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POROUS DESULFURIZATION SORBENT PELLETS CONTAINING A REACTIVE METAL OXIDE AND AN INERT ZIRCONIUM COMPOUND

Inventors: Todd H. Gardner
Lee D. Gasper-Galvin
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Todd H. Gardner
Lee D. Gasper-Galvin

METC: NONE
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Origin of the Invention

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Field of the Invention

This invention relates generally to removal of gaseous sulfur compounds from the product stream of coal gasification and more particularly to desulfurization sorbents for removing hydrogen sulfide from a reducing gas mixture at a high temperature and to methods of preparing such sorbents.

Background of the Invention

One of the problems associated with energy-producing systems utilizing gasification of coal is that most types of coal contain substantial amounts of sulfur that is converted to gaseous sulfur compounds, particularly hydrogen sulfide, in the gasification process. Upon combustion of the gasification product, the hydrogen sulfide is in turn converted to sulfur dioxide, which is a precursor to polluting "acid rain." Removal of hydrogen sulfide is therefore necessary. A widely studied approach to removal of hydrogen sulfide from a hot reducing gas
mixture has been to contact the mixture with a sorbent pellet bed in which the sulfide gas is converted to a solid compound. The bed is regenerated for reuse over repeated cycles by reaction with an oxidizing gas.

Numerous requirements and desirable features exist for sorbent materials for this purpose. The sorbent material should include an active compound which shows maximum reactivity with hydrogen sulfide and other components as required for physical strength and durability during repeated cycles of sorption and regeneration. The capability of being formed into durable pellets of a selected size for various types of reactors is also needed.

Hot gas desulfurization sorbents have typically contained zinc oxide as a reactive component. Zinc oxide by itself, however, is unsuitable for absorption because at the hot temperatures and highly reductive atmospheres required in coal gasification it is susceptible to being reduced to elemental zinc and to undergo volatilization when reduced. Some improvement has been obtained by reacting zinc oxide with oxides of other metals such as iron and titanium, forming a mixed metal oxide or solid solution made up of zinc ferrite or zinc titanate. These measures have provided added stability by enhancing strength, reducing susceptibility to being reduced to elemental zinc, and enhancing sintering resistance. It has been reported, however, that both zinc ferrite and zinc titanate decrepitate or spall due to the formation of zinc sulfide and zinc sulfate. Such reactions expand the lattice of these
crystalline materials by as much as 45 volume percent in the case of zinc titanate reacting to zinc sulfide, and by a larger volume expansion for the sorbents reacting to form zinc sulfate. Also, the initial mechanical strength of these sorbent materials may not be sufficient to withstand a fluidized bed or transport reactor environment or to withstand circulation from the reactor to the regenerator in a moving bed system. Zinc oxide-containing sorbents with enhanced strength obtained by the addition of significant quantities of inert materials, such as silica and alumina, have also been used. These sorbents are normally produced by a sol-gel technique. Zinc based sorbents containing silica and alumina have been tested for their ability to remove hydrogen sulfide from coal gases at 900° to 1,000° F. Difficulties have been encountered due to the lack of resistance of these sorbents to steam-induced degradation and loss of reactivity over as few as 20 cycles. It is believed that the loss of reactivity may be due to a slow solid-state reaction of zinc oxide with silica and alumina to form zinc silicate and zinc aluminate, respectively. Zinc silicate and zinc aluminate are essentially inert with respect to hydrogen sulfide, and therefore overall efficiency is reduced.

Summary of the Invention

This invention is directed to porous desulfurization pellets comprising a reactive metal oxide, preferably zinc oxide, mixed with an inert zirconium compound and other components as required to maintain pellet integrity under
conditions of high temperature and pressure through repeated cycles of desulfurization and regeneration. Processes for making the pellets are also provided by this invention.

The pellets may be prepared by mixing fine particles of zinc oxide and a suitable zirconium compound, along with other required components, granulating the mixture into pellets and firing the pellets, or by spray drying an aqueous slurry of such a mixture as well as by impregnating porous catalyst-carrier type zirconium-containing pellets with an aqueous solution of a zinc salt, followed by firing in air. Other components needed for use in pellets prepared by granulation or spray drying may include one or more organic or inorganic binders and promoters.

