adsorbents in the sequential sulfur adsorbent system. For the removal of various sulfur compounds, it is preferable to place the calcium exchanged zeolite in the sequential sulfur adsorbent system prior to both the hydrated alumina adsorbent and the selective sulfur adsorbent. In a more preferred embodiment the sequence of the components of the sulfur adsorbent system is first the calcium exchanged zeolite, followed by the hydrated alumina and finally the selective sulfur adsorbent.

[0027] Sulfur adsorption by this system is further enhanced because some sulfur compounds, which may be synthesized to larger and more difficult to remove sulfur compounds by a particular selective sulfur adsorbent, are removed from the feed stream by the zeolite adsorbent, particularly the calcium-exchanged zeolite adsorbent and/or the hydrated alumina adsorbent when used in a sequential combination, prior to synthesis by the selective sulfur adsorbent.

[0028] Useful selective sulfur adsorbents are selected from a group of adsorbents including, but not limited to, an adsorbent comprising substantially manganese compounds; an adsorbent which includes manganese compounds, copper oxide and a binder; an adsorbent which includes manganese compounds, iron oxide and a support, particularly alumina, most particularly a hydrated alumina; an adsorbent which includes zinc oxide and a carrier, particularly alumina; an adsorbent which includes activated carbon with copper oxide; an adsorbent which includes a zinc oxide/copper oxide blend, preferably containing small quantities of carbon and alumina; an adsorbent which includes copper oxide with alumina; an adsorbent which includes a copper oxide/zinc oxide blend mixed with alumina, preferably a hydrated alumina; an adsorbent which includes nickel on silica or alumina and various known selective sulfur adsorbents which include copper and zinc. Various quantities of the individual components of each of these selective sulfur adsorbents can be utilized and the quantity of the individual components can be modified to enhance the adsorption capacity of the overall desulfurization system, depending on the particular sulfur compounds that are present in the hydrocarbon fuel cell fuel stream and the quantity thereof.

[0029] In one preferred embodiment, the selective sulfur adsorbent includes one or more manganese compounds blended with iron oxide on a support, such as alumina, silica, silica-alumina, titania, and other inorganic refractory oxides. The preferred quantity of the support comprises from about 5 to about 25% by weight, preferably from about 5 to about 20% by weight, and most preferably from about 5 to about 15% by weight of the total weight of this selective sulfur adsorbent. One primary function of the support material is to provide a large and accessible surface area for deposition of the active metal compounds.

[0030] The metal compounds which are deposited on or incorporated within the support of this selective sulfur adsorbent, other than the one or more manganese compound(s), include iron oxide. In a preferred embodiment the iron oxide and manganese compound(s) together comprise at least about 60% by weight, preferably at least about 70% by weight and most preferably about 80% to about 90% of this selective sulfur adsorbent, by weight.

[0031] In a preferred embodiment the quantity of iron oxide present in this selective sulfur adsorbent exceeds the quantity of the manganese compound(s). It is preferred that the ratio of the iron oxide to the manganese compound(s) by weight, should be at least about 1:1 and preferably from about 1:1 to about 6:1. The preferred loading of iron oxide on the support is in the range of about 40 weight percent to about 80 weight percent and, more preferably from about 50 to about 70 weight percent of the total weight of the selective sulfur adsorbent. Various forms of iron oxide may be used, such as FeO and Fe_2O_3 and mixtures thereof.

[0032] The one or more manganese compound(s) comprise from about 15 weight percent to about 40 weight percent, preferably from about 20 weight percent to about 40 weight percent of the total weight of the selective sulfur adsorbent. Various forms of manganese compounds can be used including MnO_2, Mn_2O_3, Mn_3O_4 and $Mn(OH)_4$ and mixtures thereof.

[0033] A promoter or promoters may also be added to this selective sulfur adsorbent, preferably an alkali or alkaline earth metal oxide, promoter and more preferably calcium oxide, in quantities from about 5 to about 15% by weight. While calcium oxide is the preferred promoter, alkali or other alkaline earth metal oxide promoters, such as magnesium oxide, may also, or alternatively, be utilized in combination with the calcium oxide.

[0034] The iron oxide/manganese compound(s) selective sulfur adsorbent according to the present invention may be prepared by coprecipitation, decomposition, impregnation or mechanical mixing. Preferably, this selective sulfur adsorbent is produced by coprecipitation or decomposition. The method chosen should guarantee that there has been an intensive blending of the components of the selective sulfur adsorbent.

