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**METHODS, SYSTEMS, AND DEVICES FOR  
DEEP DESULFURIZATION OF FUEL GASES****CROSS REFERENCE TO RELATED  
APPLICATION**

This application claims priority from Provisional application No. 60/944,621 filed 18 Jun. 2007.

**FEDERALLY-SPONSORED RESEARCH AND  
DEVELOPMENT**

This invention was made with Government support under Contract DE-AC0576RLO1830 awarded by the U.S. Department of Energy. The Government has certain rights in the invention.

**BACKGROUND OF THE INVENTION**

Syngas generated by the gasification of coal or biomass has many potential applications, including the production of hydrocarbon transportation fuels, chemicals (including hydrogen), and electric power. Most syngases contain impurities that may make it unsuitable for various end uses. Sulfur-containing molecules, primarily H<sub>2</sub>S and COS, are especially troublesome catalyst poisons that must be removed to the parts per billion levels for the production of fuels and chemicals. Although technical approaches exist for removal of these sulfur species, these approaches typically tend to be rather costly, require temperature fluctuations, and in many cases backup sacrificial adsorbents. Since catalytic processes for the production of fuels and chemicals typically operate in the range of 225-300° C., a process that requires the cooling of syngas followed by a re-heating is energy inefficient. A process that is capable of removing sulfur gases to the 50 ppb level at or somewhat above the temperature of the synthesis step is much preferred.

Syngas composition is a function of several parameters, including gasifier type, operating conditions and fuel source. In the case of coal, a combination of zinc oxide with a regenerable downstream polishing bed is a promising approach. For biomass, which typically generates less than 100 ppm of sulfur gases, a stand-alone regenerable sulfur sorbent may provide an attractive approach. In the past, the development of regenerable metal sorbents has typically been stymied by the strong tendency of the metals to sinter or aggregate during the regeneration process. This results in a loss of surface area and therefore sulfur adsorbent capacity. What is needed, therefore, is a method, system and device that allows for deep (ppb) desulfurization of fuel gasses. What is also needed is a regenerable desulfurization system. What is also needed is a desulfurization system that performs effective desulfurization at warm temperatures. The present invention provides a solution to these needs.

Additional advantages and novel features of the present invention will be set forth as follows and will be readily apparent from the descriptions and demonstrations set forth herein. Accordingly, the following descriptions of the present invention should be seen as illustrative of the invention and not as limiting in any way.

**SUMMARY OF THE INVENTION**

The present invention is a highly effective and regenerable method, system and device that enables the deep desulfurization of warm fuel gases by passing these warm gasses over metal-based sorbents arranged in a mesoporous substrate.

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This technology protects Fischer-Tropsch synthesis catalysts and other sulfur sensitive catalysts, without drastic cooling of the fuel gases, and without sintering or agglomeration of the metal sorbents during the regeneration process. This allows for much more energy efficient processes for deep desulfurization to be designed. The system is characterized by active metal-based sorbents such as transient metals like Cr, Fe, Co, Ni, Cu, Ru, Rh, Pd, Ag, Pt, Au and mixtures and alloys thereof that are attached to a porous substrate, particularly a mesoporous silicate such as SBA-16.

These devices enable a process whereby warm fuel gasses such as natural gas, syngas, H<sub>2</sub>, CO, and hydrocarbon gases, mixtures of hydrocarbon gasses, and mixtures of hydrocarbon gases and inert gases, having a temperature between 20 and 900 degrees C. are passed over these sorbents to effect desulfurization of these gases down to a ppb level. These devices also allow for the regeneration of these materials after use by a cycling "oxidation-reduction" process that utilizes H<sub>2</sub>, CO, O<sub>2</sub>, N<sub>2</sub>, air, inert gases and steam in various combinations, at temperatures between 100° C. and 900° C. These processes can be utilized in a process either alone or alongside other separation processes. For high sulfur coal gas cleanup, the nanostructured metal-based sorbent bed may be attached to a separate process that can remove sulfur to ppm level (such as zinc oxide and related oxide absorbents). The present invention will then polish this gas stream by removing sulfur to ppb level. The present invention allows the total sulfur in such a gas to be reduced to less than 100 ppb and in some instances as low as 10 ppb.

The present invention utilizes stabilized active metal sorbent particles dispersed on a controlled nanoporous substrate that enables for desulfurization of warm fuel gasses. In some embodiments of the invention the metal-based sorbents comprise 0.1 to 100 weight percent metals relative to the substrates. Examples of various types of metals that can act as sorbents include: Cr, Mn, Fe, Co, Ni, Cu, Zn, Ru, Rh, Pd, Ag, Pt, Au and their alloys. Of this group particular success has been shown in systems that utilize transient metals selected from the group consisting of Ni, Cu, Fe, Ag, Co and their alloys.

Examples of various types of substrates include silica-based materials (including mesoporous silica in any form, fumed silica in any form, and zeolites in any form). These types of materials may be combined in a variety of forms and may be utilized to treat a variety of gasses including but not limited to natural gas, syngas (including both coal and biomass syngas), H<sub>2</sub>, CO, and other hydrocarbon gases, their mixtures, and their mixtures with inert gases. Examples of the types of materials that may be captured include but are not limited to H<sub>2</sub>S, COS, mercaptans, sulfides, disulfides, and thiophenes.

These metal-mesoporous materials may be incorporated into a system wherein warm fuel gases having a temperature in the range between ambient temperature (20° C.) to 900° C. can be effectively treated. In one embodiment of the invention this temperature is preferably between 100° C. to 700° C. and more preferably from 150° C. to 500° C. After these sorbents have been filled in this treatment process, these sorbents can be regenerated through a combination of "oxidation-reduction" treatments, over a series of cycles. Typically, this regeneration step is performed between one and ten cycles and preferably between 2 to 5 cycles. This "oxidation-reduction" regeneration process can be carried out using any gas stream that can oxidize metal sulfides (such as O<sub>2</sub> and its mixtures with inert gases and steam) and any gas stream that can reduce metal oxides (such as H<sub>2</sub>, CO, syngas, and their mixtures with