Desulfurization pellets of this invention are highly effective in removing hydrogen sulfide from coal gasification gas, and they overcome numerous limitations and disadvantages of materials employed in the prior art. The sorbents selectively remove hydrogen sulfide to levels below 10 to 15 ppmv over a wide range of temperatures and pressures. Their reactivity with hydrogen sulfide is high, and the pellets also show complete regenerability in oxygen-containing atmospheres. Interactions of the reactive metal oxide with zirconium compounds or catalyst carrier support materials as well as with other required components, which would result in formation of undesired inactive phases, are avoided. Furthermore, the sorbent pellets are resistant to contact with steam, to which they might be exposed during both sulfidation and regeneration, so that loss of porosity and surface area, sintering, and migration of active
metals from such exposure is avoided. The pellets do not show any indication of decrepitation or spalling, and instead exhibit attrition resistance and mechanical strength, with a crush strength over twice that of zinc titanate. No loss of zinc oxide through reduction and volatilization of the metal is shown for these materials.

**Detailed Description of the Invention**

The invention is broadly applicable to removal of gaseous sulfur compounds, primarily hydrogen sulfide, from reducing gas mixtures at an elevated temperature. In particular, it is useful for gas product streams emerging from coal gasifiers. Typically, such product streams have a strongly reducing character owing to the presence of carbon monoxide in the amount of 7 to 65 volume percent and hydrogen at 15 to 30 percent. Other major components may include carbon dioxide, hydrogen, and water vapor. Hydrogen sulfide is typically contained in the mixture at about 1 percent, and removal of this component to levels to 10 to 15 parts per million is desired to allow environmentally compatible release to the atmosphere after combustion. The starting hydrogen sulfide-containing gas mixture may also be derived from other sources such as petroleum processing streams and natural gas.

The high temperature sorbents prepared by methods of this invention selectively remove hydrogen sulfide to a level below 10 to 15 ppmv for extended periods of time from coal gas at temperatures of 650° to 1,300° F for zinc-based sorbents; 650°
to 1,600° F, and particularly 650° to 1,000° F for copper-based sorbents, at pressures from atmospheric up to 600 pounds per square inch.

The absorbent material of the present invention is provided in the form of porous pellets having a selected size depending upon the type of reactor in which a bed of the pellets is to be used. For moving bed reactors, a pellet size of 3 to 5 mm is preferred; for transport reactors, 65 to 150 microns; for fixed bed reactors, 3 to 6 mm; and for fluidized bed reactors, 200 to 3,000 microns. Uniformity of particle size and shape are also desired. In preparation of the pellets by impregnation of zirconium-containing catalyst carrier materials, the particle size of the existing material onto which the active oxide is to be infused is controlling, while in methods using granulation or spray drying absorbent particle size may be obtained by control of process steps. Regardless of how the pellets are prepared, a porosity of 20 to 60 percent is preferred to provide optimum gas-solid contact.

The reactive metal oxide component of the sorbent pellets may in general comprise from 5 to 60 weight percent thereof. In the case of the preferred active material, zinc oxide, an amount of 20 to 60 weight percent may be used when the pellets are prepared by mixing and granulation or spray drying of the mixture while 5 to 50 percent may be used for pellets prepared by infusion of catalyst-carrier pellets. Oxides of copper, or mixtures containing copper, manganese, and molybdenum may be used in place of zinc oxide in similar amounts. An inorganic
binder in the form of calcium sulfide or sodium bentonite or a mixture thereof may be provided in an amount of 2 to 10 percent. Optionally, a promoter such as cobalt oxide may be used in an amount up to 10 weight percent. An organic binder may optionally be provided in an amount of up to 5 percent. A zirconium compound which may comprise zirconia, zirconium silicate, or a zirconium derivative may be provided in an amount of at least 30 weight percent. The term "zirconium derivative" as used herein is intended to mean particles containing zirconia and other metallic oxides, as exemplified by materials disclosed in International Application No. WO95/04012. For pellets made by mixing and granulation or by spray drying, an amount of zirconium compound of 30 to 65 weight percent is preferred. For catalyst carrier impregnated particles, the previously prepared pellets will typically comprise major amounts of zirconium oxide and silicon dioxide, 50 to 52 weight percent, and 39 to 41 weight percent, respectively, in the combined form of zirconium silicate. Use of catalyst carrier particles with these amounts is preferred. Other components such as oxides of potassium, titanium, sodium, and hafnium and ferric oxide may also be included in small amounts.