[0035] The pore volume of the iron oxide/manganese compound(s) adsorbent produced by those procedures determined by mercury porosimetry is preferably from about 0.3 cc/g to about 0.6 cc/g. In addition, this selective sulfur adsorbent preferably has a compacted bulk density of about 0.4 to about 1.1 g/cc. Once the material is in its preliminary product form, it can be further processed to form the final selective sulfur adsorbent by pelletizing or extrusion. This selective sulfur adsorbent preferably is formed into moldings, especially in the form of spheres or pellets, preferably ranging in size from about 0.1 cm to about 1 cm in diameter. The materials for this selective sulfur adsorbent are preferably chosen to achieve a surface area of at least about 100 m^2/g and more preferably from about 100 m^2/g to about 300 m^2/g.

[0036] This iron oxide/manganese compound(s) selective sulfur adsorbent when used alone has shown especially good sulfur adsorption when the sulfur compounds contained in a fuel cell fuel stream comprise hydrogen sulfide, carbonyl sulfide (COS), tertiary butyl mercaptan (TBM) and ethyl mercaptan (EM). This selective sulfur adsorbent, when utilized with the calcium-exchanged zeolite adsorbent and the hydrated alumina adsorbent, has shown enhanced utility for adsorption of sulfur compounds that are commonly present in a fuel cell fuel stream including COS, tetra hydro thiophene (THT) and dimethyl sulfide (DMS), especially when the zeolite is placed in a adsorption system in sequence before the hydrated alumina adsorbent followed by the iron oxide/manganese compound(s) adsorbent in the sequential sulfur adsorbent system.

[0037] An additional preferred selective sulfur adsorbent that can be utilized with the zeolite adsorbent and the hydrated alumina adsorbent in the sequential sulfur adsorbent system includes one or more manganese compound(s), copper oxide and small quantities of a binder. The manganese compound(s) of this selective sulfur adsorbent may be utilized in any of the forms previously described for the manganese compound of the selective sulfur adsorbent described above. The manganese compound(s) of this selective sulfur adsorbent comprise from about 50 to about 80% and preferably from about 60 to about 75% of this selective sulfur adsorbent, by weight. The copper oxide comprises from about 15 to about 40% and preferably from about 15 to about 30%, by weight, of this selective sulfur adsorbent. The binder comprises from about 5 to 20%, by weight, of this selective sulfur adsorbent. In a preferred embodiment the binder may be selected from a wide variety of clays including bentonite, diatomaceous earth, attapulgite, kaolin, sepiolite, illite and mixtures thereof. More preferably, the binder comprises bentonite clay. Promoters may be added to this selective sulfur adsorbent to enhance its operating characteristics. This adsorbent is prepared by conventional procedures. The materials for this selective sulfur adsorbent are chosen so that the surface area of this manganese compound(s)/copper oxide with binder ranges from about 100 to about 300 m^2/g, preferably from about 200 to about 300 m^2/g.

[0038] This manganese compound(s)/copper oxide/binder selective sulfur adsorbent when used alone has shown great utility for the adsorption of hydrogen sulfide, carbonyl sulfide, tertiary butyl mercaptan, ethyl mercaptan and mixtures thereof. In addition, this manganese compound(s)/copper oxide/binder selective sulfur adsorbent, when utilized in sequence after the zeolite adsorbent and the hydrated alumina in the sequential sulfur adsorbent system, has shown significant adsorption for sulfur compounds contained in hydrocarbon fuel cell feed streams of the same type as those described above where the selective sulfur adsorbent composition comprises iron oxide, manganese compound(s) and small quantities of a support. This selective sulfur adsorbent has shown particular utility when it is necessary to reduce the level of carbonyl sulfide in the feed stream to extremely low levels, as low as 50 ppb or so, especially without the addition of any hydrolyzing agent to the feed stream.

[0039] An additional selective sulfur adsorbent, that can be utilized with the zeolite adsorbent and the hydrated alumina adsorbent in the sequential adsorbent system, comprises copper oxide, zinc oxide and alumina, preferably a hydrated alumina. The quantity of copper oxide present is from about 15 to about 25%, the quantity of the zinc oxide is from about 5 to about 15%, and the quantity of the alumina is from about 65 to about 85%, by weight. The adsorbent is prepared by conventional procedures. The materials for this selective sulfur adsorbent are chosen so that its surface area is from about 100 to about 300 m^2/g, preferably from about 150 to 300 m^2/g. This selective sulfur adsorbent catalyst is prepared by conventional procedures.

[0040] This selective sulfur adsorbent when used alone is particularly useful for the adsorption of hydrogen sulfide, carbonyl sulfide, tertiary butyl mercaptan, ethyl mercaptan, and mixtures thereof. This selective adsorbent has shown particular utility for the adsorption of carbonyl sulfide for extended periods of time before "breakthrough" occurs, especially without the addition of any hydrolyzing agent to the feed stream.

[0041] An additional selective sulfur adsorbent that can be utilized with the zeolite adsorbent and the hydrated alumina adsorbent in the sequential sulfur adsorbent system in place of, or in addition to, the above described selective sulfur adsorbents comprises zinc oxide alone or in combination with a carrier. While alumina is the preferred carrier, other carriers with similar performance characteristics can be utilized. In a preferred embodiment, the zinc oxide comprises at least about 60%, preferably from about 60 to about 95%, and more preferably from about 70 to about 90%, by weight, of the selective sulfur adsorbent with the remaining portion preferably comprising alumina. Additives may be added to this selective sulfur adsorbent to enhance its capacity to absorb sulfur compounds or other performance characteristics. The surface area of this selective sulfur adsorbent ranges from 5 to about 75 m^2/g and preferably from about 10 to about 50 m^2/g. This zinc oxide/alumina selective sulfur adsorbent is prepared by conventional procedures.

[0042] The zinc oxide alumina selective sulfur adsorbent when used alone as a sulfur adsorbent has shown good sulfur adsorption when the sulfur compounds contained within the fuel cell fuel stream comprise hydrogen sulfide and ethyl mercaptan and mixtures thereof.

[0043] Another selective sulfur adsorbent that can be utilized with the zeolite adsorbent and the hydrated alumina adsorbent in the sequential sulfur adsorbent system is comprised of activated carbon containing small quantities of copper oxide. In a preferred embodiment the activated carbon comprises from about 80 to about 95%, preferably 85 to 95%, by weight, of this selective sulfur adsorbent with the remaining portion comprising copper oxide. Additives may be added to the composition to enhance its performance. The activated carbon/copper oxide selective sulfur adsorbent is prepared by conventional procedures. The surface area of the composition ranges from about 300 to about 1000 m^2/g, with the preferred surface area being from about 500 m^2/g to about 1000 m^2/g. This selective sulfur adsorbent is prepared by conventional procedures.

[0044] This activated carbon with copper oxide selective sulfur adsorbent when used alone has shown great utility for the adsorption of tetra hydro thiophene, tertiary butyl mercaptan, ethyl mercaptan and mixtures thereof.

[0045] Another useful selective sulfur adsorbent that can be utilized with the zeolite adsorbent and the hydrated alumina adsorbent in a sequential sulfur adsorbent system comprises copper oxide and zinc oxide with alumina, preferably with small quantities of carbon. In a preferred embodiment the copper oxide comprises from about 50 to about 65% and more preferably from about 50 to about 60% of the selective sulfur adsorbent, by weight. The zinc oxide comprises from about 20 to about 35% of the selective sulfur adsorbent and the alumina comprises from about 5 to about 20%, preferably from about 10 to 20% of the selective sulfur adsorbent, by weight. The quantity of the carbon, if used, should be less than 10%, preferably from about 1 to about 10%, by weight. The surface area of this selective sulfur adsorbent containing copper oxide, zinc oxide, alumina, and preferably small quantities of carbon, is from about 100 to about 300 m^2/g and preferably from about 100 to about 200 m^2/g. The process for the preparation of this selective sulfur adsorbent is conventional.

[0046] This copper oxide/zinc oxide/alumina, preferably with small quantities of carbon, selective sulfur adsorbent when used alone is especially useful for the adsorption of hydrogen sulfide, tertiary butyl mercaptan, ethyl mercaptan, carbonyl sulfide and mixtures thereof.

[0047] An additional selective sulfur adsorbent that can be utilized with the zeolite adsorbent and the hydrated alumina adsorbent in the sequential sulfur adsorbent system, comprises manganese compound(s), used alone, which may be utilized in a number of forms including MnO_2, Mn_2O_3, Mn_3O_4 and $Mn(OH)_4$ or mixtures thereof. The surface area of the manganese compound(s) range from about 100 to about 300 m^2/g, and preferably from about 200 to about 300 m^2/g. Additional materials may be combined with the manganese compound(s) including calcium, silver and magnesium to promote the performance of the manganese compound(s). Conventional methods are utilized for the formation of this selective sulfur adsorbent.

[0048] The manganese compound(s) selective sulfur adsorbent when used alone has shown great utility for the adsorption of hydrogen sulfide, tertiary butyl mercaptan, ethyl mercaptan and mixtures thereof.

[0049] An additional selective sulfur adsorbent, that can be utilized with the zeolite adsorbent and the hydrated alumina adsorbent in the sequential sulfur adsorbent system, comprises copper oxide with alumina, wherein the quantity of the copper oxide is from about 5 to about 25%, preferably from about 10 to about 20%, by weight, and the quantity of the alumina is from about 75 to about 95%, preferably from about 80 to about 90%, by weight. The surface area of this selective sulfur adsorbent is from about 100 to about 300 m^2/g and preferably from about 150 to about 300 m^2/g. This selective sulfur adsorbent is prepared by conventional procedures.