Sorbents embodying the invention may be prepared by mixing fine particles in the amounts given above, adding water to form a paste or slurry, granulating the paste or spray drying the slurry, and firing the resulting pellets or by impregnating or infusing existing catalyst-carrier pellets with a solution of a suitable salt of the active metal, drying, and firing the
impregnated pellets. The impregnation procedure may be performed repeatedly to obtain a desired loading of active oxide within and on the pellets.

In the process using granulation, the starting materials preferably in the form of particles 1 to 5 microns in size are mixed by means such as a ball mill mixer until homogeneity is obtained. The mixture is then wetted to form a paste which is suitable for extrusion or agglomeration into spherical pellets of a desired size. Conventional equipment may be used for these purposes. The pellets are then dried at a temperature of 212° to 300° F for a period up to 5 hours. After drying, the pellets are calcined in air at a temperature of 1400° F to 1,472° F for a period of 1 hour to impart a high degree of strength and durability. This method is suitable for making pellets 0.5 to 6 mm in size, which pellets would be useful for fixed or moving bed reactors.

Pellet preparation using spray drying may be carried out by mixing particles, preferably between 0.1 and 1 micron in size, containing 30 weight percent of an active oxide, a zirconium compound and a binder in water. The resulting slurry is then thoroughly agitated, and a small amount, for example, 50 ml per liter of water, of sulfuric acid may be added to help dissolve some of the solids, along with 25 weight percent of isopropyl methyl cellulose to increase viscosity of the slurry. In addition, an acid stabilized surfactant may be provided to promotion attrition resistance in the pellets. The slurry is then atomized and spray dried at a temperature of 536° to 572°
F, followed by calcination under conditions as given above. This procedure is useful for making pellets of 65 to 150 microns in size, which size pellets would be useful for fluidized bed and transport reactors.

**EXAMPLES**

The invention is further illustrated by the following examples:
Example 1

Sorbent pellets are prepared by combining powders having a particle size of 1 to 5 microns of zinc oxide, zirconia, calcium sulfate, bentonite, and methyl cellulose at amounts of 28, 64, 2, 3, and 3 weight percent, respectively. The powders are then mixed in a ball mill until homogeneity is obtained. A sufficient amount of water is added to the mixture to form a dry paste, which is suitable for extrusion or agglomeration into spherical pellets. This technique is useful for making pellets 0.5 to 6 mm in diameter.

Example 2

Powders between 0.1 and 1 micron in size of zinc oxide, zirconia, and sodium bentonite are combined at amounts of 33, 65, and 2 weight percent, respectively. The powders are then mixed with water to form a slurry containing 30 weight percent solids, which is kept under constant agitation. Sulfuric acid in an amount of 50 ml per liter of water is added to help dissolve some of the solids. Up to 25 weight percent isopropyl methyl cellulose (DuPont methocel K - 100M™) is then added to increase viscosity of the slurry. Up to 0.5 weight percent of an acid surfactant is then added as necessary to promote attrition resistance. The resulting slurry is atomized and dried by spray drying. This procedure is suitable for making particles 65 to 150 microns in diameter.

Example 3
Pellets of zirconia or zirconium silicate catalyst-carrier are infused with a 1 molar solution of zinc acetate or other metal salt by contacting the pellets with the solution. The mixture is then partially dehydrated in a rotary vacuum evaporator at 70° C (158° F) and at a pressure of less than 2 inches of mercury absolute. The dried sorbent is then calcined in a muffle furnace at 760° C (1,400° F) for a period not to exceed 2 hours. The infusion procedure is repeated three or more times to obtain a desired loading.

The above examples are merely illustrative and are not to be construed as limiting the scope of the invention, which is limited only as indicated by the appended claims.
Abstract of the Disclosure

Sorbent pellets for removing hydrogen sulfide from coal gas are prepared by combining a reactive oxide, in particular zinc oxide, with a zirconium compound such as an oxide, silicate, or aluminate of zirconium, and an inorganic binder and pelletizing and calcining the mixture. Alternately, the zinc oxide may be replaced by copper oxide or a combination of copper, molybdenum, and manganese oxides. The pellet components may be mixed in dry form, moistened to produce a paste, and converted to pellets by forming an aqueous slurry of the components and spray drying the slurry, or the reactive oxide may be formed on existing zirconium-containing catalyst-carrier pellets by infusing a solution of a salt of the active metal onto the existing pellets and firing at a high temperature to produce the oxide. Pellets made according to this invention show a high reactivity with hydrogen sulfide and durability such as to be useful over repeated cycles of sorption and regeneration.