[0050] This selective sulfur adsorbent when used alone has shown particularly usefulness for the adsorption of hydrogen sulfide, carbonyl sulfide, tertiary butyl mercaptan, ethyl mercaptan and mixtures thereof.

[0051] The preferred sequence of use of the adsorbents in the desulfurization system is the zeolite adsorbent placed prior to the hydrated alumina adsorbent and followed by the selective sulfur adsorbent. The preferred ratio of the zeolite adsorbent to the combination of the hydrated alumina adsorbent and selective sulfur adsorbent is from about 1:3 to 3:1 and preferably 1:2 to about 2:1 and most preferably in the range from about 1:1, by volume.

[0052] The inventors have discovered that while a number of selective sulfur adsorbents may be utilized with the combination of the calcium exchange zeolite and the hydrated alumina to remove sulfur compounds from a feed stream, the preferred selective sulfur adsorbents, especially when carbonyl sulfide is present, particularly for hydrogen generation, comprise: a) one or more manganese compounds blended with copper oxide on small quantities of a binder, b) copper oxide, zinc oxide and alumina, preferably a hydrated alumina, and c) one or more manganese compounds, iron oxide and a support.

[0053] The inventors have surprisingly discovered that while several types of ion exchanged zeolites may be useful as the zeolite adsorbent for this sequential sulfur adsorbent system, the preferred ion exchanged zeolite is a calcium exchanged zeolite. While a number of calcium exchanged zeolites are known, including calcium exchanged zeolite A, zeolite X, zeolite Y, zeolite ZSM-5, zeolite Beta, synthetic mordenite and blends thereof, the preferred calcium exchanged zeolite for this desulfurization system is a calcium exchanged zeolite X. A particularly preferred calcium exchanged zeolite X is a calcium exchanged, low silica zeolite X, known as "LSX", or calcium exchanged low silica faujasite, known as "LSF". Zeolite X generally has a Si:Al equivalent ratio of about 1.0 to about 1.25. In one example, a conventional, non-calcium exchanged precursor synthesized LSF has the following anhydrous chemical composition: $2.0\ SiO_2:Al_2O_3:0.73\ Na_2O:0.27K_2O$, although the ratio between sodium and potassium cations can vary, sometime significantly, depending upon the process of manufacture of the LSF.

[0054] In one embodiment of the invention, a substantial percentage of the cations of the zeolite X are preferably ion exchanged with calcium ions using conventional ion exchange procedures, such as by treatment of the zeolite X with calcium salts, such as, but not limited to, calcium chloride. Several methods can be used for the ion exchange procedure with ion exchange preferably occurring after the zeolite adsorbent has been formed into its preferred final form, such as a bead or an extrudate. The zeolite X is ion exchanged to a level of at least about 50%, preferably at least 60%, more preferably at least 70%, and most preferably 85 to 95% of the exchangeable metal ions. The remaining ions may be sodium and/or potassium ions. (For reference purposes the term "calcium exchanged zeolite X" means a zeolite X containing at least about 50% calcium cations.) The calcium exchanged zeolite X of one embodiment of the invention generally contains some sodium or potassium ions in addition to the calcium ions after the calcium ion exchange. However, a portion, up to substantially all of these sodium/potassium ions, can be ion exchanged with other cations to enhance or modify the performance characteristics of the calcium exchanged zeolite X, especially for sulfur adsorption. For example, the additional cations that may be ion exchanged onto the zeolite X to enhance its performance include zinc, cadmium, cobalt, nickel, copper, iron, manganese, silver, gold, scandium, lithium and combinations thereof. The percentage of ion exchange of these additional metal ions can range from as little as about 1% up to about 40% or so, depending upon the level of calcium exchange of the zeolite X. The particular metal ions that are ion exchanged onto the calcium exchanged zeolite depend on the particular sulfur compounds which are intended to be removed from the fuel cell fuel stream by the sequential sulfur adsorbent system of the invention.

[0055] The calcium exchanged zeolite, when utilized as a sulfur adsorbent, has shown significant capability for the adsorption of various sulfur materials, particularly tetra hydro thiophene (THT), di-methyl sulfide (DMS), tertiary butyl mercaptan (TBM) and ethyl mercaptan (EM).

[0056] The alumina component of the invention comprises substantially a hydrated alumina. For purposes of this invention the terms "alumina hydrate" or "hydrated alumina" comprise aluminum hydroxides that commonly have the formula $Al(OH)_3$ or AlO(OH). The crystalline forms of these hydrated aluminas are trihydroxides and include gibbsite, bayerite and nordstrandite. Hydrated alumina also includes aluminum oxide-hydroxides such as boehmite, pseudo-boehmite, and diaspore. The preferred forms of hydrated alumina for the alumina component of various forms of the invention include boehmite, pseudo-boehmite and gibbsite. The percentage of the alumina, which comprises hydrated alumina of the type described above, is greater than 60%, preferably greater than 80%, and most preferably it approaches 100%.

[0057] While non-activated hydrated aluminas are the preferred form of hydrated alumina for the desulfurization system, "activated" hydrated aluminas may also have utility for some sulfur removal applications. For purposes of this invention, "activation" of a hydrated alumina requires impregnation of a hydrated alumina with one or more alkali metal or alkaline earth metal ions, preferably in an amount from about 0.01 to about 10 wt. %, wherein the wt. % is measured as a percentage weight of the impregnated alkali metal or alkaline earth metal to the total weight of the alkali metal/alkaline earth metal and aluminum in the composition. Activated hydrated alumina is generally activated by impregnation with alkali metal ions, most preferably sodium or potassium ions. Activated hydrated alumina of this type is prepared by methods recognized in the art, such as those disclosed, for example, in U.S. Pat. Nos. 3,058,800 and 4,835,338, both of which patents are incorporated herein by reference.

[0058] It has been surprisingly discovered that the capability of the selective sulfur adsorbents described above, when used individually, the hydrated alumina described above, and the calcium exchanged zeolite, when used individually, can be enhanced dramatically by the sequential use of the calcium exchanged zeolite X and the hydrated alumina when placed prior to the selective sulfur adsorbents in the flow of the feed stream to form the sequential sulfur adsorbent system for the desulfurization of a hydrocarbon fuel cell feed stream. The use of this combination of calcium exchanged zeolite, hydrated alumina and selective sulfur adsorbent placed in sequence, permits the adsorption of a broader range of sulfur containing compounds than has been conventionally been adsorbed using any of the components alone. For example, it has been surprisingly discovered that by the use of calcium exchanged zeolite X, hydrated alumina, and selective sulfur adsorbents placed in sequence, enhanced sulfur adsorption of a broad range of sulfur compounds, including carbonyl sulfide, hydrogen sulfide, tetra hydro thiophene, dimethyl sulfide, and various mercaptans, including ethyl, methyl, propyl, and tertiary butyl mercaptan and combinations thereof, is possible. This combination of materials when used in this sequence has shown particular utility for the removal of carbonyl sulfide from the feed stream, even when the level of conventional hydrolysis agents, such as water, ethanol, and methanol, in the feed stream is low, i.e. less than about 500 ppm. Efficient removal occurs even without the addition of conventional hydrolysis agents. In addition, especially efficient removal of carbonyl sulfide to levels as low as 50 ppb has been achieved when the selective sulfur adsorbent comprises one or more manganese compounds, copper oxide and small quantities of a binder, as previously discussed.

[0059] It has also been surprisingly discovered that the breakthrough time for sulfur compounds commonly present in a hydrocarbon fuel system can be extended by the use of the calcium exchanged zeolite X, hydrated alumina and selective sulfur adsorbent placed in sequence in the feed stream in the preferred order of the components. This breakthrough time is enhanced over a desulfurization system containing only the calcium exchanged zeolite and the selective sulfur adsorbent when used in combination. This extension of breakthrough time is particularly apparent when the selective sulfur adsorbent comprises copper oxide, zinc oxide and alumina, as previously discussed.

[0060] It has also been surprisingly discovered that by placement of the calcium exchanged zeolite X prior to the hydrated alumina, which is then followed by the selective sulfur adsorbent in the sequential sulfur adsorption system, the likelihood of the production of synthesized sulfur compounds is substantially reduced.

[0061] The inventors have also surprisingly discovered that the sequential sulfur adsorbent system as described herein can be utilized at temperatures lower than normally utilized for conventional sulfur adsorption systems. While conventional chemical sulfur adsorbents require temperatures for the feed stream of at least about 150° C. to about 400° C., embodiments of the sequential sulfur adsorbent system can be utilized effectively to adsorb the sulfur contaminants at temperatures below 100° C. Such embodiments can be especially effective for removal of some sulfur compounds at temperatures from ambient temperature to 100° C., particularly from ambient to 60° C.

[0062] In addition, when the sequential sulfur adsorbent system as described is used, the pressure on the feed stream can be reduced to a range from about 1 bar to about 18 bar, preferably from about 1.7 bar to about 7 bar. These pressure ranges are lower than normally are utilized for the adsorption of sulfur compounds in a conventional fuel cell processing train.

[0063] In addition, when the sequential sulfur adsorbent system as described herein is used, the applicants have surprisingly discovered that it is not necessary that there be a conventional hydrolysis agent, such as water, ethanol, or methanol in the feed stream to enhance sulfur removal. In previous sulfur adsorbent systems, especially those used for the removal of carbonyl sulfide, it was necessary that a hydrolyzing agent, either be present in the feed stream or be added to the feed stream in significant quantities. The inventors have surprisingly discovered that efficient and effective sulfur removal, especially for the removal of carbonyl sulfide, can occur when the sequential sulfur adsorbent system of the invention is utilized, even when the quantity of water or other hydrolyzing agents in the feed stream is less than 500 ppm. In fact, the absence of water or other hydrolyzing agents from the feed stream in amounts greater than 500 ppm is a preferred composition for a feed stream utilizing the sequential sulfur adsorbent system of the invention to reduce the likelihood that the calcium exchanged zeolite absorbs excessive levels of water or other hydrolyzing agents.

[0064] The inventors have also surprisingly discovered a method for supplying a substantially desulfurized hydrocarbon fuel stream to a fuel cell processor using the sequential sulfur adsorbent system described herein. In this process a sulfur contaminated hydrocarbon fuel stream is passed over or through the sequential sulfur adsorbent system of a fuel cell processor at a temperature from about ambient to about 100° C., preferably less than 60° C., and more preferably at ambient temperatures. By passing a hydrocarbon fuel stream comprising, for example, natural gas, propane or LPG, containing sulfur components at levels up to 500 ppm, a substantial reduction in the quantity of those sulfur compounds, preferably down to a level of less than about 50 ppb, can be achieved. It has also been surprisingly discovered that this reduction in sulfur occurs even when the level of water or other hydrolyzing agents in the fuel stream is less than 500 ppm. Utilization of feed streams with this low level of water or other hydrolyzing agents is a preferred embodiment.

[0065] The inventors have also discovered that the above-described sequential sulfur adsorbent system of the invention can be used in a desulfurizer, particularly for use in a fuel cell processing train. This desulfurizer includes an inlet for receiving the nondesulfurized hydrocarbon fuel stream, such as natural gas, propane or LPG, the sequential sulfur adsorbent system, as described herein, which is placed in a location to desulfurize the hydrocarbon fuel stream, and an outlet where the desulfurized hydrocarbon fuel stream is passed down stream for further processing. For example, the desulfurized hydrocarbon fuel stream can be passed through the fuel cell processing train to the fuel cell stack for the production of electricity.

[0066] The inventors have also surprisingly discovered that this method for supplying a substantially desulfurized hydrocarbon fuel stream is more advantageous than methods using conventional desulfurization systems as it permits desulfurization of a broader range of sulfur compounds, increases the sulfur compound breakthrough time for the system, reduces the production of synthesized sulfur compounds, reduces the required temperature of and pressure on the feed stream, does not require the presence of substantial quantities of water or other hydrolyzing agents in the feed stream, and permits the choice of different selective sulfur adsorbents to be used in the sequential sulfur adsorbent system depending on the sulfur compounds that are present in the particular feed stream. The compositions and methods of the processes also permit the production of a substantially desulfurized hydrocarbon fuel stream containing levels of sulfur below those achievable with conventional desulfurizing processes.

[0067] The inventors have also discovered that the sequential sulfur adsorbent system as described herein can be used in fuel cell processors for a longer period of time than conventional adsorbents and still achieve high levels of sulfur absorbency.

[0068] The inventors have also discovered that the sequential sulfur adsorbent system as described herein is also not subject to desorption of the adsorbed sulfur compounds when the conditions surrounding the sulfur adsorbent system change, as often occurs with some conventional sulfur adsorbents.

EXAMPLES

[0069] The following examples are intended to be illustrative of one embodiment of the invention and to teach one of ordinary skill in the art to make and use this embodiment. These examples are not intended to limit the invention in any way.

[0070] In order to illustrate the operation of one embodiment of the invention, the inventors have compared the performance of a first sulfur adsorbent system containing, in sequence, a calcium-exchanged zeolite X followed by a particular selective sulfur adsorbent with a second sulfur adsorbent system containing the same calcium-exchanged zeolite X and selective sulfur adsorbent to which has been added hydrated alumina. In the two component system, the volume of the adsorbents (10 ccs) consists of fifty percent (50%) of each component with the calcium-exchanged zeolite X placed in the system prior to the selective sulfur adsorbent. In the three component system, the same overall volume of the adsorbents (10 ccs) consists of fifty percent (50%) by volume of the calcium-exchanged zeolite X followed by twenty-five percent (25%) by volume of the hydrated alumina, and twenty five (25%) by volume of the selective sulfur adsorbent.

[0071] In each example, a synthetic natural gas feed stream is utilized comprising 93% methane, 3% ethane, 2% propane, 0.2% butane, 1% carbon dioxide and 0.75% nitrogen. Also included in this synthetic natural gas is 10 ppm (as sulfur) of carbonyl sulfide. This synthetic natural gas is passed through an artificial reactor containing the two or three component sulfur adsorbent systems. The zeolite adsorbent is in the form of 2 mm spheres. The selective sulfur adsorbent is a 1.18 mm×0.85 mm mesh particulate, typically produced by grinding 1.6 mm extrudates. The hydrated alumina is in the form of 3.2 mm extrudates ground into 1.18 mm×0.85 mm mesh particles. The various components are sized and loaded into the reactor and the synthetic natural gas feed stream is passed through the reactor. The temperature of the feed stream is maintained at 38° C. with a space velocity of 3000 hr^{-1} at a pressure of 2 bar. "Breakthrough" for this test occurs when an amount greater than 1 ppm of sulfur in the form of carbonyl sulfide is observed in the natural gas feed stream after passage through the adsorbent systems.

[0072] To determine the gas phase sulfur level of the feed stream, analysis is performed using an Agilent 6890 gas chromatograph attached to an Antek 7090 sulfur analyzer. The gas chromatograph utilizes a 60 m×320 micron DB-1 capillary column for sulfur compound separation. The Antek 7090 utilizes a sulfur chemiluminescense detector (SCD) for sulfur detection. The operational detection limit for the system is approximately 50 ppb (mole). The test unit is controlled by automation software.

Example 1

[0073] The synthetic natural gas containing carbonyl sulfide is passed through a reactor containing, in sequence, calcium-exchanged zeolite X and the selective sulfur adsorbent. The zeolite X has an Si:Al equivalent ratio of 1.17 and a calcium exchange of 70% with the remaining metal ions comprising sodium and/or potassium. The selective sulfur adsorbent comprises 70% by weight manganese compounds, 21% copper oxide comprising Cuo and 9% silica. The temperature of the reactor is maintained at 38° C. and the pressure is maintained at about 2 bar. The sulfur adsorbency of the two component system is shown on **FIG. 1**, and shows breakthrough occurring at 136 hours. The percent S in the form of COS that is removed by this system is listed in **FIG. 2**.

Example 2

[0074] A further test is run wherein the calcium exchanged zeolite and selective sulfur adsorbent of Example 1 are used in combination with a hydrated alumina in the reactor. The hydrated alumina is commercial pseudoboehmite. The hydrated alumina is placed in sequence in the system after the calcium-exchanged zeolite X and before the selective sulfur adsorbent. Fifty percent of the components by volume is composed of the zeolite X and 25% is composed of each of the selective sulfur adsorbent and the hydrated alumina. A total of 10 ccs of the components is used. The operating conditions and the composition of the feed stream are the same as for Example 1. The percent S in the form of COS that was removed by the system is listed in **FIG. 2**. When the feed stream is passed through the reactor, breakthrough does not occur until 204 hours, as shown in **FIG. 1**. In addition, as shown in **FIG. 2**, a higher percentage of sulfur is removed from the feed stream by breakthrough utilizing the three component system than occurs with the two component system.

[0075] As is clear from these examples, the combination of the calcium exchanged zeolite with the hydrated alumina adsorbent followed by the selective sulfur adsorbent increases the time of sulfur breakthrough and extends the lifetime of the sequential sulfur adsorbent system.

[0076] As many changes and variations in the disclosed embodiments may be made without departing from the inventive concept, the invention is not intended to be limited by this description.

1. A process for desulfurization of a hydrocarbon feed stream comprising

providing a hydrocarbon feed stream, which is contaminated with sulfur compounds, including carbonyl sulfide,

passing the sulfur contaminated feed stream through a sequential sulfur adsorbent system comprising in sequence zeolite, hydrated alumina, and a selective sulfur adsorbent to produce a hydrocarbon feed stream which has been substantially desulfurized.

2. The process of claim 1, where the zeolite comprises a calcium exchanged zeolite X or LSX.

3. The process of claim 2, wherein the calcium exchanged zeolite X or LSX is exchanged with calcium ions at least about 50%.

4. The process of claim 3, wherein the calcium exchanged zeolite X or LSX is further exchanged with metal ions selected from the group consisting of zinc, cadmium, cobalt, nickel, copper, iron, manganese, silver, gold, scandium, lithium and combinations thereof.

5. The process of claim 1, wherein the Si:Al ratio of the zeolite is from about 1.0 to about 1.25.

6. The process of claim 1, wherein the composition of the hydrated alumina is selected from boehmite, pseudo-boehmite and gibbsite.

7. The process of claim 1, wherein the composition of the hydrated alumina is selected from $Al(OH)_3$ and $AlO(OH)$.

8. The process of claim 1, wherein the selective sulfur absorbent comprises zinc oxide, copper oxide and a binder.

9. The process of claim 1, wherein the selective sulfur absorbent comprises copper oxide and one or more manganese compounds.

10. The process of claim 1, wherein the selective sulfur absorbent comprises one or more manganese compounds and an iron compound.

11. The process of claim 1, wherein the temperature of the sequential sulfur adsorbent system, as the feed stream passes therethough, is from ambient to about 100° C.

12. The process of claim 1, wherein the temperature of the sequential sulfur adsorbent system, as the feed stream passes therethough, is from ambient to about 60° C.

13. The process of claim 1, wherein the feed stream contacts the zeolite prior to contacting either the hydrated alumina or the selective sulfur absorbent.

14. The process of claim 1, wherein the feed stream contacts the zeolite prior to contacting the hydrated alumina and contacts the selective sulfur adsorbent after contacting the hydrated alumina.

15. A process for desulfurization of a hydrocarbon fuel cell feed stream comprising

providing a hydrocarbon feed stream to a fuel cell processing train, wherein the feed stream is contaminated with sulfur compounds, including carbonyl sulfide,

passing the sulfur contaminated feed stream through a sequential sulfur adsorbent system comprising, in sequence, calcium-exchanged zeolite, hydrated alumina and a selective sulfur adsorbent to produce a hydrocarbon feed stream which has been substantially desulfurized, and

delivering the substantially desulfurized hydrocarbon feed stream to remaining components of the fuel cell processing train.

16. The process of claim 15, wherein the temperature of the sequential sulfur adsorbent system as the feed stream passes therethough is from ambient to about 100° C.

17. A process for the desulfurization of a hydrocarbon fuel cell feed stream comprising

providing the hydrocarbon feed stream to a fuel cell processing train, wherein the feed stream is contaminated with sulfur compounds, including one or more compounds selected from the group consisting of carbonyl sulfide, hydrogen sulfide, tetra hydro thiophene, dimethyl sulfide, mercaptans, disulfides, thiophenes, sulfoxides, other organic sulfides, and higher molecular weight organic sulfur compounds and combinations thereof,

passing the sulfur contaminated feed stream through a sequential sulfur adsorbent system comprising, in sequence, calcium exchange zeolite X or LSX, hydrated alumina, selected from the group consisting of boehmite, pseudo-boehmite and gibbsite and mixtures thereof, and a selective sulfur adsorbent selected from the group consisting of a blend of components selected from a) copper oxide, a manganese compound and a binder; b) copper oxide, a zinc compound and a binder, and c) a manganese compound, an iron compound and a support to produce a hydrocarbon feed stream which has been substantially desulfurized, and delivering the substantially desulfurized hydrocarbon feed stream to remaining components of the fuel cell processing train.

18. The process of claim 17, wherein the temperature of the sequential sulfur adsorbent system as the feed stream passes therethrough is from ambient to about 100° C.

19. The process of claim 17, wherein the pressure of the sulfur contaminated feed stream as it passes through the sequential sulfur adsorbent system is from about 1 bar to about 18 bar.

20. A sequential adsorbent system for use in a fuel cell processing train comprising in sequence calcium exchanged zeolite, hydrated alumina and a selective sulfur adsorbent, wherein the calcium exchanged zeolite comprises calcium exchanged zeolite X or LSX ion exchanged to at least 50% of the available metal ions with calcium ions; wherein the hydrated alumina is selected from the group consisting of gibbsite, boehmite, pseudo-boehmite and mixtures thereof; and wherein the selective sulfur adsorbent comprises from about 60 to about 80% by weight of one or more manganese compounds selected from the group consisting of MnO_2, Mn_2O_3, Mn_3O_4 and $Mn(OH)_4$ and mixtures thereof, from about 15 to about 40% by weight of copper oxide, and a binder.

21. A sequential adsorbent system for use in a fuel cell processing train comprising in sequence calcium exchanged zeolite, wherein the calcium exchanged zeolite comprises calcium exchanged zeolite X or LSX, ion exchanged to at least 50% of the available metal ions with calcium ions; hydrated alumina selected from the group consisting of gibbsite, boehmite, pseudo-boehmite and mixtures thereof, and a selective sulfur adsorbent comprising from about 15 to about 40 copper oxide, from about 5 to about 15 of a zinc compound and at least about 40% alumina.

22. A sequential adsorbent system for use in a fuel cell processing train comprising in sequence calcium exchanged zeolite X or LSX, ion exchanged to at least 50% of the available metal ions with calcium cations; hydrated alumina selected from the group consisting of gibbsite, boehmite, pseudo-boehmite and mixtures thereof, and a selective sulfur adsorbent comprising from about 20 to about 40% of a manganese compound or compounds selected from the group consisting of MnO_2, Mn_2O_3, Mn_3O_4, $Mn(OH)_4$ and mixtures thereof, from about 40 to about 80% of iron oxide, and a support.

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